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The Synthesis and Utilisation of Ionic Liquids in the Removal of Harmful Impurities from Fuel

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Declaration

The work described within this thesis was, unless clearly stated and referenced undertaken by myself during the period July 2013 – July 2016

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Abstract

The development of a pure and thus efficient fuel is of increasing importance in the use of a finite resource to be environmentally responsible and economically viable. Trace amounts of dissolved sodium has been identified as a suspect leading to the formation of internal diesel injector deposits (IDIDs) which proves problematic by reducing fuel efficiency in high pressure diesel injectors. Zinc contaminants have been identified as suspects leading to nozzle deposit formation and copper contaminants quickly reduce the oxidation stability of diesel fuel. I demonstrate in this research the successful extraction of ppm levels of Na^+ , Zn^{2+} and Cu^{2+} from model diesel fuels. A range of ionic liquids (ILs) with a variety of cations and anions were examined for their effectiveness at different loadings of IL relative to the fuel. Results provide several clear trends with some exceptional capabilities of the ILs in the extractions. The tunable properties of the ILs ions allow the 'design' to meet the requirements for a particular target and here provide several potential candidates for the extractions

^{23}Na NMR was used in the determination of donor number (DN) and Kamlet-Taft parameters were gathered for each IL providing information of possible hydrogen-bond acidity / basicity (α / β) and dipolarity/polarizability solvent strength (π^*). In addition the non-random two liquid model (NRTL) was applied to correlate the experimental extraction results and determine τ parameters for each of the ILs. Donor number (DN), τ parameters and β values in addition to interfacial tension and viscosity provide information of the extraction mechanisms and predict performance, enabling a chemical design of ILs that are ideal for fuel purification.

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Nomenclature

DBT	Dibenzothiophene
DMSO-d6	Deuterated DMSO
DN	Donor Number
DTC	Dithiocarbamate
EDS	Extractive Desulfurisation
H-bonding	Hydrogen bonding
HDS	Hydrodesulfurisation
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
IDIDs	Internal Diesel Injector Deposits
IFT	Interfacial Tension
IL	Ionic Liquid
KT	Kamlet Taft
LC	Local Composition
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance
NRTL	Non-random Two-liquid Equation
OAc	Acetate Functional Group
ODS	Oxidative Desulfurisation
ppm	Parts per million
PTFE	Polytetrafluoroethylene
RT	Room Temperature (298.15 K)
SILP	Solid-Supported Ionic Liquid Phase
Tf	Trifluoromethanesulfonate Functional Group
TSILs	Task Specific Ionic Liquids
ULSD	Ultra Low Sulfur Diesel
UV-Vis	Ultraviolet-Visible

1 Introduction and Background

1.1 Introduction

The performance, and in particular fuel economy, of internal combustion engines must not be considered in isolation, but in terms of the refinery and delivery process.¹ Diesel fuel can contain a range of undesirable compounds gained throughout production, transport or storage which can affect its physical and chemical properties in a variety of ways. For example, if the fuel is too volatile, when it is used at high ambient temperatures it is liable to vaporise in the fuel lines and form vapour locks.¹ The volatility of the fuel depends on the blend. Different distillates will be affected by the ambient temperature according to their boiling points. The specific environment in which the fuel is used should be taken into consideration as this has an effect on the running temperature of the fuel. The octane number is a measure of resistance to self-ignition and cetane number indicates how readily the fuel ignites; these are key properties in fuel performance. These all need to be taken into careful consideration when introducing new molecules to the system due to the requirements fuel needs to meet (e.g. planes, tractors or road vehicles).

Solvents and detergents are already used in a range of processes throughout the fuel industry, including the extraction of undesired molecules in the fuel. Ionic liquids are proving to be solvents of ever greater interest and utility.² They have found use in many applications such as biomass processing, catalysis and lubricants.³⁻⁷ They have been the subject of widespread academic study in recent years and have already been applied to a number of commercial processes most notably the BASF BASIL™ (Basic Acid Scavenging utilising Ionic Liquids) process.⁴ Exploiting the advantageous solvent properties of ionic liquids could prove very beneficial to the energy industry. As a result of their ionic character, ILs have negligible vapour pressure under standard process operating conditions, thus rendering them easily recoverable from molecular volatile compounds and avoiding losses to the atmosphere; increasing safety and potentially benefitting the environment compared to volatile organic solvents. Moreover, a judicious selection of their

constituent ions can tune the properties of the ionic liquids to a considerable extent, thus allowing the 'design' of the ionic liquid to meet the requirements for a particular target i.e. task-specific ionic liquids (TSILs).⁸

This research concept originates from the idea of using 'designed' ILs to remove the impurities from diesel fuels via liquid-liquid extraction or cartridge filtration. An industry standard test for a model diesel fuel (hexadecane) using sodium naphthanate and DDSA the fuel to produce a one of the surrogates due to the soap deposits being defined by the presence of sodium and carboxylic acid functionality.⁹ Zinc neodecanoate and Cu(acac)₂ were used to prepare the other two fuel surrogates. To the best of my knowledge, only limited research has been conducted on extractions using ionic liquids with diesel fuels outside of desulfurization/denitrogenation. I believe this work presents the first study in the extraction of contaminant sodium, zinc and copper ions from surrogate and commercial fuel using ionic liquids therefore providing a pathway for the future use of ionic liquids in the biphasic extraction of metal impurities from hydrocarbon streams. The low solubility and non-aqueous nature of the ILs, combined with the ability to synthetically tailor the solvents to extract Na, Zn and Cu contaminant ions, provide a unique platform for metal extraction.

1.2 Application of ILs in the Desulfurisation and Denitrogenation of Fuels

This study presents the first research into the extraction of Na⁺, Zn²⁺ and Cu²⁺ from diesel fuel however, research has been carried out in the field of ILs for the extraction of other unwanted components from hydrocarbon streams.

In recent years a great deal of attention has been paid to the deep desulfurisation of fuels due to the gradual reduction in statutory sulfur emissions.¹⁰ The combustion of fuels containing sulfur leads to the emission of SO_x that interacts with atmospheric water to form environmentally damaging sulfates and acid rain.¹¹ The reduction in sulfur content in the fuels is also beneficial to prevent the

corrosion of the equipment used. Hydrodesulfurisation (HDS) is a desulfurisation technique effective in the removal of thiols, sulfides, and disulfides, but the method is inefficient in the removal of dibenzothiophene (DBT) and its derivatives to meet the current emission standards.¹² This is due to sulfur being bound in an aromatic structure which provides steric hindrance in catalytic desulfurisation causing HDS to require severe operating conditions and a large operating cost (expensive catalysts).¹³ To overcome this a development was designed to be able to selectively oxidise DBT and its derivatives producing their corresponding sulfoxides and sulfones, which are then removed via a subsequent extraction process.¹⁴ This process is known as oxidative desulfurisation (ODS) but due to the extractants potentially being both volatile and flammable this presents safety and environmental issues.

Similar research has been carried out in the removal NO_x compounds which in combination with SO_x contributes to air contamination and ozone consumption.¹⁵ Currently in industry, the removal of nitrogen and sulfur compounds in fuels is conducted via simultaneous HDS and hydro-denitrogenation (HDN). These methods cause C-S and C-N bond cleavage to produce highly undesirable H_2S and NH_3 , respectively.^{16,17}

Alternatively, methods employing ILs in the extraction of sulfur and nitrogen compounds have been put forward to provide a sustainable substitute to the current desulfurisation and denitrogenation techniques. Due to their extractability, non-volatile nature and possibility to be non-corrosive they offer a promising alternative. Already a wide range of ILs have been assessed in the extraction of organosulfur compounds from fuel oils and show some excellent results. This has predominantly been achieved using varied imidazolium¹⁸, pyridinium¹⁹ and thiazolium²⁰ ILs but there is great potential by variation of the constituent cation. Research in this field has shown that an important consideration for the implementation of ILs to a fuel application is the IL–fuel mass ratio. This is due to a minimum quantity of IL being desirable in the extractions to reduce cost thus a compromise must be made between IL cost and sulfur extraction. A high IL–fuel

mass ratio provides a high sulfur extraction and this is shown using the IL $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$. The order of sulfur extraction efficiency indicates the order; $1 : 5 < 1 : 4 < 1 : 3 < 1 : 2 < 1 : 1$ (w/w) IL–fuel.²¹ Similarly a range of $[\text{MeSO}_4]^-$ and $[\text{BF}_4]^-$ based ILs provide the same trend.^{22,23} Studies have shown that multiple extractions can produce very promising results providing complete sulfur removal from fuels via the recycling of ILs.²⁴ $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ has been shown to remove 100% of sulfur after five cycles.²⁵ The mutual solubility of the ILs and fuels have been considered which has shown the solubility of an IL in fuel is negligible and the solubility of fuel in an IL is affected by the nature of the fuel.¹⁸ This is important in this application as losses of either component need to be accounted for to provide an efficient system. With regards to temperature, N-methylpyrrolidone hydrogen sulfate ($[\text{HNMP}][\text{HSO}_4]$) has shown that an increase in temperature from 40 °C to 70 °C increases the sulfur extraction from 48% to 63%.²⁴ However, it has been shown that increasing in temperature with high viscosity ILs increases the sulfur extraction efficiency and low viscosity ILs show the reverse trend.²⁵ This could be caused by a cleaner partition at lower temperatures, while mass transfer is better at higher temperatures thus the mutual solubility increasing with temperature. The ILs can be regenerated for repeated use in this application. This proceeds with negligible loss in extraction efficiency of sulfur after a limited number of runs.^{26,27} Experiments have been conducted for fuels used in the industry and provide similar conclusions however, the efficiency in the extraction of sulfur is decreased.²⁵ This would be due to the complex make-up of the market fuels leading to competition of other fuel components with the ILs. To date ILs have provided a very promising alternative to extract sulfur from fuels. To further improve the extraction and applicability of ILs they can be tailored to provide an increased performance for real fuel used in the industry.

Similarly denitrogenation using ILs has proved promising results in combination with desulfurisation but the research is not as vast and thus not as detailed. Successful extractions have been achieved using dicyanamide based ILs²⁸, pyridinium based ILs²⁹ and imidazolium based ILs in which Zn containing species

show double extraction efficiency of nitrogen.³⁰ The effect of the physical environment (temperature, IL-fuel mass ratio etc.) on nitrogen extraction is shown to be similar to the extraction of sulfur as discussed earlier in this section.

1.3 Application of ILs in the Extraction of Metals

1.3.1 Mercury Removal from Natural Gas

Extractions utilising ILs has not been limited only to desulfurisation and denitrogenation applications of fuels but has found widespread use in metal extraction, notably from natural gas and waste water streams. An application related to the research carried out in this project is the removal of mercury from natural gas via the utilisation of ionic liquids. Within the oil and gas industry mercury removal is of increasing importance, to protect the workers and equipment used in industry processes. There are increasing regulations of mercury levels in all aspects of the oil and gas industry which originates naturally from the earth's crust and is subsequently released into the environment.³¹ Research has been carried out developing ILs into a solid-supported ionic liquid phase (SILP) material for the removal of mercury from natural gas. This has been scaled to full industrial implementation within four years and accomplished on various scales. The scale of the application does not hinder the ability to digest large amounts of mercury (up to 20 wt%).³² The development of this technology has outlined a commercially competitive mercury adsorbent for the natural gas industry.

1.3.2 Sulfamic Acid ILs

Protonated sulfamic acid ILs have been designed to act as super strong acids to enable the increased extraction of metals and are safer to handle than known super strong acids.³³ Sulfamate ions are known to provide vast coordination chemistry forming a variety of complexes such as Zn^{2+} , Co^{2+} , Ni^{2+} and rare-earth ions (La–Lu,

Y) which bond through the oxygen atom, while sulfamate complexes of Pt^{2+} , Pt^{4+} , Cr^{3+} , and Ru^{3+} are bonded through the nitrogen atom.^{34–39} The strong affinity for metal ions and the differences in coordination behaviour suggest that N-alkylated sulfamic acid ILs could be an excellent candidate for the extraction of metals.

1.3.3 Metal Extraction From Waste Water

Extraction of metals from waste water is of great importance with the aim of removing hazardous metals or recycling precious metals. The European Union has set stringent guidelines for high Environmental Quality Standards (EQS) for substances of priority in surface water; this outlines the maximum concentrations allowed in surface water.⁴⁰ The list of priority substances includes 33 organic/inorganic compounds that are known to be problematic in the aquatic environment due to their toxicity and bioaccumulation in the food chain. Metals such as Hg, Pb, Ni, and Cd and their compounds belong to this list of priority substances.⁴⁰ Using ILs to extract metals from aqueous systems proved to be inefficient due to the metal ion preferably remaining in the aqueous phase in the hydrated form. It is therefore necessary to utilise an extractant molecule that can complex directly with the metal ions to increase their hydrophobicity.^{41–43} This provides a difficult task of finding extractant molecules that remain in the IL phase in a complex system.

Research has mainly focused around the synthesis and design of novel task-specific ILs which have been tailored to chelate the desired target. Novel compounds have been designed to act as both ILs and extract heavy metal ions. For instance a range of ILs have been designed by manipulating a 1-alkyl-3-methylimidazolium structure to produce a range of $[\text{PF}_6]^-$ based ILs for the extraction of Hg^{2+} and Cd^{2+} .⁴⁴

A vast study has been carried out to evaluate the feasibility of functionalised ammonium and phosphonium based ILs as extractants of metals of significance; Cd, Ni, Hg, Pb as well as for As, Cr, Cu, Pt, Sn, Zn.⁴⁵ The ILs in this study prove to be promising candidates for the selective purification of waste water. The most

efficient systems were concluded to be the use of thiol and thioether functionalised ILs for treatment of communal waste water and the use of tricaprylmethylammonium thiocyanate for industrial waste water with high levels of Zn. However, ILs containing thiol groups did not have a high affinity towards planar intact platinum complexes due to the polarity of the complexes thus strongly hydrophobic and apolar ILs need to be employed in the extraction process. The hydrophobicity and polarisability of IL has a direct impact on the extraction processes, thus the design of hydrophobic, apolar ILs needs to take place to allow the extraction of the platinum complexes.

Research has been carried out the separation of fission products such as Cs^+ and Sr^{2+} from aqueous samples. This has been achieved promising results through the design and synthesis of monoaza-crown ILs, which has shown to increase the diffusion of the cations into the IL phase.^{46,47}

In the utilisation of ILs in metal extractions it is known that future work needs to focus on the methods to recover metals from the ILs in addition to the recycling of ILs for use on a larger scale. Previously heavy metals have been stripped successfully from the commercially available anion functionalized IL trioctylmethylammonium thiosalicylate via oxidation of the thiol-group with HNO_3 .⁴⁸ Likewise this was successfully achieved with uranium and tricaprylmethylammonium thiosalicylate.⁴⁹

Overall, previous research has shown that ILs display the ability to offer a safer and highly selective alternative to extract metal ions from various media. This therefore deems them an exceptional candidate in the removal of metal ions from diesel fuel responsible a range of significant problems within the oil and gas industry.

1.4 Problems Caused by the Presence of Metals in Diesel Fuel

1.4.1 Internal Diesel Injector Deposits (IDIDs)

When considering modern diesel fuel injectors a remarkable challenge exists. Internal diesel-injector deposits (IDIDs), which cause what is descriptively called 'injector sticking', are being observed in increasing numbers and appear detrimental to new injector technologies.⁹ Technical papers have been published describing work on a number of investigations into the character and origins of these internal diesel injector deposits.^{50–52} The deposits tend to build up around the needle valve (Figure 1.1) causing sticking. The deposits can lead to rough idling, power loss, high emissions, high-pressure fuel pump wear, injector sticking, internal component corrosion and of course ultimately engine failure.⁵¹

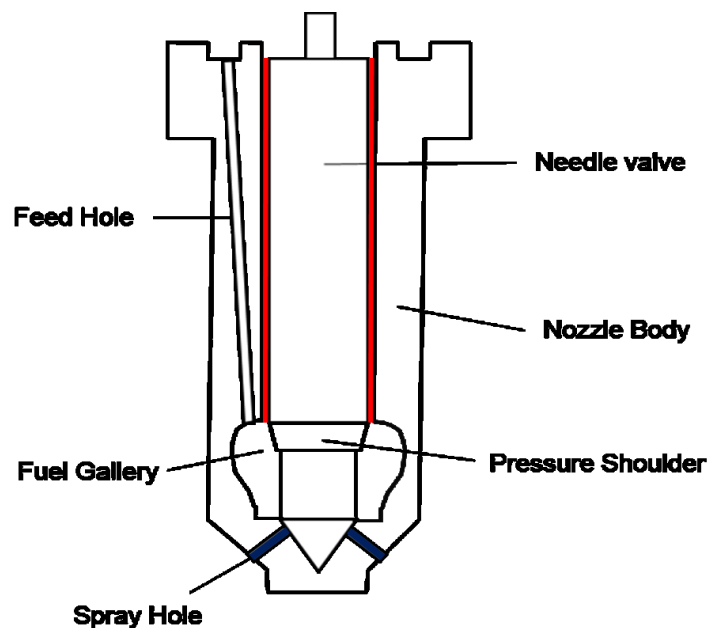


Figure 1.1 - Schematic diagram of a high pressure diesel fuel injector, red indicates typical location of internal diesel injector deposits (IDIDs) and dark blue indicates the location of typical carbonaceous deposits

It has been determined that sodium present in the fuel is one of the most likely suspects linked to the cause of these deposits. Sodium compounds are found in fuel due to the use of drying agents (e.g. sodium sulfate, Na_2SO_4), corrosion inhibitors and through inclusion during transportation. Sodium hydroxide, for example, is now commonly used in the refining process to produce ultra-low sulfur diesel (ULSD) fuel from crude oil.⁵³ Fuel has always contained trace amounts of sodium but modern acidic additives such as dodecenyl succinic acid (DDSA), a corrosion inhibitor, react to form sodium soaps which could increase the formation of IDIDs. There are currently no regulations on sodium concentration in crude oil although most producers do state it in the fuel specifications.

Here, to the best of our knowledge only limited research has been conducted on extractions using ionic liquids with diesel fuels outside of desulfurization or denitrogenation. We believe we present the first study in the extraction of contaminant sodium ions from commercial fuel using ionic liquids therefore providing a pathway for the future use of ionic liquids in the biphasic extraction of metal impurities from hydrocarbon streams. The low solubility and non-aqueous nature of the ILs, combined with the ability to synthetically tailor them to extract Na^+ ions, provide a unique platform for metal extraction from fuels.

1.4.2 Nozzle Deposits

In recent years great improvements in the design of diesel engines have been achieved particularly by the advances in the diesel injector systems. A decrease in diameter of the nozzle orifice to enhance spray characteristics lead to increased spray pressures enabling high power densities and decreased emissions.⁵⁴ However, this leaves injectors vulnerable to the formation of nozzle deposits.⁵⁵ Zinc can contaminate diesel fuels via contact with dust or surfaces containing zinc, this then acts as a catalyst in the formation of carbon deposits which induce nozzle deposit formation.⁵⁶ These deposits tend to form in the spray holes blocking partially, or completely hindering, the smooth delivery of a fuel injection (Figure 1.1). Similarly to IDIDs these types of deposit impact the correct performance of the

engine. However, whilst IDIDs cause sticking in injectors preventing them from working entirely, nozzle deposits block the nozzle holes preventing efficient fuel flow. Therefore, nozzle deposits will affect the spray of fuel into the engine, leading to worse emissions and reduced power, whilst IDIDs can prevent a vehicle from working at all. I show here that ILs can remove zinc from the diesel fuel and thus prevent deposit formation.

1.4.3 Oxidation Stability

Diesel fuel stability is an important factor to take into account when adjusting the chemical composition of diesel fuels. This can refer to stability of the fuel during storage under ambient conditions for extended periods or to thermal stability with short exposure to higher temperatures in end use equipment.

Degradation in the stability of diesel can be shown in a number of ways such as colour change, development of particulate matter and can normally be followed by the formation of insoluble sediments. Changes in physical and chemical properties can also take place. Sediments can lead to fuel filter plugging and other engine difficulties.⁵⁷

The fuel stability can be heavily affected by temperature, oxygen levels and storage. The promotion of oxidation in the diesel fuel can be linked to high temperatures, high oxygen content, exposure to light and prolonged storage times. Also some metals like copper accelerate fuel aging reactions.⁵⁸

This is shown to significantly reduce the oxidation stability of diesel fuel, determined via the rancimat oxidative stability test.⁵⁶ I show here that ILs can be used to remove copper from the diesel fuel and thus prevent reduction in the oxidation stability of the fuel.

1.5 Metal Chelation

1.5.1 Background and Theory

Upon the selection of ILs for the extraction of Na^+ , Zn^{2+} and Cu^{2+} we need to consider how the chelation of the ILs to the metal ions present in the fuels will take place. Towards the end of the 19th century, Alfred Werner unveiled the puzzle of the “double salts”, which metal complexes were then known as. The problem involved with transition-metal complexes was that they were shown to have higher valences. Neutrality principles were satisfied by anions but other species were present and associated with the metals, producing more complex stoichiometries (e.g. $\text{CoCl}_2 \cdot 6\text{NH}_3$).⁵⁹ The discovery to the mystery underlying bonding in transition metals was proposed by Alfred Werner, who was awarded the Nobel Prize for Chemistry in 1913. His concept outlined a double valence for transition-metal ions, a primary valence, satisfying principles of neutrality, plus a secondary valence, providing a ‘coordination number’, often consisting of additional species beyond those necessary to satisfy the charge.⁶⁰ A range of concepts are involved with coordination chemistry which are outlined in this section to provide a detailed understanding of the application throughout this study:

- **Ligand** - A ligand can be defined as an ion or a molecule that is bonded to the central atom(s).⁶¹ They can frequently bind via more than one donor atom, the number of these donors are referred to as the ligand’s denticity. The ILs used in the initial screening study will bind to the metals via one donor atom making them monodentate ligands. The novel ILs and additives synthesised (Chapter 6) will potentially bind to the metals via multiple atoms.

- **Oxidation State** - The oxidation state of an element in a compound is the overall charge on the central atom(s) when the ligands are removed.⁶² The metals used in the model fuels in this research will have the form of Na^+ , Zn^{2+} and Cu^{2+} giving the oxidation states of +1, +2 and +2 respectively. This will coordinate with the corresponding number of the ligands (IL anion) to satisfy the overall charge.
- **Bonding** – The bonding that takes place in coordination complexes ranges from completely ion-dipole to covalent in which there is an overlap between the metal and ligand valence orbitals.⁶¹ Most complexes reside between these two providing a mixed character. Small and highly charged metal ions, such as Na^+ tend to form more ionic compounds. Metals in lower oxidation states or those with unfilled sub-shells such as the transition metals such as Zn^{2+} and Cu^{2+} tend to form more covalent complexes with well-defined coordination geometries.⁶¹
- **Coordination Number** – Describes the number of atoms or ligands attached to a metal centre.⁶³

The Principle of Hard and Soft Acids and Bases (HSAB) states that hard acids form more stable complexes with hard bases and soft bases form more stable complexes with soft acids.⁶⁴ When referring to the orbitals the hard molecules have a large gap between the HOMO and LUMO, soft molecules have a small gap between the HOMO and LUMO. Na^+ is defined as a hard acid whilst Zn^{2+} and Cu^{2+} are borderline acids. Therefore the design of the ILs can be manipulated to form more stable complexes based on this knowledge.

1.5.2 Metal Chelation in this Study

Ligands used in metal ion extraction have conjoined functional groups (e.g., carboxylic acids) or contain donor atoms (e.g., crown ethers) that interact to form complexes with metal ions. Ligands containing soft donor atoms such as N or S have been explored in other systems for the extraction of heavy metals through the use of thioether⁶⁵, thiourea⁶⁶, and urea⁶⁷ functional groups. With the ILs, bonding is likely to take place through the S, N or O atoms of the anion as previously shown in metal extractions from aqueous solutions.⁶⁸ A previous study has shown that the [NTf₂]⁻ based ILs are a weaker coordinating anion with the zinc cation in comparison to tosylate based ILs, indicating that the coordination of the ether chain would dominate stripping of zinc ions.⁶⁹ The coordination mode of the Cu²⁺ ions in the ionic liquids having chelate amine have been studied using NMR and visible electronic spectra.⁷⁰ The metals in the complexes present in the model fuels have the following electronic configuration:

- Sodium dodecenylsuccinic acid (Na⁺): 1s²2s²2p⁶
- Zinc neodecanoate (Zn²⁺): 1s²2s²2p⁶3s²3p⁶3d¹⁰
- Copper acetylacetonate (Cu²⁺): 1s²2s²2p⁶3s²3p⁶3d⁹

The electronic configurations it is shown that that Na⁺ and Zn²⁺ both have full outer shells providing a higher stability than the Cu²⁺ complex. This information needs to be taken into consideration when examining the ability of the ILs to complex with the metal ions present in the fuels.

1.6 Outline of Work

The aim of the research carried out was to synthesise a range of ILs and carry out a screening study for the extraction of Na^+ , Zn^{2+} and Cu^{2+} from n-hexadecane determining the most desirable properties for the maximum extraction efficiency. The best candidates were then taken and novel ILs synthesised to extract the metals from market fuel samples.

Chapter 2 outlines the experimental methods and synthetic methodology, including the methods for the ICP-OES technique carried out to analyse metal concentrations in fuel samples.

Chapter 3 provides the characterisation of the ionic liquids synthesised for this study to deduce suitable extraction mechanisms and analyse the most desirable properties of the ionic liquids for the extraction of each metal contaminant.

Chapter 4 investigates the application of ILs in the extraction of Na^+ from a model fuel linking the properties of the ILs to the extraction efficiency and fitting the results to an NRTL equation.

Chapter 5 studies the application of ILs in the extraction of dicationic metals ($\text{Zn}^{2+}/\text{Cu}^{2+}$) from model fuels linking the properties of the ILs to the extraction efficiency and fitting the results to an NRTL equation. A comparison of all metal extractions is drawn.

Chapter 6 looks at the synthesis of novel task specific ILs through characterisation and screening of the initial set of ILs designed for this application. The task specific ILs and most successful candidates are assessed for their ability to extract metals from market fuels.

Chapter 7 summarises the overall conclusions from this work and documents the future possible direction of this research area.

1.7 Ionic Liquids Selection

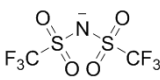
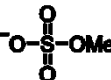
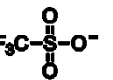
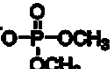
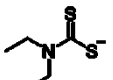
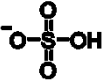
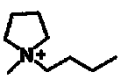
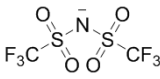
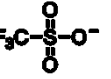
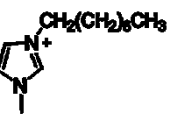
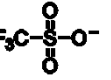
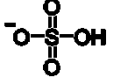
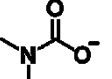
Cation	Anion
 $[C_4C_1im]^+$	 $[N(Tf)_2]^-$  $[MeSO_4]^-$  $[OTf]^-$  $[OAc]^-$  $[Me_2PO_4]^-$  $[S_2CN(C_2H_5)_2]^-$  $[HSO_4]^-$
 $[C_4C_1pyrr]^+$	 $[N(Tf)_2]^-$  $[OTf]^-$
 $[C_8C_1im]^+$	 Cl^-  $[OTf]^-$  $[HSO_4]^-$
 $[(CH_3)_2NH_2]^+$	 $[(CH_3)_2NCOO]^-$

Figure 1.2 - Range of ILs synthesised for use in this study $[C_4C_1im][N(Tf)_2]$, $[C_4C_1im][MeSO_4]$, $[C_4C_1im][OTf]$, $[C_4C_1im][OAc]$, $[C_4C_1im][Me_2PO_4]$, $[C_4C_1im][S_2CN(C_2H_5)_2]$, $[C_4C_1im][HSO_4]$, $[C_4C_1pyrr][N(Tf)_2]$, $[C_4C_1pyrr][OTf]$ $[C_8C_1im]Cl$, $[C_8C_1im][HSO_4]$ and $[(CH_3)_2NH_2][(CH_3)_2NCOO]$

Formula	Name
[C₄C₁im][N(Tf)₂]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C₄C₁im][MeSO₄]	1-butyl-3-methylimidazolium methylsulfate
[C₄C₁im][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[C₄C₁im][OAc]	1-butyl-3-methylimidazolium acetate
[C₄C₁im][Me₂PO₄]	1-butyl-3-methylimidazolium dimethylphosphate
[C₄C₁im][S₂CN(C₂H₅)₂]	1-butyl-3-methylimidazolium diethyldithiocarbamate
[C₄C₁im][HSO₄]	1-butyl-3-methylimidazolium hydrogen sulphate
[C₄C₁pyrr][N(Tf)₂]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[C₄C₁pyrr][OTf]	1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate
[C₈C₁im]Cl	1-methyl-3-octylimidazolium chloride
[C₈C₁im][OTf]	1-methyl-3-octylimidazolium trifluoromethanesulfonate
[C₈C₁im][HSO₄]	1-methyl-3-octylimidazolium hydrogen sulphate
[(CH₃)₂NH₂][(CH₃)₂NCOO]	Dimethylammonium dimethylcarbamate

A wide range of ionic liquids with varying functional groups were synthesised (Figure 1.2) to determine which cationic and anionic components of ILs are effective in the extraction of Na^+ , Zn^{2+} and Cu^{2+} from n-hexadecane (a model diesel fuel). Dialkylimidazolium (with methyl and butyl or octyl alkyl chains) and dialkylpyrrolidinium (with methyl and butyl alkyl chains) based ILs were selected due to their varying cationic properties, with individual ring structures, and their alkyl chain lengths yielding variety of structure without the incorporation of additional functional groups. Specific to the structures, the imidazolium-based cations contain a delocalised charged ring whereas the pyrrolidinium-based cations provide a charged atom. The anions in this study were employed for a number of reasons in addition to being thought of as suitable candidates to coordinate to the metals. Specific details are below:

1. The $[\text{N}(\text{Tf})_2]^-$ and $[\text{OTf}]^-$ anions were selected due to being widely used and thus there exists vast amounts of physical property data about them.
2. The $[\text{OAc}]^-$ anion contains only atoms of CHNO, which is most appealing to a fuel application to meet emission standards of sulfur.
3. The $[\text{Me}_2\text{PO}_4]^-$ and $[\text{Me}_2\text{SO}_4]^-$ anions were selected to provide information on whether a sulfur or phosphorus centre is preferable in the chelation of the metals.
4. The $[\text{HSO}_4]^-$ anion was employed to allow the determination of whether anion-based H bond donation could have a major role in chelation.
5. The chloride (Cl^-) anion was selected to examine possible formation of a metal precipitate within the extraction (after strong direct metal-anion coordination), and to determine how this could affect the purification approach.

6. Finally, the carbamate ILS $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ and $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ (Figure 1.3) were selected as they possess an excellent ability to form metal complexes. Carbamates have displayed the ability to form stable complexes with every transition metal in the periodic table⁷¹ which originates from their flexible electronic nature. In $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ the sulfur atoms possess σ -donor, and π -back-donation, characteristics of equal magnitude. Furthermore, the planar delocalised π -orbital system also enables additional π -electron flow from nitrogen to sulfur.⁷² $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ is excellent candidate due to containing atoms of CHNO only.

2 Synthesis and Methodologies

2.1 Introduction

A variety of room temperature ionic liquids were synthesised for use in this study. Some are used for the extraction themselves but others were utilised purely in characterisations and comparisons. It must also be noted that not all ILs gave conclusive results in the extraction of some metals so will only be referred to and not used in some comparisons. All reactions requiring an inert atmosphere were performed under standard Schlenk techniques using dry nitrogen. All commercially acquired chemicals were obtained from Sigma-Aldrich, and were used without further purification unless otherwise stated. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent purification system.

2.2 Naming of Ionic Liquids

With the large increase of researchers working with or synthesising ionic liquids there becomes great difficulty in keeping the nomenclature to a standard universal naming system. It almost appears that there is a constant stream of novel functional ILs that naming becomes difficult to keep track of and of course the argument of whom is correct.

Most commonly used i.e. 1-butyl-3-methylimidazolium chloride, displayed as [bmim][Cl] or [BMIM][Cl]. However, to avoid confusion in this work an alphanumeric naming system for ionic liquids has been implemented as follows:

1. The cation is abbreviated e.g. an imidazolium cation would be im, while a pyrrolidinium cation is abbreviated to pyrr (see IL synthesis and figure 2.1 for abbreviations).

2. The alkyl chains of the ILs are abbreviated, with a subscript number to provide the chain length e.g. C₄ would contain a butyl chain and C₈ would contain an octyl chain.

2.3 Instrumentation for Characterisation

2.3.1 NMR Analysis

NMR spectra were recorded on Bruker 400 MHz Ultrashield Avance III HD NMR spectrometers (¹H NMR (400 MHz), ¹³C (100.7 MHz)). The sample was placed into an NMR tube and dissolved in DMSO – d₆. Chemical shifts are reported in ppm (relative to the DMSO-d₆ residual peak) and J-coupling constants given in Hz.

2.3.2 Mass Spectrometry

0.1 - 0.2 mg of the sample was dissolved in the appropriate solvent (usually DCM) and run on the appropriate mass spectrometer. LSIMS was run on a Micromass Autospec Premier using Cs ions in either positive or negative mode.

ES mass spectrometry was performed on a Waters LCT Premier using the column; Waters BEH Acquity C18, 50 mm x 2.1 mm at a temperature of 40 °C and an injection volume of 10 µL. ES+ was run using a capillary voltage of 2kV, sample cone voltage 30 V, desolvation temperature of 350 °C, Source Temperature of 120 °C, cone gas flow (nitrogen) of 10 L hr⁻¹, desolvation gas flow (nitrogen) of 400 L hr⁻¹ and an MCP Voltage of 2.1 kV. ES- mode was run using a capillary voltage of 2.5 kV, sample cone voltage 150 V, desolvation temperature of 350 °C, Source Temperature of 120 °C, cone gas flow (nitrogen) of 10 L hr⁻¹, desolvation gas flow (nitrogen) of 400 L hr⁻¹ and an MCP Voltage of 2.1 kV.

2.3.3 Melting Point Analysis

The sample was added to a melting point tube. Melting point measurements were carried out on a Stanford Research Systems 'OptiMelt' automated melting point system, with a heating rate of 1 °C min⁻¹. Melting point values are uncorrected.

2.3.4 Elemental Analysis

Elemental analysis experiments were carried out by the London Metropolitan University service. The instrument used was a Thermo Scientific (Carlo Erba) Flash 2000 Elemental Analyser, configured for %CHN (+/- 0.30% for a pure compound).

2.3.5 Donor Number Measurements

The ILs were dried *in vacuo* overnight prior to the measurements and were stored in J. Young valve NMR tubes. The probe substances (Na(NTf)₂ or NaOTf) were added to the IL under an inert atmosphere to give 0.2 M solutions. The samples were then sonicated at 30 °C to ensure all of the sodium compounds dissolved into the ionic liquid. The chemical shift of the samples were measured at 298 K on a Bruker 400 AVANCE III HD spectrometer running TopSpin 3.2 and equipped with a z-gradient bbo/ 5 mm tuneable SmartProbe™.

Sodium spectra were acquired at a frequency of 105.82 MHz using a spectral width of 21307 Hz (~ 200 ppm centred at 0.0 ppm) and 8192 data points giving an acquisition time of 0.192 s. A deuterium lock was provided via a DMSO-*d*₆ capillary tube insert. The Bruker pulse programme zg (i.e. a 90° pulse) and relaxation delay of 0.1 s were used. The data was processed using 8192 data points and an exponential window function of 50 Hz. Chemical shift calibration was achieved by employing a secondary reference of a saturated NaCl/H₂O solution with a DMSO-*d*₆ capillary tube insert (= 0 ppm).

The recorded spectra were evaluated using MestReNova's NMR software and the DN values were assigned to the ILs by using a linear calibration line consisting of values for 16 different organic solvents as used in previous literature, the calibration line had a fit coefficient of around 0.95 of which the data can be found in Appendix A.⁷³

2.3.6 Kamlet Taft Measurements

Dye solutions of Reichardt's Dye 30 (0.9 mM), *N,N*-diethyl-4-nitroaniline (0.6 mM), and 4-nitroaniline (0.7 mM) were freshly prepared in dichloromethane (DCM). The appropriate volume of dye for the ionic liquids was then determined in 1 mL of DCM to give an absorbance value within the range of 0.5-1.0.

The ionic liquids (1 mL), were placed in to 5 mL round bottomed flasks and dried *in vacuo* overnight at 60 °C prior to each measurement. The appropriate volume of freshly made dye was added the flask before the DCM was removed at 60 °C *in vacuo* for 1 h. The sample was allowed to cool and cuvettes were washed prior to each use with, acetone (x 3), industrially methylated spirit (x 3) and DCM (x 3) before drying under a stream of dry nitrogen.

2.3.6.1 UV/Vis Spectroscopy

The UV-Visible spectrum of each sample measured at 25 °C via a thermostatic circulator controlling the sample holder temperature on a Perkin-Elmer Lambda 25 spectrophotometer calibrated to ± 0.2 nm using a holmium oxide standard, with an accuracy of 0.5 nm and using 0.1 cm zirconium cells. (200-1100 nm). The regression used in the determination of the Kamlet Taft parameters were calculated according to literature procedures.⁷⁴

2.3.7 Water Content Analysis

All ionic liquids were dried *in vacuo* prior to measurement and the water content were measured via Karl-Fischer titration on a Mettler Toledo C30 Compact Karl Fischer Coulometer. The measurements were repeated three times to ensure reliability.

The instrument was fully calibrated a small amount of the sample (0.3 -0.5 mL) was drawn up into a syringe and weighed using a balance. The sample was then slowly injected into the top of the flask until the display asked for the weight of the sample. The syringe was weighed again and the calculated weight of the IL was entered on the display. Upon completion the water content of the IL was given.

