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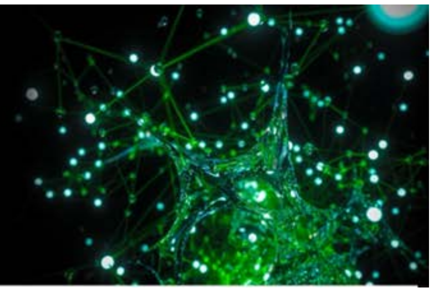

QUILL
Quarterly Reports

November 2023 – January 2024

CONFIDENTIAL (up to February 2027)

Contents

QUILL Quarterly Report

November 2023 – January 2024

Name:	Haris Amir		
Supervisor(s):	Professor John Holbrey		
Position:	PhD student		
Start date:	10/01/2020	**Anticipated end date:**	09/2024
Funding body:	ESPRC/UKRI		

Design of New, Non-Coordinating, and Hydrophobic Anions for Functional Ionic Liquids

Background

New boron containing anions are of interest for the development of new ionic liquid anions with a wide range of potential applications including electro- and photo- chemistry, and for the separation and extraction of metals and waste. In this work, functional borate anions formed as complexes with O-, O/N-, and N- chelators for ionic liquid applications have been designed and investigated.

Thesis tile: **Designing new Borate anions for ionic liquids**
Submission date: **To be decided**

Thesis structure:

Chapter list:

1. Introduction + literature review
2. Synthesis & characterisation
3. Halogen free sodium borate salts as electrolytes for sodium ion batteries
4. Conductivity of borate based ionic liquids
5. Borate based Organic plastic crystals (OIPCs)
6. PDADMA FSI doped with sodium borate salts for solid state electrolytes
7. Concluding remarks

QUILL Quarterly Report

November 2023 – January 2024

Name:	Oguzhan Cakir		
Supervisor(s):	Professor Peter Nockemann		
Position:	PhD student		
Start date:	09/01/2023	**Anticipated end date:**	31/11/2026
Funding body:	Turkish Government (TENMAK)		

Magneto-Structural Properties of Boron-containing Rare-Earth Magnets Synthesised Through Ionic Liquid Pathways

Background

Molecular nanoclusters constitute an intermediate state of matter between molecules and nanoparticles. The advantage of these materials is that, in contrast to conventional nanoparticles, they have a defined molecular structure that can exhibit cooperative spin-spin interactions, which might be used for magnetic high-density data-storage on a molecular level. We propose to investigate the synthesis of novel and interesting molecular cluster magnets using ionic liquid pathways; the aim is to achieve control over magnetic materials at cluster size with defined structures by using ground-breaking new synthetic methodologies.

Molecular cluster magnets provide a rich playground of different magnetic interactions in well-defined nanostructures, occupying the space between the quantum and classical world. Other interesting possibilities are clusters with antiferromagnetic or ferromagnetic intra-molecular couplings, which may exhibit bulk ferro- or ferrimagnetic interactions. Studying their physical properties contributes to our understanding of magnetic interactions in complex molecular structures. The use of ionic liquids allows for fundamentally different synthetic pathways resulting in compounds not accessible through conventional solvent-based synthesis.

Objective of this work

- Synthesise novel molecular cluster magnets with spin-cooperative behaviour using ionic liquid pathways.
- Understand synthesis of molecular cluster magnets through ionic liquid pathways including the formation mechanism
- The magneto structural properties of both the liquid precursor and the solid-state molecular cluster magnets as a function of varying syntheses conditions.
- Use the understanding of formation mechanisms and magneto structural property relationships to inform the design of further molecular cluster magnets.

Progress to Date:
I have completed several post-graduate training programs to enrich my research skills:

- "How to Read Critically and Take Good Notes" workshop by Fabiana McCracken at Queen's University
- "Training on Pure and the Research Portal" by Rebecca Clarke at Queen's University
- 8-week academic writing course by Rachael O'Neill at Queen's University

Additionally, I have conducted an extensive literature review on relevant topics including ionic liquids, molecular magnets, and magnetic ionic liquids. The key findings were compiled into a structured review and presented to Prof. Nockemann (see structure of the literature review below).