2.3.8 Density Measurements

All samples were dried *in vacuo* prior and density measurements were carried out on a LiquiPhysics™ DM40 density metre at 25 °C and repeated three times to give an average result. The error associated with the measurement has been given as $\pm 0.001 \text{ g cm}^{-3}$ by the manufacturer.

A small amount (1 - 2 mL) of the sample was placed into the clean, dry sample U tube of the instrument using a syringe. It was ensured that the sample tube was completely filled and that no gas bubbles were present. After the instrument displayed a steady reading to four significant figures, the temperature equilibrium had been reached and the density was recorded.

2.3.9 Interfacial Tension Measurements

The interfacial tension values were determined via a pendant drop analysis using a Krüss EasyDrop Tensiometer. A 1 cm³ cuvette was filled with n-hexadecane (lighter phase) and a pendant drop of the IL (denser phase) was suspended within the fuel

using a one millilitre syringe on a computer controlled syringe driver. A wide bore stainless steel needle with a diameter of 1.830 mm was used to minimise the chance of the ionic liquid climbing the outside of the needle. The ionic liquid was injected until it was the largest stable pendant drop possible and the droplet was equilibrated for 5 minutes before the image was 'frame-grabbed' from the video. The drop was illuminated from behind and the camera at the front recorded an image of the drop. The DSA1 software was used to analyse the drop and calculate interfacial tensions.

2.3.10 Viscosity Measurements

Viscosity measurements were determined using an AR2000EX rheometer (TA Instruments) at 25 °C fully calibrated prior to loading the sample. The temperature was controlled through the use of a Peltier plate and measurements were recorded under an inert atmosphere using a truncated cone geometry of 40 mm, 2° steel cone geometry. The device was controlled and data was recorded using Rheology Advantage software. Measurements were recorded over a range of temperatures with angular velocities between 0.1 and 10 rad per second.

2.4 Synthetic Methods

2.4.1 Synthesis of 1-butyl-3-methylimidazolium chloride

[C₄C₁im]Cl

Freshly distilled 1-chlorobutane (102.85 g, 1.11 mol) was added dropwise (slowly) to a mixture of freshly distilled 1-methylimidazole (82.92 g, 1.01 mol) and ethyl acetate (100 mL) at RT. The temperature was increased to 45 °C for three days and once a biphasic mixture had formed the temperature was increased to 75 °C and stirred for a further 4 days. The colourless biphasic mixture was placed in a freezer

overnight, a white precipitate formed and the solvent was removed via Schlenk techniques. The remaining white crystals were washed with ethyl acetate and then recrystallised in acetonitrile. The residual solution was carefully decanted off, and the solid was dried *in vacuo* to yield 1-butyl-3-methylimidazolium chloride (88.21 g, 50 %) as a white crystalline solid. Found: m.p. 69-72 °C, ^1H NMR (400 MHz, DMSO- d_6): δ 9.37 (s, 1H), 7.84 (t, J = 1.7 Hz, 1H), 7.76 (t, J = 1.7 Hz, 1H), 4.19 (t, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.77 (p, J = 7.2 Hz, 2H), 1.26 (h, J = 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ 137.14, 128.78, 124.07, 122.74, 48.90, 36.19, 31.84, 19.24, 13.76. m/z (LSIMS $^+$): 139 (100%) $[\text{C}_4\text{C}_1\text{im}]^+$. m/z (LSIMS $-$): 35 (100%) $[\text{Cl}]^-$, 37 (19%) $[\text{Cl}]^-$. Calc. for $\text{C}_8\text{H}_{15}\text{ClN}_2$: C, 55.01; H, 8.66; N, 16.04%. Found: C, 55.04; H, 8.76; N, 15.89%.

2.4.2 Synthesis of 1-ethyl-3-methylimidazolium

bis(trifluoromethylsulfonyl)imide $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$

A solution of lithium bis(trifluoromethylsulfonyl)imide (54.55 g, 0.19 mol) in water (50 mL) was added to a solution of 1-ethyl-3-methylimidazolium chloride (29.69 g, 0.17 mol) in dichloromethane (100 mL) and stirred vigorously at room temperature for 8 hours. The lower phase from the biphasic mixture was collected and washed repeatedly with water (10 x 100 mL) until no chloride traces remained in the washings (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ^1H (ppm) (400 MHz, DMSO- d_6): 9.10 (1H, s), 7.77 (1H, s), 7.69 (1H, s), 4.18 (2H, q, J = 7.3 Hz), 3.84 (3H, s), 1.41 (3H, t, J = 7.3 Hz). ^{13}C NMR (101 MHz, DMSO): 136.45, 123.79, 122.18, 118.36, 44.34, 35.89, 15.28. m/z (LSIMS $^+$): 111 ($[\text{C}_2\text{C}_1\text{im}]^+$, 100 %). m/z (LSIMS $-$): 280 ($[\text{NTf}_2]^-$, 100 %). Calc. for $\text{C}_{10}\text{H}_{15}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: C, 24.65 (24.55); H, 2.66 (2.83); N, 10.64 %. Found: C, 24.55; H, 2.83; N, 10.60 %.

2.4.3 Synthesis of 1-methyl-3-propylimidazolium

bis(trifluoromethylsulfonyl)imide [C₃C₁im][N(Tf)₂]

A solution of lithium bis(trifluoromethylsulfonyl)imide (54.55 g, 0.19 mol) in water (50 mL) was added to a solution of 1-methyl-3-propylimidazolium chloride (29.69 g, 0.17 mol) in dichloromethane (100 mL) and stirred vigorously at room temperature for 8 hours. The lower phase from the biphasic mixture was collected and washed repeatedly with water (10 x 100 mL) until no chloride traces remained in the washings (silver nitrate test – AgCl solubility in water = 1.3×10^{-5} mol L⁻¹).⁷⁵ The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed in vacuo (24 hours) giving 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): 9.10 (1H, s, C(2)H), 7.76 (1H, s, d 1H (ppm) (400 MHz, DMSO-d₆): 9.10 (1H, s, C(2)H), 7.76 (1H, s, C(4)H), 7.70 (1H, s, C(5)H), 4.12 (2H, t, NCH₂CH₂CH₃), 3.85 (3H, s, -NCH₃), 1.80 (2H, sextet, 3JHH = 7.3 Hz, 0.86 (3H, t, J = 7.4 Hz). ¹³C NMR (101 MHz, DMSO): 136.51, 123.64, 122.26, 118.35, 50.27, 35.73, 22.83, 10.38. m/z (LSIMS+): 125 ([C₃C₁im]⁺, 100 %). m/z (LSIMS-): 280 ([NTf₂]⁻, 100 %). Calc. for C₁₀H₁₅F₆N₃O₄S₂: C, 26.83; H, 3.27; N, 10.45 Found: C, 26.67; H, 3.23; N, 10.26%.

2.4.4 Synthesis of 1-butyl-3-methylimidazolium

bis(trifluoromethylsulfonyl)imide [C₄C₁im][N(Tf)₂]

A solution of lithium bis(trifluoromethylsulfonyl)imide (54.55 g, 0.19 mol) in water (50 mL) was added to a solution of 1-butyl-3-methylimidazolium chloride (29.69 g, 0.17 mol) in dichloromethane (100 mL) and stirred vigorously at room temperature for 8 hours. The lower phase from the biphasic mixture was collected and washed repeatedly with water (10 x 100 mL) until no chloride traces remained in the

washings (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless and highly viscous liquid. Found: ^1H NMR (400 MHz, DMSO- d_6): δ 8.01 (s, 1H), 6.94 – 6.88 (m, 1H), 6.83 (t, J = 1.7 Hz, 1H), 3.61 (t, J = 7.4 Hz, 2H), 1.35 – 1.22 (m, 2H), 0.77 (h, J = 7.4 Hz, 2H), 0.33 (t, J = 7.4 Hz, 3H). ^{13}C NMR in progress. m/z (LSIMS $^+$): 139 (100%) [$\text{C}_4\text{C}_1\text{im}$] $^+$. m/z (LSIMS $^-$): 280 (100%) [NTf_2] $^-$. Calc. for $\text{C}_{10}\text{H}_{15}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: C, 28.64; H, 3.61; N, 10.02%. Found: C, 28.69; H, 3.50; N, 10.16%.

2.4.5 Synthesis of 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [$\text{C}_{10}\text{C}_1\text{im}$][$\text{N}(\text{Tf})_2$]

A solution of lithium bis(trifluoromethylsulfonyl)imide (22.19 g, 0.08 mol) was added to a solution of 1-decyl-3-methylimidazolium chloride (12.86 g, 0.07 mol) in dichloromethane (100 mL) and stirred vigorously at room temperature for 2 days. The white precipitate was removed and the lower phase from the biphasic mixture was collected and washed repeatedly with water (10 x 100 mL) until no chloride traces remained in the washings (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ^1H NMR (400 MHz, DMSO- d_6): δ 8.01 (s, 1H), 6.94 – 6.88 (m, 1H), 6.83 (t, J = 1.7 Hz, 1H), 3.61 (t, J = 7.4 Hz, 2H), 1.35 – 1.22 (m, 2H), 0.77 (h, J = 7.4 Hz, 2H), 0.33 (t, J = 7.4 Hz, 3H). m/z (LSIMS $^+$): 139 (100%) [$\text{C}_4\text{C}_1\text{im}$] $^+$. m/z (LSIMS $^-$): 280 (100%) [NTf_2] $^-$. Calc. for $\text{C}_{10}\text{H}_{15}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: C, 28.64; H, 3.61; N, 10.02%. Found: C, 28.69; H, 3.50; N, 10.16%.

2.4.6 Synthesis of 1-butyl-3-methylimidazolium methyl sulphate [C₄C₁im][MeSO₄]

Dimethyl sulphate (54.23 g, 0.43 mol) was added dropwise (slowly) to mixture of 1-butylimidazole (48.43 g, 0.39 mol) and toluene (100 ml) cooled by an ice bath with stirring. After one hour at RT the upper layer was removed via Schlenk techniques and the lower layer was washed three times with 50 ml of toluene. The solvent was removed *in vacuo* (24 hours) giving 1-butyl-3-methylimidazolium methyl sulphate (89.81 g, 92 %) as a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 8.55 (s, 1H), 7.27 (s, 1H), 7.18 (s, 1H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.95 (s, 3H), 1.21 (p, *J* = 7.2 Hz, 2H), 0.63 (h, *J* = 7.4 Hz, 2H), 0.19 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 136.66, 123.12, 121.93, 53.12, 48.40, 35.14, 31.26, 18.54, 12.50. *m/z* (LSIMS⁺): 139 (100%) [C₄C₁im]⁺, 83 (59%). *m/z* (LSIMS⁻): 111 (100%) [MeSO₄]⁻. Calc. for C₉H₁₈N₂O₄S: C, 43.19; H, 7.25; N, 11.19%. Found: C, 42.99; H, 7.17; N, 11.05%.

2.4.7 Synthesis of 1-butyl-3-methylimidazolium hydrogen sulphate [C₄C₁im][HSO₄]

1-butyl-3-methylimidazolium methyl sulphate (152.19 g, 0.61 mol) was diluted with deionized water (100 ml) and sulfuric acid (6 drops) in a 500ml round-bottomed flask. The solution was then heated for 3 hours at 170 °C with vigorous stirring and deionized water was added dropwise throughout the reaction via a dropping funnel. Upon completion the solution was allowed to cool to room temperature and deionized water (50 ml) was added. The solution was purified from activated charcoal followed by filtration through a cellulose micro filter. The water was then removed via rotary evaporation and the resulting liquid was dried *in vacuo* to give 1-butyl-3-methylimidazolium hydrogen sulphate (102.36 g 71.02 %) as a colourless

viscous liquid. Found: ^1H NMR (400 MHz, DMSO- d_6): δ 9.54 (s, 1H), 9.21 (s, 1H), 7.81 (t, J = 1.8 Hz, 1H), 7.74 (t, J = 1.8 Hz, 1H), 4.17 (t, J = 7.2 Hz, 2H), 1.75 (p, J = 7.2 Hz, 2H), 1.24 (h, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ 137.18, 124.06, 122.76, 48.90, 40.52, 40.31, 40.10, 39.26, 36.12, 31.87, 19.21, 13.72. m/z (LSIMS $^+$): 139 (100%) [$\text{C}_4\text{C}_1\text{im}$] $^+$. m/z (LSIMS $^-$): 97 (100%) [HSO_4] $^-$. Calc. for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_4\text{S}$: C, 40.67; H, 6.83; N, 11.86%. Found: C, 40.55; H, 6.79; N, 11.76%.

2.4.8 Synthesis of 1-butyl-3-methylimidazolium trifluoromethanesulfonate [$\text{C}_4\text{C}_1\text{im}$][OTf]

Lithium trifluoromethanesulfonate (54.60 g, 0.35 mol) was added to a mixture of 1-butyl-3-methylimidazolium chloride (55.96 g, 0.32 mol) and dichloromethane. The solution was stirred for 48 hours at RT. Upon completion the reaction mixture was filtered and washed with dichloromethane (2x30 mL). The organic extracts were combined and product extraction was carried out in a liquid-liquid extractor (water/DCM) system over 4 days. The organic phase was separated and the solvent was removed *in vacuo* (24 hours) giving 1-butyl-3-methylimidazolium trifluoromethanesulfonate (50.03 g, 54.19 %) as a colourless viscous liquid. Found ^1H NMR (400 MHz, DMSO- d_6): δ 8.34 (s, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 3.63 (t, J = 7.3 Hz, 2H), 1.24 (p, J = 7.3 Hz, 2H), 0.69 (h, J = 7.4 Hz, 2H), 0.26 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 136.22, 125.06, 122.91, 121.88, 121.69, 118.69, 115.51, 48.57, 35.01, 31.03, 18.37, 18.30, 12.12, 12.00. m/z (LSIMS $^+$): 139 (100%) [$\text{C}_4\text{C}_1\text{im}$] $^+$, 83 (59%). m/z (LSIMS $^-$): 149 (100%) [CF_3SO_3] $^-$. Calc. for $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_4\text{S}$: C, 37.50; H, 5.24; N, 9.72%. Found: C, 37.61; H, 5.19; N, 9.93%.

2.4.9 Synthesis of 1-butyl-3-methylimidazolium acetate

[C₄C₁im][OAc] (a)

Barium hydroxide octahydrate (141.88 g, 0.50 mol) was added to deionized water (10 ml per 1 g of barium hydroxide octahydrate), and the solution was heated at 70 °C for 1 hour. Separately, 1-butyl-3-methylimidazolium hydrogen sulphate (106.27 g, 0.45 mol) was diluted with an equal volume of deionized water and added dropwise to the hot aqueous barium hydroxide solution over ten minutes, whereupon a white precipitate formed. The mixture was then heated at 70 °C for a further hour, cooled to room temperature and refrigerated for a minimum of 30 minutes, to encourage all barium sulphate to precipitate out. The cold solution was filtered, generating an aqueous solution of 1-butyl-3-methylimidazolium hydroxide.

The basic aqueous solution of 1-butyl-3-methylimidazolium hydroxide was treated with the conjugate carboxylic acid H[A] (1 equiv.), until the pH of the solution had reached ca. 7. The water was removed by rotary evaporation and the ionic liquid was filtered to remove small quantities of solid material. The ionic liquid was dried *in vacuo* (24 hours) giving 1-butyl-3-methylimidazolium acetate (56.32 g, 63.13 %) a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 9.17 – 9.11 (m, 1H), 7.43 (s, 1H), 7.34 (s, 1H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.45 (s, 3H), 1.19 (d, *J* = 10.0 Hz, 5H), 0.64 (h, *J* = 7.4 Hz, 2H), 0.20 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 176.22, 136.83, 123.50, 122.27, 48.40, 35.32, 31.55, 24.24, 24.21, 18.57, 12.66. *m/z* (LSIMS⁺): 139 (100%) [C₄C₁im]⁺. *m/z* (LSIMS⁻): 59 (100%) [OAc]⁻. Calc. for C₁₀H₁₈N₂O₂: C, 60.58; H, 9.15; N, 14.13%. Found: C, 60.55; H, 9.33; N, 13.99%.

2.4.10 Synthesis of 1-butyl-3-methylimidazolium acetate

[C₄C₁im][OAc] (b)

1-butyl-3-methylimidazolium chloride (16.42 g, 0.094 mol) and silver acetate (14.18 g, 0.085 mol) were carefully weighed into a 100 ml round-bottomed flask, and the flask was wrapped in aluminium foil to prevent photodegradation of the silver acetate. Deionized water (50 ml) was added, and the solution was stirred at room temperature for three days, during which time a white precipitate formed. The solution was then filtered and tested for the presence of excess Ag⁺ or Cl⁻ as follows: one or two drops of the impure aqueous ionic liquid solution were added to two glass vials, and both were diluted with deionized water (1 ml). To the first vial was added a few drops of 1 M aqueous hydrochloric acid, and to the other a few drops of 1 M aqueous silver nitrate. The tests indicated that there was a slight excess of Ag⁺. Aqueous solutions of 1-butyl-3-methylimidazolium chloride and silver acetate were added dropwise to the acetate ionic liquid, alternately with stirring, until no further precipitate formation was observed. The opaque solution was filtered, giving a colourless solution, which tested negative with both 1 M aqueous hydrochloric acid and 1 M aqueous silver nitrate. The water was removed via rotary evaporation, and the product was dried *in vacuo*, to give 1-butyl-3-methylimidazolium acetate (14.71 g, 87.29 %) as a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 10.19 (s, 1H), 8.09 (s, 1H), 7.94 (s, 1H), 5.26 (s, 1H), 3.95 – 3.87 (m, 2H), 1.28 (p, *J* = 7.3 Hz, 2H), 1.20 (s, 3H), 0.67 (h, *J* = 7.5 Hz, 2H), 0.26 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 174.50, 174.45, 138.28, 123.78, 122.74, 48.06, 35.00, 31.77, 25.14, 18.69, 12.68, 12.64. *m/z* (LSIMS⁺): 139 (100%) [C₄C₁im]⁺. *m/z* (LSIMS⁻): 59 (100%) [OAc]⁻. Calc. for C₁₀H₁₈N₂O₂: C, 60.58; H, 9.15; N, 14.13%. Found: C, 60.55; H, 9.33; N, 13.99%.

2.4.11 Synthesis of 1-butyl-3-methylimidazolium dimethyl phosphate [C₄C₁im][Me₂PO₄]

Trimethyl phosphate (157.4 g, 1.12 mol) was added dropwise to a cold mixture of 1-butylimidazole (126.9 g, 1.02 mol) and ethyl acetate (150 ml) with vigorous stirring. The reaction was stirred for 24 hours at 80 °C and then distilled water (60 ml) was added to produce a biphasic mixture. The IL phase was isolated and the solvent was removed via rotary evaporation to produce a colourless viscous liquid. The liquid was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm) and dried in vacuo to give 1-butyl-3-methylimidazolium dimethyl phosphate (206.2 g 78.03 %) as a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 9.39 (s, 1H), 7.70 (s, 1H), 7.54 (s, 1H), 4.29 (s, 2H), 3.78 (t, *J* = 6.6 Hz, 2H), 2.78 (d, *J* = 10.8 Hz, 6H), 1.18 (p, *J* = 7.3 Hz, 2H), 0.60 (h, *J* = 7.3 Hz, 2H), 0.17 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, DMSO-weak): δ 137.23, 123.54, 122.53, 51.05, 50.99, 48.12, 35.07, 31.67, 18.53, 12.54. *m/z* (LSIMS⁺): 139 (100%) [C₄C₁im]⁺. *m/z* (LSIMS⁻): 125 (100%) [Me₂PO₄]⁻. Calc. for C₁₀H₂₁N₂O₄P: C, 45.45; H, 8.01; N, 10.60%. Found: C, 45.39; H, 8.09; N, 10.47%.

2.4.12 Synthesis of 1-butyl-3-methylimidazolium diethyldithiocarbamate [C₄C₁im][S₂CN(C₂H₅)₂]

An ion exchange column was prepared using Amberlite® IRA-400 chloride form (267.27 g, 1.4 eq/L, 0.782 mol). The resin was soaked overnight in distilled water and then flushed through with additional distilled water until the solution ran colourless. A solution of sodium diethyldithiocarbamate (528.58 g, 2.346 mol) and distilled water was prepared and run through the column (flow rate 1ml/min). Ion exchange chromatography was carried out to ensure no chloride traces remained. A solution of 1-butyl-3-methylimidazolium chloride (92.73 g, 0.531 mol) in distilled water was prepared and run through the column (flow rate 1ml/min) to produce

an orange solution. This was run through a C18 column and the solvent was removed in vacuo to produce a pale yellow viscous liquid, 1-butyl-3-methylimidazolium diethyldithiocarbamate (96.14 g, 62.98%). Found: ^1H NMR (400 MHz, DMSO- d_6) δ 9.73 (d, J = 2.2 Hz, 1H), 7.86 (t, J = 1.8 Hz, 1H), 7.78 (t, J = 1.8 Hz, 1H), 4.23 (t, J = 7.2 Hz, 2H), 4.00 (q, J = 7.0 Hz, 4H), 3.91 (s, 3H), 1.84 – 1.71 (m, 2H), 1.32 – 1.18 (m, 2H), 1.09 (t, J = 7.0 Hz, 6H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 212.58, 123.94, 122.75, 48.89, 46.50, 36.13, 31.99, 19.27, 13.77, 13.02. m/z (LSIMS $^+$): 139 (100%) $[\text{C}_4\text{C}_{1\text{im}}]^+$. m/z (LSIMS $^-$): 149 (100%) $[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]^-$. Calc. for $\text{C}_{13}\text{H}_{25}\text{N}_3\text{S}_2$: C, 54.31; H, 8.77; N, 14.62%. Found: C, 54.26; H, 8.79; N, 14.57%.

2.4.13 Synthesis of 1-butyl-1-methylpyrrolidinium chloride

$[\text{C}_4\text{C}_1\text{pyrr}]\text{Cl}$

Freshly distilled N-methylpyrrolidine (311.65 g, 3.66 mol) was added dropwise to a mixture of freshly distilled 1-chlorobutane (309.18 g, 3.33 mol) and ethyl acetate (300 mL). The reaction was heated for 3 days at 75 °C and upon completion the solution was cooled to give a white precipitate. The mixture was placed in a freezer overnight to encourage precipitation and then the solvent was removed via Schlenk techniques. The remaining white crystals were washed with ethyl acetate and then recrystallised in acetonitrile. The residual solution was carefully decanted off, and the solid was dried *in vacuo* to yield 1-butyl-1-methylpyrrolidinium chloride (356.66 g, 60.3 %) as a white crystalline solid. ^1H NMR (400 MHz, DMSO- d_6) δ 3.55 – 3.28 (m, 3H), 2.99 (s, 2H), 2.08 (q, J = 3.8 Hz, 2H), 1.75 – 1.62 (m, 1H), 1.32 (h, J = 7.4 Hz, 1H), 0.94 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 63.83, 63.29, 47.91, 39.38, 25.41, 21.53, 19.80, 13.99. m/z (LSIMS $^+$): 142 (100%) $[\text{C}_4\text{C}_1\text{py}]^+$. m/z (LSIMS $^-$): 35 (100%) $[\text{Cl}]^-$, 37 (19%) $[\text{Cl}]^-$. Calc. for $\text{C}_9\text{H}_{20}\text{ClN}$: C, 60.83; H, 11.34; N, 7.88%. Found: C, 60.74; H, 11.42; N, 7.83%.

2.4.14 Synthesis of 1-butyl-1-methylpyrrolidinium

bis(trifluoromethylsulfonyl)imide [C₄C₁pyrr][N(Tf)₂]

A mixture of 1-butyl-1-methylpyrrolidinium chloride (33.78 g, 0.19 mol) and dichloromethane (50 mL) was added to lithium bis-(trifluoromethylsulfonyl)imide (60.29 g, 0.21 mol) and stirred vigorously at room temperature for 24 hours. The mixture was filtered and washed repeatedly with deionized water (10 x 100 mL) until no chloride traces remained (test with silver nitrate solution). The ionic liquid in dichloromethane was purified through a short alumina column topped with a thin layer of activated charcoal (ca < 5 mm). The solvent was then removed *in vacuo* (24 hours) giving 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (71.29 g, 89 %) as a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆) δ 3.53 – 3.39 (m, 1H), 3.38 – 3.25 (m, 1H), 2.98 (s, 1H), 2.16 – 2.01 (m, 2H), 1.75 – 1.62 (m, 1H), 1.32 (h, J = 7.4 Hz, 1H), 0.94 (t, J = 7.4 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 124.76, 121.56, 118.37, 63.89, 63.39, 47.95, 40.62, 40.41, 40.20, 39.99, 39.78, 39.58, 39.36, 25.38, 21.53, 19.76, 13.88. m/z (LSIMS⁺): 142 (100%) [C₄C₁pyrr]⁺. m/z (LSIMS⁻): 280 (100%) [NTf₂]⁻. Calc. for C₁₁H₂₀F₆N₂O₄S₂: C, 31.28; H, 4.77; N, 6.63%. Found: C, 31.29 H, 4.80; N, 6.70%.

2.4.15 Synthesis of 1-butyl-1-methylpyrrolidinium

trifluoromethanesulfonate [C₄C₁pyrr][OTf]

A mixture of 1-butyl-1-methylpyrrolidinium chloride (67.88 g, 0.38 mol) and acetone (50 mL) was added to sodium trifluoromethanesulfonate (71.92 g 0.42 mol) and the reaction was stirred for 48 hours at room temperature. The resulting organic phase was filtered and washed with water until chloride tests proved negative (silver nitrate test). The solvent was then removed via rotary evaporation and the ionic liquid was passed through a short alumina column topped with a layer of activated charcoal (ca < 5 mm). The remaining liquid was dried *in vacuo* (24 hours)

giving 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (72.15 g, 65.18 %) a colourless viscous liquid. Found ^1H NMR (400 MHz, DMSO- d_6) δ 3.53 – 3.37 (m, 3H), 3.39 – 3.25 (m, 2H), 2.98 (s, 3H), 2.08 (dq, J = 4.9, 3.2, 1.9 Hz, 4H), 1.75 – 1.62 (m, 2H), 1.32 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 125.97, 122.76, 119.56, 63.90, 63.86, 63.38, 47.94, 25.38, 21.52, 19.75, 13.90. m/z (LSIMS $^+$): 142 (100%) $[\text{C}_4\text{C}_1\text{pyrr}]^+$. m/z (LSIMS $^-$): 149 (100%) $[\text{CF}_3\text{SO}_3]^-$. Calc. for $\text{C}_{10}\text{H}_{20}\text{F}_3\text{NO}_3\text{S}$: C, 41.23; H, 6.92; N, 4.81%. Found: C, 41.42; H, 7.09; N, 4.91%.

2.4.16 Synthesis of 1-methyl-3-octylimidazolium chloride

$[\text{C}_8\text{C}_1\text{im}]\text{Cl}$

Freshly distilled 1-chlorooctane (258.69 g, 1.74 mol) was added dropwise to a cold mixture of freshly distilled 1-methylimidazole (129.72 g, 1.58 mol) and ethyl acetate (200 mL) with vigorous stirring. The reaction was continued for 1 week at 75 °C, cooled to room temperature and the solvent was removed via rotary evaporation. The remaining liquid was washed with ethyl acetate (3x200 mL) and removed by freezing the ionic liquid over dry ice and evacuating via a fritted filter. The product was dried *in vacuo* (24 hours) giving 1-methyl-3-octylimidazolium chloride (291.70 g, 80 %), a colourless viscous liquid. Found: ^1H NMR (400 MHz, DMSO- d_6): δ 9.27 (s, 1H), 7.81 (d, J = 1.9 Hz, 1H), 7.74 (t, J = 1.9 Hz, 1H), 4.17 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.78 (p, J = 7.2 Hz, 2H), 1.26 (dh, J = 10.9, 6.6, 5.6 Hz, 11H), 0.90 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, DMSO- d_6): δ 138.19, 127.64, 119.95, 48.50, 35.74, 32.81, 31.41, 31.22, 29.73, 28.64, 28.50, 25.62, 22.00, 13.37. m/z (LSIMS $^+$): 195 (100%) $[\text{HC}_8\text{C}_1\text{im}]^+$. m/z (LSIMS $^-$): 35 (100%) $^{35}\text{Cl}^-$, 37 (19%) $^{37}\text{Cl}^-$. Calc. for $\text{C}_{12}\text{H}_{23}\text{ClN}_2$: C, 62.45; H, 10.05; N, 12.14%. Found: C, 62.34; H, 10.13; N, 12.24%.

2.4.17 Synthesis of 1-methyl-3-octylimidazolium hydrogen sulphate [C₈C₁im][HSO₄]

A round-bottomed flask was fitted with two oil bubblers (1 M sodium hydroxide) and a dropping funnel. Sulfuric acid 98% (22.18 g, 0.23 mol) was added dropwise to a cold mixture of 1-methyl-3-octylimidazolium chloride (50.00 g 0.22 mol) and water (50 ml) over a period of one hour. The water was removed via rotary evaporation and the remaining liquid was dried *in vacuo* (24 hours) 1-methyl-3-octylimidazolium hydrogen sulphate (62.48 g, 97.1%) a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 11.25 (s, 2H), 8.56 (s, 1H), 7.12 (d, *J* = 18.6 Hz, 2H), 3.38 (s, 3H), 1.26 (s, 2H), 0.66 (s, 5H), 0.56 (s, 6H), 0.16 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆): δ 136.24, 135.19, 123.22, 122.90, 121.88, 119.27, 48.87, 40.39, 40.18, 39.97, 39.76, 39.55, 35.58, 35.37, 31.18, 29.56, 29.45, 28.55, 28.44, 25.55, 21.97, 13.29. *m/z* (LSIMS⁺): 195 (100%) [C₈C₁im]⁺. *m/z* (LSIMS⁻): 97 (100%) [HSO₄]⁻. Calc. for C₁₂H₂₄N₂O₄S: C, 49.29; H, 8.27; N, 9.58%. Found: C, 49.14; H, 8.34; N, 9.57%.

2.4.18 Synthesis of 1-methyl-3-octylimidazolium trifluoromethanesulfonate [C₄C₁im][OTf]

A mixture of 1-methyl-3-octylimidazolium chloride (66.93 g, 0.29 mol) and acetone (100 mL) was added to sodium trifluoromethanesulfonate (54.89 g, 0.31 mol) and the reaction was stirred for 48 hours at room temperature. The resulting organic phase was filtered and washed with water until chloride tests proved negative (silver nitrate test). The solvent was then removed via rotary evaporation and the remaining liquid was dried *in vacuo* (24 hours) giving 1-methyl-3-octylimidazolium trifluoromethanesulfonate (66.28 g, 66.2 %) a colourless viscous liquid. Found: ¹H NMR (400 MHz, DMSO-d₆): δ 8.46 (s, 1H), 7.17 (s, 1H), 7.09 (s, 1H), 3.69 (t, *J* = 6.8 Hz, 2H), 1.34 (q, *J* = 6.8 Hz, 2H), 0.80 – 0.67 (m, 11H), 0.31 (t, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, DMSO-weak): δ 137.64, 136.31, 127.92, 125.14, 123.03, 121.95,

121.77, 119.89, 118.77, 115.58, 48.95, 40.20, 39.99, 39.78, 35.13, 32.04, 31.06, 29.35, 28.36, 28.27, 25.40, 21.88, 13.09, 12.97. m/z (LSIMS⁺): 195 (100%) [C₈C₁im]⁺. m/z (LSIMS⁻): 149 (100%) [CF₃SO₃]⁻. Calc. for C₁₃H₂₃F₃N₂O₃S: C, 45.34; H, 6.73; N, 8.13%. Found: C, 45.45; H, 6.73; N, 8.23%.

2.4.19 Synthesis of 1-butyl-aza-[18-C-6H][OAc]

NaH (80 mmol, 60 % dispersion in mineral oil, 2.68 g) and dry THF (200 mL) were added to a 1 L round bottomed flask and cooled to 0 °C in an ice bath. N-butyl-diethanolamine (20 mmol, 3.22 g) was dissolved in dry THF (200 mL) and added dropwise to the cooled system during 1 h. the ice bath was then removed and the mixture was heated to reflux for 2 h. The system was cooled to 0 °C in an ice bath and then a solution of THF (200 mL) and tetraethylene glycol ditosylate was added (20 mmol, 10.05 g). The ice bath was then removed and the mixture was stirred under reflux for 48 h. Upon completion of the reaction, the mixture was concentrated and water was added (100 mL). The mixture was extracted with DCM (3 x 140 mL). The combined organic layer was washed with water (3 x 100 mL) and dried by anhydrous MgSO₄. The yellow oily product was collected by evaporating the solvent *in vacuo* and stored in a refrigerator.

Acetic acid (6 mmol) was then added to the solution of the product with water (80 mL) and THF (80 mL). The mixture was then stirred for 24 h at room temperature. The THF and existing excess aza-crown ether were extracted off with DCM (5 x 40 mL). The excess water was removed in vacuo and 1-butyl-aza-[18-C-6H][OAc] was obtained. ¹H NMR (400 MHz, DMSO-d₆): ¹H NMR (400 MHz, DMSO-d₆) δ 5.76 (s, 1H), 3.59 – 3.36 (m, 16H), 2.62 (t, *J* = 6.0 Hz, 5H), 2.44 (dt, *J* = 16.5, 7.3 Hz, 3H), 1.91 (s, 5H), 1.41 – 1.19 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 4H). ¹³C NMR (101 MHz, DMSO-weak): δ 172.52, 70.56, 70.43, 70.17, 69.84, 59.63, 57.04, 55.37, 55.31, 54.25, 29.60, 21.58, 20.40. m/z (LSIMS⁺): 320 (100%) C₁₆H₃₄NO₅⁺. m/z (LSIMS⁻): 59 (100%) [OAc]⁻. Calc. for C₁₈H₃₇NO₇: C, 56.97; H, 9.83; N, 3.69%. Found: C, 57.12; H, 10.01; N, 3.58%.

2.4.20 Synthesis of 2,6-Bis{[bis(2-pyridylmethyl)amino]methyl}-4-methylphenol (H-bpmp)

Under N₂, a mixture of bis(2-pyridylmethyl)amine and triethylamine in anhydrous THF was added dropwise to a stirred solution of 2,6-bis(chloromethyl)-4-methylphenol also in dry THF at 0 °C. Upon completion, the mixture was allowed to warm to room temperature. After 2 days, the resulting mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was dissolved in methylene chloride, washed with brine, and dried over anhydrous Na₂SO₄. Following filtration the solution was evaporated to dryness under reduced pressure, and a crude product was obtained as a sticky solid. Recrystallization from hexane : ether (1:1) afforded pure H-bpmp as a light yellow solid. Characterisation in agreement with reference.⁷⁶

2.5 Metal Extraction

2.5.1 Sample Preparation

The metal extractions were performed for each IL by contacting 1 mL of the ionic liquid with varying volumes of the model fuel (10 – 100 mL) at a uniform concentration for 1 min on a Heidolph Multi Reax Vortex Shaker subsequently leaving overnight to phase separate and settle. 2 mL of the fuel phase was then transferred to a centrifuge tube and contacted with 2 mL of a 4M HNO₃ solution for 1 min on the shaker. This was also left to settle overnight and 1 mL of the acid (HNO₃) phase was then transferred to a centrifuge tube and diluted with 3 mL of distilled water to produce a 1M solution. All extractions were run and left overnight in a temperature regulated room at 22 °C. Once a range of samples were prepared the metal concentration was determined via ICP-OES and partition coefficients for each sample were calculated via excel and processed through Origin.

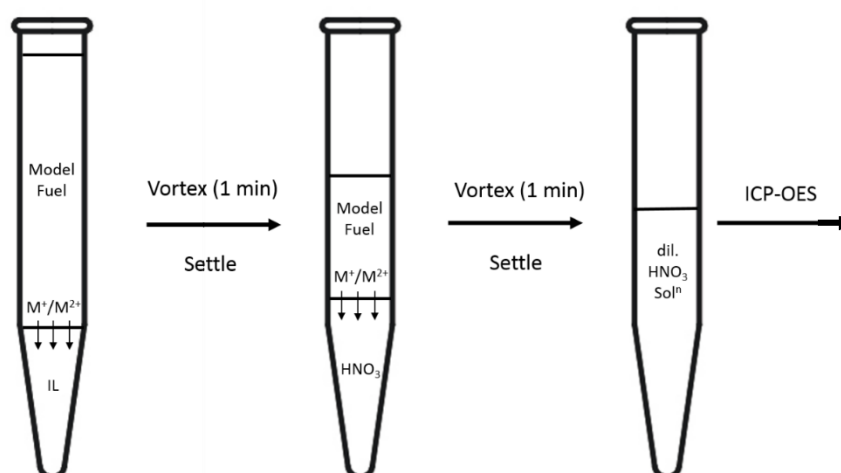


Figure 2.1 - Schematic Diagram for the Stepwise Extraction of Metals from n-hexadecane using ILs

2.5.2 Inductively coupled plasma – Optical Emission Spectroscopy (ICP- OES)

2.5.2.1 Methodology

The concentration of metal ions were determined for each sample via ICP-OES after performing a calibration and background check for each of the expected ions. Standards for calibration were prepared using multielement standard solution 1 TraceCERT® in 10% nitric acid at concentrations of 0.2, 5 and 25 mg kg⁻¹. To ensure that the data was reliable data points were repeated three times for each sample. The partition coefficients of these extractions were then calculated via Excel and experiments were repeated three times to provide error bars across the range of volumes.

3 Properties of Ionic Liquids

3.1 Introduction

To synthesise the most suitable IL candidate for an application in the extraction of Na^+ , Zn^{2+} and Cu^{2+} from diesel fuel, there has to be a core understanding of the properties of the ILs. The cation and especially anion effects within the extraction of the desired metal from diesel need to be fully described. It must be ensured that the designed ILs are immiscible with the fuel and possesses the optimal physical properties to provide the greatest partitioning of the metal from the fuel to the IL phase. A range of characterisations thought to be essential in this application were carried out to determine the main factors that affect the extraction mechanisms in this study.

The properties of the ILs investigated include:

1. Donor Number via ^{23}Na NMR
2. Kamlet Taft Solvent Parameters
3. Water Content Analysis
4. Density Measurements
5. Computational Critical Property Calculations
6. Interfacial Tension (IFT) between ILs and n-hexadecane
7. Viscosity

3.2 Donor Number (DN)

3.2.1 Background

Donor number, DN, was determined to investigate which ILs have an increased affinity for the extraction of metals in diesel fuel. Victor Gutmann defined DN as a quantitative measure for the tendency to donate electron pairs to acceptors. He demonstrated that DN can be used to measure the electron pair donation ability of a solvent.⁷⁷ There has been much development on this work to define the

effectiveness of solvents as electron pair donors.⁷⁸ The DN of an IL allows the prediction of the strength of an interaction between the IL's anion and the targeted metal ions, or other Lewis acids. It could also be used to produce a database that will predict the probability for the coordination of the ILs anions to metal centres or other electrophilic substrates.⁷³

²³Na NMR was used in this research to determine DNs of the ILs defining their Lewis basicity. Here, DN was used to determine the strength of interaction of IL anions with metal ions. The purpose of which was to quantify the potential for extracting metal ions dissolved from market fuels and the corresponding models. Quantification and comparison of the ILs interactions provided information on how the extraction mechanism proceeds.

3.2.2 Results and Discussion

The top performing candidates for the extraction of metals from diesel fuel will have a high DN as this shows an increased electron pair donation ability of the IL. The data shows a diverse range of DNs for the ILs selected for this study providing a good indication of which ILs will be most efficient for the partition of metals into the IL phase via a biphasic extraction. [NTf₂]⁻ ILs with varying chain lengths were measure to determine if the length of the alkyl chain had an effect on the DN value. It is clear to see from the data that as the chain length decreases the DN and thus strength on interaction with the metal increases (C₂ > C₃ > C₄ > C₁₀). The ILs [C₄C₁im][Me₂PO₄], [C₄C₁im][S₂CN(C₂H₅)₂] and [C₈C₁im]Cl display the highest DNs which implies they should give high partitioning of metals into the IL phase via a biphasic extraction. However, due to their elemental constituents containing phosphate, sulfur and chlorine atoms a fuel application may not be suitable due to emission standards. These ILs still remain of great interest from a theoretical stand point and data can be translated across to other applications.

Table 3.1 - ^{23}Na NMR chemical shift data and determined donor numbers

Ionic Liquid	^{23}Na	
	Donor Number [kcal mol ⁻¹] (ref)	Chemical Shift [ppm]
[C ₂ C ₁ im] [NTf ₂]	10.8	-10.4
[C ₃ C ₁ im] [NTf ₂]	8.8	-11.4
[C ₁₀ C ₁ im] [NTf ₂]	6.3	-12.5
[C ₄ C ₁ im][N(Tf) ₂]	9.9 (10.2) ⁷³	-10.9
[C ₄ C ₁ im][OTf]	19.8	-6.2
[C ₄ C ₁ im][MeSO ₄]	19.6	-6.3
[C ₄ C ₁ im][Me ₂ PO ₄]	28.6	-2.0
[C ₄ C ₁ im][HSO ₄]	13.6	-9.1
[C ₄ C ₁ im][OAc]	21.3	-5.4
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	32.2	-0.3
[C ₄ C ₁ pyrr][N(Tf) ₂]	7.4	-12.0
[C ₄ C ₁ pyrr][OTf]	16.4	-7.7
[C ₈ C ₁ im]Cl	70.0 (69.2) ⁷³	17.7
[C ₈ C ₁ im][OTf]	18.5 (18.6) ⁷³	-6.8
[C ₈ C ₁ im][HSO ₄]	19.4	-6.4
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	24.6	-3.9

[C₄C₁im][OAc] and [(CH₃)₂NH₂][(CH₃)₂NCOO] give slightly lower DN's but are of particular interest as they contain atoms of CHNO only. This suggests they will be some of the best performing candidates as a compromise between performance and requirement. DN will be used in addition to other physical and chemical properties to determine the optimum properties for an efficient extraction of metals from diesel fuel. To provide a more in-depth study and the reliability of trends solvency properties were defined by another method.

3.3 Kamlet-Taft Measurements

3.3.1 Background

Kamlet-Taft solvent descriptors have been used to define polarity across a wide range of solvents including applications such as sub- and supercritical fluorinated ethane solvents, hydrofluoroethers and hydrofluoroether azeotropic mixtures and a range of solvents of interest in green chemistry.^{79–81} In the field of ILs Kamlet-Taft solvent descriptors have been used in a number of applications such as explanations of their reactivity with anionic nucleophiles⁸² and predicting how ILs work in catalysis.⁸³ Using solvachromatic dyes, Kamlet-Taft values were gathered for each IL to determine their hydrogen-bond acidity / basicity (α / β) and dipolarity/polarizability (π^*) effects which explain the ways in which solvents interact with solutes. These are capable of capturing the complexity of interactions that give rise to a solvent's overall polarity. The multi-parameter polarity scales introduced by Kamlet and Taft are based upon Linear Solvation Energy Relationships composed of the complimentary orthogonal scales of α , β and π^* (Equation 3.1).⁸⁴ These scales combined provide greater detail on the polarity of a solvent in comparison to single parameter scales.

$$(XYZ) = (XYZ)_0 + a\alpha + b\beta + s\pi^* \quad (3.1)$$

π^* is the value that most resembles 'polarity' in the absence of any hydrogen bonding effects. The IL values for π^* are relatively high in comparison with most non-aqueous molecular solvents (Table 3.2 and 3.3). π^* values remain steady for each of the ILs used in this study suggesting that their 'polarity' is similar.

$$\pi^* = 0.314 (27.52 - \nu_{\text{N,N-diethyl-4-nitroaniline}}) \quad (3.2)$$

The α -values are largely determined by the nature of the cation, with a smaller anion effect, and fall between 0.44 – 0.65 for the ILs measured in this study. The α values describes the ability of a solvent to donate a proton in a solvent-solute hydrogen bond. In this study the α parameter will be of importance in the understanding how the extraction mechanism proceeds. The ILs cation could extract the metals counter part within the additive directly affecting a successful extraction.

$$\alpha = 0.0649E_T^{30} - 2.03 - 0.72\pi^* \quad (3.3)$$

Where Reichardt's E_T^{30} scale displays the hydrogen bond donating ability of the IL:

$$E_T^{30} = \frac{28592}{\lambda_{max}} \quad (3.4)$$

For this study, the greatest interest lies in the Kamlet Taft β -values which is directly related to the anion of the IL. This allows correlation between the coordination ability of the IL anion and metal in diesel fuel. This value has the greatest variation throughout the ILs used in this study (Table 3.2 and Table 3.3).

$$\beta = \frac{1.035 \nu_{N,N\text{-diethyl-4-nitroaniline}} + 2.64 - \nu_{4\text{-nitroaniline}}}{2.80} \quad (3.5)$$

3.3.2 Results and Discussion

The Kamlet Taft parameters were determined via the Reichardt's 30 dye set (Figure 3.1) following the methodology outlined in chapter 2.

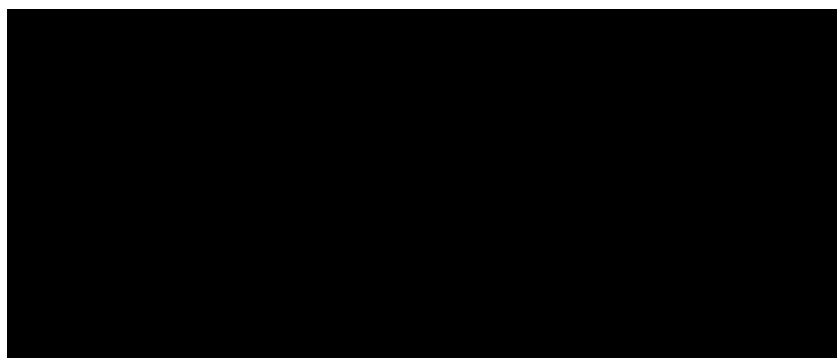


Figure 3.1 - Structures of the dyes used in the determination of Kamlet-Taft parameters; a) Reichardt's Dye 30, b) *N,N*-diethyl-4-nitroaniline and c) 4-nitroaniline

Not all of the Kamlet-Taft values for the synthesised ILs could be measured via this method (Chapter 2).

Table 3.2 - Kamlet-Taft parameters determined for the ILs used in this study acquired using Reichardt's Dye 30, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline (via equations 3.2, 3.3, 3.4 and 3.5).

Ionic Liquid	α (ref)	β (ref)	π^* (ref)
[C ₄ C ₁ im][N(Tf) ₂]	0.65 (0.62) ⁸⁵	0.24 (0.24) ⁸⁵	0.92 (0.98) ⁸⁵
[C ₄ C ₁ im][OTf]	0.65 (0.63) ⁸⁵	0.50 (0.46) ⁸⁵	0.94 (1.01) ⁸⁵
[C ₄ C ₁ im][MeSO ₄]	0.57 (0.53) ⁷⁴	0.67 (0.66) ⁷⁴	1.02 (1.06) ⁷⁴
[C ₄ C ₁ im][Me ₂ PO ₄]	0.48 (0.45) ⁷⁴	1.13 (1.13) ⁷⁴	0.93 (0.98) ⁷⁴
[C ₄ C ₁ im][OAc]	0.60 (0.57) ⁸²	1.26 (1.18) ⁸²	0.93 (0.89) ⁸²
[C ₄ C ₁ pyrr][N(Tf) ₂]	0.45 (0.73) ⁸⁶	0.20 (-0.11) ⁸⁶	0.90 (0.89) ⁸⁶
[C ₄ C ₁ pyrr][OTf]	0.44 (0.40) ⁸⁷	0.47 (0.46) ⁸⁷	0.94 (1.02) ⁸⁷
[C ₈ C ₁ im]Cl	0.47	1.00	0.94
[C ₈ C ₁ im][OTf]	0.65	0.53	0.91
Ethanol	(0.86) ⁸⁸	(0.75) ⁸⁸	(0.54) ⁸⁸

The acidic nature of $[\text{HSO}_4]^-$ ILs caused them to react with the dyes and the high viscosity of $[\text{C}_4\text{C}_1\text{im}][\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ made loading cuvettes in the absence of air bubbles difficult and hence obtaining spectra. However, the data provides a large enough range to correlate the ability of the IL extraction towards the metal in diesel fuel.

The α parameters here do show variation which could affect the extraction if the mechanism proceeds via the cation extracting the metal's counterpart in the additive present in the n-hexadecane.

The β values for the ILs show a good agreement with literature (Table 3.2) and display a similar trend to the DN values described earlier in this chapter. Their correlation will be discussed further in Chapter 4. The $[\text{N}(\text{Tf})_2]^-$ ILs have the lowest β values which would suggest that their ability to interact with the metals in diesel fuel would be the weakest but still have the ability to extract the metals. The $[\text{OTf}]^-$ and $[\text{MeSO}_4]^-$ ILs provide intermediate β values (0.47 – 0.67) suggesting that they would extract the metals to a greater extent based on these parameters. As with the DN analysis the highest values were given by $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ and $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$. This provides further evidence to suggest that these ILs will provide the largest partitioning of metals into the IL phase via a biphasic extraction. Of particular interest is $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ giving the highest of all β values measured at 1.26 and having a chemical composition which is highly suitable for a fuel application.

The Kamlet Taft parameters were determined via two different dye sets to ensure the reliability of the trends given via these solvent descriptors. The second set of parameters were determined with a similar methodology (Chapter 2) but different set of dyes; Reichardt's Dye 33 (0.9 mM), 4-nitrophenol (0.6 mM) and 4-nitroanisole (0.7 mM) (Figure 3.2).

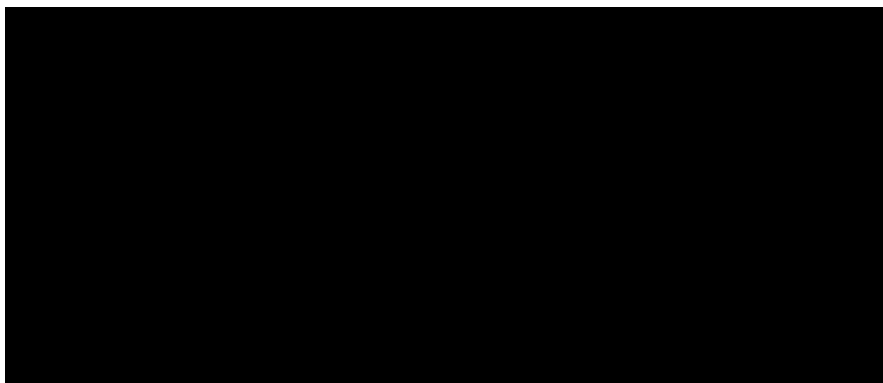


Figure 3.2 - Structures of the dyes used in the determination of Kamlet-Taft parameters; a) Reichardt's Dye 33, b) 4-nitrophenol and c) 4-nitroanisole.

The following calculations were employed in the determination of the α , β and π^* values for the ILs:

$$\alpha = 0.649 E_T^{33} - 2.03 - 0.72\pi^* \quad (3.6)$$

$$\beta = 0.346 (35.045 - \nu) - 0.57 \pi^* - 0.12 \delta \quad (3.7)$$

$$\pi^* = 0.427 \cdot (34.12 - \nu) \quad (3.8)$$

Where E_T^{33} is determined via:

$$E_T^{30} = 0.9986 E_T^{33} - 8.6878 \quad (3.9)$$

Generally the Kamlet Taft values are higher than the values determined with the Reichardt's 30 dye set. A similar trend is shown through these values, with the $N(Tf)_2$ ILs giving the lowest β values and the $[OTf]^-$ and $[MeSO_4]^-$ anion based ILs providing intermediate β values (0.59 – 0.74). The strongest candidates for this application are also assumed to be $[C_4C_{1im}][Me_2PO_4]$, $[C_4C_{1im}][OAc]$ and $[C_8C_{1im}][Cl]$ from this data. However, $[C_4C_{1im}][OAc]$ is still a strong candidate but does not

display the highest β values in this dye set and is outperformed by [C₄C₁im][Me₂PO₄]

Table 3.3 - Kamlet-Taft parameters determined for the ILs used in this study acquired using Reichardt's Dye 33, 4-nitrophenol and 4-nitroanisole (via equations 3.6. 3.7 and 3.8).

Ionic Liquid	α (ref)	β (ref)	π^* (ref)
[C ₄ C ₁ im][N(Tf) ₂]	0.72 (0.69) ⁸⁹	0.45 (0.41) ⁷⁴	0.84 (0.97) ⁸⁹
[C ₄ C ₁ im][OTf]	0.69 (0.62) ⁸⁹	0.59 (0.60) ⁷⁴	0.94 (1.03) ⁸⁹
[C ₄ C ₁ im][MeSO ₄]	0.59	0.74	1.04
[C ₄ C ₁ im][Me ₂ PO ₄]	0.48	1.16	1.04
[C ₄ C ₁ im][OAc]	0.41	1.02	1.20
[C ₄ C ₁ pyrr][N(Tf) ₂]	0.57	0.42 (0.41) ⁷⁴	0.82
[C ₄ C ₁ pyrr][OTf]	0.53	0.62	0.88
[C ₈ C ₁ im]Cl	0.49 (0.33) ⁹⁰	0.95 (0.90) ⁹⁰	1.02 (1.09) ⁹⁰
[C ₈ C ₁ im][OTf]	0.74	0.71	0.88

The purpose of using a secondary dye set was to support the trends of the solvent parameters determined for the ILs alongside the referenced values thus increasing the reliability of the data. The graph (Figure 3.3) shows the comparison of the β values for each of the ILs determined via 4-nitroaniline from the first dye set and 4-nitrophenol from the second dye set. The β value was selected for comparison as this the most interesting parameter for this study. This is because the β value provides hydrogen-bond basicity of the IL thus displaying how effective the anion is likely to be at chelating to the metal in n-hexadecane.

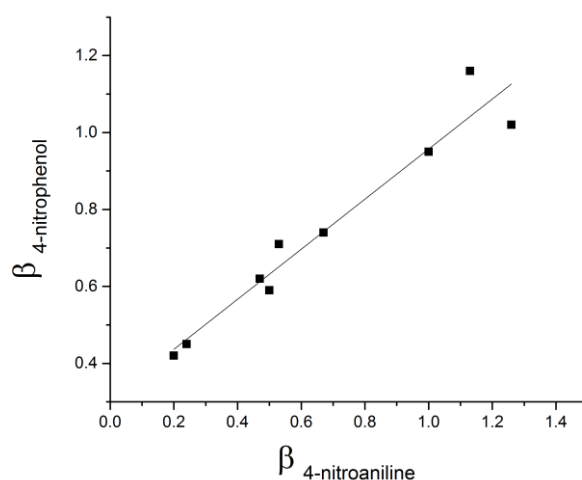


Figure 3.3 - Kamlet Taft β Value Comparison for the dyes 4-nitrophenol and 4-nitroaniline

The graph shows a clear correlation of the β values determined via two different dyes increasing the reliability of the solvent descriptor of the measurable ILs. It must be noted that only the first dye set will be used further in the study as vast amounts of data is available on ILs using these dyes. DN and Kamlet Taft parameters have indicated how the IL will interact with the metal but properties of the liquid and other components present need to be evaluated.

3.4 Water Content

3.4.1 Background

Karl Fischer titration is an analytical method that can determine the water content within a sample using volumetric or coulometric titration. The German scientist Karl Fischer introduced this method in 1935.⁹¹ At volumetric titration the added volume is measured and the demanded value is calculated by a stoichiometric equation. The sensitivity of a volumetric titration is 10 μg of water.⁹² The water content for the ILs used in this study was measured after drying the ILs for 24 hours *in vacuo* at 60 °C. The purpose of the Karl Fischer titration was to determine how the water

content could affect the extractions or characterisation of the ILs in their most dehydrated form.

3.4.2 Results and Discussion

Table 3.4 - Water content data for ILs used in this study calculated via Karl Fischer titration.

Ionic Liquid	Water Content [ppm]	Molarity [mol/L]
[C ₄ C ₁ im][N(Tf) ₂]	107	0.006
[C ₄ C ₁ im][Me ₂ PO ₄]	1337	0.074
[C ₄ C ₁ im][MeSO ₄]	1195	0.066
[C ₄ C ₁ pyrr][OTf]	139	0.008
[C ₄ C ₁ im][OTf]	224	0.012
[C ₄ C ₁ pyrr][N(Tf) ₂]	142	0.008
[C ₄ C ₁ im][OAc]	1129	0.063
[C ₈ C ₁ im][OTf]	159	0.009
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	3290	0.183
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	3514	0.195
[C ₄ C ₁ im][HSO ₄]	2238	0.124
[C ₈ C ₁ im][HSO ₄]	778	0.043
[C ₈ C ₁ im]Cl	1699	0.094
[C ₂ C ₁ im][NTf ₂]	98	0.005
[C ₃ C ₁ im][NTf ₂]	101	0.006
[C ₁₀ C ₁ im][NTf ₂]	105	0.006

A variety of water contents displayed were post-drying with the highest water content being 0.33 % (3290 ppm) for [C₄C₁im][S₂CN(C₂H₅)₂] and lowest being 0.01 % (98.4 ppm) for [C₂C₁im][NTf₂] which would be expected due to the [N(Tf)₂]⁻ ILs

being the most hydrophobic ILs used in this study.⁹³ This information proves beneficial as we can show how water content affects the extractions and if they are applicable for a fuel application. Determining if the ILs are hydrophilic or hydrophobic can provide other uses such as a dehydrating agent in addition to a metal extractor. A low water content would be desirable so that we can confirm that the ILs ability in the extraction of metals is purely due to the IL itself. Water would also extract metals from the fuel phase. It must be noted that water in the fuel would not be desirable in the fuel industry. It is known that water in storage tanks causes algae growth and would be preferable to be removed from the system. However, it is assumed that water would reside in the IL layer in the application and could even benefit the industry by removing water from 'wet' fuel.

3.5 Density Measurements

3.5.1 Background

Density is a core property of any matter and applied in this study. For ILs it has been measured in a range of experimental and theoretical studies.^{94–97} ILs with a greater density than n-hexadecane are required so the IL can reside at the bottom of the fuel post biphasic mixing. The measurements were also taken into consideration to determine if density has any direct effect on the extraction of the metal from diesel fuel. In addition to this, the density measurements were required for the calculation of other properties in this study including viscosity and interfacial tension.

Density, ρ , was measured using a vibrating U-tube where the natural frequency of the liquid is measured whilst temperature remains constant.

$$\tau = 2\pi \sqrt{\frac{\rho v + m}{c}} \quad (3.10)$$

The period τ , is provided by the density of the liquid, cell volume, v , the cell mass, m , and the spring constant C .

$$\rho = \frac{\tau^2 - B}{A} \quad (3.11)$$

where,

$$A = \frac{4\pi^2 v}{c}, B = \frac{4\pi^2 m}{c} \quad (3.12)$$

The unit can be calibrated with two different substances to determine the constants A and B thus determining the density of the liquid.

3.5.2 Results and Discussion

Table 3.5 - Density Measurements (25 °C) for the ILs Used in this Study

Ionic Liquid	Density [g cm ⁻³] (Ref)
[C ₄ C ₁ im][N(Tf) ₂]	1.43 (1.43) ⁹⁸
[C ₄ C ₁ im][OTf]	1.30 (1.30) ⁹⁹
[C ₄ C ₁ im][MeSO ₄]	1.20 (1.21) ¹⁰⁰
[C ₄ C ₁ im][Me ₂ PO ₄]	1.16 (1.16) ¹⁰¹
[C ₄ C ₁ im][HSO ₄]	1.27
[C ₄ C ₁ im][OAc]	1.07 (1.05) ¹⁰²
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	1.08
[C ₄ C ₁ pyrr][N(Tf) ₂]	1.39 (1.40) ¹⁰³
[C ₄ C ₁ pyrr][OTf]	1.25 (1.25) ¹⁰⁴
[C ₈ C ₁ im]Cl	1.02 (1.00) ⁹⁸
[C ₈ C ₁ im][OTf]	1.20 (1.20) ¹⁰⁵
[C ₈ C ₁ im][HSO ₄]	1.16
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	1.05

The data shows that the $[\text{N}(\text{Tf})_2]^-$ ILs have the highest density of the ILs measured in this study. From these results it is shown that the cation has an effect on the density of the IL. The butylimidazolium cation gives higher densities which can be seen when a decrease in value occurs for the both $[\text{NTf}_2]^-$ and $[\text{OTf}]^-$ ILs when the cation is changed for a pyrrolidinium cation with a butyl side chain. A further decrease in density with the $[\text{OTf}]^-$ ILs can be seen when the imidazolium cation with an octyl side chain is present suggesting that longer alkyl chain lengths decrease the density of the ILs. This will be due to an increase in packing distance increasing the free volume and thus the liquid having an overall lower density.¹⁰² $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ possesses the lowest density of all the ILs used in this research. Theoretically a lower density would be preferable. This would allow ease of migration of the metal ions from the fuel phase into the IL phase due to the molecules being less closely packed together in the IL. It is shown from the data that $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$, $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ and $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ all give relatively low densities, which would perform well in this application. For the fuel industry $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ and $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ would be most suitable due to their chemical constituents. In addition to this these ILs have been shown to have other desirable properties for this application such as high DN and high β values, making them some of the best candidates so far. ILs densities have been shown to decrease with increasing temperature suggesting that an elevated temperature could increase the partitioning of metals from the fuel to the IL phase.¹⁰⁶

The critical property values for the ILs (Appendix C) calculated via the methodology stated previously (Chapter 2) were used to calculate density via a model (Equation 3.13) designed by Valderrama-Robles.¹⁰⁷ This was used to draw a comparison between the calculated and experimental density values.

Table 3.6 – Calculated and Experimental Density for the ILs Used in This Study

Ionic Liquids	ρ_{calc}	ρ_{exp}	% $\Delta\rho$
[C ₄ C ₁ im][N(Tf) ₂]	1.39	1.43	-2.8
[C ₄ C ₁ im][OTf]	1.31	1.29	1.5
[C ₄ C ₁ im][MeSO ₄]	1.21	1.20	0.8
[C ₄ C ₁ im][Me ₂ PO ₄]	1.11	1.16	-4.4
[C ₄ C ₁ im][HSO ₄]	1.23	1.27	-3.2
[C ₄ C ₁ im][OAc]	1.07	1.07	0.0
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	0.87	1.08	-21.5
[C ₄ C ₁ pyr][N(Tf) ₂]	1.34	1.39	-1.6
[C ₄ C ₁ pyr][OTf]	1.23	1.25	-1.7
[C ₈ C ₁ im]Cl	1.02	1.02	0.0
[C ₈ C ₁ im][OTf]	1.20	1.20	0.0
[C ₈ C ₁ im][HSO ₄]	1.14	1.16	-1.7
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	1.11	1.05	5.5

Constants A and B, temperature T, normal boiling point temperature T_b and critical temperature T_c are used to calculate model density ρ (Equation 3.13);

$$\rho(g\text{ cm}^{-3}) = (A/B) + (2/7) \cdot \{(A \cdot \ln B)/B\} \frac{(T - T_b)}{(T_c - T_b)} \quad (3.13)$$

where;

$$A = a + b \cdot M/V_c \quad \text{and} \quad B = (c/V_c + d/M) \cdot V_c^\delta \quad (3.14 \text{ and } 3.15)$$

molecular mass M, critical volume V_c and constants, a = 0.3411, b = 2.0443, c = 0.5386, d = 0.0393 and e = 1.0476 are used in the calculation of the constants A and B. The ρ calculated from the model is then compared with the experimental values including % deviation (Table 3.6). A majority deviate by 4% and below with the exception of the carbamate ILs which seem to have a larger deviation from the

experimental value. This can be explained by the Valderrama-Robles model accounting for common ILs and these contain less common components.

This comparison was employed to confirm the reliability of the density results as this is an important property with regards to this research. Density is utilised in other calculations and calibrations in this work, including the measurement of IFT and viscosity. The calculated density was also used in Aspen to define the ILs in the NRTL model.

3.6 Interfacial Tension Measurements (IFT)

3.6.1 Background

Interfacial tension (IFT) is an important parameter when it comes to the analysis of biphasic extractions in a liquid-liquid system. The IFT influences the miscibility of the two phases and the transport of the metal ions between them. As a result of the density measurements the IFT was measured via the pendant drop method as it was assumed that an interface could be formed (Chapter 2). This was first derived in 1883 by Bashforth and Adams.¹⁰⁸ The IFT is determined via the Young-Laplace equation which takes into account the differences in pressure (Δp) above and below a curved section of a droplet that has principal radii of curvature r_1 and r_2 , and an interfacial tension (γ) (Equation 3.14).

$$\Delta p = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3.16)$$

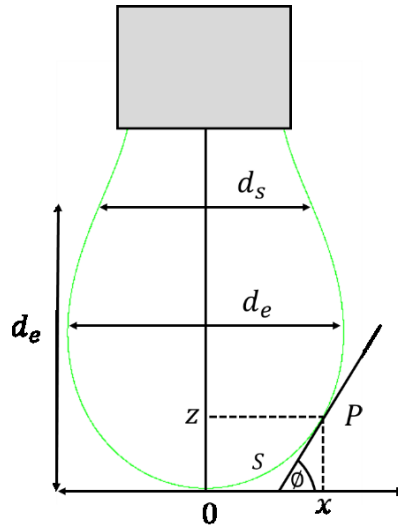


Figure 3.4 - displays the parameters involved in the fit of the Young-Laplace equation; s is the length of the arc along the drop profile, ϕ is the angle between the tangents at point $P(x, z)$ and the x -axis. d_e is the diameter at the equator and d_s is the diameter at the selected plane at a height d_e from the x -axis.

3.6.2 Results and Discussion

IFT values were obtained for six of the ILs in this research (Table 3.7). For the remainder of the ILs, IFT was immeasurable by the instrumentation used due to the IFT being too low between the IL and hexadecane phases. This impacted the ability to draw conclusions but to utilise the results the IFT values for these ILs are assumed to be lower than the measurable ILs in this study. A desirable IL for this application would require a low IFT during mixing to enable the metal ions to transfer to the IL phase. However, a reasonable IFT will still be required so that once transferred the metal ions will remain in the IL phase and provide a good separation with n-hexadecane.

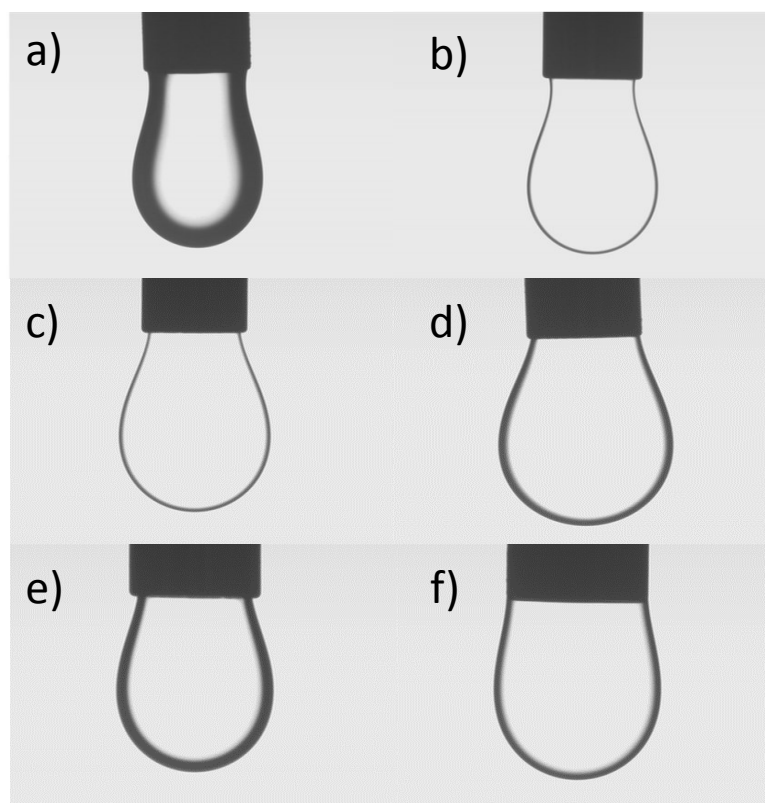


Figure 3.5 - Images of IL droplets in n-hexadecane; a) $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$, b) $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$, c) $[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_4]$, d) $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$, e) $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$, f) $[\text{C}_8\text{C}_1\text{im}][\text{HSO}_4]$

The image profiles of the droplets (Figure 3.5) display the individuality of the ILs at their maximum before descending from the needle tip to the bottom of n-hexadecane in the cuvette. Due to the decreased sample range via the employed instrumentation it was difficult to draw conclusions for the IFT data individually.

Table 3.7 – IFT Values for the ILs Used in This Study

Ionic Liquid	IFT [N.m]
[C ₄ C ₁ im][MeSO ₄]	2.34 ± 0.00
[C ₄ C ₁ im][Me ₂ PO ₄]	2.02 ± 0.08
[C ₄ C ₁ im][OAc]	2.54 ± 0.09
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	0.96 ± 0.01
[C ₈ C ₁ im]Cl	0.88 ± 0.02
[C ₈ C ₁ im][HSO ₄]	1.71 ± 0.00

From the data gathered (Table 3.7) it can be seen that the ILs possessing the imidazolium cation with a butyl chain generally display a higher IFT than that of the ILs containing the imidazolium cation with an octyl chain. This cannot be definitive as there are no ILs measured with the same anion but varying cation. However, in previous research it is shown that with imidazolium and pyrrolidinium based ILs there is a decrease in surface tension values for ILs with longer alkyl side chains on both cation and anion.¹⁰⁹ Therefore it can be assumed that the longer the alkyl side chain of the cation and anion the more favourable is self-aggregation and aggregation of mixtures. The IFT measurements have provided important insight to the ILs behaviour and how this property will affect the biphasic extraction of metals from diesel fuel. It is shown that a longer alkyl chain and thus overall low IFT would be preferred in the extraction of metals so that during vortex aggregation of the IL and n-hexadecane is favourable. This would allow the migration of metal ions from the diesel fuel to the IL phase. Therefore transfer of the metal ions will be dependant on IFT but chelation relies on other properties.

3.7 Viscosity Measurements

3.7.1 Background

Rheology is the study of how matter responds to deformation resulting from the application of force.¹¹⁰ The viscosity, η , of ILs is an essential parameter for their use in this application and is formally defined as the fluid's resistance to flow. The viscosity of ILs have been shown to be determined by three main factors; size, shape, and the interaction between the cation and the anion.¹¹¹ In the extraction of metals from n-hexadecane it is important determine the most desirable viscosity of the IL. This can help to increase the partitioning of the target metal from the fuel phase to the IL phase in a biphasic extraction. The two plates model is used to define the parameters used here. In this case the top plate with a wide contact area, A , is sheared with a force, F .

Shear Stress is given by:

$$\tau = \frac{F}{A} \quad (3.17)$$

Shear stress, τ , is known as the ratio of shear force, F , and the shear area, A .

With a shear rate:

$$\dot{\gamma} = \frac{v}{h} = \frac{dv}{dh} \quad (3.18)$$

Shear rate, $\dot{\gamma}$, with v representing the velocity (m s^{-1}) and h (m) displaying the distance between the two plates. The variables dh and dv are applicable for the case of planar fluid layers.

Viscosity can thus be given as a ratio of shear rate and shear stress:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3.19)$$

The viscosity in this case is measured using the cone-and-plate rheometer (Figure 3.6) by syringing the specified small amount of liquid between the cone and plate and moving these with a measured force and speed. Using this type of rheometer the cone is used to measure the rotating geometry with an angle, α , of less than 4° using the plate as the stationary counterpart. In addition to this the conical shape is able to remove any air bubbles once the geometry gap is set. You can use truncated and non-truncated cones. In this set up we used truncated which has the following advantages:

- Zero friction between the cone and plate gives no static or kinetic friction contributions, which could affect the torque and thus final measurement.
- The cone or plate do not wear thus there are no changes of geometry parameters.

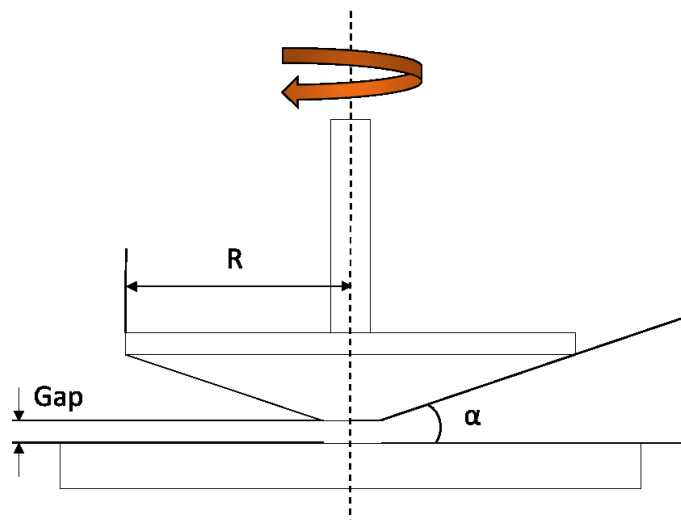


Figure 3.6 – Cone and Plate Rheometer Equipment

When using the cone and plate system it is vital that the filling takes place correctly and the shear gap must be filled completely to measure the liquid. The liquid should overflow approximately 1 mm from the cone edge (Figure 3.7).

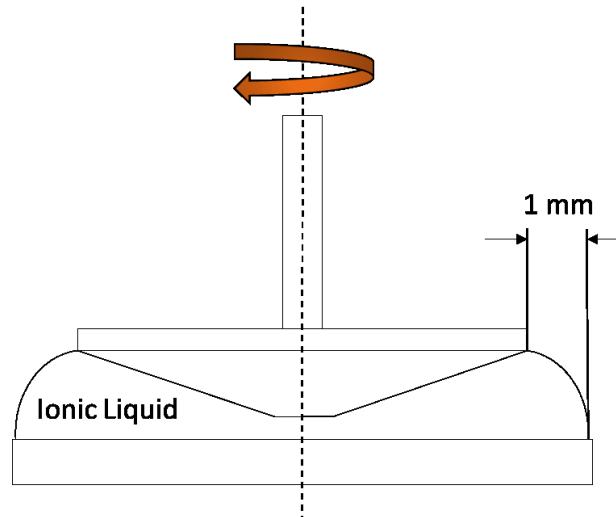


Figure 3.7 – Ideal loading of an IL on Cone and Plate Rheometer

The shear stress, τ , in a cone and plate measuring system is shown to be:

$$\tau = \frac{3M}{2\pi R^3} \quad (3.20)$$

M gives applied torque, R the radius of the cone.