My project so far has focused on synthesising and characterising novel boron-containing rare-earth molecular magnets using ionic liquid pathways. The work is divided into three main stages:

1. Synthesis and characterisation of ionic liquid precursors
2. Synthesis and characterisation of rare-earth coordination complexes
3. Synthesis and characterisation of final boron-containing rare-earth magnets

I have successfully completed stages 1 and 2, with promising results. I am currently optimising the experiments for stage 3 to obtain the target materials. If successful, I will apply for my annual progress review and present my work at the upcoming QUILL conference through a slide presentation and poster.

The next phase will involve investigating the magneto-structural properties of the synthesised compounds in detail. Overall, the project is progressing well in line with the initial timeline.

Here is the proposed structure of a literature review on the topic of boron-containing rare-earth magnets synthesised through ionic liquid pathways:

Introduction

- Background on rare-earth magnets and their importance
- Brief overview of conventional synthesis methods and their limitations
- Introduction to ionic liquids and their potential as solvents for inorganic synthesis

Ionic Liquids

- Properties of ionic liquids relevant to inorganic synthesis (negligible vapor pressure, thermal stability, etc.)
- Use of ionic liquids as solvents in inorganic chemistry
- Types of ionic liquids suitable for rare-earth and boron chemistry

Molecular Magnets

- Fundamentals of molecular magnetism
- Important classes of molecular magnets (e.g. single-molecule magnets)
- Strategies for designing/improving molecular magnets

Synthesis of Molecular Magnets

- Common synthetic techniques
- Use of conventional solvents and limitations

- Emerging non-conventional techniques (hydro/solvothermal, microwave, mechanochemical, etc.)

Rare-Earth Borates

- Structural motifs and magnetic properties of rare-earth borates
- Current synthetic approaches to rare-earth borates and limitations
- Characterisation techniques for structure and magnetism

Ionic Liquids for Rare-Earth Borate Synthesis

- Recent examples demonstrating utility of ionic liquids.
- Structures and properties of rare-earth borates achieved through ionic liquid synthesis.
- Proposed mechanisms for ionic liquid synthesis and advantages

Outlook and Conclusions

- Summary of key points and current state of literature
- Remaining challenges and unanswered questions
- Proposed directions for future research

QUILL Quarterly Report

November 2023 – January 2024

Name:	Aodhán Dugan		
Supervisor(s):	Prof Peter Nockemann, Dr Oana Istrate & Dr Paul Kavanagh		
Position:	PhD student		
Start date:	Oct 2023	**Anticipated end date:**	Sep 2026
Funding body:	Shell/DfE		

Parametric Study of Electrolyte Flow in 3D-Printed Operando Redox Flow Cells

Overview

The aim of this project is to improve the electrochemical activity of redox flow batteries through electrode/electrolyte interaction enhancement. This is achieved through using novel techniques to improve otherwise limiting factors in certain systems such as poor electrode wettability (due to the hydrophobic nature of carbon) and electrochemically active surface area (ECSA). This can be achieved through electrode surface treatment which can be achieved through several methods including heat treatment, plasma treatment, acid/base treatment or the deposition of nanocatalysts such as carbon-based catalysts, metal-based catalysts and metal-oxide based catalysts. Each of these treatments provide different advantages and disadvantages in terms of repeatability, level of improved electrochemical activity and economic feasibility. Each of these factors is key in improving the electrochemical capability in these systems, which could see redox flow battery technology could be a viable alternative to large scale traditional renewable energy storage. A lot of focus has been geared towards vanadium redox flow batteries seeing it become arguably the most widely developed and widely integrated, but expensive active materials has resulted in attention being gazed elsewhere, such as all-iron redox flow batteries. The abundant nature of iron makes it an ideal candidate for the large-scale ideals of redox flow battery application, but the battery performance is below the standards at the minute. Transferring our knowledge from VRFB to IRFB could be the key to unlocking the potential within.

Objective of this work

The objective of this work is to develop a redox flow battery technology that is sustainable economically and electrochemically, and that can be applied on a global scale. This project hopes to achieve this through electrode treatment technologies and transferring knowledge form VRFB to IRFB.

Work to date

To date, a potential metal-based group of electrocatalysts has been identified in the form of polyoxometalates. These structures have unique mechanical, physical and redox-active properties that make them ideal candidates for electrocatalysis.

To date, tetrabutylammonium hexamolybdate $[(n\text{-}C_4H_9)_4N]_2[Mo_6O_{19}]$ has been successfully synthesised and characterised using FTIR and Single-Crystal X-Ray Diffraction. This product was then deposited on carbon-felt electrode via hydrothermal deposition and the treated felt was characterised by SEM. The most important finding of work to date is that the product has been successfully deposited on the electrode.