The shear rate, $\dot{\gamma}$, in this system is determined by the rotation of the cone, the angular velocity, ω , and cone angle, α (Figure 3.6).

$$\dot{\gamma} = \frac{\omega}{\alpha} \quad (3.21)$$

Thus, the viscosity of the liquids using a cone and plate rheometer can be calculated integrating the above equations via:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{3M\alpha}{2\pi R^3 \omega} \quad (3.22)$$

A large radius cone and applied torque ensures that the liquid is not ejected from the cone when the shear is applied, this is essential when dealing with samples of a low viscosity. In addition to this measuring viscosity with a larger area, and thus the sensitivity will be greater, and hence you can measure low viscosities better. The radius, R, plays a large part in the calculation of viscosity, thus correct filling is essential. When shear is applied the ILs usually follow a Newtonian behaviour, which shows shear stress and shear rate being proportional thus viscosity being a function of temperature and pressure, constant at all Shear rates.¹¹² There can be two effects known as ‘shear-thickening’ and ‘shear-thinning’ when the shear rate is increased the liquid’s viscosity increases or decreases respectively.¹¹²

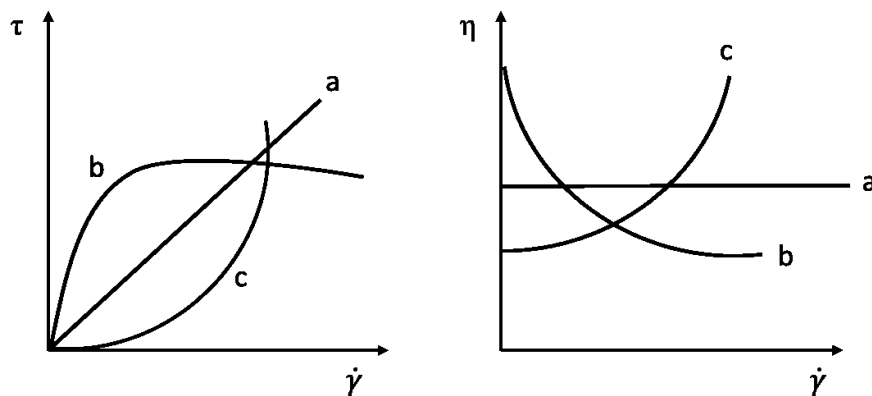


Figure 3.8 – The left hand graph represents shear stress (τ) vs. the shear rate ($\dot{\gamma}$); the right hand plot represents viscosity (η) vs. shear rate ($\dot{\gamma}$) with (a) displaying ideal Newtonian, behaviour, (b) displaying shear-thinning behaviour and (c) displaying shear thickening behaviour

The determination of the viscoelastic properties for a liquid can be carried out by performing creep and creep recovery shear stress steps. Continuous deformation will be displayed if constant stress is applied to an ideally viscous liquid.

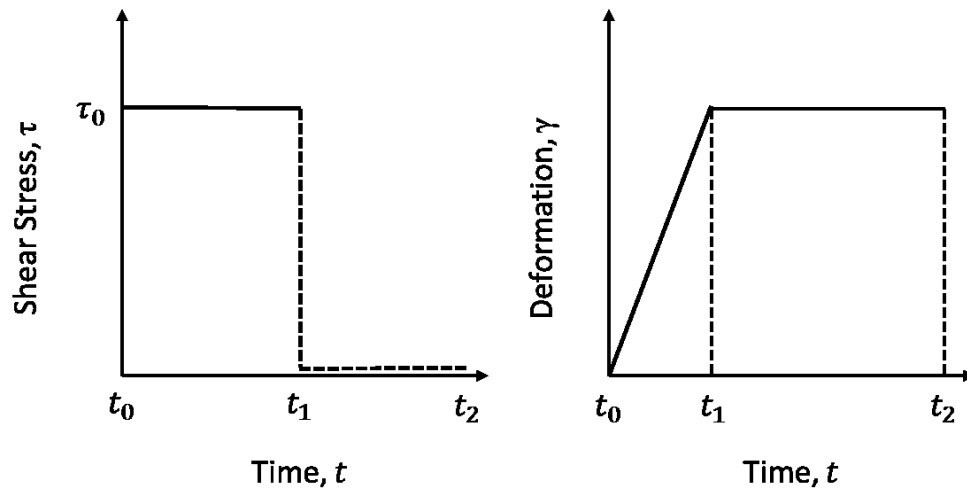


Figure 3.9 – The left hand graph illustrates the application and removal of shear stress, the right hand graph illustrates creep and creep recovery steps.

As there is no elastic property linked to the liquid when the stress is removed no reformation will occur. In the case of this study deformation energy is applied during the loading but cannot be stored thus once the load is removed the liquid remains deformed. The viscoelastic properties of the ILs and fuels were determined using the creep test which consists of two parts:

1. Constant shear stress (τ_0) is applied from t_0 to t_1
2. The stress is removed and the sample is left to rest from t_1 to t_2

The creep and recovery graph (Figure 3.9 - Right) resemble the curves of the ILs and fuels used in this study.

3.7.2 Results and Discussion

Table 3.8 – Viscosity of ILs used in this study at 25° C

Ionic Liquid	Viscosity at 25° C [mPa s] (Ref)
[C ₂ C ₁ im] [NTf ₂]	29.18 ± 1.31 (31.79) ¹¹³
[C ₃ C ₁ im] [NTf ₂]	41.80 ± 0.16 (43.70) ¹¹⁴
[C ₄ C ₁ im][N(Tf) ₂]	57.24 ± 0.15 (50.70) ¹¹⁵
[C ₄ C ₁ im][OTf]	77.95 ± 0.30 (84.40) ¹¹⁶
[C ₄ C ₁ im][MeSO ₄]	97.02 ± 2.08 (182.0) ¹¹⁷
[C ₄ C ₁ im][Me ₂ PO ₄]	136.20 ± 3.07 (585.0) ¹⁰¹
[C ₄ C ₁ im][OAc]	158.90 ± 0.23 (300.0) ¹¹⁸
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	2394.00 ± 9.91
[C ₄ C ₁ pyrr][N(Tf) ₂]	72.31 ± 0.08 (77.60) ¹¹⁹
[C ₄ C ₁ pyrr][OTf]	131.8 ± 0.17 (160.0) ¹²⁰
[C ₈ C ₁ im]Cl	3155.00 ± 25.90
[C ₈ C ₁ im][OTf]	181.00 ± 0.28
[C ₈ C ₁ im][HSO ₄]	2922.00 ± 8.90
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	53.45 ± 1.52
Water	(0.89) ¹²¹

The viscosity data for the ILs used in this study (Table 3.8) was measured and referenced to literature where feasible. Water content can effect the viscosity value and varies from different sources for hydrophilic ILs. There is an increase in the formation of clusters at high water concentrations and the anions become hydrated and weakens the interaction between the cations and anions at low water concentrations.¹²²

The hydrophobic ILs were referenced to show the reliability of viscosity measurements via the cone and plate rheometer.

It is evident from the viscosity data that a decrease in alkyl chain length causes an increase in viscosity e.g. $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{Tf})_2] < [\text{C}_3\text{C}_1\text{im}][\text{N}(\text{Tf})_2] < [\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$. Thus if the extraction is viscosity dependant then the length of the alkyl chain will have an indirect effect on the extraction efficiency of the ILs in the extraction of metal from n-hexadecane. The highest viscosities observed (2394 – 3155 mPa. s) are displayed by $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$, $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_8\text{C}_1\text{im}][\text{HSO}_4]$. This shows a vast difference between the ILs with high viscosity and the remainder of ILs measured in this study. The remaining ILs viscosities are below 181 mPa s with $[\text{C}_8\text{C}_1\text{im}][\text{OTf}]$ displaying the highest viscosity. We can see evidence again from the $[\text{OTf}]^-$ ILs viscosities that the cation has an affect on overall viscosity of the ILs with the viscosity decreasing with decreasing chain length and exchange for a pyrrolidinium cation. $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$, $[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ display relatively high viscosities in the lower bracket. The $[\text{N}(\text{Tf})_2]^-$ ILs generally give the lowest viscosities from this data set particularly the imidazolium based ILs. Correlation of this data with partition coefficients from the extractions will allow a clear insight to determine if viscosity has a direct affect on the biphasic extractions of metals from diesel fuel.

Table 3.9 – Viscosity of Fuel Samples at 25° C

Fuel Sample	Viscosity at 25° C [mPa s]
Na DDSA Model Fuel	2.81 ± 0.04
Zn neodecanoate Fuel Model	2.07 ± 0.02
Cu (acac) ₂ Fuel Model	2.10 ± 0.04
Market Fuel	2.99 ± 0.12

The viscosities of the fuel samples were determined (Table 3.9) to see if there was any direct affect on the biphasic extraction of metals using ILs. The market fuel has the greatest viscosity which will be due to a manipulation of the fuel product via

industry using additives. The model fuels produced in this research showed a variety of viscosities with the following trend; Na > Cu > Zn. However, the Zn and Cu models have little variation whilst the Na model displays much higher viscosity than the other two models. This indicates that the Na DDSA additive plays a role in the increase of viscosity within the fuel as the market fuel also contains this. Correlation of fuel viscosities and extraction efficiencies of the different metals will be analysed to determine if the fuel viscosity has a direct effect on the extraction.

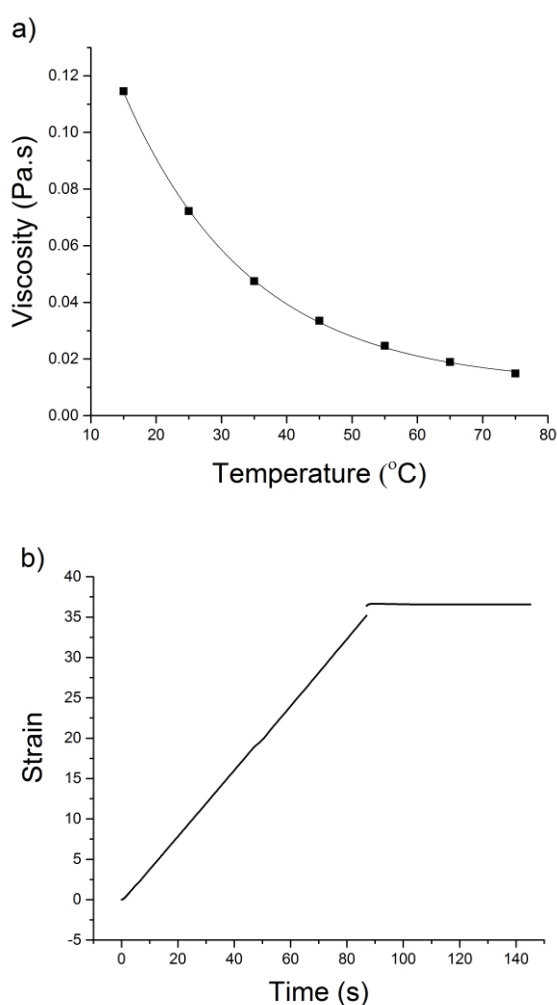


Figure 3.10 – Viscosity profile for $[C_4C_1pyrr][N(Tf)_2]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

The viscosity of all ILs used in this research were measured over a temperature range of 15 – 75 °C. Figure 3.10a shows an example IL [C₄C₁pyrr][N(Tf)₂] over the temperature ranges stated, all of the ILs in this study display a similar trend. The initial drop (0.042 Pa. s) in viscosity is the greatest from 15 – 25 °C. The viscosity drops 0.025 Pa. s from the temperature range 25 – 35 °C almost half of the initial decrease in viscosity. For the remainder of the temperature increase (35 – 75 °C) the viscosity values 0.014, 0.0088, 0.0057 and 0.0041 Pa. s are given respectively. This shows a decrease in the viscosity drop when higher temperatures are reached. An example creep and creep recovery as discussed above can also be seen (Figure 3.10b). The creep and creep recovery graph displays a typical Newtonian behaviour of the [C₄C₁pyrr][N(Tf)₂] IL for which all of the ILs showed in this study. The viscosity profiles for all of the liquids used in this study can be found in the appendix B.

3.8 Conclusion

When considering a biphasic extraction, the properties and interactions of the individual phases need to be defined and accounted for to provide the most efficient extraction system possible. From these results it is possible to gain an insight to the properties that will deem an IL successful and applicable to an application in fuel. Thus so far the general criteria for the highest possible extraction efficiency can be achieved via the following points:

1. Immiscible with the diesel fuel (all ILs in this study will be).
2. Low IFT so that metal ions can easily migrate across the phases and aggregation of both liquids will be increased during vortex mixing.
3. Highest possible DN (Lewis basicity) and Kamlet Taft β value to increase chelation of ILs to target metals in fuel.
4. Relatively high viscosity to ‘encapsulate’ metal ions once in the IL phase.
5. Ideally contain atoms of only CHNO to meet emission standards.
6. Low density to allow the flow of metal ions into the IL phase.

Density and viscosity of a liquid are not directly related as when temperature is altered viscosity will change but density will remain approximately the same. However, the kinematic viscosity represents the dynamic viscosity of a fluid per unit density. These results allow the definition of the properties of the ILs and fuels employed in this study to best satisfy the above criteria. The ILs best fit to this criteria are $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$, $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$, $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$, $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ and $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ hence defining the most suitable candidates for the application. These properties are taken into account and related to each extraction in Chapters 4, 5 and 6.

4 Extraction of Sodium from Diesel Fuel

4.1 Introduction

Sodium present in the fuel is one of the most likely suspects linked to the cause of Internal Diesel Injector Deposits (IDIDs). In this research it was found that ILs can extract up to 99.1 % of Na^+ from a model diesel fuel at a Na^+ concentration of just 3 mg kg^{-1} in the fuel; factors affecting the extent of extraction were investigated *via* correlation with experimental solvent descriptors. ^{23}Na NMR was used in the determination of donor number (DN) and Kamlet-Taft parameters were gathered for each IL providing information on possible hydrogen-bond acidity / basicity (α / β) and dipolarity solvent strength (π^*). In addition the non-random two liquid thermodynamic model (NRTL) was applied to correlate the experimental extraction results and determine the binary interaction parameter (τ) of the NRTL model for each of the ILs with Na^+ . It was determined that the extraction is controlled strongly by the hydrogen bond basicity of the IL which is directly related to the ability of the anion of the IL to complex Na^+ and thereby remove it from the fuel. DN, τ parameters and β in addition to interfacial tension and viscosity provide further information of the extraction mechanisms and predict performance, enabling a chemical design of ILs that are ideal for fuel purification.

4.2 Results and Discussion

The initial consideration for this study focused on the selection of ILs to provide comprehensive insight of mechanisms underlying the IL-based extraction of Na^+ from diesel fuel. ILs possess many desirable properties such as high thermal stability, low volatility, and excellent solubility.¹²³ They also show good extraction ability for metals from various media^{44,46,124}, and are immiscible with aliphatic liquids such as oil.¹²⁵ For this research a broad range of ILs, with varying physical properties, were synthesised which were thought to be feasible for the extraction of sodium ions from hydrocarbon streams due to reasons stated in Chapter 1. Additionally, interactions of any potential IL losses to the fuel when run through an engine were accounted for. One of the main points which needs consideration is

the feasibility of the IL for an application in fuel, as residual IL contaminating the fuel would enter the diesel chamber. However, this requirement had to be balanced against obtaining the maximum amount of chemical understanding of the system behaviour. We therefore included ILs with only CHNO atoms, in addition to ILs containing different components such as sulfur and phosphorus. However, it is considered that most ILs would decompose at the temperature conditions found in diesel engines, and decomposition products would then combust or vaporize. After analysis of the fuel phase (post-extraction) we found that the ILs used have negligible solubility within the fuel phase to the level of being undetectable via ^1H NMR or mass spectrometry.

The anions were selected to give variety in their possible interaction with the sodium ions to determine the properties of the ILs that are desired (and required) for this application. We postulated that this proceeds via the IL extracting the sodium ions directly from the fuel phase in a biphasic extraction. The sulfate, phosphate and acetate anions were selected because of being known for strongly interacting towards metals, through the formation of chelated complexes. It has been identified that sulphur-based species are not suitable for a fuel additive¹²⁶ and the choice of the ILs with these anions is purely for screening purposes in order to gain understanding of the underlying chemical effects controlling the extraction.

4.2.1 Extraction Experiments

After screening the ILs outlined in Chapter 1 the graphs (Figures 4.1, 4.2 and 4.3) show all of the ILs could be considered to be successful in the biphasic extraction of Na^+ . The ILs were run in a biphasic extraction with an increasing Fuel:IL ratio to isolate high performing candidates for further study. The extractions were analysed, the partition coefficient for sodium between two phases was calculated and plotted against Fuel:IL ratio. This provides an insight into the efficiency of the IL in the extraction of Na^+ from n-hexadecane. $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ extracts 95.2 % of the sodium present in the model fuel at a 100:1 Fuel:IL ratio giving a high

partitioning of Na^+ into the IL phase. However this IL is not most suited to an application in fuel due containing atoms of sulfur thus not fitting for current emission standards. $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ in the extraction of Na is highly effective giving a partition coefficient of up to 1865 and the chemical make-up has a greater suitability for fuel application.

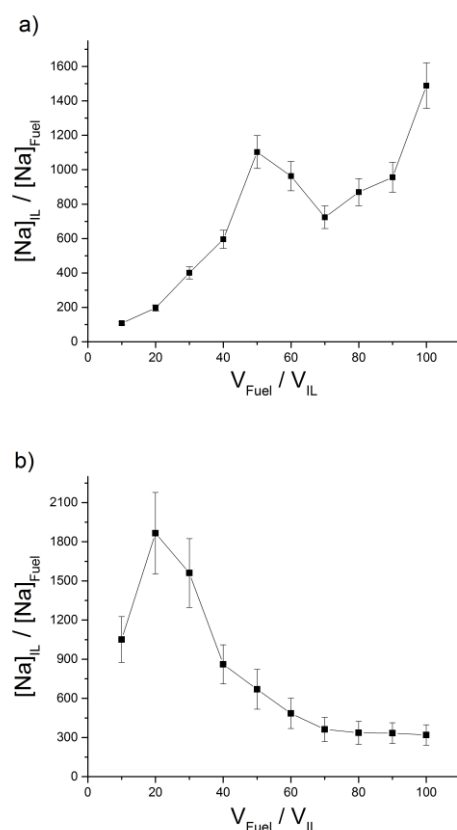


Figure 4.1 - ILs with high partitioning of Na^+ into the IL phase; (a) $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ and (b) $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$.

$[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ is capable of achieving high partition coefficients at low fuel loadings but these decrease to 319 at a 100:1 Fuel:IL ratio whereas $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ increases from 100 to 1489 over the full range of ratios investigated and manages to maintain a large partitioning of Na^+ into the IL phase. It should be noted that there is a fluctuation in the trend between the 50:1 and 70:1 Fuel:IL ratio which provides a higher partitioning of Na^+ into the IL phase than expected. The

partition maximum coefficient for $[(CH_3)_2NH_2][(CH_3)_2NCOO]$ translates to an extraction of 99.1% of Na from the Fuel in the IL phase (Table 4.1). It would be expected that the partition coefficient would decrease with an increasing Fuel:IL due to the volume of IL remaining constant and the fuel increasing thus providing a greater amount of sodium to extract. This is not the case for some of the ILs which perform better at higher fuel loading and at 10:1 Fuel:IL there is a lower than expected partition coefficient for $[(CH_3)_2NH_2][(CH_3)_2NCOO]$. This could be caused by the interfaces being too close together at smaller volumes, causing contamination when sampling.

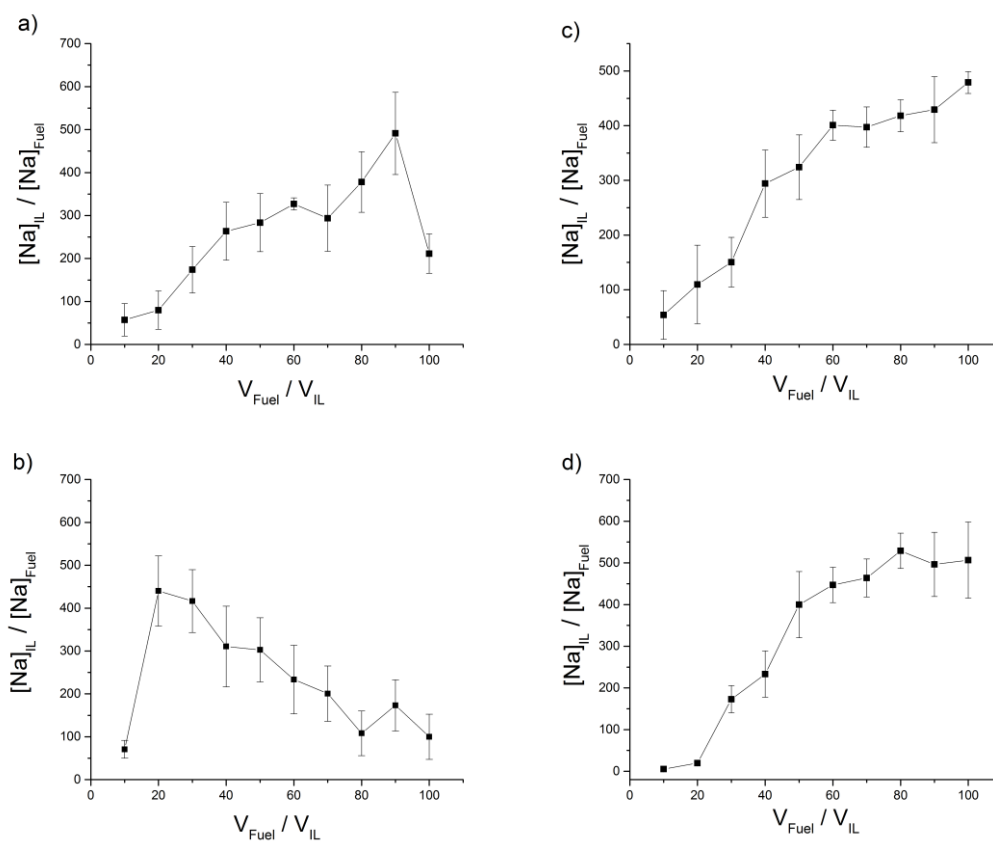


Figure 4.2 - ILs with intermediate partitioning of Na^+ into the IL phase; (a) $[C_4C_1im][Me_2PO_4]$, (b) $[C_4C_1im][OAc]$, (c) $[C_4C_1im][N(Tf)_2]$ and (d) $[C_4C_1pyrr][N(Tf)_2]$.

$[C_4C_1im][Me_2PO_4]$ and $[C_4C_1im][OAc]$ ILs give intermediate partition coefficients which we have classified as reaching between 400 - 1000. The partitioning into

[C₄C₁im][Me₂PO₄] increased with the volume of fuel up to 540 and then decreases dramatically; almost oppositely [C₄C₁im][OAc] starts with a partition coefficient of 440 and then gradually decreases to 100 at a volume ratio of 100. The low partition coefficient for [C₄C₁im][OAc] at 10:1 Fuel:IL can be again explained due to the low volume of fuel phase resulting in contamination when sampling. The [N(Tf)₂]⁻ ILs give an intermediate partition efficiency in the extraction of sodium ions which also increases with increasing volume of fuel. One explanation for this could be that as the volume of fuel increases, the flow of the fuel increases thus the ability to aggregate the IL at the bottom of the centrifuge tube would increase. With these particular ILs this effect outweighs the increase of sodium in the system. Another explanation could be when the fuel is sampled the volume is small and thus close to the interface which could contain Na⁺, this would explain the low partition coefficients at a volume ratio of 10 : 1. One would expect that at higher fuel loadings there will be more Na⁺ in the IL (more total Na in the system relative to IL), and the small IL solubility in the fuel could carry relatively greater amounts of Na⁺ with it; this is not what we often observed.

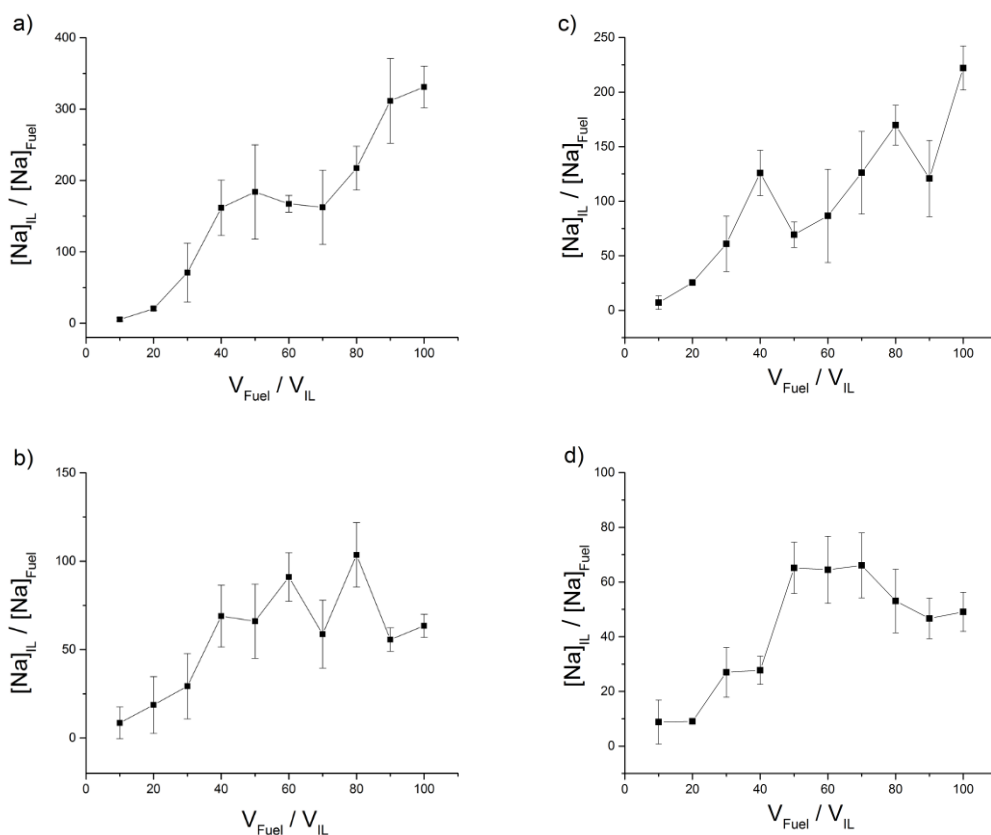


Figure 4.3 - ILs with a low partitioning of Na^+ into the IL phase, (a) $[C_4C_{1im}][OTf]$, (b) $[C_4C_{1pyrr}][OTf]$, (c) $[C_8C_{1im}][OTf]$ and (d) $[C_4C_{1im}][MeSO_4]$.

From the ILs used in this study the $[OTf]^-$ and $[MeSO_4]^-$ based ILs appeared to have the lowest partitioning of Na^+ to the IL phase giving coefficients of 400 and below, and in general did not extract sodium from fuel to the same extent as the other ILs. $[OTf]^-$ and $[MeSO_4]^-$ again would have a higher affinity for $[M]^{2+}$ metal ions over Na^+ due to the nature of the oxygen anion which could offer an explanation for the low partitioning of the singly charged Na^+ into the IL phase. $[C_8C_{1im}][OTf]$ shows two fluctuation in the partition coefficient trend, one higher than expected at 40:1 and one at 90:1 lower than expected. Again $[C_4C_{1pyrr}][OTf]$ displays two fluctuations in the trend at 60:1 and 80:1 which are higher than expected.

Upon comparing the extractions with $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$ and $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ one can visibly see that a precipitate of NaCl forms when $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ is mixed with the Na DDSA model. After this has been left overnight a precipitate was observed at the bottom of the vessel.

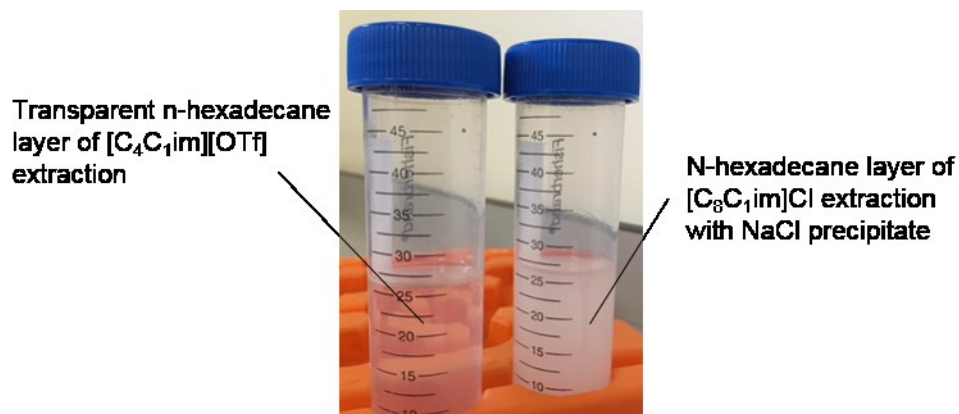


Figure 4.4 Photograph displaying model fuel post extraction with $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$ (left) and $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ (right).

This could be beneficial to the fuel industry as the sodium could easily be removed via this route (for example in storage tanks). The rest of the ILs did not form a precipitate so the Na^+ resides encapsulated within the IL phase. The IL could then be ‘cleaned’, via an appropriate method e.g. aqueous washing, and reused for further extractions.

4.2.2 Extraction Percentages

The extractions are evaluated via partition coefficients, due to the difficulty of achieving exact concentrations when preparing the model fuels each time. This section displays an exemplar run though with each of the ILs displaying the maximum extraction for each metal within the volume range and the concentration of the model fuel used. This is believed to provide a simplified data output so that the percentage of Na^+ extracted from n-hexadecane can clearly be seen.

Table 4.1 – Peak Percentage Extraction of Na⁺ for ILs in This Study Including Metal Concentrations.

Ionic Liquid	Peak Na ⁺ Extraction (%)	Na ⁺ Concentration in Model Fuel (mg L ⁻¹)
[C ₄ C ₁ im][N(Tf) ₂]	87.7	2.39
[C ₄ C ₁ im][OTf]	53.9	2.65
[C ₄ C ₁ im][MeSO ₄]	65.5	2.78
[C ₄ C ₁ im][Me ₂ PO ₄]	90.9	2.65
[C ₄ C ₁ im][OAc]	96.7	2.49
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	93.1	2.56
[C ₄ C ₁ pyr][N(Tf) ₂]	86.3	2.78
[C ₄ C ₁ pyr][OTf]	65.4	2.33
[C ₈ C ₁ im][OTf]	58.2	2.65
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	99.1	2.40

4.2.3 IL Characterisation and Na⁺ Extraction

Factors affecting the extent of extraction were investigated *via* correlation with experimental solvent descriptors. ²³Na NMR was used to determine donor numbers (electron donating ability) and Kamlet-Taft data was gathered for each IL giving α , β and π^* values. Upon comparison of the data possible mechanisms were derived for the extractions with each IL.

4.2.4 Donor Number and Na⁺ Extraction

To provide a comparison of the extraction data and donor number a ranking system was designed to order the ILs into ability of high (H), Intermediate (I) and low (L) in the extraction of Na⁺ from n-hexadecane (Table 4.2). Due to [HSO₄]⁻ ILs giving erratic readings through the extraction experiments their characterisation will be displayed but will not be used in further discussion. An explanation for these readings can be related to the high viscosity of the [HSO₄]⁻ ILs (Chapter 3). The fuel would not have been able to aggregate the ILs from the bottom of the centrifuge

tube efficiently each time. This would inhibit sufficient mixing to achieve consistent partitioning of Na⁺ into the IL phase each time thus providing erratic readings.

Table 4.2 - Hierarchy of ILs for this study in the ability to extract Na⁺ from n-hexadecane.

Ionic Liquid	Donor Number [kcal mol⁻¹]	IL ability in the Extraction of Na
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	32.2	H
[C ₄ C ₁ im][Me ₂ PO ₄]	28.6	I
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	24.6	H
[C ₄ C ₁ im][OAc]	21.3	I
[C ₄ C ₁ im][OTf]	19.8	L
[C ₄ C ₁ im][MeSO ₄]	19.6	L
[C ₈ C ₁ im][OTf]	18.5	L
[C ₄ C ₁ pyrr][OTf]	16.4	L
[C ₄ C ₁ im][N(Tf) ₂]	9.9	I
[C ₄ C ₁ pyrr][N(Tf) ₂]	7.4	I

The ILs were reordered in terms of DN. It is clear that the ILs with a higher ability to extract Na⁺ have a larger DN. The only discrepancy was found in the liquids that possess an [N(Tf)₂]⁻ anion which provide an accelerated extraction ability upon comparison of their DN. This could be due to the effect of the physical properties of the ILs, as opposed to their chemical make-up, such as the free flow of these low viscosity ILs. To further explain the relationship between the extraction of Na⁺ and IL, Kamlet Taft solvent parameters were determined. DN displays the effect of the anions but KT allows comparisons between individual component ions of the IL.

4.2.5 Kamlet Taft Paramters in Relation to Na⁺ Extraction

The measurement and methodology in the determination of Kamlet Taft Paramters of the ILs used in this study are outlined in Chapter 3.

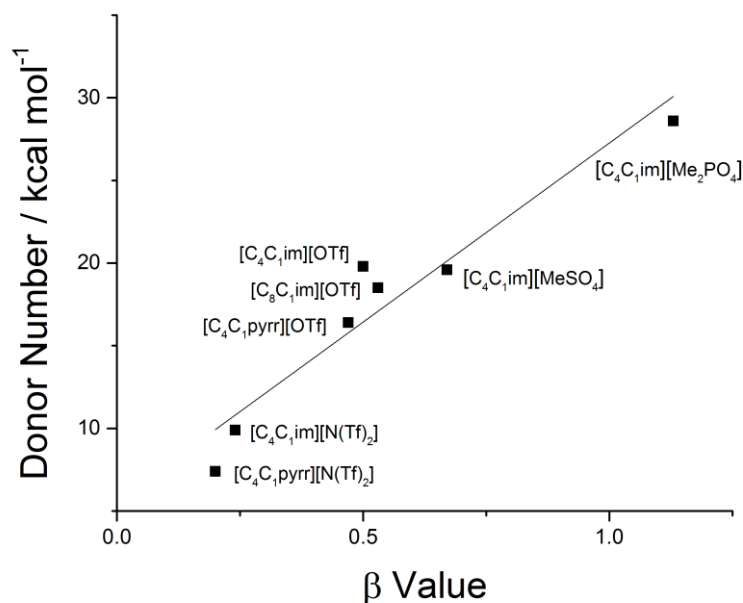


Figure 4.5 - DN values vs. Kamlet Taft β values for the range of ILs used in this study which were feasible for β value measurements.

There is a strong correlation between the donor number and Kamlet Taft β values for the ILs, although DN provides information about the whole IL with the β shows the anion effect only.^{73,74} [C₈C₁im]Cl was removed from this comparison due the donor number value being too large to scale with β values as they usually range from 0 - 1.5. The donor number values were compared to a large study of ²³Na NMR in the determination of donor number for ILs to ensure results were reliable.⁷³ [C₄C₁im][OAc] gives a high β value due to its high hydrogen bond basicity but would not chelate to Na⁺ well in the study of donor number because it has a higher affinity for [M]²⁺ ions such as Zn or Cu. When comparing the [OTf]⁻ and [N(Tf)₂]⁻ anions with both DN and β , the values decrease by roughly half on both scales from [OTf]⁻ to [N(Tf)₂]⁻ (Table 4.3). This further emphasises that both scales play a role on the extraction mechanism of Na⁺ via ILs. There is little correlation between the α parameter and extractability of Na⁺ thus different assays will need to be utilised to determine in the extraction mechanism proceeds via this route.

Table 4.3 - Comparison of $[\text{N}(\text{Tf})_2]^-$ and $[\text{OTf}]^-$ anions according to their DN and Kamlet Taft, β , parameters.

Ionic Liquids	DN [kcal mol^{-1}]	β Values
$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$	9.9	0.24
$[\text{C}_4\text{C}_1\text{pyrr}][\text{N}(\text{Tf})_2]$	7.4	0.20
$[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$	19.8	0.50
$[\text{C}_4\text{C}_1\text{pyrr}][\text{OTf}]$	16.4	0.47

4.2.6 Optimum IL Properties for Increased Extraction of Na^+

Table 4.4 - Rheological, DN and Droplet Analysis for ILs in this study (- = unmeasurable IFT).

Ionic Liquid	Peak Partition Coefficient	Donor	IFT [mN m^{-1}]	Viscosity [mPa s]
		Number [kcal mol^{-1}]		
$[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$	1488	32.2	0.96	2394.00
$[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$	491	28.6	2.02	136.20
$[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$	1865	24.6	-	53.45
$[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$	440	21.3	2.54	158.90
$[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$	331	19.8	-	77.95
$[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_4]$	66	19.6	2.34	97.02
$[\text{C}_8\text{C}_1\text{im}][\text{OTf}]$	222	18.5	-	181.00
$[\text{C}_4\text{C}_1\text{pyrr}][\text{OTf}]$	103	16.4	-	131.80
$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$	479	9.9	-	57.24
$[\text{C}_4\text{C}_1\text{pyrr}][\text{N}(\text{Tf})_2]$	528	7.4	-	72.31

To provide an overall insight to the extraction mechanism, interfacial tension (IFT) and viscosity of the ILs were compared to the peak partition coefficient each IL displays within the volume ratio range (1:10-1:100) (Table 4.4). In some instances the ILs IFT was immeasurable by the instrumentation due to the IFT being very low and is therefore assumed to be lower than the ILs measured in this study. It appears that the extraction of sodium ions relies on a combination of all three factors, i.e. DN, IFT and viscosity. For example $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ has a high electron donating ability (DN) and low IFT, enabling the Na^+ ions to cross over into the IL phase, and high viscosity to keep the Na^+ within the IL. This appears to be the ideal condition to provide the highest possible partitioning into the IL phase. $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ gives a relatively high DN but has a high IFT and low viscosity so in the extraction of Na^+ does not perform as well. Meanwhile $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$, having roughly the same viscosity, displays a higher DN and lower IFT thus giving an increased extraction.

4.3 Computational Modelling of a Binary System

Accurate thermodynamic models are capable of reproducing the behaviour of the systems. Models are useful in the understanding of trends, predicting values when there is limited data and process design. The most frequently used models for liquid-liquid equilibrium are based on the Gibbs Energy and are powerful tools in the field of liquid-liquid extractions (LLE). Wilson¹²⁷, NRTL¹²⁸ and UNIQUAC¹²⁹ are the most known models which will be discussed and the NRTL equation will be utilised.

The mixing of molecules is never entirely random due to the intermolecular forces involved thus models have been designed to take into account a non-randomness parameter and provide better models and descriptions of phase behaviour.¹³⁰ In this study we applied one of the local composition (LC) models (Figure 4.6) of which there are several. The whole idea of these models is based on the 'non random' mixing of molecules and this is achieved via 'local compositions' which are different to the overall concentration due to the short ranges of intermolecular forces. Due

to the non-randomness character of LC models they provide a much more realistic idea of the phase behaviour. Some of these models have been developed into predictive group contributions and thus do not require experimental data. However all of the LC models have defects some practical and some theoretical which we will discuss briefly in this section

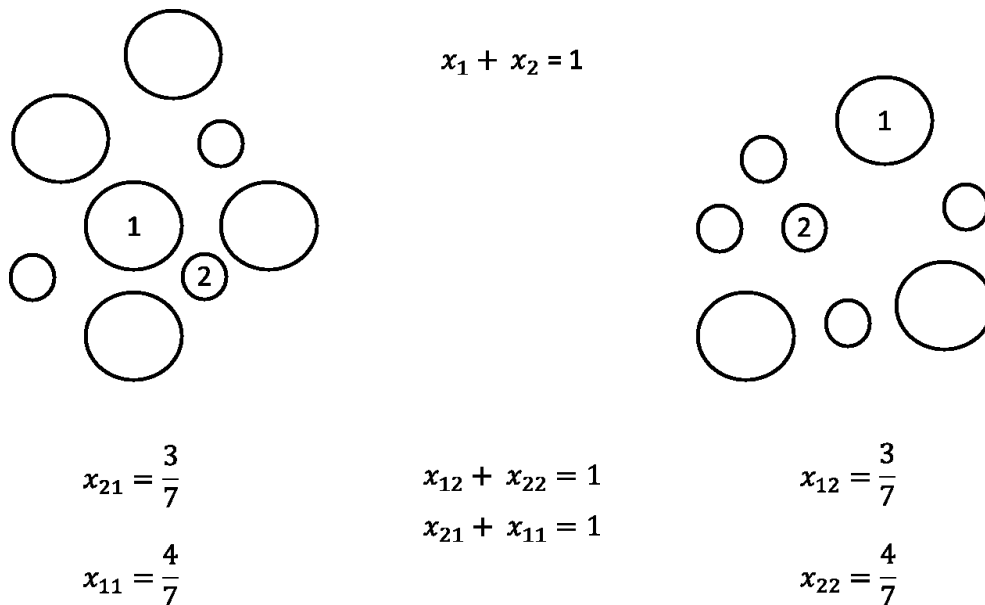


Figure 4.6 – The concept of local compositions, where x_{ij} indicates the mole fraction of compound i (number of molecules i over total number of molecules) around a central molecule j . Note that the local compositions differ from the overall ones ($x_i = 0.5$).

4.3.1 Choice of Equation

Careful consideration was taken when selecting a model for this system and all have their limitations. These are the main points considered in the selection of the equation:

- All of the models contain parameters with a temperature dependency and are applicable to multicomponent VLE systems, however Wilson cannot be applied to LLE. LLE is necessary for this study therefore the Wilson equation was not used in this study.

- UNIQUAC and NRTL can be used with VLE and LLE relatively well, UNIQUAC is used especially for binary mixtures, but not so much in multicomponent mixtures which is required for this study as we have three components being the fuel, IL and metal.
- Whereas UNIQUAC provides temperature dependent parameters, this is not important to this study because the extraction study was conducted at isothermal conditions.
- NRTL is widely applicable to most cases and suitable for ILs.

After considering the above points it was concluded that the NRTL model would be the best fit for this application due to working best with multicomponent LLE systems. In addition to this successful LLE modelling for the separation of ethanol has been demonstrated.¹³¹

4.3.2 Non-random Two-Liquid Equation (NRTL)

In this study, the activity coefficients of the Na⁺ in the IL and n-hexadecane (diesel) phases were evaluated using the non-random two-liquid (NRTL) model. This model has been shown to be useful for correlating the experimental liquid-liquid equilibrium data of the systems containing ILs.¹³² The parameters of the NRTL model are fitted using experimental data from the extractions (Equation 4.1) where g is an intermolecular pair energy and α is a non-randomness factor and in this research found between 0.1 – 0.5. The mixture is considered to be an ideal solution (completely random) when the value of α is 0. The non-randomness parameter enables the NRTL model to be applied to various binary and tertiary mixtures due to the additional degree of freedom that it offers.

$$\frac{g^E}{RT} = \chi_1 \chi_2 \left[\frac{\tau_{21} G_{21}}{\chi_1 + \chi_2 G_{21}} + \frac{\tau_{12} G_{12}}{\chi_1 G_{12} + \chi_2} \right] \quad (4.1)$$

where;

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT}; \tau_{21} = \frac{g_{12} - g_{11}}{RT} \quad (4.2)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}); G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (4.3)$$

4.3.2.1 Configuration of NRTL Model

The NRTL model was configured using mole fraction (w_i) values calculated from the experimental data from the ICP-OES. To carry out a comparison, estimates against experimental mole fractions were plotted for Na^+ in both n-hexadecane and the IL using the $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ extraction as an exemplar (Figure 4.7). Similarly all ILs showed a good correlation.

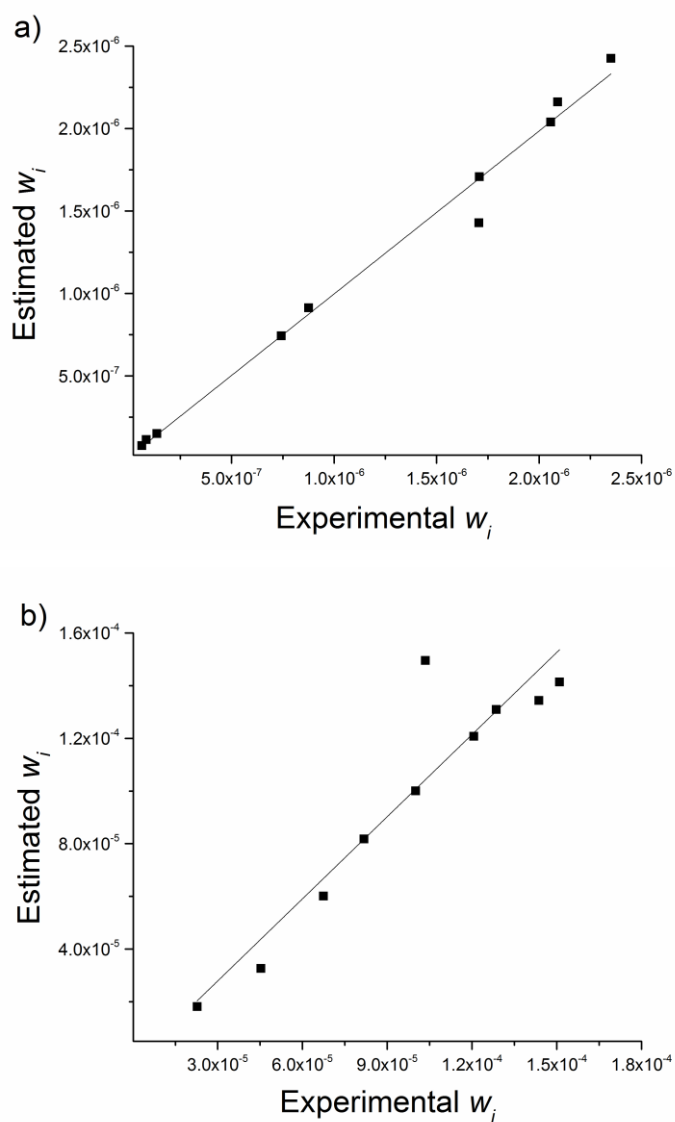


Figure 4.7 - Experimental mole fraction (w_i) vs calculated for (a) Na^+ in n-hexadecane and (b) Na^+ in $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$.

4.3.2.2 Experimental vs. Model τ values

A comparison of the τ values calculated via the model against τ values calculated from the extraction data was carried out to further ensure that the NRTL model fit the experimental data (Figure 4.8).

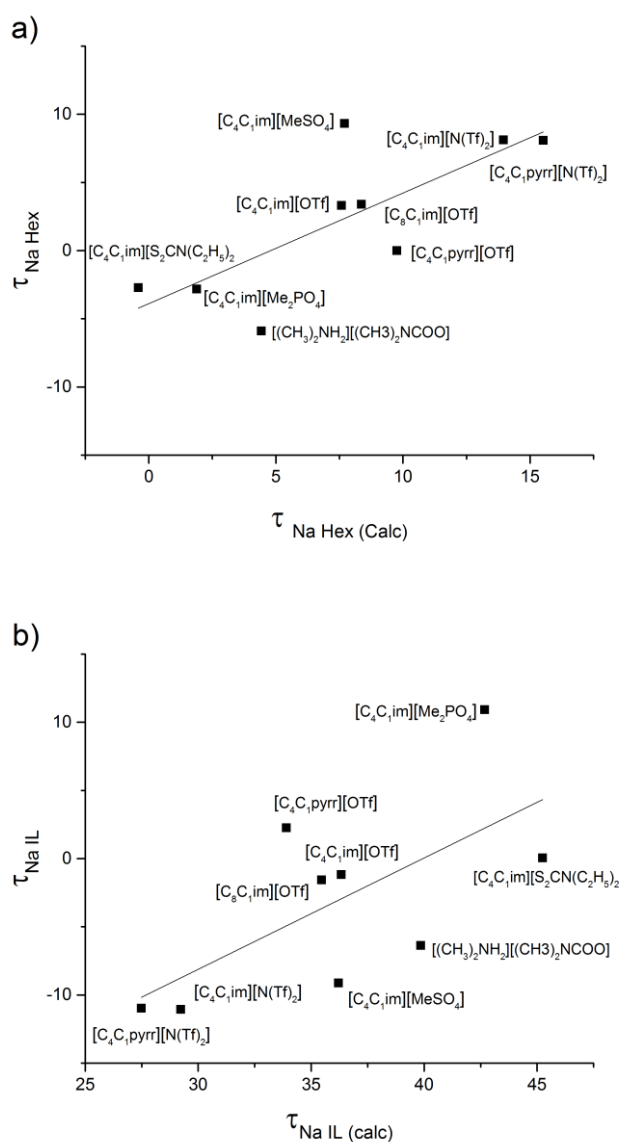


Figure 4.8 - Comparison of calculated (from experimental DN values) and NRTL model τ parameters (a) Na^+ in n-hexadecane and (b) Na in IL

This was calculated via a linear regression with DN as this experimental descriptor is expected to provide information on the whole liquid opposed to β which provides data relating to the anion of the IL. Again $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ were removed from the DN work in this section due to reasons stated previously.

To carry out the liquid–liquid equilibrium calculation, phase compositions were obtained by solving an isothermal liquid–liquid flash at a given temperature and pressure. The flash calculation consists of the following system of equations.

Equilibrium equation:

$$x_i^{L1}\gamma_i^{L1} - x_i^{L2}\gamma_i^{L2} = 0, \quad i = 1, N_c \quad (4.4)$$

Equation of summation:

$$\sum_i x_i^{L1} - \sum_i x_i^{L2} = 0 \quad (4.5)$$

where, x_i is the amount of component i in the mixture; x_i^{L1} is the amount of component i in liquid phase $L1$; x_i^{L2} , is the amount of component i in liquid phase $L2$; and N_c is the number of constituents of the liquid phases.

For a multicomponent system such as this, the activity coefficient of component i is given by the general expression:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j \tau_{ji} x_j} + \sum_j \frac{G_{ji} x_j}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_j \tau_{kj} G_{kj} x_k}{\sum_j \tau_{ji} G_{kj} x_k} \right) \quad (4.6)$$

With $\ln G_{ij} = -\alpha_{ij}\tau_{ij}$, $\alpha_{ij} = \alpha_{ji}$ and $\tau_{ii} = 0$ where τ_{ij} and τ_{ji} are binary interaction parameters, and α_{ij} is the non-randomness parameter. The non-randomness parameter enables the NRTL model to be applied to various binary and ternary mixtures because of the additional degree of freedom given by ij .

4.3.2.3 Donor Number and τ Comparison

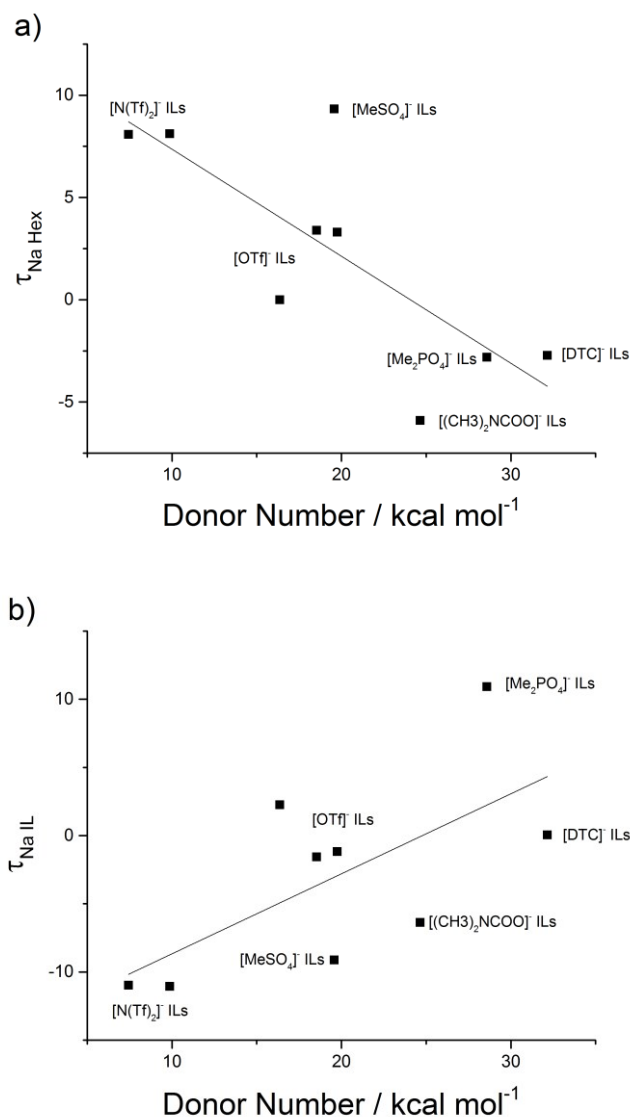


Figure 4.9 - τ vs Donor Number (a) Na⁺ in n-hexadecane and (b) Na⁺ in IL.

The correlation between DN and τ values was analysed (Figure 4.9) displaying again that ILs with particular anions group into families. From this data, generally as DN increases the τ parameter decreases providing a correlation between the anion effect and which phase the sodium ions has a higher affinity for in the extraction

system. Again when considering the Na^+ in the IL layer it appears to have the corresponding opposite trend. This analysis demonstrates that the NRTL model could be used to predict the Na^+ partitioning into various ILs, or at least IL anion families, provided the β values (and therefore DN and therefore τ) are known. A list of τ parameters for Na^+ in both the fuel and IL phase can be found in Appendix D.

4.4 Conclusions

In summary, a range of ILs have been synthesised and examined for their ability to extract sodium from n-hexadecane model fuels at a concentration of 3 mg kg^{-1} of sodium. They have shown a variety of different partition coefficients in the extraction of sodium ions. The results from our analysis show that the extraction is highly related to the constituent anions. This achieved up to 99.1 % extraction at a 100:1 (Fuel: IL) volume ratio using $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ as the best performing IL. The most suitable IL in terms of an industrial viewpoint would be $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ due to the low cost, high partition coefficient, and suitable elemental make-up for a fuel application. Additionally, the presence of the IL within the n-hexadecane was below detectable levels on NMR spectroscopy and mass spectroscopy and therefore all of the successful ILs in this study could also be considered for this application. Minimal loss of IL to the n-hexadecane phase is also beneficial for industrial applications due to minimal usage of the IL and negligible contamination of the processed fuel in addition to the possibility of recycling the IL. The effectiveness of each IL was determined via the calculation of the partition coefficients for Na^+ into each IL over an increased volume of fuel. This was carried out by relating the Fuel:IL volume ratio to the concentration in each of the phases post-extraction. Factors affecting the extent of extraction were investigated *via* correlation with experimental solvent descriptors, providing a strong link between the ILs ability to extract sodium ions and Kamlet-Taft's β values and ^{23}Na donor number. The NRTL model was applied to the experimental data to determine τ values for each of the ILs, this was found to be strongly coordinated to the DN

values of the ILs. All the data gathered was put together to determine the most suitable extraction mechanism for the ILs. However, some of the ILs in this study gave a low partitioning of sodium ions into the IL phase which is thought to be caused by the low affinity of the anion for sodium ions or related to the IFT and the IL viscosity.

5 Utilisation of Ionic Liquids to Remove Harmful M^{2+} Contaminants from Hydrocarbon Streams

5.1 Introduction

Zinc contaminants have been identified as suspects leading to nozzle deposit formation and copper contaminants rapidly reduce the oxidation stability of diesel fuel. Ionic liquids (ILs) are commonly referred to as ‘designer solvents’, due to the great degree of fine-tuning of their physical and chemical properties afforded by modification of their constituent cations and anions. These tunable properties of the ILs ions allow the ‘design’ to meet the requirements for a particular target and thus be a potential candidate for the extraction of the zinc and copper from diesel fuel. It is shown for the first time that ILs can extract up to 99.3 % of Zn^{2+} at a Zinc concentration of 2 mg kg^{-1} and Cu^{2+} can be extracted up to 99.7 % at a Copper concentration of 1 mg kg^{-1} from a model diesel fuel which are very low levels of metal; factors affecting the extent of extraction were investigated *via* correlation with experimental descriptors:

1. ^{23}Na NMR was used in the determination of donor number (DN)
2. Kamlet-Taft parameters were gathered for each IL providing information of possible hydrogen-bond acidity / basicity (α / β), and dipolarity/polarizability effects (π^*).
3. The non-random two liquid model (NRTL) was applied to determine τ parameters for each of the ILs.

These showed that the extraction is controlled strongly by the hydrogen bond basicity of the IL, which is directly related to the ability of the anion of the IL to complex zinc and copper ions thus removing them from the fuel. DN, τ parameters and β , in addition to interfacial tension and viscosity, provide further information of the extraction mechanisms and allow performance to be predicted, enabling a chemical design of ILs that are tuned for fuel purification.

5.2 Results and Discussion

The initial consideration for this study focused on the selection of ionic liquids to provide a comprehensive insight into the mechanisms underlying the IL-based extraction of Zn^{2+} and Cu^{2+} from diesel fuel. A broad range of ILs, with varying physical properties, were synthesised which were thought to be feasible for the extraction of zinc and copper ions from hydrocarbon streams due to possessing many desirable properties such as high thermal stability, low volatility, and excellent metal ion solubility.¹²³ They also show good extraction ability for metals from various media^{44,46,124}, and are immiscible with aliphatic liquids such as oil.¹²⁵ Additionally, interactions of any potential IL losses to the fuel when run through an engine needed to be accounted for. One of the main points which needs consideration is the feasibility of the IL for an application in fuel, as residual IL contaminating the fuel would enter the diesel chamber. However, this requirement had to be balanced against obtaining the maximum amount of chemical understanding of the system behaviour. We therefore included ILs with only CHNO atoms, in addition to ILs containing different elements such as sulfur and phosphorus. However, it is considered that most ionic liquids would decompose at the temperature conditions found in diesel engines, and the decomposition products would then combust or vaporize. After analysis of the fuel phase (post-extraction) we found that the ILs used have negligible solubility within the fuel phase to the level of being undetectable via ^1H NMR or mass spectrometry.

The anions were selected to give variety in their possible interaction with the zinc and copper ions to determine the properties of the ionic liquids that are desired (and required) for this application. We postulated that this proceeds via the ionic liquid extracting the zinc and copper ions directly from the fuel phase in a biphasic extraction. The sulfate, phosphate and acetate anions were selected because of being known for strongly interacting towards metal ions, through the formation of chelated complexes. It has been identified that sulfur is not suitable for a fuel

additive¹²⁶ and the choice of the ionic liquids with these sulfur containing anions is purely for screening purposes in order to gain understanding of the underlying chemical effects controlling the extraction.

5.2.1 Extraction Experiments

The graphs (Figures 5.1, 5.2, 5.3, 5.4, 5.5 and Figure 5.7) show the ILs feasibility in the successful biphasic extraction of Zn^{2+} and Cu^{2+} from the model fuels. The ILs were run in a biphasic extraction with an increasing Fuel to IL volume ratio to isolate high performing candidates for further study. For example $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ (Figure 5.1 c) can extract 99.0% of the zinc ions present in the model fuel at a 100:1 (Fuel:IL), and would ideally be suited to a fuel application due to it consisting of only CHNO atoms.

The extractions were analysed, and the partition coefficient for zinc between the two phases calculated and plotted against Fuel:IL ratio. This provides an insight into the efficiency of the IL for the extraction of Zn^{2+} and Cu^{2+} from n-hexadecane. $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ in the extraction of Zn^{2+} is highly effective giving a partition coefficient of up to 8294 (70:1 Fuel:IL) but due to the anion containing a phosphorus atom the suitability of this IL for fuel applications is debatable.

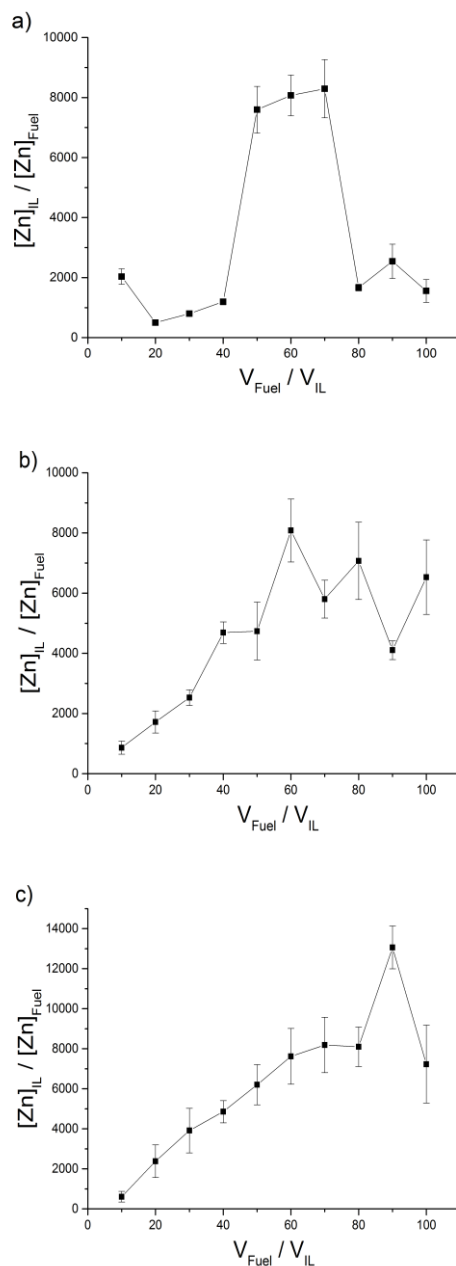


Figure 5.1 - ILs with high partitioning (H) of Zn^{2+} into the IL phase; (a) $[C_4C_{1im}][Me_2PO_4]$ (b) $[C_4C_{1im}][S_2CN(C_2H_5)_2]$ (c) $[C_4C_{1im}][OAc]$

$[C_4C_{1im}][S_2CN(C_2H_5)_2]$ and $[C_4C_{1im}][OAc]$ are capable of high partition coefficients and generally increase when the fuel loading is increased whereas, $[C_4C_{1im}][Me_2PO_4]$ provides an optimal range in which the partitioning of Zn^{2+} into

the IL is greatest. High partition coefficients (H) have been classified as those reaching above 3000 for Zn^{2+} . The partition maximum partition coefficient for $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ translates to an extraction of 99.2% of Zn^{2+} from the fuel model in the IL phase. Fluctuations in the partition coefficient trends can be seen with $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ at 60:1, higher and 90:1, lower than expected. Also $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ at 90:1 Fuel:IL displays a higher than expected value.

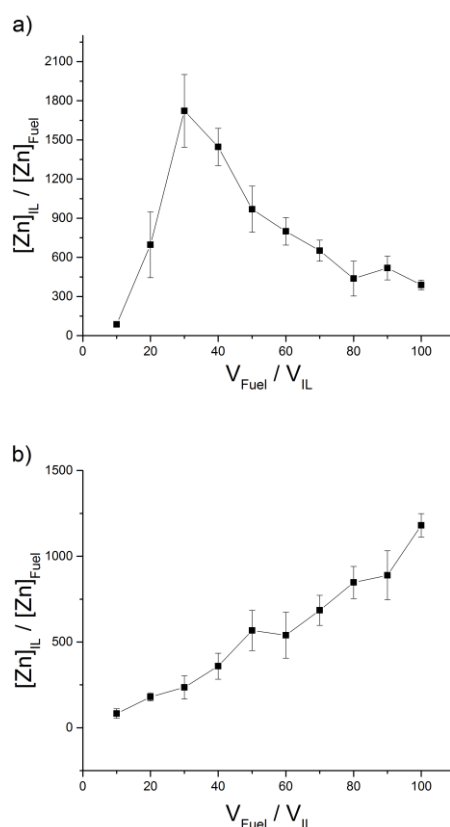


Figure 5.2 - ILs with intermediate partitioning (I) of Zn^{2+} into the IL phase; (a) $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ (b) $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$

It would be expected that the partition coefficient would decrease with an increasing fuel to IL ratio due to the volume of ionic liquid remaining constant and the fuel increasing thus providing a greater amount of zinc ions to extract. This is not the case for $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ which perform better at higher fuel loading. The ILs $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ and $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ give an intermediate partition coefficient

(I) which is classified as a peak partition coefficient reaching between 1000 – 3000 for Zn^{2+} .

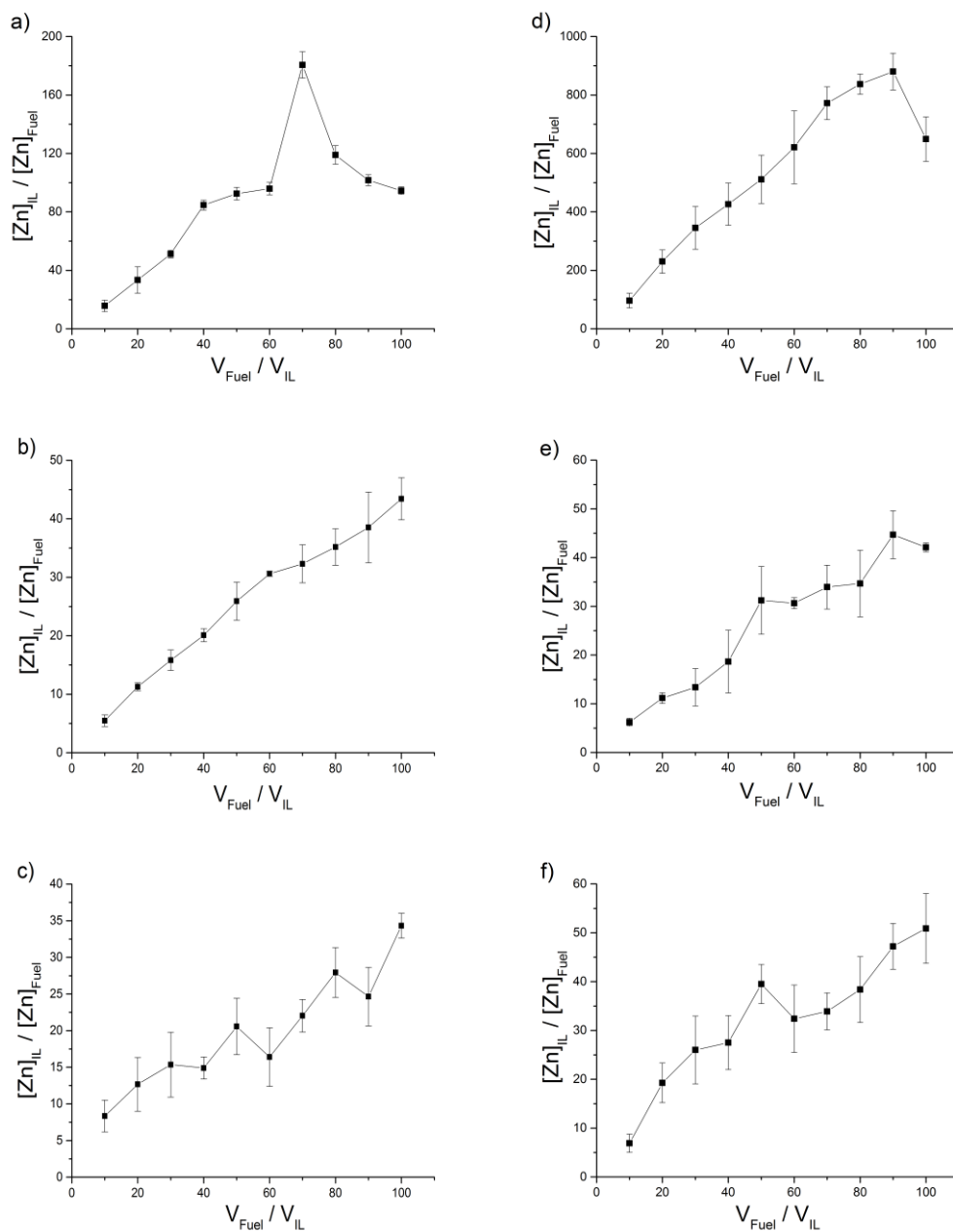


Figure 5.3 - ILs with a low partitioning (L) of Zn^{2+} into the IL phase, (a) $[\text{C}_4\text{C}_{1\text{im}}][\text{MeSO}_4]$, (b) $[\text{C}_4\text{C}_{1\text{im}}][\text{OTf}]$ (c) $[\text{C}_4\text{C}_{1\text{pyrr}}][\text{OTf}]$, (d) $[\text{C}_8\text{C}_{1\text{im}}][\text{OTf}]$ and (e) $[\text{C}_4\text{C}_{1\text{im}}][\text{N}(\text{Tf})_2]$ (f) $[\text{C}_4\text{C}_{1\text{pyrr}}][\text{N}(\text{Tf})_2]$

Partitioning of zinc ions into $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ increased with the volume of fuel up to 1722 (1:30 Fuel:IL) and then decreases dramatically with further increased (Fuel:IL). The partitioning of Zn into $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ gradually increases when the (Fuel:IL) volume ratio is increased.

Those ILs with a peak partition coefficients below 1000 have been classified as low (L) extractors. A major fluctuation with these partition coefficient trends is shown with $[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_4]$ at the 70:1 Fuel:IL ratio which provides the peak partition coefficient. The $[\text{N}(\text{Tf})_2]^-$ and $[\text{OTf}]^-$ anion based ILs give low partition efficiencies in the extraction of Zn^{2+} but the partition coefficient increases as the volume of fuel increases. One would expect that at higher fuel loadings there will be more metal in the IL (more total metal in the system relative to IL), and the small IL solubility in the fuel could carry relatively greater amounts of metal with it; this is not what we often observed. Explanations for this effect could be the following:

- With increasing volume of fuel the total amount of the ionic liquid lost into the fuel could increase during vortex mixing during extraction. As the volume of fuel increases the flow of the fuel and thus the ability to aggregate the IL at the bottom of the centrifuge tube would increase with these particular ILs, so much that it outweighs the increase of metal in the system.
- When the fuel is sampled the volume is small and thus close to the interface which could contain the metal, this would explain the low partition coefficients at a volume ratio of 10.

For the $[\text{N}(\text{Tf})_2]^-$ and $[\text{OTf}]^-$ anion based ILs the low partition coefficient is likely due to the fluorine groups which are electron withdrawing, decreasing the interaction between the anion of the IL and positively charged metal. Leading to a decreased partitioning of the metal into the IL phase.

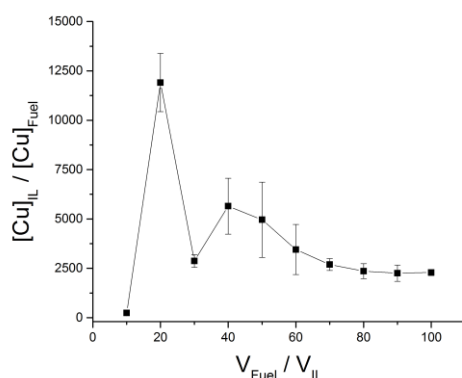


Figure 5.4 - ILs with high (H) partitioning of Cu^{2+} into the IL phase; $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$

$[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ and $[\text{C}_4\text{C}_1\text{im}][\text{MePO}_4]$ were employed in the removal of Cu^{2+} from fuel due to their exceptional ability in the extraction of Zn^{2+} and were expected to extract Cu in a similar manner due to copper and zinc both containing M^{2+} species. The same hierarchical system that was used for Zn^{2+} was used for Cu^{2+} i.e. high (H), intermediate (I) and low (L). $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ in a similar fashion to Zn^{2+} , extracts Cu^{2+} with a high partitioning giving a maximum partition coefficient of 11908 (Figure 5.4). The low partitioning of Cu^{2+} at 10:1 (Fuel:IL) would be expected due to the fuel sample volume being small and thus close to the interface which could contain the metal.

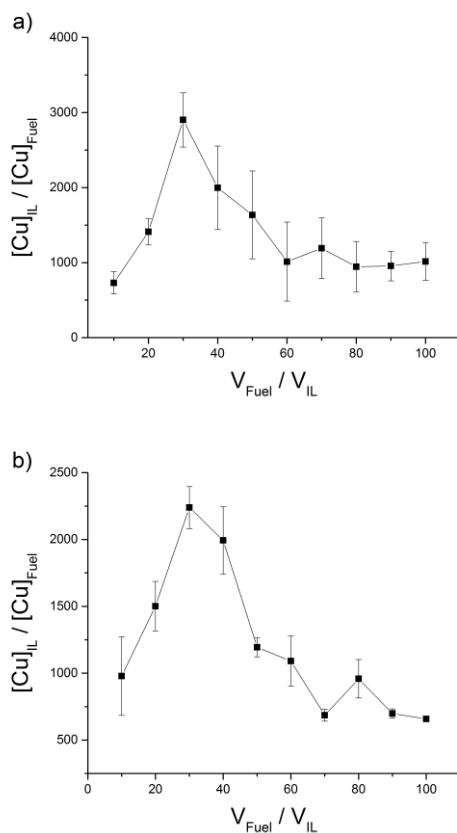


Figure 5.5 - ILs with an Intermediate (I) partitioning of Cu^{2+} into the IL phase, (a) $[\text{C}_8\text{C}_{1\text{im}}]\text{Cl}$, (b) $[\text{C}_8\text{C}_{1\text{im}}][\text{OTf}]$

$[\text{C}_8\text{C}_{1\text{im}}]\text{Cl}$ gave an intermediate partitioning of Cu^{2+} into the IL phase during the biphasic extraction. It is thought that at low fuel loadings low partitioning was recorded for both intermediate ILs is due to the sample volume being too small and close to the interface where the metal resides rather than in the bulk phase. The partition coefficient of $[\text{C}_8\text{C}_{1\text{im}}]\text{Cl}$ and $[\text{C}_8\text{C}_{1\text{im}}][\text{OTf}]$ then increases to a maximum of 2902 and 2239 respectively. The partition coefficients then decrease at higher fuel loadings and $[\text{C}_8\text{C}_{1\text{im}}][\text{OTf}]$ displays a lower than expected partition coefficient at 70:1 Fuel:IL. Both intermediate ILs for the extraction of Cu^{2+} possess an octylimidazolium cation suggesting that this aids the partitioning of Cu^{2+} into the IL phase. An explanation for this could be the increased aggregation of the two phases caused by the long alkyl chain of the octylimidazolium cation. The long alkyl chain

(non – polar tail) would have a higher affinity for the fuel phase and the polar head would have a higher affinity for the IL phase (Figure 5.6). The octylimidazolium ILs therefore act as a surfactant lowering surface tension between the phases and this would likely lead to an increased extraction of Cu^{2+} . This trend can also be seen in the extraction of Zn^{2+} as from the three $[\text{OTf}]^-$ anion based ILs, $[\text{C}_8\text{C}_1\text{im}][\text{OTf}]$ provides the largest peak partition coefficient. However, this trend was not clear in the Na^+ extractions thus this effect could be outweighed by another property (Chapter 4).