Conclusion and future work

To conclude, a Mo-based polyoxometalate has been successfully synthesised, characterised and deposited onto a carbon-based electrode. Going forward, the treated electrode will be subject to electrochemical characterisation in the form of cyclic voltammetry and electrochemical impedance spectroscopy to determine whether there has been any improvement in electrochemical activity towards the redox active species, vanadium.

QUILL Quarterly Report

November 2023 – January 2024

Name:	Nia Foster		
Supervisor(s):	Dr Paul Kavanagh & Prof Peter Robertson		
Position:	PhD student		
Start date:	October 2023	**Anticipated end date:**	September 2026
Funding body:	Department of Economy		

Electro-Photo Generation of Highly Reducing Radical Anions for CO_2 Activation

Background

Electrochemistry has recently been a huge area of interest in chemistry, being used in areas such as synthesis, batteries, and analysis. It is commonly used in homogeneous redox catalysis, where a voltage is applied across the electrochemical cell, allowing for electron transfer between the electroactive substrate and the electrode.

The focus here is on electrochemical homogeneous redox catalysts that carry out reductions. The issue is that it can be difficult to get a catalyst to a high enough energy level to be able to reduce difficult substrates such as CO_2. The limits are due to multiple factors, such as electrolyte degradation and the energy input required to maintain a very low potential. We require a technique that can raise the catalyst to a higher energy level while surpassing these limitations within the cell.

While these reactions involving electrolysis alone are successful, the electro-active catalysts are not very strong and sometimes require additional reactants such as acids or bases to activate harder-to-reduce species. Ideally, we want to avoid additives that are harmful chemicals and that cause more waste, therefore we turn to photochemistry to try and excite the catalyst to a higher energy level.

Studies on homogeneous electrophotocatalysis emerged around the late 1970’s, with Moutet and Revardy’s research into using phenothiazine as an oxidising agent being one of the most popular examples. Interest in electrophotocatalysis continued through the 80’s however interest dwindled. It wasn’t until 2019 when academics such as Xu, Stahl, and Lambert sparked renewed interest in the area with their papers on Mes-Acr, iodide ions and TAC, respectively.

Objective of this work

The current title of my PhD is the Electro-photo generation of highly reducing radical anions for CO_2 activation. The plan is to study a series of homogeneous redox electrophotocatalysts, specifically reductive electrophotocatalysts. By activating these catalysts though applying a negative potential and exciting them using light, they will have a very high energy that ideally will be used to reduce more difficult substrates such as carbon dioxide or nitrogen.

The reason that there is a focus on carbon dioxide reduction is due to the harm it causes to the environment. Ideally, we want to remove it from the atmosphere, which is why carbon capture has become a huge industry.

Progress to date

The first part of my PhD that I have been working on is categorising a series of homogeneous redox electrophotocatalysts that have previously been mentioned in papers. I wanted to compare them all and be able to find their redox potential, their diffusion co-efficient and their electron transfer constant. By keeping all other variables the same, I tested 12 redox catalysts, shown in below:

Mediator	**E^o vs Fc/Fc$^+$**	**D**	**k^o**
Oxidation catalysts	Vs^{-1}	cm^{2}s^{-1}	s^{-1}
TPPD	0.1663	D_o=2.62x10^{-7} D_r=2.23x10^{-7}	7.68x10^{-4}
phenothiazine	0.2158	D_o=1.837x10^{-5} D_r=1.604x10^{-5}	5.61x10^{-3}
10-Methylphenothiazine	0.340	D_o=2.05x10^{-5} D_r=1.23x10^{-5}	5.79x10^{-3}
10-Phenylphenothiazine	0.294	D_o=1.96x10^{-5} D_r=1.00x10^{-5}	1.79x10^{-3}
Reduction catalysts			
9-Mesityl-10-methylacridinium perchlorate (Mes-Acr)	-0.935	D_o=7.22x10^{-6} D_r=1.43x10^{-5}	8.137x10^{-3}
9,10 Anthracenedicarbonitrile*	-1.292	D_o=2.37x10^{-7} D_r=8.46x10^{-7}	1.57x10^{-3}
Anthracene*	-2.41	D_o=1.07x10^{-6} D_r=2.27x10^{-6}	2.03x10^{-4}
9-fluorenone*	-1.66	D_o=2.98x10^{-6} D_r=7.96x10^{-6}	2.258x10^{-3}
Pyrene*	-2.5325	D_o=3.16x10^{-6} D_r=4.51x10^{-6}	1.47x10^{-3}
napthalene	-1.3685	D_o=5.17x10^{-6} D_r=4.22x10^{-5}	3.39x10^{-6}
thianthrene	0.8035	D_o=6.79x10^{-6} D_r=5.59x10^{-6}	3.68x10^{-3}
phenazine	-0.961	D_o=1.25x10^{-5} D_r=6.56x10^{-5}	4.55x10^{-5}