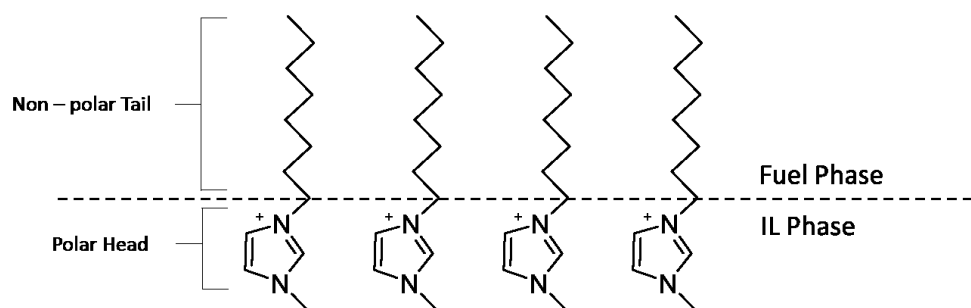


Figure 5.6 – Arrangement of the octylimidazolium cation at an interface between IL and fuel phases

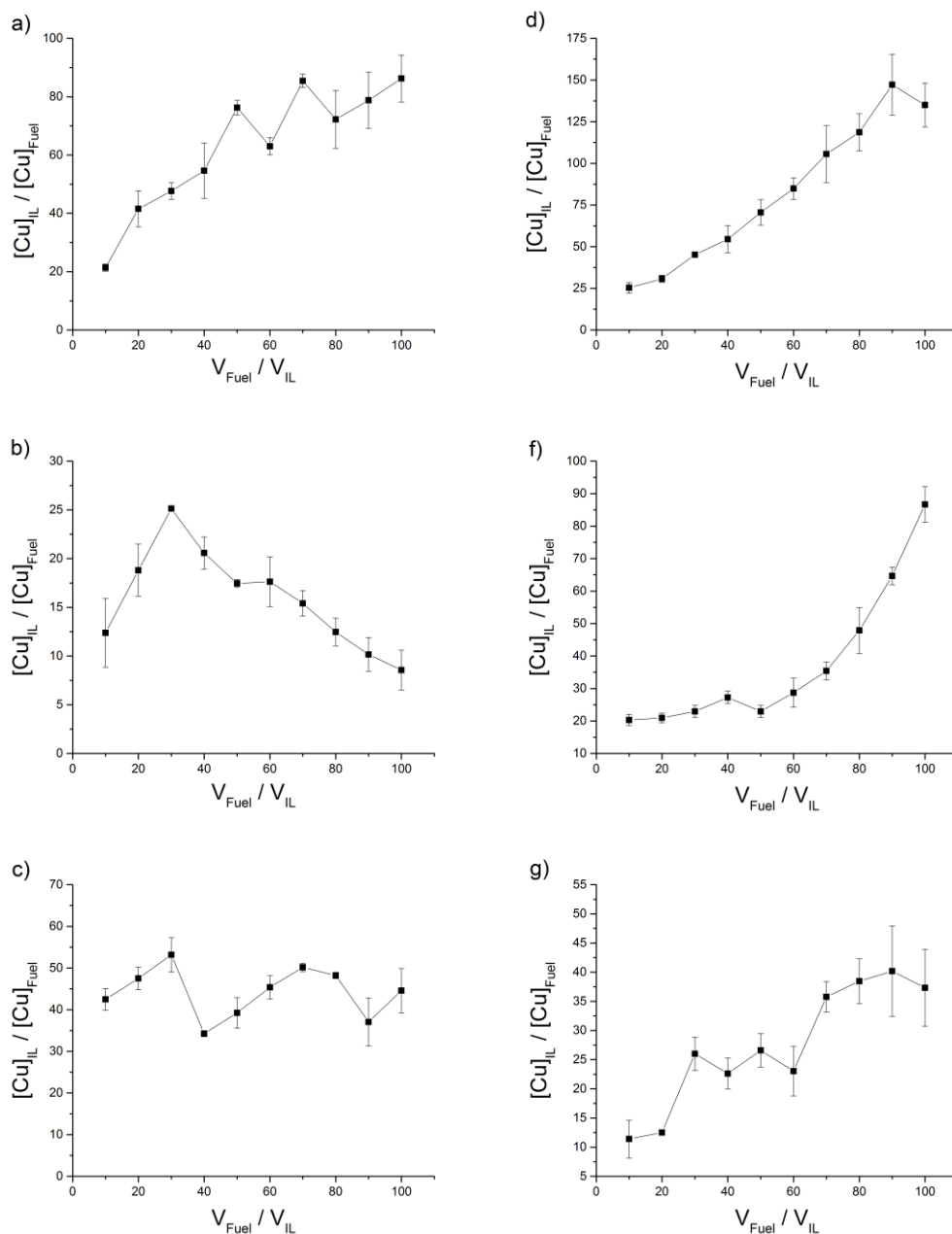


Figure 5.7 - ILs with a low (L) partitioning of Cu^{2+} into the IL phase, (a) $[C_4C_1im][Me_2PO_4]$, (b) $[(CH_3)_2NH_2][(CH_3)_2NCOO]$, (c) $[C_4C_1im][MeSO_4]$, (d) $[C_4C_1im][N(Tf)_2]$, (e) $[C_4C_1pyrr][N(Tf)_2]$, (f) $[C_4C_1im][OTf]$, (g) $[C_4C_1pyrr][OTf]$

[C₄C₁im][MePO₄] and [(CH₃)₂NH₂][(CH₃)₂NCOO] both, compared to Zn²⁺, give low partition coefficients for the removal of Cu²⁺ (Figure 5.7). [C₄C₁im][Me₂PO₄] displays a low partitioning of Cu²⁺ into the IL phase displaying a peak partition coefficient of only 86.25 (100:1 Fuel:IL) ratio which, in comparison with the peak partition of 8294 (1:70 Fuel:IL) for the extraction of Zn²⁺ is significantly less. [C₄C₁im][Me₂PO₄] displays two anomalies within the partition coefficient trend at 50:1 and 70:1 Fuel:IL which are higher than expected. Similarly for [(CH₃)₂NH₂][(CH₃)₂NCOO] the peak partition coefficient is 25.13 at a (30:1 Fuel:IL) ratio compared with the peak partition coefficient of Zn²⁺ at 1722 (30:1 Fuel:IL). An explanation for this could be the composition of the metal complexes present within the n-hexadecane, as the peak partition coefficient in the extraction of Zn²⁺ is far greater than for Cu²⁺ for all the ILs. The acetylacetonate of the Cu(acac)₂ used in the copper model fuel as a source of Cu²⁺ is known to be a strong chelating agent.¹³³ This could affect the ability of the ILs to preferentially chelate to the metals. [C₄C₁im][MeSO₄], the [N(Tf)₂]⁻ anion based ILs and the [OTf]⁻ anion based ILs, excluding [C₈C₁im][OTf], all fall into the low partition coefficient bracket in the extraction of all tested metals so is not unusual to see them with this ranking. [C₄C₁im][MeSO₄] shows a higher fluctuation in the trend at 90:1 Fuel:IL and [C₄C₁pyrr][OTf] shows two fluctuations at both 30:1 and 60:1 Fuel:IL higher and lower than expected respectively.

5.2.2 Extraction Percentages

This section displays an exemplar run though with each of the ILs displaying the maximum extraction for each metal within the volume range and the concentration of the model fuel used. This is believed to provide a simplified data output so that the percentage of both Zn²⁺ and Cu²⁺ extracted from n-hexadecane can clearly be seen.

Table 5.1 - Peak percentage extraction of Zn²⁺ for ILs in this study including metal concentrations.

Ionic Liquid	Peak Zn²⁺ Extraction (%)	Zn²⁺ Concentration in Model Fuel (mg L⁻¹)
[C ₄ C ₁ im][N(Tf) ₂]	54.5	1.59
[C ₄ C ₁ im][OTf]	39.3	1.66
[C ₄ C ₁ im][MeSO ₄]	72.3	1.62
[C ₄ C ₁ im][Me ₂ PO ₄]	99.6	1.62
[C ₄ C ₁ im][OAc]	99.4	2.67
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	99.3	1.62
[C ₄ C ₁ pyrr][N(Tf) ₂]	54.4	1.59
[C ₄ C ₁ pyrr][OTf]	50.6	1.45
[C ₈ C ₁ im][OTf]	93.2	1.45
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	98.5	1.59

Table 5.2 – Peak percentage extraction of Cu²⁺ for ILs in this study including metal concentrations.

Ionic Liquid	Peak Cu²⁺ Extraction (%)	Cu²⁺ Concentration in Model Fuel (mg L⁻¹)
[C ₄ C ₁ im][N(Tf) ₂]	74.0	1.11
[C ₄ C ₁ im][OTf]	68.5	0.65
[C ₄ C ₁ im][MeSO ₄]	90.6	1.18
[C ₄ C ₁ im][Me ₂ PO ₄]	69.5	1.28
[C ₄ C ₁ im][OAc]	99.9	1.28
[C ₄ C ₁ pyrr][N(Tf) ₂]	72.5	1.11
[C ₄ C ₁ pyrr][OTf]	57.0	0.65
[C ₈ C ₁ im][OTf]	99.2	0.65
[C ₈ C ₁ im]Cl	99.4	1.18
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	60.9	1.03

5.2.3 IL Characterisation

The extent of extraction was investigated by correlation with experimental solvent descriptors. ^{23}Na NMR determined donor numbers (electron donating ability) and Kamlet-Taft data was gathered for each IL giving hydrogen-bond acidity / basicity (α / β) and dipolarity/polarizability effect (π^*) values. Mechanisms were then derived for each of the extractions for each IL via comparison of the data.

5.2.3.1 Donor Number Analysis

The donor number, DN, (defined by Na^{23} NMR) of the ILs was used in this study to define the Lewis basicity of the ILs. This is a term previously used to display and quantify solvent properties by Victor Gutmann.⁷⁷ He demonstrated that donor number could be used as a quantitative measure for the ability of the solvent to donate electron pairs to acceptors. Information on the donor number of ILs in this study allowed an estimation/determination of the strength of the interactions between the ILs anions and the dissolved zinc and copper ions in the model fuels. To provide a comparison of the extraction data and donor number the ranking system, high (H), Intermediate (I) and low (L) was used in the extraction of Zn^{2+} and Cu^{2+} from n-hexadecane. Due to $[\text{HSO}_4]^-$ anion based ILs giving erratic readings through the extraction experiments their characterisation will be displayed but will not be used in further discussion.

Table 5.3 - Hierarchy of ILs for this study in the ability to extract Zn^{2+} from n-hexadecane

Ionic Liquid	Donor Number [kcal mol⁻¹]	Ionic Liquid Ability to Extract Zn^{2+}
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	32.2	H
[C ₄ C ₁ im][Me ₂ PO ₄]	28.6	H
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	24.6	I
[C ₄ C ₁ im][OAc]	21.3	H
[C ₄ C ₁ im][OTf]	19.8	L
[C ₄ C ₁ im][MeSO ₄]	19.6	L
[C ₈ C ₁ im][OTf]	18.5	L
[C ₄ C ₁ pyrr][OTf]	16.4	L
[C ₄ C ₁ im][N(Tf) ₂]	9.9	L
[C ₄ C ₁ pyrr][N(Tf) ₂]	7.4	L

The ILs were ordered in terms of their DN and it is clear to see that the ILs with a higher ability to extract Zn^{2+} have a larger DN (Table 5.3). However, there is a discrepancy with [(CH₃)₂NH₂][(CH₃)₂NCOO] which provides only an intermediate extraction ability but has a relatively high DN. This difference could be caused by the physical parameters of the system such as its viscosity or density.

Table 5.4 - Hierarchy of ILs for this study in the ability to extract Cu²⁺ from n-hexadecane

Ionic Liquid	Donor Number [kcal mol ⁻¹]	Ionic Liquid Ability to Extract Cu ²⁺
[C ₈ C ₁ im]Cl	70.0	I
[C ₄ C ₁ im][Me ₂ PO ₄]	28.6	L
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	24.6	L
[C ₄ C ₁ im][OAc]	21.3	H
[C ₄ C ₁ im][OTf]	19.8	L
[C ₄ C ₁ im][MeSO ₄]	19.6	L
[C ₈ C ₁ im][OTf]	18.5	I
[C ₄ C ₁ pyrr][OTf]	16.4	L
[C ₄ C ₁ im][N(Tf) ₂]	9.9	L
[C ₄ C ₁ pyrr][N(Tf) ₂]	7.4	L

The ILs were ordered in terms of their DN and measured against their ability to extract Cu²⁺. However, the trend is not as evident for the extraction of Cu²⁺ as with Zn²⁺ (Table 5.4). [C₄C₁im][OAc] has a highest partitioning of Cu²⁺ into the IL phase but possesses a lower DN than [(CH₃)₂NH₂][(CH₃)₂NCOO] and [C₄C₁im][Me₂PO₄] which provide a low partition coefficient. This could be explained again by the chemical make-up of the metal Cu²⁺ complex in n-hexadecane. Showing that certain ILs would have a higher ability to extract the copper based on their chemical properties. These results imply that octylimidazolium cations and acetate anions are preferable and therefore [C₈C₁im][OAc] would give the best extraction of Cu²⁺ from n-hexadecane.

To deliver a more in-depth understanding of the extraction mechanism, the densities and viscosities of the ILs were compared to the peak partition coefficient for each IL within the volume ratio range used (1:10 - 1:100) (Table 5.5).

Table 5.5 - Comparison of peak partition coefficient with rheological, DN, and Density measurements for ILs in the extraction of zinc ions.

Ionic Liquid	Peak Partition Coefficient Zn ²⁺	Donor Number [kcal mol ⁻¹]	Viscosity [mPa s]	Density [g cm ⁻³]
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	8081	32.2	2394.00	1.083
[C ₄ C ₁ im][Me ₂ PO ₄]	8294	28.6	136.20	1.158
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	1722	24.6	53.45	1.050
[C ₄ C ₁ im][OAc]	13061	21.3	158.90	1.066
[C ₄ C ₁ im][OTf]	43	19.8	77.95	1.295
[C ₄ C ₁ im][MeSO ₄]	180	19.6	97.02	1.200
[C ₈ C ₁ im][OTf]	880	18.5	181.00	1.201
[C ₄ C ₁ pyrr][OTf]	34	16.4	131.80	1.249
[C ₄ C ₁ im][N(Tf) ₂]	44	9.9	57.24	1.431
[C ₄ C ₁ pyrr][N(Tf) ₂]	50	7.4	72.31	1.394

It appears that the extraction of Zn²⁺ could be influenced by these physical properties in addition to each ILs' DN. Upon comparison of the data, the ILs which work best generally have a high DN, high viscosity and a low density. For example [C₄C₁im][OAc] has a high electron donating ability (DN), a relatively low density enabling the Zn²⁺ ions to cross over into the IL phase, and high viscosity to keep the Zn²⁺ within the IL. This suggests these are the ideal conditions to aid the highest possible partitioning of Zn²⁺ into the IL phase but the trend is not so evident to suggest that these are the only factors involved. [C₄C₁im][S₂CN(C₂H₅)₂] gives the highest DN and has an exceptionally high viscosity but in the extraction of Zn²⁺ does not perform as well even though the density is only marginally higher than that of [C₄C₁im][OAc]. Looking to balance the effects and probably have a have a high DN and viscosity with a reduced density.

Table 5.6 - Comparison of peak partition coefficient with rheological, DN, and Density measurements for ILs in the extraction of copper ions.

Ionic Liquid	Peak	Donor	Viscosity [mPa s]	Density [g cm ⁻³]
	Partition Coefficient Cu ²⁺	Number [kcal mol ⁻¹]		
[C ₈ C ₁ im]Cl	2902	70.0	3155.00	1.016
[C ₄ C ₁ im][Me ₂ PO ₄]	86	28.6	136.20	1.158
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	25	24.6	53.45	1.050
[C ₄ C ₁ im][OAc]	5647	21.3	158.90	1.066
[C ₄ C ₁ im][OTf]	85	19.8	77.95	1.295
[C ₄ C ₁ im][MeSO ₄]	53	19.6	97.02	1.200
[C ₈ C ₁ im][OTf]	2239	18.5	181.00	1.201
[C ₄ C ₁ pyrr][OTf]	40	16.4	131.80	1.249
[C ₄ C ₁ im][N(Tf) ₂]	147	9.90	57.24	1.431
[C ₄ C ₁ pyrr][N(Tf) ₂]	167	7.40	72.31	1.394

As with Zn²⁺ the Cu²⁺ densities and viscosities of the ILs were compared to the peak partition coefficient for each IL within the volume ratio range used (1:10 - 1:100) (Table 5.4). It is clear to see that the best performing ILs in the extraction of Cu²⁺ from diesel fuel are [C₈C₁im]Cl, [C₄C₁im][OAc] and [C₈C₁im][OTf]. However, there does not appear to be such an obvious trend as with Zn²⁺ in relation to the physical properties measured (Table 5.6). It was concluded that the ideal properties of the IL in the extraction of Zn²⁺ were high DN, high viscosity and low density. [C₄C₁im][OAc] seems to maintain this trend as it gives the highest partitioning of Cu²⁺ into the IL phase and possesses these properties. However, [C₄C₁im][Me₂PO₄] and [(CH₃)₂NH₂][(CH₃)₂NCOO] give significantly decreased partitioning of Cu²⁺ into the IL phase even though the properties are not too dissimilar to that of [C₄C₁im][OAc]. This suggests that the chemical composition of ILs plays a larger role in the extraction Cu(acac)₂ in addition to the physical properties of the ILs. The most

surprising result is the exceptional performance of [C₈C₁im][OTf] in the extraction Cu²⁺ regardless of its relatively low DN. [C₈C₁im]Cl displays an extremely high DN and viscosity in addition to a low density giving a higher peak partition coefficient than [C₈C₁im][OTf]. This can be explained via the high viscosity and intermediate density in addition to the octylimidazolium cation potentially causing an increased aggregation at the Fuel/IL interface.

5.2.4 Non-random Two-Liquid Equation (NRTL)

To finalise the study on the removal of dicationic metals, the activity coefficients of the Zn²⁺ and Cu²⁺ in the IL and n-hexadecane (diesel) phases were assessed using the NRTL model. This model has been shown to be useful for correlating the experimental liquid-liquid equilibrium data of systems containing ILs.¹³² The results from the extractions were fitted to the NRTL model as documented earlier with Na⁺ (Chapter 4).

5.2.4.1 Zinc Extraction

The configuration of the NRTL model was processed via mass fraction values calculated from the experimental data obtained from the ICP-OES. To draw up a comparison, using the [C₈C₁im][OTf] Zn²⁺ extraction as an exemplar, estimates against experimental mass fractions (W_i) were plotted for Zn²⁺ in both n-hexadecane and the IL (Figure 5.8). Similarly all ILs showed a good correlation for zinc ions.

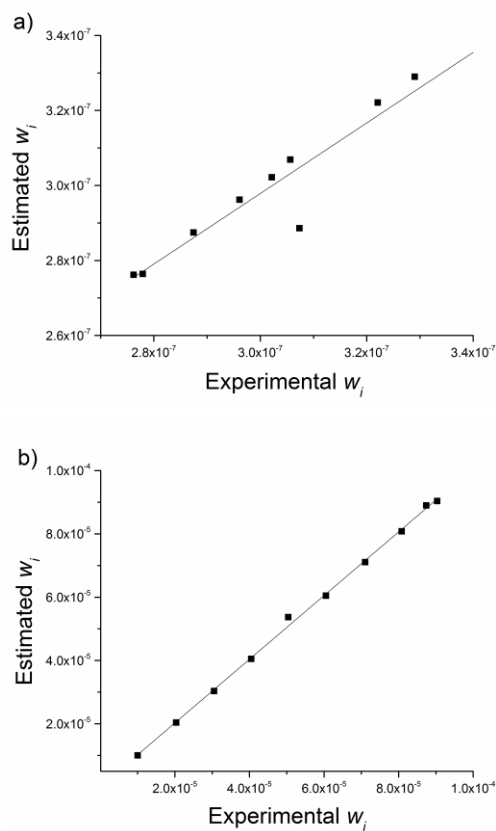


Figure 5.8 - Experimental mass fraction (w_i) vs calculated for (a) Zn^{2+} in n-hexadecane and (b) Zn^{2+} in $[\text{C}_8\text{C}_1\text{im}][\text{OTf}]$

τ values calculated via the model were compared with τ values calculated from the extraction data to ensure that the NRTL model was in line with the experimental data (Figure 5.9). $[\text{C}_4\text{C}_1\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ was removed from figure 5.7a and $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ was removed from both figure 5.8a and 5.8b to provide a clear trend between the τ values. A linear regression with DN was used as this factor provides information on the whole liquid opposed to β which only provides data relating to the anion of the ionic liquid. $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ was removed from the DN work in this section due to having an exceptionally high DN in comparison to other ILs. To carry out the liquid–liquid equilibrium calculation, phase compositions were obtained by solving an isothermal liquid–liquid flash at a given temperature and pressure.

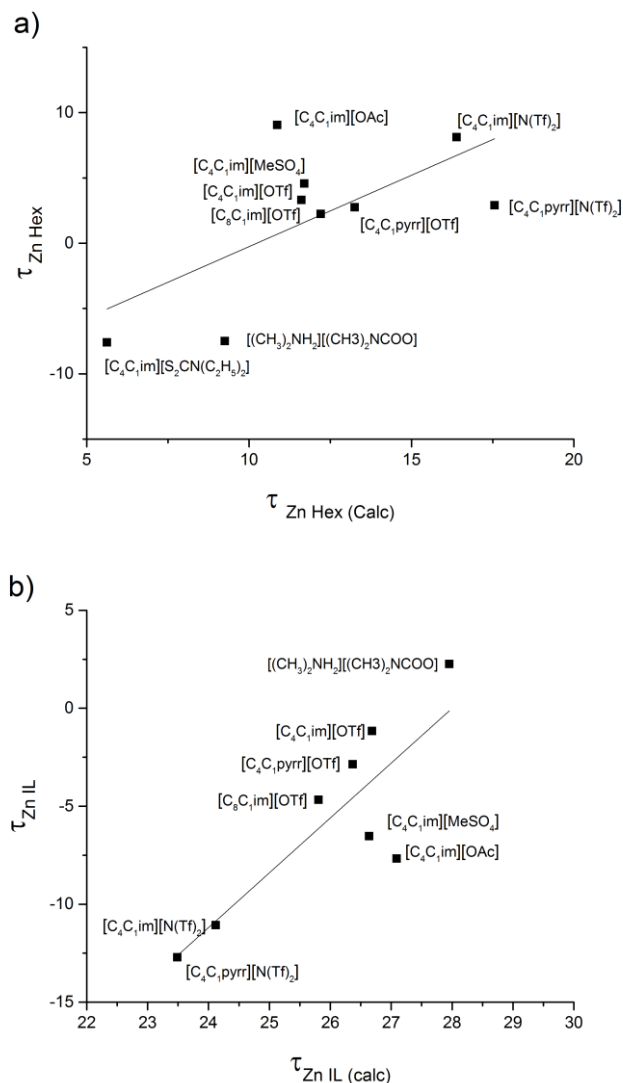


Figure 5.9 - Comparison of calculated (from experimental DN values) and NRTL model τ parameters (a) Zn^{2+} in n-hexadecane and (b) Zn^{2+} in IL

The correlation between DN and τ values was analysed (figure 5.10) displaying the same trend as in the Na^+ study ILs with particular anions group into clusters. In this data, the line was used to guide the eye as opposed to a best fit but generally as DN increases the τ parameter decreases for Zn^{2+} in n-hexadecane and increases for Zn^{2+} in the IL. This provides a trend showing the anion effect and which phase is preferable for the Zn^{2+} cations in the extraction system. This analysis demonstrates

that the NRTL model could be used to predict the Zn^{2+} and potentially Cu^{2+} partitioning into various ILs, or at least IL anion families, provided the β values (and therefore DN and τ) are known.

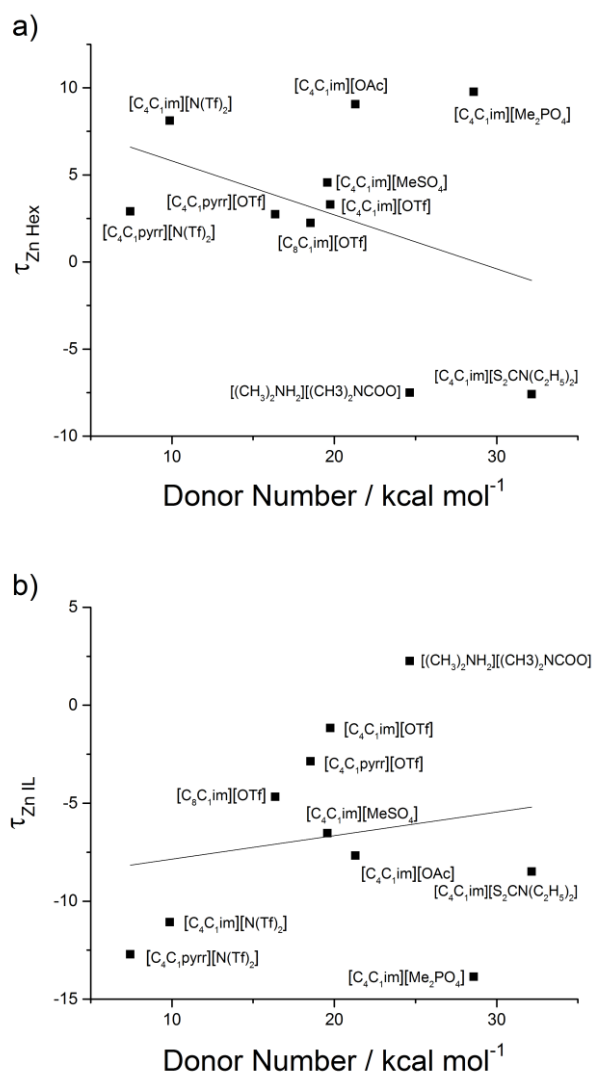


Figure 5.10 - τ vs Donor Number (a) Zn^{2+} in n-hexadecane and (b) Zn^{2+} in IL

5.2.4.2 Copper Extraction

The NRTL model was configured in the same manner as for Zn^{2+} via the mass fraction values calculated from experimental Cu^{2+} extraction data. To draw up a comparison, estimates against experimental mass fractions (w_i) were plotted for Cu^{2+} in both n-hexadecane and the IL using the $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ Cu^{2+} extraction as an exemplar (Figure 5.11). Similarly all ILs showed a good correlation for experimental and calculated copper mass fraction values.

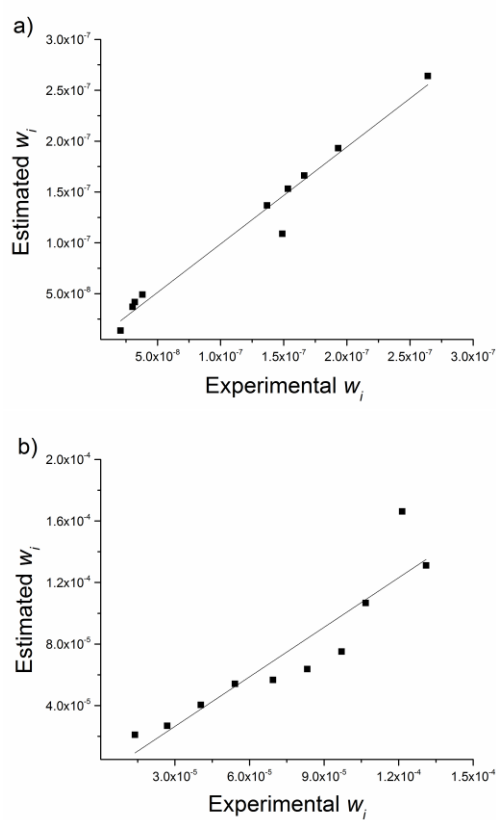


Figure 5.11 - Experimental mass fraction (w_i) vs calculated for (a) Cu^{2+} in n-hexadecane and (b) Cu^{2+} in $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$

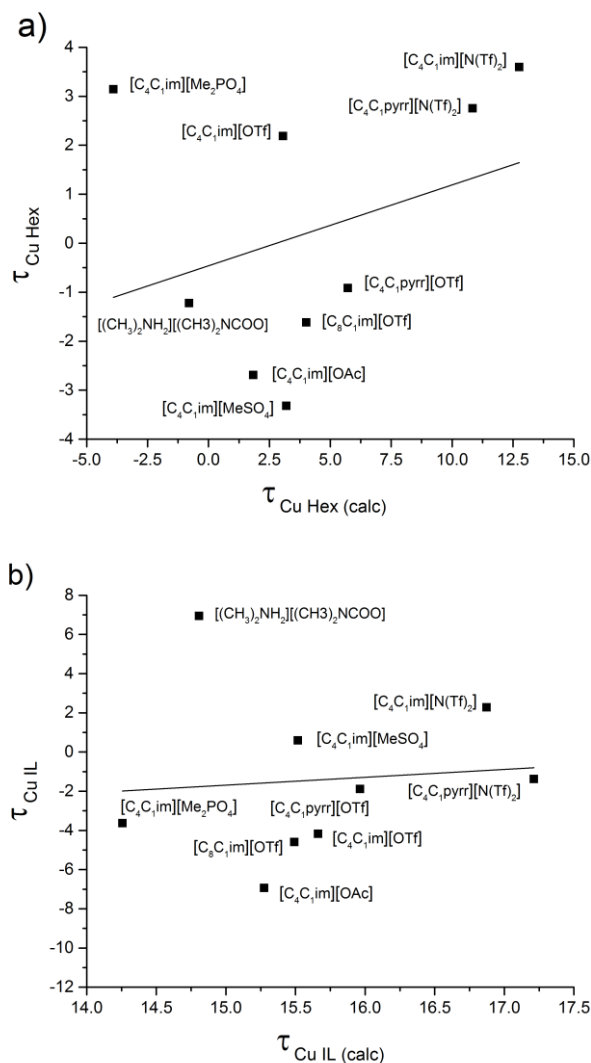


Figure 5.12 - Comparison of calculated (from experimental DN values) and NRTL model τ parameters (a) Cu^{2+} in n-hexadecane and (b) Cu^{2+} in IL

As with zinc ions, the copper ion extraction τ values calculated via the NRTL model were compared with τ values calculated from the extraction data to ensure that the NRTL model was in line with the experimental data (Figure 5.12). A regression with DN was utilised to provide the calculated τ values. $[\text{C}_8\text{C}_1\text{im}]\text{Cl}$ was also removed from the Cu^{2+} DN work due to having an exceptionally high DN in comparison to other ILs. Phase compositions were also obtained by solving an isothermal liquid–liquid flash at a given temperature and pressure. The linear fits (Figure 5.12a and

5.12b) are used here as guidance and not to provide clear trends. As with τ comparisons for Na^+ and Zn^{2+} it can be shown that the ILs with the same anions cluster together as displayed by the $[\text{N}(\text{Tf})_2]^-$ and $[\text{OTf}]^-$ based anion ILs (Figure 5.12). From this data it is clear to see that the $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$ IL does not fit this assumption.

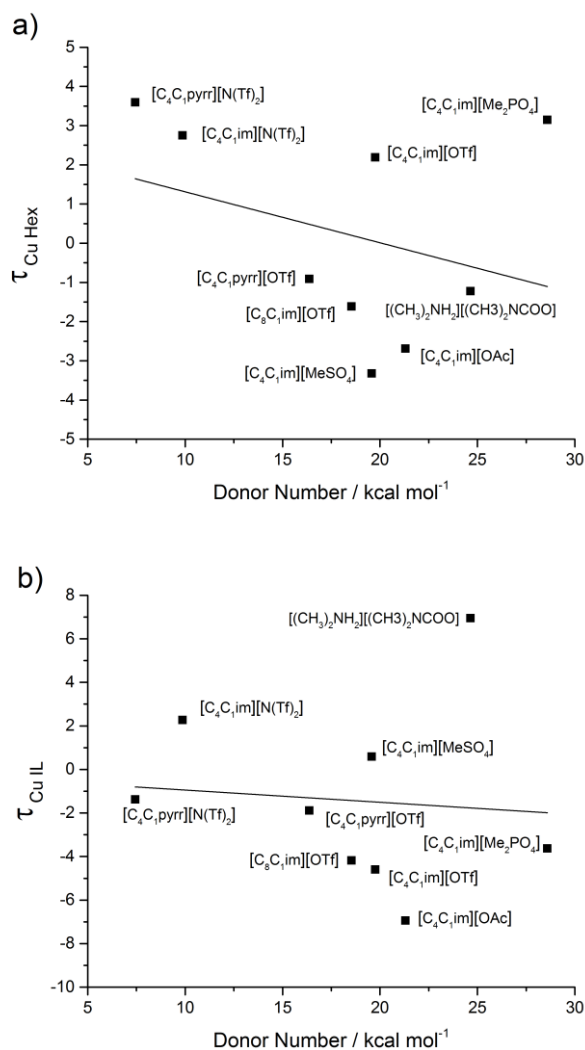


Figure 5.13 - τ vs Donor Number (a) Cu^{2+} in n-hexadecane and (b) Cu^{2+} in IL

The correlation between DN and τ values was analysed (figure 5.13) displaying the same trend as in the Na^+ and Zn^{2+} studies displaying ILs with particular anions

grouping into clusters. However, as with the τ comparisons there seems to be an exception of $[\text{C}_4\text{C}_1\text{im}][\text{OTf}]$ in this data. The line also was used to guide the eye as opposed to a best fit but generally as DN increases the τ parameter decreases for both for Cu^{2+} in n-hexadecane and Cu^{2+} in the IL. This provides a trend showing the anion effect and which phase is preferable for the Zn^{2+} cations in the extraction system. The analysis of Cu^{2+} extractions via the NRTL model demonstrates that it can be used to predict the Cu^{2+} partitioning into various ILs, or at least IL anion families. A list of τ parameters for Zn^{2+} and Cu^{2+} in both the fuel and IL phase can be found in Appendix D.

5.3 Conclusions

Overall, a wide selection of ILs were synthesised and examined for their extraction efficiency in removal of zinc and copper ions from n-hexadecane model fuels at a concentration of 2 and 1 mg kg^{-1} respectively. They have shown an array of trends in the extraction of zinc and copper ions, and show different partition coefficients between them. At a 100:1 (Fuel:IL) volume ratio using $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$, the best performing IL for the extraction of both metals, 99.3 % of Zn^{2+} and 99.7% of Cu^{2+} was extracted. This is the most suitable IL in terms of an industrial viewpoint due to high partition coefficient, and suitable elemental make-up for a fuel application (CHNO). In addition to this, ILs within the n-hexadecane were undetectable via NMR spectroscopy and mass spectroscopy thus all of the successful ILs in this study can be considered for an application in metal ion extraction from fuels. Minimal loss of ILs to the n-hexadecane phase is also beneficial for industrial applications due to minimal usage of the ILs and negligible contamination of the processed fuel in addition to the possibility of recycling the ILs.

The ILs ability to extract the metal ions were determined via partition coefficients for Zn^{2+} and Cu^{2+} over an increased volume of fuel (10-100 mL). Factors affecting the extent of extraction were investigated *via* correlation with experimental solvent descriptors, implying a strong link between the ILs ability to extract zinc and copper

ions with Kamlet-Taft's β values and ^{23}Na donor number. Application of the NRTL model to the experimental data determined τ values for each of the IL, showed some correlation to the DN and β values. All the data was taken into consideration when deducing a suitable extraction mechanism for the ILs. However, some of the ILs in this study gave a low partitioning of zinc and copper ions into the IL phase which is thought to be caused by the low affinity of the anion towards zinc and/or copper ions in addition to the properties of the ILs i.e. viscosity and density.

6 Application – Increasing Extraction Efficiency of Metals from Model and Market Fuels

6.1 Introduction

After a number of vigorous screening studies the most suitable ILs for the biphasic extraction of metals from diesel fuel were selected based on their partition coefficient and chemical make-up (CHNO). In addition, the synthesis and design of novel additives and ILs were undertaken to maximise the extraction based on prior information gained. A diesel sample was provided by Shell Global Solutions that was found to foul engines due to its metal content. This portion of the research is of great importance to the project as the ILs have proven to work in the extraction of Na^+ , Zn^{2+} and Cu^{2+} from surrogate fuels of n-hexadecane but diesel fuel on the market contains a wide range of additives included to optimise the fuel's desired properties. These could affect the extractions in a number of ways including inhibiting the effective partitioning of the metal into the IL. $[\text{C}_4\text{C}_{1}\text{im}][\text{OAc}]$ and $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ were the most successful candidates and were assessed in a 'one pot' extraction of the metals from a market fuel in addition to the use of a novel monoaza-crown IL.

6.2 Additive - 2,6-bis{[bis(2-pyridylmethyl)amino]methyl}-4-methylphenol (H-BPMP)

6.2.1 Background

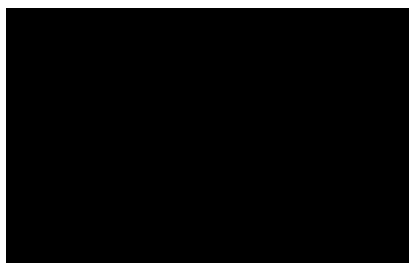


Figure 6.1 – Structure of 2,6-bis{[bis(2-pyridylmethyl)amino]methyl}-4-methylphenol, abbreviated to (H-BPMP)

The H-BPMP (Figure 6.1) was selected as an additive to take advantage of the metal ligand interaction, it is water soluble and therefore was assumed it would reside in the IL layer in a biphasic extraction with n-hexadecane and an IL, unlike the crown complexes that appeared to cross over the n-hexadecane phase. H-BPMP has been shown to form a crystalline dinuclear complex with Co^{II} and is thought to chelate well to the Zn^{2+} species in zinc neodecanoate (Figure 6.2).¹³⁴ Previous use of the molecule has included a chemical sensor for gamma and neutron radiation and a phosphate sensing probe.^{134,135} Refer to chapter 2 for the synthesis and characterisation of this molecule.

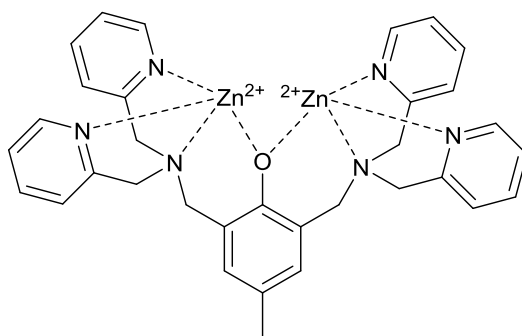


Figure 6.2 – Proposed Structure of the H-BPMP and Zn^{2+} Complex

6.2.2 Extractions

H-BPMP (15 mmol) was added to $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ and a range of $[\text{N}(\text{Tf})_2]^-$ anion based imidazolium ILs, with varying chain lengths, to monitor the effect on the partitioning of Zn^{2+} into the IL phase. The $[\text{N}(\text{Tf})_2]^-$ anion based ILs were selected due to the low partitioning of Zn^{2+} into the $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ phase and to see if chain length had any effect on extraction when using the additive. $[\text{C}_4\text{C}_1\text{im}][\text{Me}_2\text{PO}_4]$ had a high partitioning of Zn^{2+} into the IL phase (Chapter 5) so was used to compare the benefit of H-BPMP when the IL is already a high extractor.