The ideal catalyst would need to be electrochemically accessible, with the potential being more than 2.5V to produce the anion. It should have a fast diffusion through the electrolyte, ideally more than 10^{-6}cm^{2}s^{-1}. The final attribute to make a good electrophotocatalyst is that it should be fast and reversible, with the heterogeneous electron transfer constant to be more than 10^{-3}s^{-1}. Experiments marked with a * were carried out in DMF as they didn't dissolve in MeCN. Results highlighted in green fit the attributes required below. Using these parameters, from my results the ideal reducing electrophotocatalysts would be Mes-Acr, 9-fluorenone, and thianthrene. However, further research needs to be carried out to see how they react once irradiated with light.

Conclusions and future work

These catalysts will need to be tested under blue or UV light, to observe whether the catalyst is indeed a successful photocatalyst as well as an electrocatalyst, and to see how much more effective the catalyst is once photochemically excited.

There are multiple areas of research that I could investigate. The next project I plan on carrying out will be focused on electrochemistry. Ideally, I will be taking a wide range of electrocatalysts and categorising them, keeping all the conditions the same, including the electrolyte and the type of electrodes. There hasn’t previously been a study categorising a range of electrocatalysts so creating this list with accurate, essential information such as their redox potential, diffusion co-efficient and electron transfer constant will prove to be incredibly useful, providing important information for myself and other electrochemists to refer to.

Further on from that, I could possibly investigate different electrode materials and how effective they are with different types of electrocatalysts. A study could also be completed on different types of solvents or electrolytes, however, this project can go in many directions and holds lots of potential.

QUILL Quarterly Report

November 2023 – January 2024

Name:	Edwin Harvey		
Supervisor(s):	Dr Oana Istrate, Prof Peter Nockemann & Dr Stephen Glover		
Position:	PhD student		
Start date:	February 2022	**Anticipated end date:**	August 2025
Funding body:	Department for the Economy		

3D Printing for Renewable Energy Applications

Background

Redox flow batteries (RFBs) are promising candidates for grid-scale energy storage and stationary energy storage applications. They have a longer cycle life than lithium-ion and can use cheaper, safer, and more environmentally friendly electrolytes. Such systems are becoming more important as we rely more on intermittent renewable energy, such as wind and solar, as we move towards reaching net zero by 2050 (UK govt target).

The RFB design has not changed much since their inception in the 20th century (e.g. vanadium RFBs were invented in 1986 at the University of New South Wales, Australia). Electrodes are still typically made using carbon felt as these have good electrical conductivity, electrochemical activity, and are mechanically and chemically stable. However, using carbon felt as an electrode material limits cell design and is associated with a high interphase electrical resistance. Additionally, for flow-over electrode designs, flow channels must be machined into graphite plates which is complex and expensive. 3D-printable electrodes may offer a greater design freedom where, for example, flow channels can be printed as part of the design, and porous and solid elements can be combined.

Graphene nanocomposite materials may be able to replace graphite and carbon felt as an electrode material. Possible 3D-printing technologies for this material are fused deposition modelling (FDM), and stereolithography (SLA). FDM uses a heated thermoplastic filament which is extruded out of the printer nozzle, following a pre-calculated path to manufacture the part layer by layer. Graphene based nanocomposites have been printed using FDM but often suffer from agglomeration of graphene due to extruding conditions. SLA uses a liquid resin which is cured using UV light at the desired locations, also building the part layer by layer. SLA may offer improved graphene dispersion compared to FDM.

Objective of this work

To create a viable redox flow battery (RFB) electrode that has been manufactured through 3D-printing technology.

Progress to date

Initially, I spent time reading literature and planning my PhD by splitting it into work-packages that each last a few months. My first work-package is focused on manufacturing a 3D-printable RFB material utilising carbon nanofillers. After analysing the properties of various polymer matrices, I have decided to focus on acrylate-based monomers that can be polymerised in-situ with graphene. This is because various papers have shown this method to produce high electrical conductivity and excellent graphene dispersion.

During initial experimental work graphene oxide (GO) was synthesised using a modified Hummers' method. Following this, seven polymer/graphene nanocomposites were manufactured using SLA 3D-printing containing GO and graphene nanoplatelet (GNP) fillers. Nanofillers and nanocomposites were then characterised using FTIR, Raman spectroscopy, X-ray diffraction, tensile testing, and electrical testing. A literature study and experimental work were submitted as part of my differentiation which was completed in November 2022.

Since November 2022, I have been focused on manufacturing and modifying graphite powder and developing my characterisation skills. I have been undertaking an in-situ polymerisation method to produce high electrical conductivity nanocomposites which have the potential to be used as a 3D-printed electrode material.

Since February 2023, I have been focusing on a latex mixing method for producing graphite oxide nanocomposites. This has involved testing different mixing methods and adding salts to coagulate the particles into a nanocomposite.

Since May 2023, I have focused on refining the latex mixing method to produce mouldable graphene oxide composite materials. I have shaped the composite material and undertaken CV electrochemical measurements in a vanadium electrolyte which shows promising results. I've also been performing a full characterisation of the composite material (TGA, DSC, Raman, FTIR, etc.) and writing up the info for a paper submission.

Since August 2023, more detailed electrochemical characterisation has been undertaken. Oxygenated groups on graphene nanocomposites were shown to offer enhanced electrode activity in vanadium redox reactions. The focus of the project has moved back to resin 3D printing (e.g., SLA or Digital Light Processing). Using the synthesised graphite materials (expanded graphite, graphene oxide, and pristine graphene), different nanocomposite architectures have been produced using resin 3D printing. Challenges producing nanocomposites include dispersing fillers in resin, keeping viscosity at an appropriate level for printing, and final mechanical properties.

Since November 2023, we have been developing compression moulded flow fields for RFBs. Firstly, a composite material of PMMA/graphite was synthesised using methods refined through the PhD. Using a mould produced through CNC manufacturing, flow fields were successfully compression moulded with different densities. The compression moulded flow fields are electrically conductive and can be produced in similar designs to commercial machined flow fields.

Conclusions and future work
Summarise the most important finding/conclusion to date. Where do you go next?
If you published your work, please provide reference here.

Electrically conductive flow fields have been manufactured through compression moulding using PMMA/graphite composite material. Future work will test the flow fields in a RFB test cell, comparing different flow field designs and material formulations.

QUILL Quarterly Report

November 2023 – January 2024

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey & Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	01 Oct 2021	**Anticipated end date:**	March 2025
Funding body:	EPSRC		

Intrinsic FLP Systems in Ionic Liquids

Background

Frustrated Lewis acid/base pairs (FLPs) are potential metal-free alternatives to platinum group metal catalysts and have been shown to activate hydrogen for hydrogenation chemistry [1]. Typical examples of FLPs that have been studied are combinations of a sterically hindered bulky phosphine Lewis base paired with a strongly electrophilic Lewis acidic susbstituted borane. While many of the advances in FLP chemistry have sought to exploit these bulky phosphine/borane pairs, less attention has been given to alternative acid/base pairs although examples with non-boron Lewis acid FLP components are known including N-alkylacridinium cations which have been show to exhibit FLPs chemistry when paired with lutidine (2,6-dimethylpyridine) as a base [2].

Objective of this work

The goal of this research is to develop organic FLPs (eliminating the need for group 13-based Lewis acids) within an intrinsic IL medium in which, ideally, the potential catalyst concentration in the liquid is maximised and enables reaction intensification creating greener, sustainable chemistry through facile synthesis and replacement of both conventional solvents and platinum group metal catalysts.