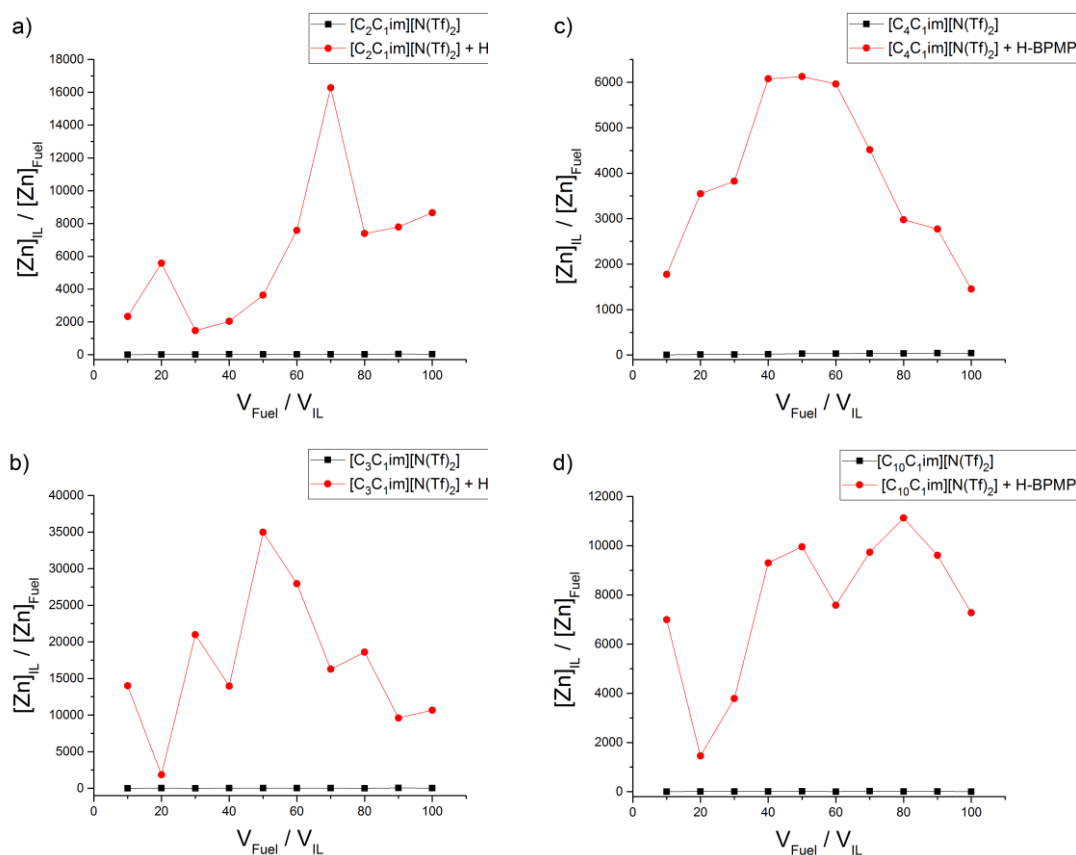


Figure 6.3 – ILs + H-BPMP partitioning of Zn^{2+} into the IL phase; a) $[C_2C_1im][N(Tf)_2]$, b) $[C_3C_1im][N(Tf)_2]$, c) $[C_4C_1im][N(Tf)_2]$ and d) $[C_{10}C_1im][N(Tf)_2]$

The addition of H-BPMP is shown to increase the partitioning of Zn^{2+} into the IL phase by a substantial amount but varies with each IL. All of the $[N(Tf)_2]^-$ anion based ILs without H-bpmp appear to be ‘flatlined’ in comparison. An interest lay in how the alkyl chain length would affect the role of the H-BPMP being added. There does not appear to be any clear trend but with higher peak partition coefficients are seen when the chain length is shorter with the optimum chain length is being propyl (C3). There however appears to be a number of fluctuation within the partition coefficients for the data which could suggest optimal vortex volumes. The maximum partition coefficient for $[C_2C_1im][N(Tf)_2]$ displays a large value at 70:1 and is an isolated data point so could be a fluctuation however, there does seem to be a gradual increase in partition coefficient with volume upto 70:1 Fuel:IL which drops

immediately as it reaches 80:1 Fuel:IL. $[C_3C_1im][N(Tf)_2]$ show initially an increased partition coefficient at 10:1 Fuel:IL which decrease at a 20:1 Fuel:IL loading which can be explained by there being no contamination at 10:1 sampling but is present at the 20:1 sampling. This pattern is again shown for the $[C_{10}C_1im][N(Tf)_2]$ IL in addition to a lower than expected partition coefficient at 60:1 Fuel:IL.

Table 6.1 - Comparison of Peak Partition Coefficients for the extraction of Zn^{2+} before and after the addition of H-bmp

Ionic Liquid	Peak Partition Coefficient	Peak Partition Coefficient with H-BPMP	Peak Zn^{2+} Extraction with H-BPMP (%)
$[C_2C_1im][N(Tf)_2]$	44.37	16275	99.9
$[C_3C_1im][N(Tf)_2]$	46.10	34975	99.9
$[C_4C_1im][N(Tf)_2]$	44.69	6076	99.4
$[C_{10}C_1im][N(Tf)_2]$	19.35	11128	99.9

Unexpectedly the partition coefficient of $[C_4C_1im][Me_2PO_4]$ was dramatically increased further than the already high partition coefficient of 8294 giving a new maximum of 34,975. It should be noted that error bars are present for the $[C_4C_1im][N(Tf)_2]$ and $[C_4C_1im][Me_2PO_4]$ without H-BPMP but cannot be seen on this scale. Time did not permit to repeat the remaining ILs with and without H-BPMP so the standard deviation was utilised from the three measurements taken for each Fuel:IL data point via ICP-OES experiments as the experimental error.

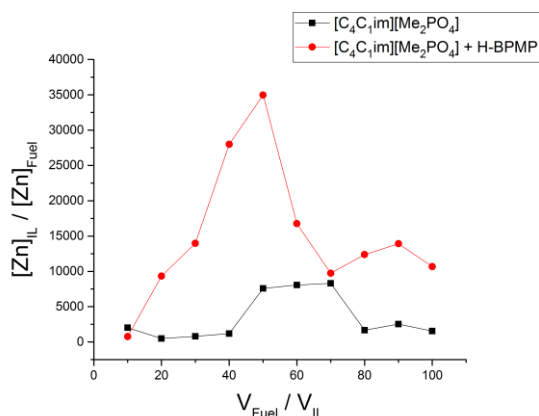


Figure 6.4 - ILs + H-BPMP partitioning of Zn into the IL phase; $[C_4C_1im][Me_2PO_4]$

6.3 Crown Ether Complexes

6.3.1 Background

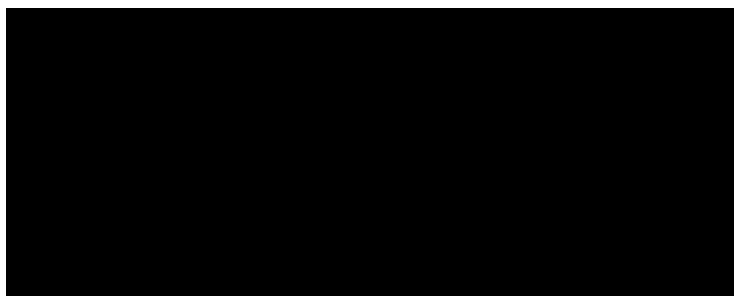


Figure 6.5 – Crown Ethers; a) 18-Crown-6 and b) 15-Crown -5

The synthesis of crown ethers has provided a new family of ligands for certain metal cations. They have found a range of applications in solvent extraction systems that are highly selective for metal ions based on the sizes of the crown-ether rings.¹³⁶ These systems utilise a crown ether phase to target metal ions from different solutions through the complexation of the metal with the specific crown ether. The idea here comes in using the crown complexes as an additive to ILs, or by producing an aza crown ring a crown ether functionalised IL can be synthesised via protonation of the nitrogen (Figure 6.6).

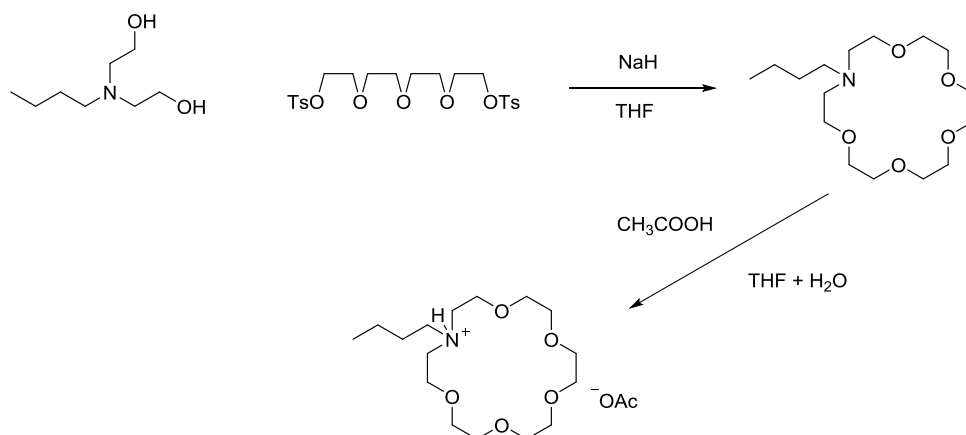


Figure 6.6 – Synthesis of 1-Butyl-aza-[18-C-6H][OAc]

6.3.2 Application

18-crown-5 and 15-crown-5 (15 mmol) were added individually to $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ and the metal concentrations of the fuels post extraction were analysed via ICP-OES. Addition of the crowns was found to decrease the partitioning of sodium from the diesel fuel into the IL suggesting that the crown competitively complexes to the target metal ion but resides in the fuel layer as it has a higher affinity for this phase (Figure 6.7). Therefore, an aza-crown IL was designed (Figure 6.6) to increase the polarity of a crown type molecule and induce a higher affinity for the IL phase. The increase in polarity was achieved by the introduction of a positively charged nitrogen atom and negatively charged acetate anion. The most suitable anion (acetate, $[\text{OAc}]^-$) for the extraction of zinc and copper (Chapter 5), was incorporated into the structure endeavouring to provide the maximum possible extraction of the metals giving rise to the number of problems within diesel engines. This monoaza-crown IL is designed to provide both a crown ether ring, and acetate anion bringing together the chelation advantages of both leading to a possible ‘one pot’ extraction approach.

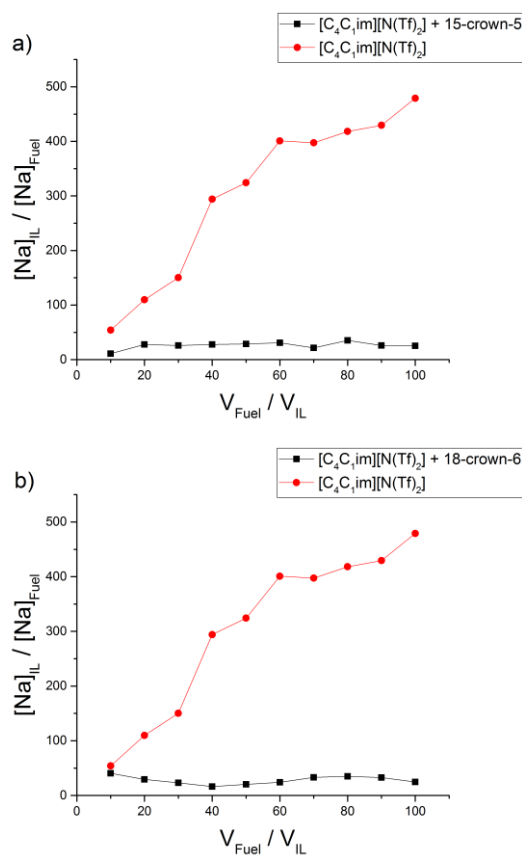


Figure 6.7 – Use of a) 15-crown-5 and b) 18-crown-6 in $[C_4C_1im][N(Tf)_2]$ as additives to monitor their effect on the partitioning of Na into the IL phase

6.3.3 Extractions

1-Butyl-aza-[18-C-6H][OAc] (15 mmol) was added to $[C_4C_1im][N(Tf)_2]$ with the purpose of providing an increased polarity over a standard crown ether thus chelating to the metals and remaining in the polar IL phase. $[C_4C_1im][N(Tf)_2]$ was selected as the bulk IL due to its availability, and ease of comparison with the H-BPMP additive study. A model was produced with concentrations of 0.715, 0.285 and 0.214 mg kg⁻¹ of Na⁺, Zn²⁺ and Cu²⁺ respectively. The standard extraction procedure as outlined in Chapter 2 was followed producing comparison graphs for each individually targetted metal for $[C_4C_1im][N(Tf)_2]$ with, and without, the 1-

Butyl-aza-[18-C-6HK][OAc] IL additive (Figure 6.8). This was to determine if there was an increase or decrease in the partitioning of metals into the IL through the addition of 1-Butyl-aza-[18-C-6H][OAc]. In the extraction of Na^+ it is clear to see that the addition of 1-Butyl-aza-[18-C-6H][OAc] drastically decreases the partitioning of Na^+ into the IL phase (Figure 6.8a). The use of the monoaza-crown IL was thought to increase the partitioning of Na^+ into the IL but this does not appear to be the case. This could be explained via a number of reasons:

- The 18-C-6 monoaza crown ring size does not provide the highest affinity for Na^+ which suggests a different sized ring will increase the affinity for the metal and thus partitioning of Na^+ into the IL phase. 15-C-5 (decreased cavity size) and 21-C-7 (increased donor atoms) crown ether ring sizes have both been shown to provide a higher affinity for Na^+ and could be utilised in further experiments to target Na^+ in n-hexadecane.¹³⁷
- The protonated nitrogen that forms part of the monoaza-crown ring could potentially skew the shape of the crown thus providing a decreased fit and thus inhibiting chelation with the desired metal. Protonation of active sites has been shown to decrease affinity of substrates in a similar manner due to a skewed shape.¹³⁸

With the extraction of Zn^{2+} it is clear to see that the addition of 1-Butyl-aza-[18-C-6H][OAc] increases the peak partitioning of Zn^{2+} into the IL phase (Figure 6.8b). This provides the largest increase in partitioning of the three metals. However, the peak partition coefficient of $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ and 1-Butyl-aza-[18-C-6H][OAc] at 5393 (40:1 Fuel:IL) (Table 6.2) is significantly less than the peak partition coefficient of $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ for Zn^{2+} at 13061 (90:1, Fuel:IL). The high affinity of $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ for Zn^{2+} displayed in Chapter 5 suggests that this increase in partition coefficient is caused by the presence of the $[\text{OAc}]^-$ anion but is limited due to the decreased concentration (15 mmol) and thus $[\text{OAc}]^-$ anion itself. Another explanation is that

the competition and chelation of Cu^{2+} to the $[\text{OAc}]^-$ anion in the model fuel would lower the peak partition coefficient.

Table 6.2 - Comparison of Peak Partition Coefficients for the extraction of Na^+ , Zn^{2+} and Cu^{2+} with and without the use of the 1-butyl-aza-[18-C-6H][OAc] additive

Target Metal	Peak partition Coefficient of $[\text{C}_4\text{C}_{11}\text{im}][\text{N}(\text{Tf})_2]$	Peak Partition Coefficient with 1-Butyl-aza-[18-C-6HK][OAc]	Peak Extraction with Additive (%)
Na^+	479.0	20.72	20.7
Zn^{2+}	44.70	5393	99.3
Cu^{2+}	147.2	424.8	95.8

As with the extraction of Zn^{2+} the peak partition coefficient of Cu^{2+} into the IL phase increases on the addition of 1-butyl-aza-[18-C-6H][OAc] to $[\text{C}_4\text{C}_{11}\text{im}][\text{N}(\text{Tf})_2]$. The peak partition coefficient increases from 147.2 (90:1 Fuel:IL) to 424.8 (30:1 Fuel:IL) suggesting that the $[\text{OAc}]^-$ anion has a higher affinity for Zn^{2+} . It has been displayed in previous research that Zn^{2+} has a higher adsorption to acetate than that of Cu^{2+} which explains this effect.¹³⁹ Both Zn^{2+} and Cu^{2+} would not strongly chelate to larger crown ring sizes due to their relatively small ionic radii thus a smaller ring such as 15-crown-5 could provide a stronger chelation.¹⁴⁰ This further emphasises that the increase in peak partition coefficient is strongly related to the presence of the $[\text{OAc}]^-$ anion in the 1-butyl-aza-[18-C-6H][OAc] IL. An exemplar run though with the IL is present in Table 6.2 displaying the maximum extraction for each metal within the volume range and the concentration of the model fuel used. It must be noted that there are two fluctuations present in the Zn^{2+} partition coefficient trend at 20:1 and 40:1 Fuel:IL which are both higher than expected this again could be caused by optimum vortex conditions thus providing an increased partition coefficient.

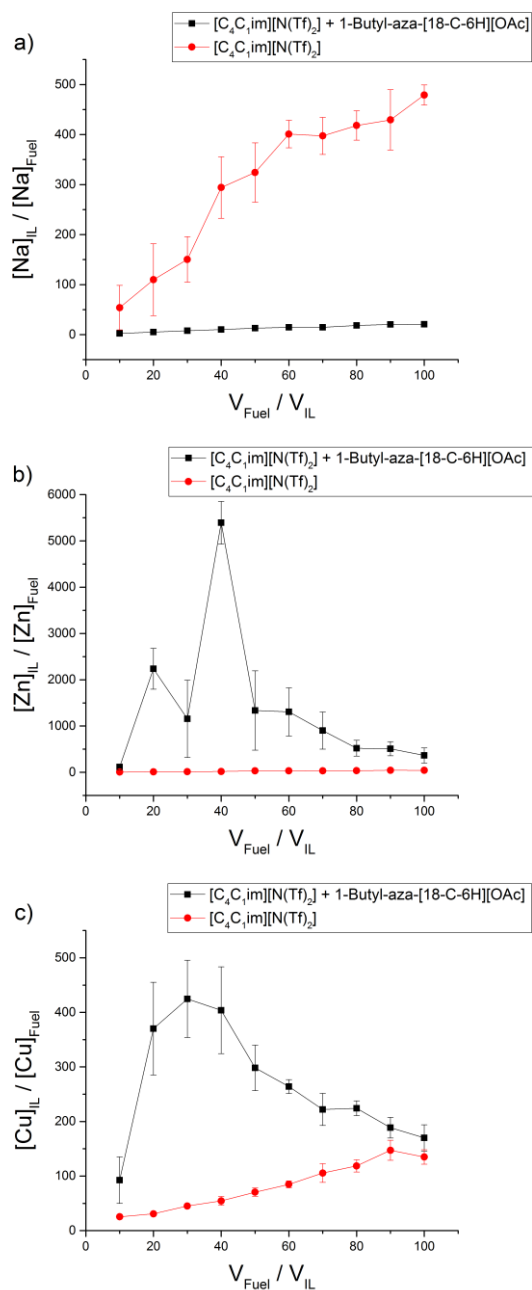


Figure 6.8 - ILs + 1-Butyl-aza-[18-C-6H][OAc] partitioning of a) Na^+ , b) Zn^{2+} and c) Cu^{2+} into the IL phase; $[C_4C_1im][N(Tf)_2]$

6.4 Market Fuels

6.4.1 Background

Shell Global Solutions provided a sample of diesel fuel used in the fuel industry. This was a CEC reference fuel (RF79-07; batch 7) blended with 1 ppm zinc neodecanoate. The fuel was blended early 2016 and failed the industry standard fouling test. This was selected due to the relevance of the study aiming to extract the metals and thus prevent fouling. $[C_4C_{1im}][OAc]$ and $[(CH_3)_2NH_2][(CH_3)_2NCOO]$ were selected as the most suitable for an application in fuel due to their ability to provide high partitioning of metals into the IL phase in addition to only containing CHNO atoms (Chapters 4 and 5).

The concentration of metals determined via ICP-OES in the market fuel was significantly less than stated for the standard industry models, to which we prepared our models to. The concentration of metals present in the fuel was $0.068 \text{ mg kg}^{-1} \text{ Na}^+$ and $0.032 \text{ mg kg}^{-1} \text{ Zn}^{2+}$. However, the models were designed to represent the highest concentrations that have been seen in the field. The RF79-07 fuel contained detectable amounts of zinc and sodium but not copper so we were unable to determine the ability of these ILs to extract copper from market fuels. As the results provided from the screening studies show that $[C_4C_{1im}][OAc]$ provides a similar peak partition coefficient for zinc and copper (Chapter 5) we can imply that it should provide similar results for copper extraction.

6.4.2 Extractions

$[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ (Figure 6.9) and $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ (Figure 6.10) were examined for their ability to extract zinc and sodium from RF79-07 in a biphasic extraction. This was carried out with the same methodologies as the screening studies (Chapter 2) and upon completion of the extractions, partition coefficients were calculated. $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ which over the range of tested volume ratios, had partition coefficients which, generally increases for both metals but are relatively low: 57.21 (70:1, Fuel:IL) and 158.1 (100:1, Fuel:IL) for Na^+ and Zn^{2+} respectively. At the fuel loading 80:1 for Zn^{2+} the partition coefficient is lower than expected. This could be caused by contamination during sampling as this point is isolated.

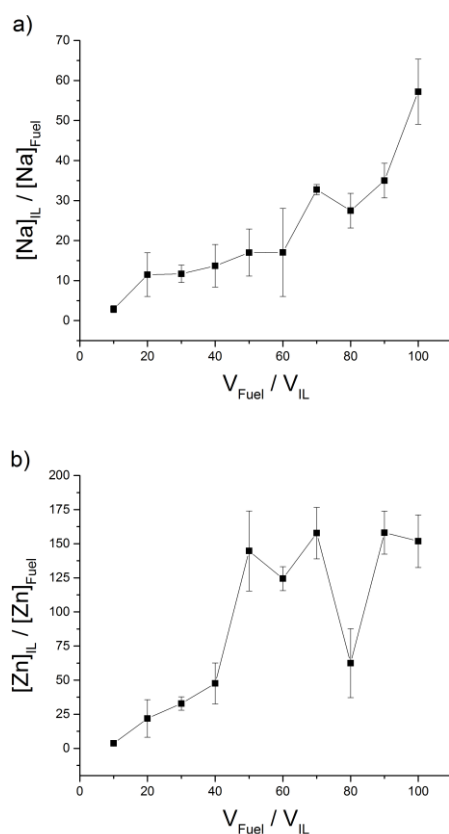


Figure 6.9 - $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ in the extraction of metals from RF79-07 market fuel; a) Na^+ and b) Zn^{2+}

Over the range of Fuel:IL ratios the partition coefficient of $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ generally increases for Na^+ . Zn^{2+} gives rise to a sharp increase (60:1, Fuel:IL) and subsequently a sharp drop (90:1, Fuel:IL). $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ performs best with the market fuel giving a peak partition coefficient of Na^+ at 2937 (70:1, Fuel:IL), compared to 50.7 (100:1, Fuel:IL) for $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$. For Na^+ the peak partition coefficient at 70:1 appears to be a fluctuation in the trend but it is just as likely that the point at 80:1 is lower than expected and thus exaggerated how increased the peak partition coefficient is.

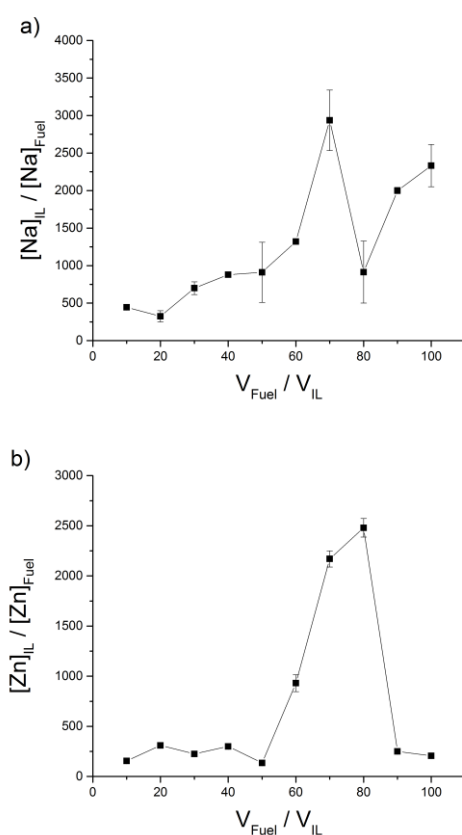


Figure 6.10 - $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ in the extraction of metals from RF79-07 market fuel; a) Na^+ and b) Zn^{2+}

The calculated peak partition coefficients for the market fuels were compared against the peak partition coefficients for the model fuels (Table 6.3). It is evident to see that the partition coefficients for the extraction of both metals from the

market fuel is significantly lower than an extraction from the model fuels. For example, $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ in the extraction of Zn from the market fuel displays a peak partition coefficient of 2480 (80:1, Fuel:IL) which, in comparison with the large 13061 (90:1, Fuel:IL) for the extraction of Zn from the model fuel shows that there will be other effects governing the chelation of the IL with the metal. However, considering the extraction of Na via $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ we can see an exceptional peak partition of 2937 (70:1, Fuel:IL) with the market fuel compared to 440 (20:1, Fuel:IL) with the model fuel. This suggests that the conditions of the market fuel can provide a more efficient extraction or the Na^+ could be in a state for which the $[\text{OAc}]^-$ has a higher affinity. An exemplar run though with each of the ILs with market fuel are present displaying the maximum extraction for each metal within the volume range and the concentration of the model fuel used.

If we use a similar classification system for the market fuel as was used for the model extractions (Chapter 4 and 5) we can categorise both metals for the individual ILs into one group due to the likeness of their values. $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ is classified as giving a low (L) peak partition coefficient (0 – 1000) for the extraction of both metals and $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ is classified as giving a high (H) peak partition coefficient (2000 and above).

Table 6.3 – Peak Partition coefficients for the extraction of Na^+ and Zn^{2+} from model and market diesel fuels.

IL + Target Metal	Peak Partition Coefficient with Model Fuel	Peak Partition Coefficient with Market Fuel	Peak Extraction with Market Fuel (%)
$[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}] + \text{Na}$	1865	57.21	47.1
$[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}] + \text{Zn}$	1722	158.1	81.3
$[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}] + \text{Na}$	440	2937	98.5
$[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}] + \text{Zn}$	13061	2480	96.8

This leads to a number of possible explanations for the values obtained in the extraction of both metals from the market fuel. Other additives in the fuel could be in competition with the metal to chelate with the ILs anion therefore limiting the amount of metal that the IL can extract. The physical properties of the market fuel such as viscosity, IFT and density could be very different. For instance the market fuel has the highest viscosity of 2.99 mPa s (Chapter 3) which would suggest that the metal ions are more likely to remain in the fuel layer if considering the previous discussion regarding the ILs viscosity in metal extraction (Chapters 4 and 5). This would explain the low partition coefficients for the extraction of metals from the market fuel. However, [C₄C₁im][OAc] has the lowest partition coefficient in the extraction of sodium from the model fuel. The Na model fuel has the second largest viscosity of 2.81 mPa s (similar to market fuel) and a high concentration of sodium dodeceny succinic acid (NaDDSA) relatively, but the main idea here is that NaDDSA has an effect on the extractions as it will be present in the market fuels and in larger concentrations within the Na model, thus effecting the chelation of ILs to metals.

6.5 Conclusion

The research undertaken in this chapter has focused on improving the extraction of metals with ILs via designed additives and the application of the most suitable ILs to market fuels. The use of H-BPMP (15 mmol) has displayed very positive results increasing the peak partition coefficients dramatically. [C₃C₁im][N(Tf)₂] with H-BPMP was able to extract Zn²⁺ with a partition coefficient of 34975 giving the highest partitioning of any metal into the IL phase recorded during this research. This is substantial considering the [N(Tf)₂]⁻ based ILs do not usually show high partitioning of Zn²⁺ into the IL phase. To further increase the extraction of Zn²⁺, H-BPMP could be added to [C₄C₁im][OAc] however, H-BPMP may not be applicable to a fuel application due to the high cost of the molecule.

The synthesised 1-butyl-aza-[18-C-6H][OAc] IL was expected to increase the extraction of all metals in a 'one pot' extraction by the addition of 15 mmol of it to

[C₄C₁im][N(Tf)₂]. However, this did not show the promising results as the use of H-BPMP did. It appears that further manipulation and design are required to increase the affinity of the IL towards Na⁺, Zn²⁺ and Cu²⁺. From the results it is clear to see that the production of a similar molecule containing a monoaza 15-crown-5 ring could provide the desired extraction levels. The extraction of metals from market fuels using [(CH₃)₂NH₂][(CH₃)₂NCOO] and [C₄C₁im][OAc] showed that it is possible to extract Na⁺ and Zn²⁺ from market diesel fuels using ILs. These of course display different partition coefficients than the extractions using model fuels as there will be a number of additive within the market fuel that could hinder the extraction via ILs. Overall, [C₄C₁im][OAc] is the most promising candidate for the application providing high partition coefficients with the market fuel and consisting of only CHNO atoms.

7 Conclusions and Further Work

7.1 Conclusion

The overall aim of the study was to exploit the advantageous solvent properties of ionic liquids and apply them to the selective biphasic extraction of Na^+ , Zn^{2+} and Cu^{2+} from diesel fuels thereby eliminating the problems caused by IDIDs, nozzle deposits and oxidation stability reduction.

A range of ILs were designed and synthesised for a diverse screening study to determine the ability of ILs to extract the metals from n-hexadecane model fuels in a liquid-liquid extraction and the desirable functionalities for high efficacy. The extractions were carried out and the remaining metal concentrations in the fuel layer were analysed by ICP-OES. Mechanisms were deduced and an 'in-depth' understanding of each IL via assessment of the relevant IL properties and selecting the most suitable candidate for the application. Further to this there are two routes in which the mechanism could proceed and further work needs to be carried out to confirm the correct extraction mechanism. Firstly this could proceed via a direct extraction of the metal from n-hexadecane via the ILs anion by direct chelation upon vortex mixing. A more likely scenario is the exchange of both the ILs constituent cation and anion with the metal and anionic component of the complex present in the fuel. Further work needs to be carried out to determine the role of the cation in the extraction of these additives to reach a final conclusion regarding the mechanism.

In an attempt to further enhance the extraction of the metals, the H-BPMP additive and a novel aza-crown IL were synthesised and added to ILs to produce 15 mmol solutions. The effects of these additives on the metal extractions and partition coefficients were monitored. The addition of H-BPMP was able to increase the extraction of Zn^{2+} up to 99.9 % and can increase the peak partition coefficients with great magnitude (Chapter 6).

All of the ILs synthesised in this study were able to extract the metals from the fuels to some extent as the results showed there was at least minimal partitioning of the metals from the fuel into the IL phase. The extent of partitioning of each metal for

each individual IL was examined and compared against the individual properties of the ILs. $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ was found to be most applicable in the extraction of Na^+ , and $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ for the extraction of Zn^{2+} and Cu^{2+} due to these ILs giving the highest partitioning of metals into the IL phase and possessing the most suitable chemical make-up for an application in fuel containing only atoms of CHNO. This study has shown that at a 100 : 1 (Fuel : IL) volume ratio:

- Na^+ can be extracted up to 99.1% from a model fuel consisting of n-hexadecane and just 3 mg kg^{-1} sodium dodecenylsuccinic acid.
- Zn^{2+} can be extracted up to 99.3% from a model fuel consisting of n-hexadecane and 2 mg kg^{-1} zinc neodecanoate.
- Cu^{2+} can be extracted up to 99.7% from a model fuel consisting of n-hexadecane and 1 mg kg^{-1} copper(II) acetylacetonate.

Properties of the ILs which appear to be directly involved in the ability of the ILs to extract the metals from diesel fuels seems to be a combination of donor number, viscosity, density and IFT depending on the metal being targeted. The most applicable ILs; $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ and $[\text{C}_4\text{C}_1\text{im}][\text{OAc}]$ were then implemented in a more 'realistic' real-world scenario to extract the target metals from market fuels obtained via Shell Global Solutions. These fuel samples contained only Zn^{2+} and Cu^{2+} and the ILs showed a reduced partition coefficient in comparison to extractions from the constituent model fuels. However, they display the ability to remove both metals successfully from diesel fuel.

In summary:

- A diverse range of ILs have been synthesised and characterised with a focus on liquid-liquid extraction of metals from diesel fuel.

- The biphasic extraction of metals from model diesel fuels using ILs has been confirmed as possible with some exceptional capabilities of individual ILs especially those candidates containing acetate and carbamate anions.
- Factors affecting the extent of extraction were investigated *via* correlation with experimental descriptors.
- Extraction data for the fuel models has been fitted to an NRTL model to ensure that the data correlates to a thermodynamic model.
- Novel mono-aza crown ILs and the H-BPMP additive have been designed and employed to provide the most efficient extraction possible.
- $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ and $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ have been assessed in the extraction of Na^+ and Zn^{2+} from market diesel fuels in a ‘one pot’ extraction proving that these metals can be extracted using ILs.
- At a 100:1 (Market Fuel : IL) volume ratio $[(\text{CH}_3)_2\text{NH}_2][(\text{CH}_3)_2\text{NCOO}]$ has been shown to extract up to 81.25 % Zn^{2+} and 38.24 % Na^+ and $[\text{C}_4\text{C}_{1\text{im}}][\text{OAc}]$ has been shown to extract upto 68.75 Zn^{2+} and 98.53 % Na^+ simultaneously.

7.2 Further Work

This study has provided a pathway to a relevant and exciting application of ILs but further refinement of the research needs to be carried out. The research offers a detailed understanding of the fundamentals in the extraction of metals from diesel fuels using ILs but now these ILs need to be investigated further to determine if they can be employed in the fuel industry via cartridge filtration or a liquid-liquid extraction in the fuel tanks.

7.2.1 Recyclability of ILs

An important and interesting area which was not undertaken in this study was the recyclability of the ILs. Once the extraction of metals has taken place it could easily be separated from the IL using one of the following procedures:

- Electrocoagulation - low cost, low purity, oxide formation
- Electrodeposition - higher cost, high purity, control state of metal.

These processes can be screened for use in this application via cyclic voltammetry; indicating if the extraction of the metal from the IL is possible and cyclic amperometry; showing the potential and maximum efficiency of the recovery. The metal could then be used in wide ranging applications or sold for use in industries that require high purity metals (e.g. electronic industries). The ILs could be reused for the extraction of metals in the fuel industry increasing the feasibility of ILs for this application.

7.2.2 Extraction Optimisation

Throughout this study it has been shown that the extractions work in a single environment due to the temperature remaining constant. However, if the conditions of the environment are altered, the optimum extraction conditions for the partitioning of the metal into the IL phase can be defined. Monitoring the effect of temperature variation (10 – 100 °C) on the extraction of metals from n-hexadecane could provide this information to allow further optimisation of the extraction. Also a saturation study could identify the maximum loading of metal in the IL and thus further emphasise that feasibility of the application providing the most suitable Fuel : IL volume ratio for each IL.

Further assessment of the IL water content and how this affects the extraction of Na^+ , Zn^{2+} and Cu^{2+} from n-hexadecane is important because water present in the

fuel could hinder the uptake of the metals. In addition to this the water content of the fuel can be monitored to determine if ILs remove water. Water can have detrimental effects during the storage of diesel fuel due to enabling the growth of algae in the tanks therefore if the ILs offer an ability to 'dry' the fuel as well as extract the metals this is an additional benefit.

7.2.3 Fuel Additives

With regards to metal extraction from the market fuel a full analysis of the components within the fuel is required. Analysis should be undertaken prior and post-extraction to display the effects that the IL has had on the composition of the fuel. Additives used in market fuels are vital to provide the desired properties of the fuel desired by the manufacturer. If any of these additives are removed it could have a detrimental effect on the performance of the fuel which is designed to provide certain criteria.

7.2.4 Further Synthesis

The further synthesis of aza-crown ILs with varying ether linkages and anions is important to fully exploit and investigate the potential of this family of ILs. This will highlight the most suitable crown ether ring size and anion to maximise the extraction of all target metals in diesel fuel. Different size rings may be required to target different metals hence a mixture of sizes may be advantageous. The synthesis of PEGylated ILs (Figure 7.1) could provide an alternative to the aza-crown ILs. The ether chain can be manipulated for a higher affinity for the desired metal. These types of ILs have already been utilised in the chelation of metals such as Mg^{2+} .¹⁴¹

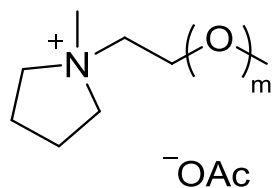


Figure 7.1 - General molecular structure for PEGylated ILs.

As displayed with the synthesised additives in this study (Chapter 6) they can be added to a common ILs such as $[C_4C_1im][N(Tf)_2]$ in mmol quantities to determine if they improve the extraction of the trace metal impurities.

The synthesis of novel cyclen and porphyrin ILs based on their high affinity for multivalent metal ions could be exploited. The synthesis would proceed via a protonation of the N groups present in the molecules aza ring. Used as a minor component, these additives could enhance performance and would be quantitatively retained in the IL.

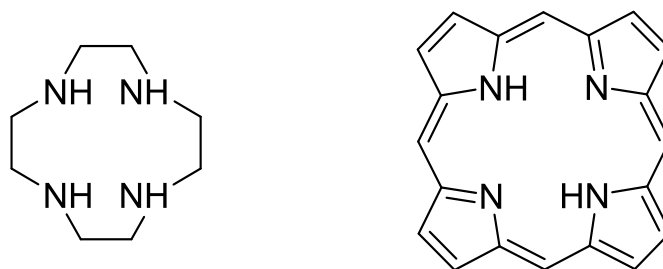


Figure 7.2 - Cyclen (left) and porphyrin (right) structures possessing potential to form ILs.

These IL designs could lead to additive IL-based processes, where extremely efficient ILs can be used in even more minuscule quantities than our present systems due to the multiple chelation effects. As the IL loadings are not presently limiting, we expect affinity or mass transport to limit loadings for a continuous or semi-continuous large-scale process. Whilst exploiting the pathway to which this study has provided to extract. The following will need to be considered in a final decision for full application:

- Economy of ILs for this application (to assess commercial feasibility).

- Chemical make-up of ILs (CHNO only is desirable to avoid potential contamination, though the IL is not at detectable levels in the fuel post-extraction).
- Are chelating additives actually necessary (to enhance performance or extraction kinetics)?

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Appendix

Appendix A

Donor Number Calibration

Table A.1 - ^{23}Na NMR data and corresponding DN for a range of solvents used in the production of a calibration line⁷³

Solvent	Donor Number (kcal mol ⁻¹)	^{23}Na shift (ppm)
Nitromethane	2.7	-12.7184
Acetanhydride	10.5	-11.3866
Benzonitrile	11.9	-6.7318
Acetonitrile	14.1	-6.9038
Acetone	17	-7.2938
γ -butyrolactone	18	-8.2835
THF	20	-7.5993
n-Pentanol	25	-2.6268
DMF	26.6	-4.2517
DMSO	29.8	-0.0245
H ₂ O	33	0
Pyridin	33.1	-0.11
Isopropanol	36	-0.6233
t-Butanol	38	-0.0733
HMPA	38.8	2 ^a
Ethylendiamine	55 ^b	12.4618

^aPopov

^bGutmann

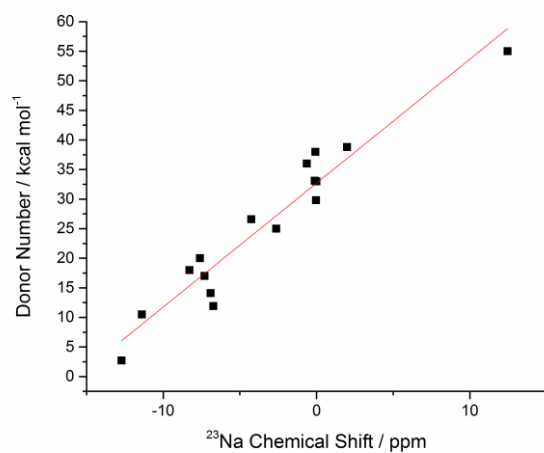


Figure A.1 - Calibration line used for the assignment of Donor Numbers and thus calculation of the DN from the chemical shift of the ²³Na signal ⁷³

$$DN \text{ (kcal mol}^{-1}\text{)} = 32.7397712308 + 2.1061380895 \times Na \delta 23 \text{ (ppm)}$$

Appendix B

Viscosity Profiles

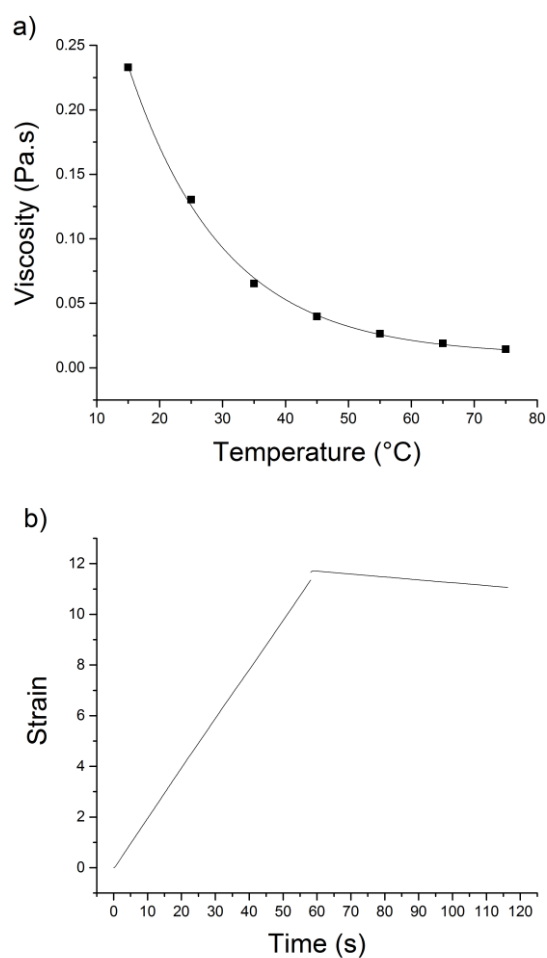


Figure A.2 - Viscosity profile for $[C_4C_1im][Me_2PO_4]$ including; a) viscosity over the temperature range of 15 – 75 $^{\circ}C$ and b) creep and creep recovery steps

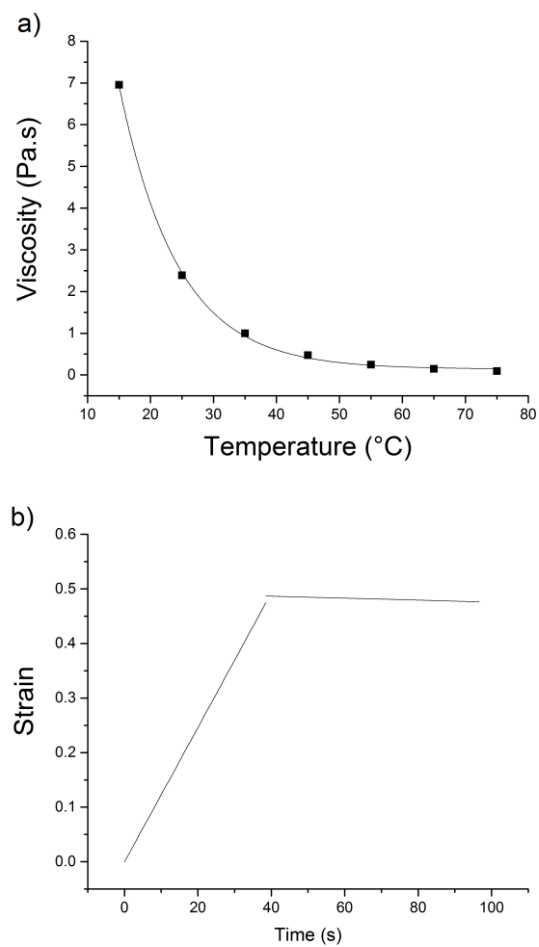


Figure A.3 - Viscosity profile for $[\text{C}_4\text{C}_{1}\text{im}][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

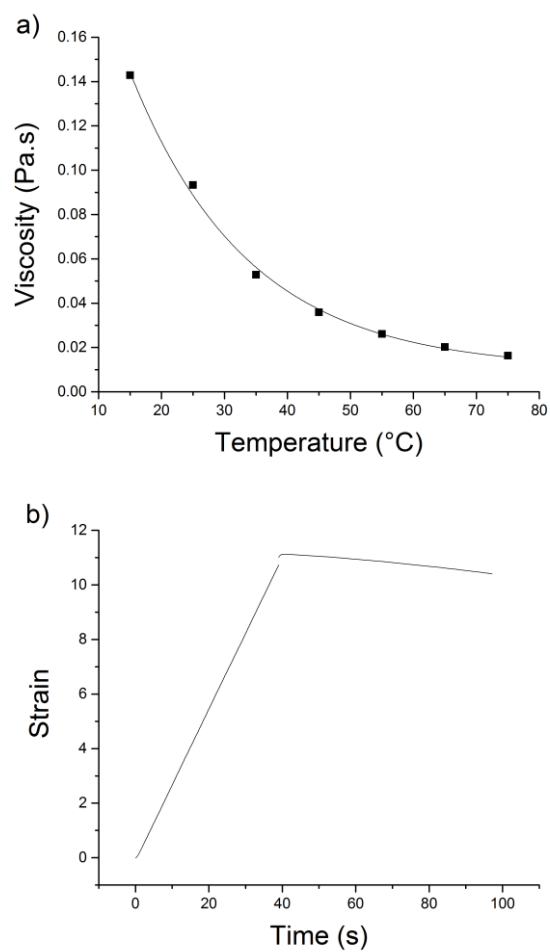


Figure A.4 - Viscosity profile for [C₄C₁im][MeSO₄] including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

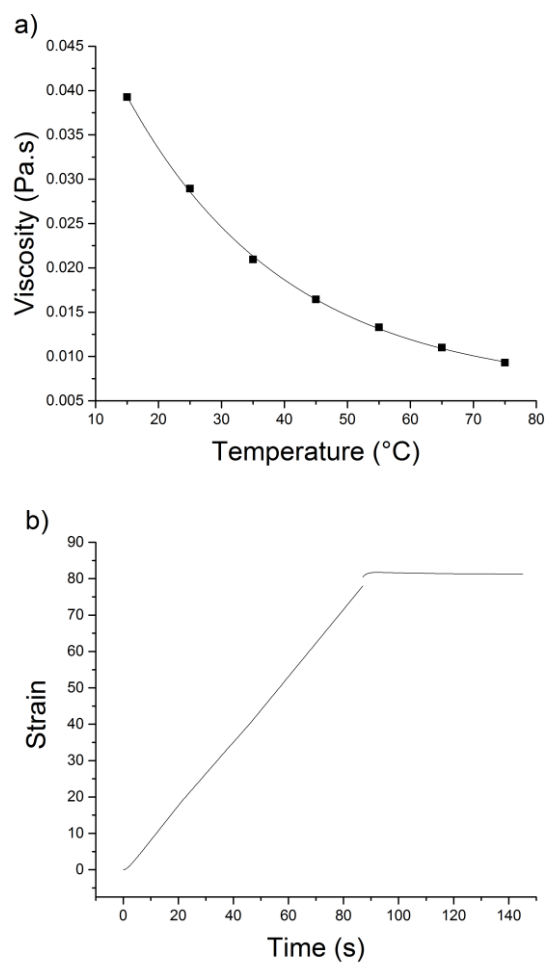


Figure A.5 - Viscosity profile for $[\text{C}_2\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

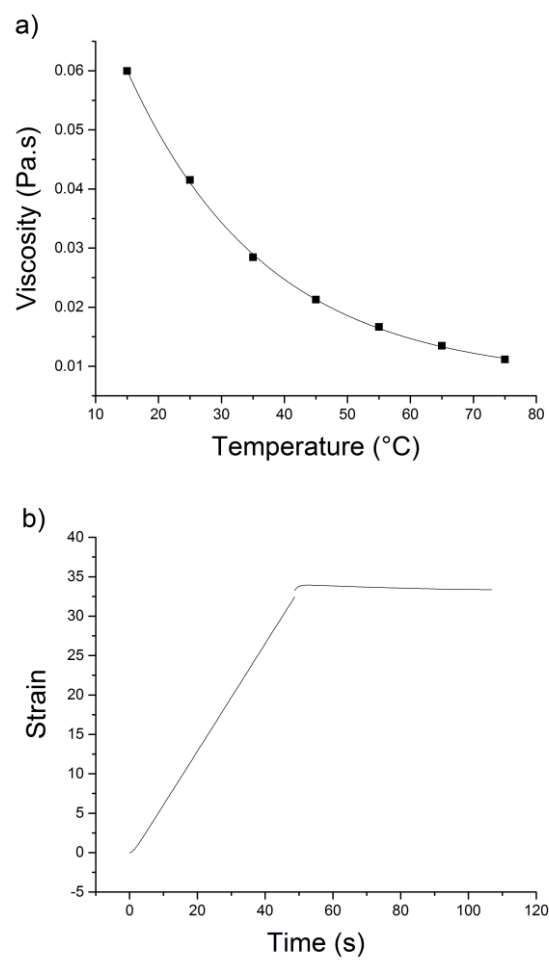


Figure A.6 - Viscosity profile for $[C_3C_{1im}][N(Tf)_2]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

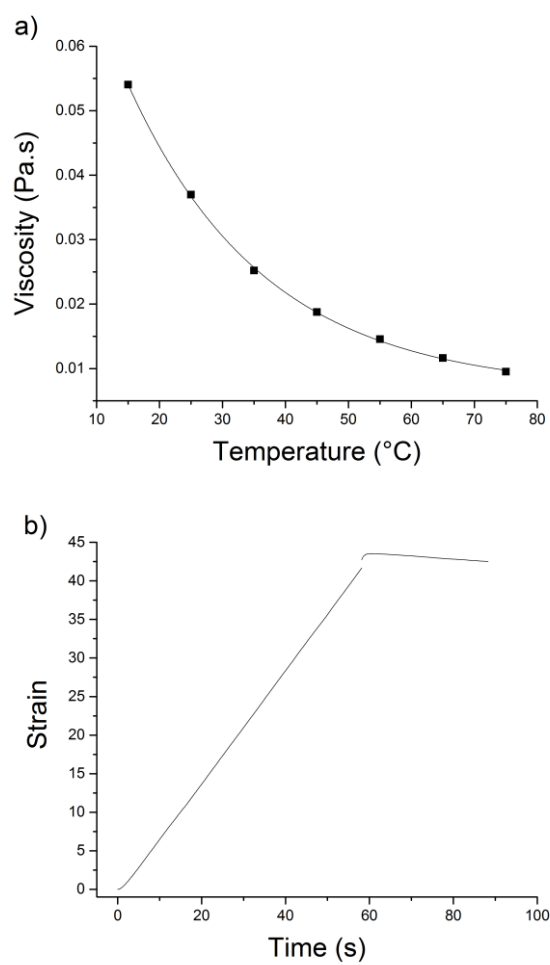


Figure A.7 - Viscosity profile for $[C_4C_{1im}][N(Tf)_2]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

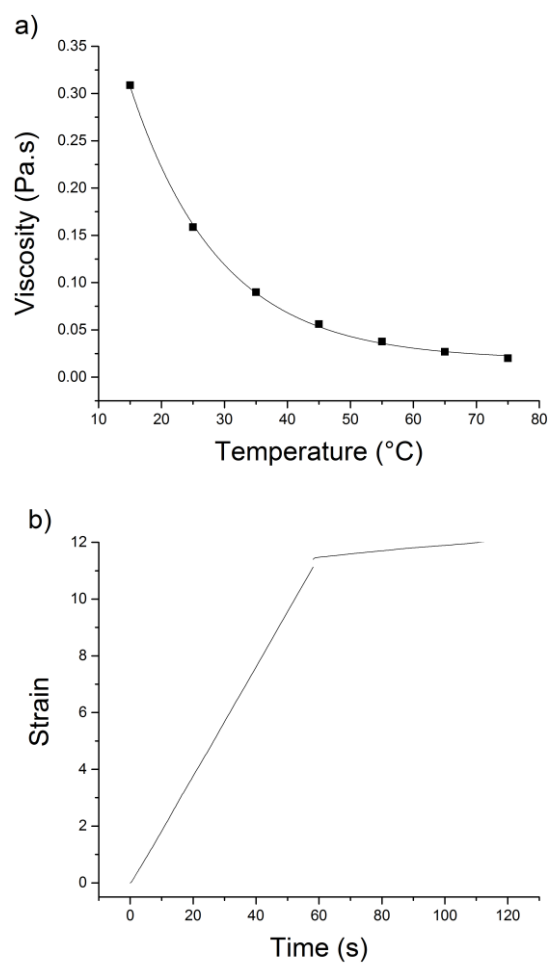


Figure A.8 - Viscosity profile for [C₄C₁im][OAc] including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

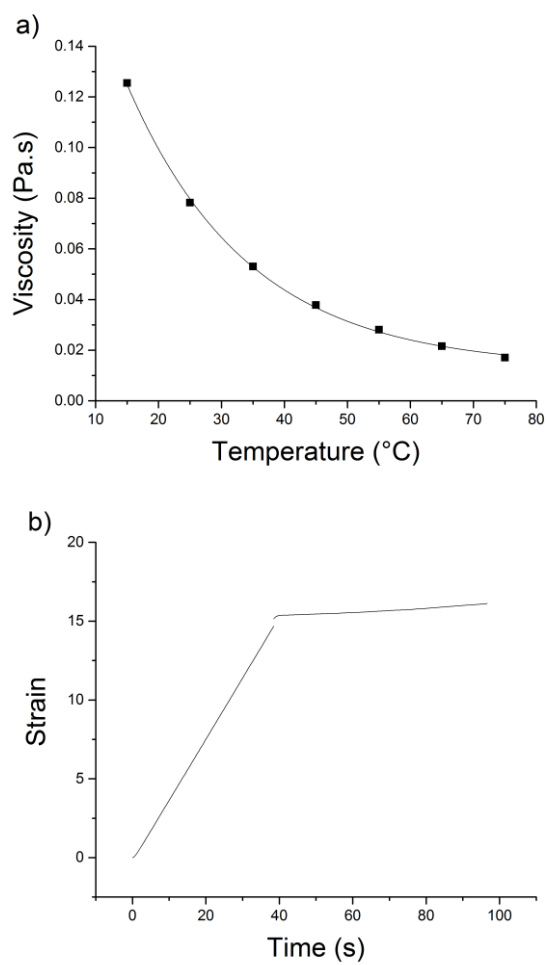


Figure A.9 - Viscosity profile for [C₄C₁im][OTf] including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

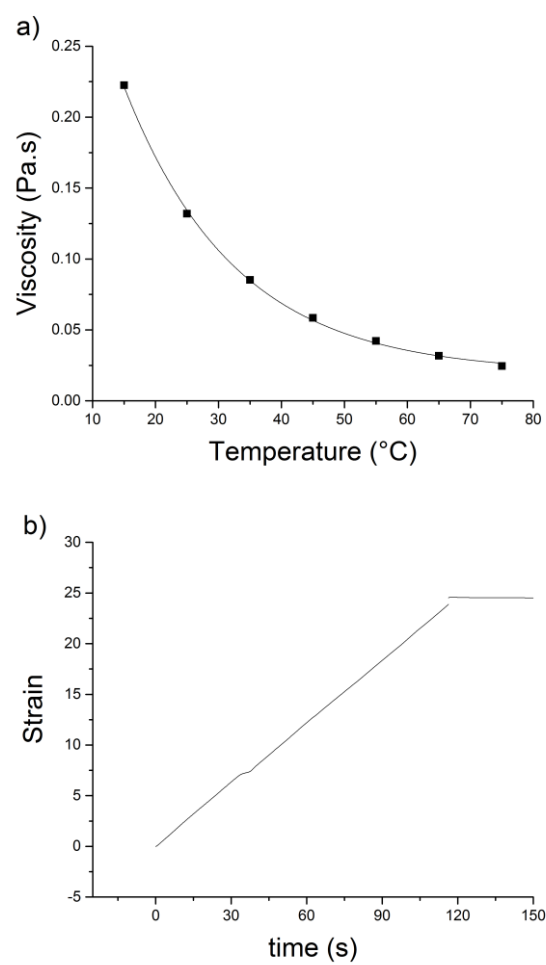


Figure A.10 - Viscosity profile for [C₄C₁pyrr][OTf] including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

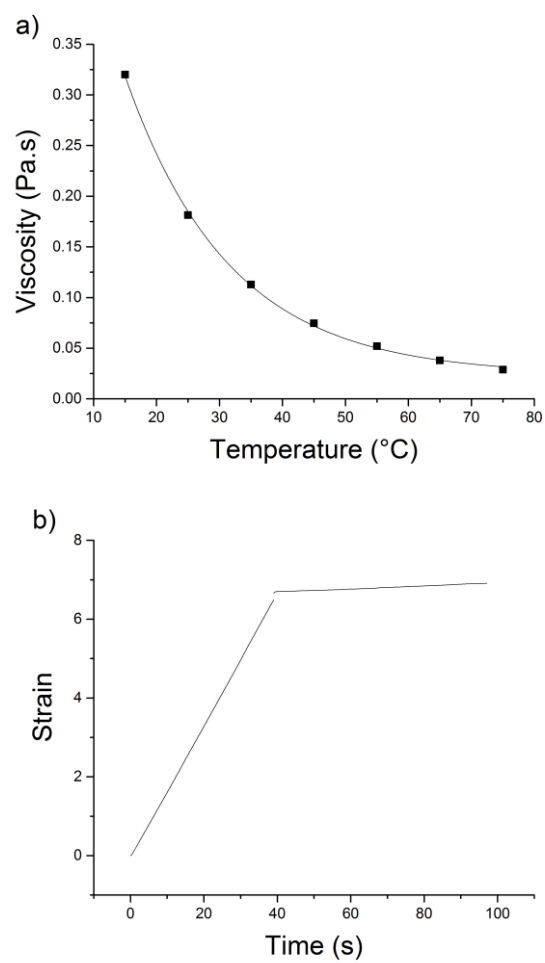


Figure A.11 - Viscosity profile for [C₈C₁im][OTf] including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

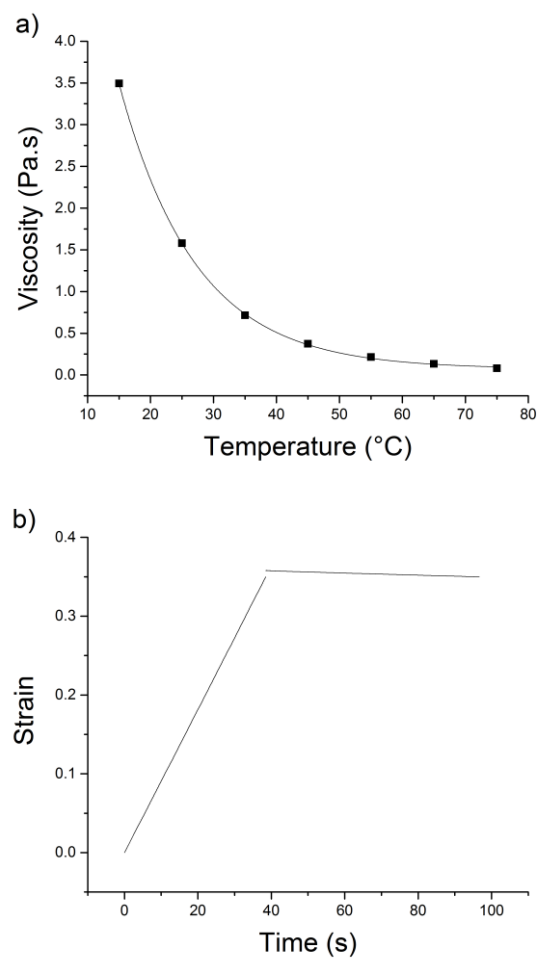


Figure A.12 - Viscosity profile for [C₈C₁im]Cl including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

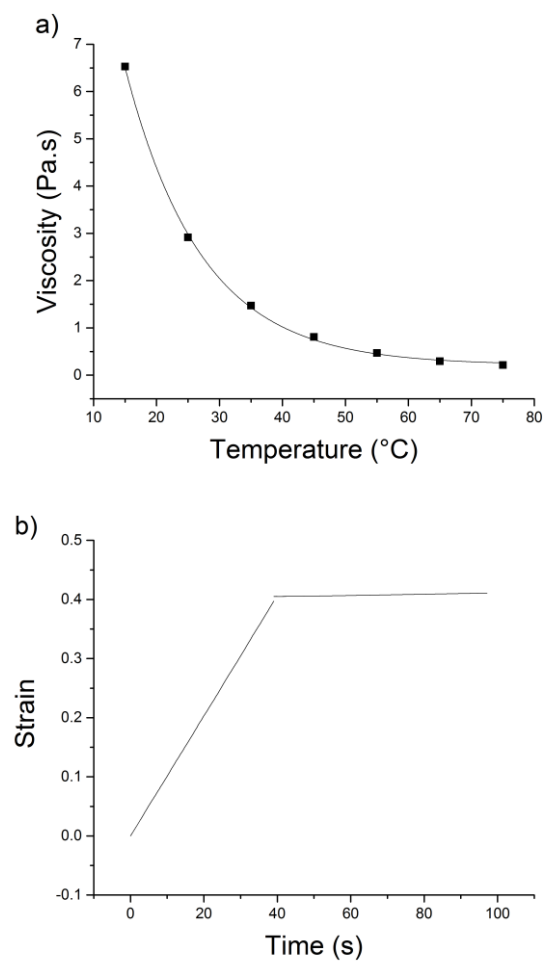


Figure A.13 - Viscosity profile for $[\text{C}_8\text{C}_{1\text{im}}][\text{HSO}_4]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

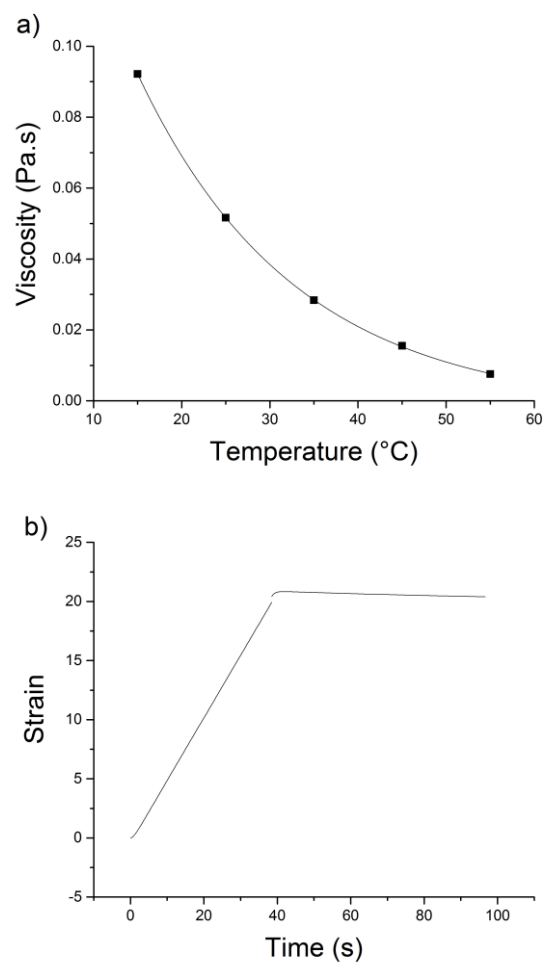


Figure A.14 - Viscosity profile for $[(CH_3)_2NH_2][(CH_3)_2NCOO]$ including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

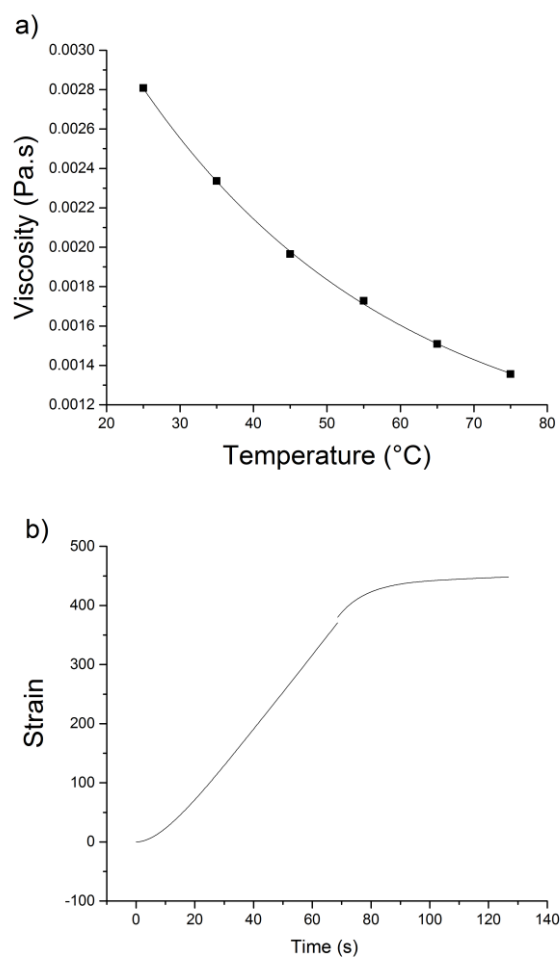


Figure A.15 - Viscosity profile for the sodium dodecenylsuccinic acid model fuel including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

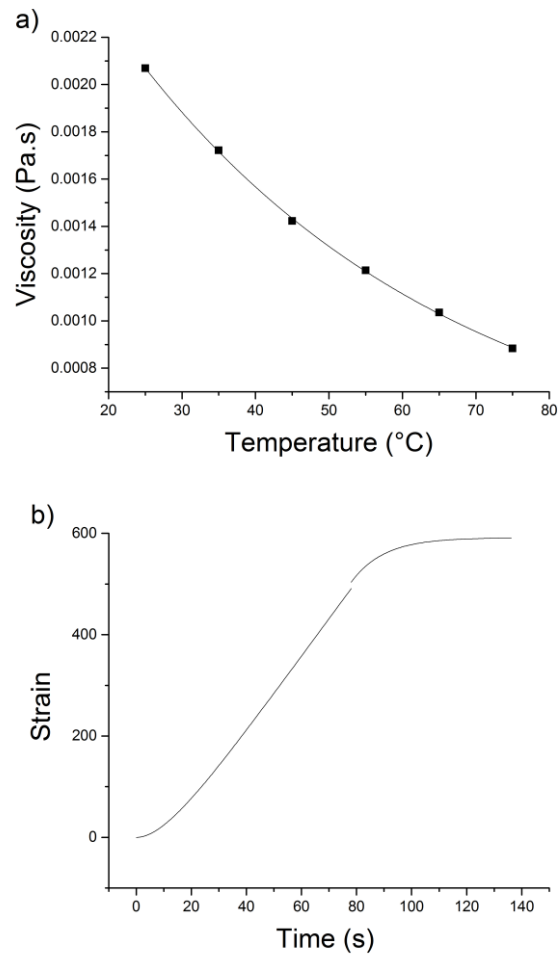


Figure A.16 - Viscosity profile for the zinc neodecanoate model fuel including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

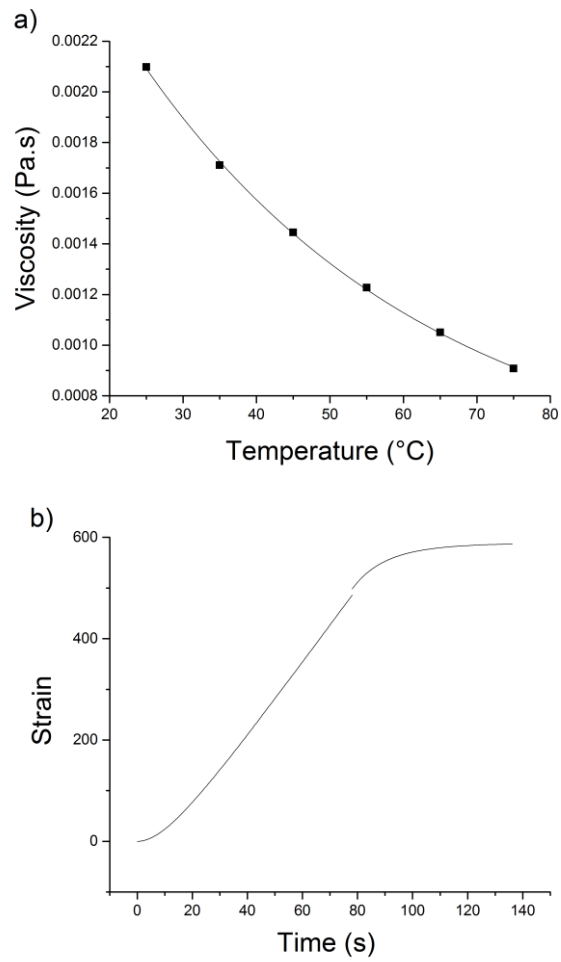


Figure A.17 - Viscosity profile for the copper acetylacetonate model fuel including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

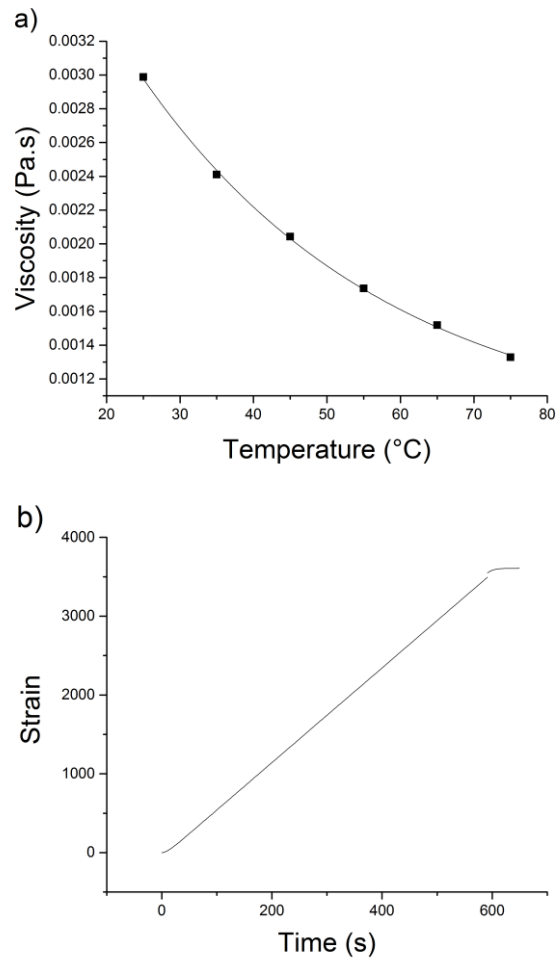


Figure A.18 - Viscosity profile for the market fuel including; a) viscosity over the temperature range of 15 – 75 °C and b) creep and creep recovery steps

Appendix C

Critical Properties of ILs

Table A.2 - Calculated Critical Properties for the ILs Used in This Study

Ionic Liquids	V_c (cm ³ mol ⁻¹)	T_b (K)	T_c (K)	P_c (bar)	Z_c	ω
[C ₄ C ₁ im][N(Tf) ₂]	1008.97	925.30	1333.15	25.97	0.24	0.37
[C ₄ C ₁ im][OTf]	750.66	707.72	1023.54	29.47	0.26	0.40
[C ₄ C ₁ im][MeSO ₄]	716.89	735.56	1081.64	36.10	0.29	0.41
[C ₄ C ₁ im][Me ₂ PO ₄]	826.58	625.76	820.56	20.59	0.25	0.81
[C ₄ C ₁ im][HSO ₄]	664.87	782.44	1103.83	43.36	0.31	0.70
[C ₄ C ₁ im][OAc]	658.24	624.58	847.31	24.45	0.23	0.67
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	1172.33	877.85	1191.47	13.39	0.16	0.35
[C ₄ C ₁ pyr][N(Tf) ₂]	1050.30	759.80	1093.10	24.25	0.28	0.35
[C ₄ C ₁ pyr][OTf]	810.83	605.08	856.20	25.11	0.29	0.44
[C ₈ C ₁ im]Cl	797.19	649.55	869.41	20.32	0.22	0.66
[C ₈ C ₁ im][OTf]	979.10	799.24	1088.70	21.59	0.23	0.58
[C ₈ C ₁ im][HSO ₄]	893.31	873.96	1167.76	28.55	0.26	0.86
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	434.55	458.59	636.11	30.92	0.25	0.65

Appendix D

NRTL τ Parameters

Listed are the τ parameters calculated from the NRTL model for Na⁺, Zn²⁺ and Cu²⁺ in n-hexadecane and Na⁺, Zn²⁺ and Cu²⁺ in the IL phase for the screening the ILs used in this study (Table A.3, A.4 and A.5). There were no obvious trends with the raw data but when compared to DN and calculated τ parameters correlations could be drawn showing that the τ parameters for Na⁺, Zn²⁺ and Cu²⁺ in a particular phase can be related to its Lewis basicity (Chapters 4 and 5).

Table A.3 – Tau Parameters for Na⁺ in both Fuel and IL phase.

Ionic Liquid	$\tau_{\text{Na Hex}}$	$\tau_{\text{Na IL}}$
[C ₄ C ₁ im][N(Tf) ₂]	8.12	-11.06
[C ₄ C ₁ im][OTf]	3.31	-1.16
[C ₄ C ₁ im][MeSO ₄]	9.33	-9.12
[C ₄ C ₁ im][Me ₂ PO ₄]	-2.82	-10.92
[C ₄ C ₁ im][OAc]	-13.0	-5.26
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	-2.71	0.05
[C ₄ C ₁ pyr][N(Tf) ₂]	8.08	-11.0
[C ₄ C ₁ pyr][OTf]	-0.01	2.25
[C ₈ C ₁ im][OTf]	24.1	5.00
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	-5.90	-6.37

Table A.4 - Tau Parameters for Zn²⁺ in both Fuel and IL phase.

Ionic Liquid	$\tau_{\text{Zn Hex}}$	$\tau_{\text{Zn IL}}$
[C ₄ C ₁ im][N(Tf) ₂]	2.97	-4.34
[C ₄ C ₁ im][OTf]	3.15	-4.21
[C ₄ C ₁ im][MeSO ₄]	4.56	-6.53
[C ₄ C ₁ im][Me ₂ PO ₄]	9.78	-13.86
[C ₄ C ₁ im][OAc]	9.05	-7.67
[C ₄ C ₁ im][S ₂ CN(C ₂ H ₅) ₂]	-7.59	-8.49
[C ₄ C ₁ pyr][N(Tf) ₂]	2.90	-12.71
[C ₄ C ₁ pyr][OTf]	2.75	-4.68
[C ₈ C ₁ im][OTf]	2.24	-2.86
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	-7.50	2.26

Table A.5 - Tau Parameters for Cu²⁺ in both Fuel and IL phase.

Ionic Liquid	$\tau_{\text{Cu Hex}}$	$\tau_{\text{Cu IL}}$
[C ₄ C ₁ im][N(Tf) ₂]	-3.51	5.69
[C ₄ C ₁ im][OTf]	4.87	-11.06
[C ₄ C ₁ im][MeSO ₄]	-3.32	0.59
[C ₄ C ₁ im][Me ₂ PO ₄]	3.14	-3.63
[C ₄ C ₁ im][OAc]	-2.69	-6.94
[C ₄ C ₁ pyr][N(Tf) ₂]	8.48	-7.06
[C ₄ C ₁ pyr][OTf]	-0.91	-1.88
[C ₈ C ₁ im][OTf]	-1.61	-4.18
[C ₈ C ₁ im]Cl	1.52	2.10
[(CH ₃) ₂ NH ₂][(CH ₃) ₂ NCOO]	-1.22	6.95