Progress to date

Five *N*-alkyl-acridinium salts and *N*-protonated heterocyclic ionic liquids, as precursors for FLP studies, have been successfully synthesised and fully characterised. *N-alkylated N-a*lkylacridinium *bis*{trifluoromethylsulfonyl}imide ([R-Ac][Tf_2N]) salts synthesised are highly soluble in H-lutidinium and H-picolinium *bis*{trifluoromethylsulfonyl}imide ([H-lut][Tf_2N] and [H-pic][Tf_2N]) ionic liquids. This contrasts with the reported poor [2] and limiting solubility of *N*-methylacridinium salts in organic solvents. Since the previous report, we have once again discovered that headspace GC is not a viable method to quantify the H_2 uptake for our system, as the results obtained do not correlate with those observed from NMR spectroscopy. We have carried out all the experimental sets for the intrinsically IL FLP “proof-of-concept” system to date, using an internal standard for quantification of results and I am currently analysing all of the results and preparing thesis chapters and a draft paper for publication. Additionally, a proposal to carry out neutron scattering studies on acid/base association in the N-methylacridinium bistrifylimide/lutidine ionic liquid FLP has been successfully granted beam-time is ISIS, RAL requiring synthesis of deuterated N-alkylacridinium salts and lutidine.

Ongoing investigations are being conducted on 3,5-dicyanopyridinium analogues of the N-alkylacridinium Lewis acid components of FLPs. We anticipated that this set of molecules may be able to be used as alternative cations (within an FLP system), due to their similar hydride ion affinity to that of the dihydromethylacridinium molecule [3]. These N-alkylated-3,5-dicyanopyridinium cations should also feature innate ability to act as IL based charge transfer materials, extending previsou work within QUILL (Hardacre, Holbrey, Mullan) on cyanopyridinium IL charge transfer complexes [4]. CT forming complexes of ILs with electron-rich donor aromatics, We also have decided to revisit a range of 4-cyanopyridinium bistrifylimide that have been examined by the Group in the past as CTMs, when paired with 1-methylnaphthalene. The aim of this work is to try and develop a deeper understanding of the charge shuttling/ transfer mechanism between these ILs and 1-Methylnaphthalene via electrochemical impedance spectroscopy (EIS), collaborating with Dr. Josh Bailey. The robustness of the electrochemical cell design required for EIS measurements has been improved, allowing reliable temperature control, and EIS conductivity studies on cyanopyridinium ILs and IL/aromatic CT complexes is underway.

Conclusions and future work

In terms of the “proof-of-concept” intrinsically IL FLP, only 5 experiments are left to complete, which include one time interval measurement and 4 control experiments. We have began to analyse all of the results and I am currently writing two thesis chapters and a publication simultaneously for this aspect of the work. It is the aim that once this work is done, we can probe the system for fluorescent activity (briefly) and hence move on to the deuteration reactions of the N-methylacridinium bistrifylimide/lutidine ionic liquid FLP, in preparation/anticipation of carrying out experiments at ISIS. In conclusion, the last bit of work that is planned for the next while is EIS spectroscopy on the 4-cyanopyridinium ILs and after completion of the analyses of these ILs, we will move on to the 3,5-dicyanopyridinium ILs.

References

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2. E. R. Clark and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2014, 53, 11306–11309.
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QUILL Quarterly Report

November 2023 – January 2024

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John D Holbrey and Dr Leila Moura		
Position:	3rd year PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2024
Funding body:	Tezpur University-Queens University Belfast joint PhD programme		

LCST Behaviour in 5-Phenyltetrazolate Based Ionic Liquids

Background

In the previous report, deuteration of tetrabutylphosphonium bromide was attempted to prepare the D-ionic liquid for neutron scattering experiments. In addition to that, posters were presented at QUILL IAB and COIL-9 conference. Here, a brief summary of the phase behaviour results of the ionic liquid water mixtures with respect to crystal structures will be explained.

Objective of this work

The ultimate objective of this research is to comprehend and elucidate the phase behaviour of certain ionic liquids known as the lower critical solubility temperature (LCST), with the purpose of establishing the boundaries and formulating a methodology for synthesizing such ionic liquids that possess the potential to function as draw solutes in the forward osmosis process for desalinating seawater. During this procedure, a series of ionic liquids containing the tetrazole moiety will be synthesized, assessed, and compared to the current ones, considering the selection of the anion or cation, which can influence the phase behaviours.

Progress to date

1. Repeat the Phase behaviour tests to generate phase diagrams for the ionic liquids with substituents in the anions including $4CH_3$, $3CH_3$, $2CH_3$, $4C_2H_5$, $4CF_3$, 2Cl, 2Br, $4OCH_3$, and $3OCH_3$. It was observed that except the ionic liquid- water systems of 2Br, $4OCH_3$, and $3OCH_3$ substituted anions in the ionic liquid, all other systems displayed a phase diagram with undefined cloud point regions at lower compositions. This was mainly due to the presence of dispersed droplets and solids at lower temperatures. One such example is shown below:

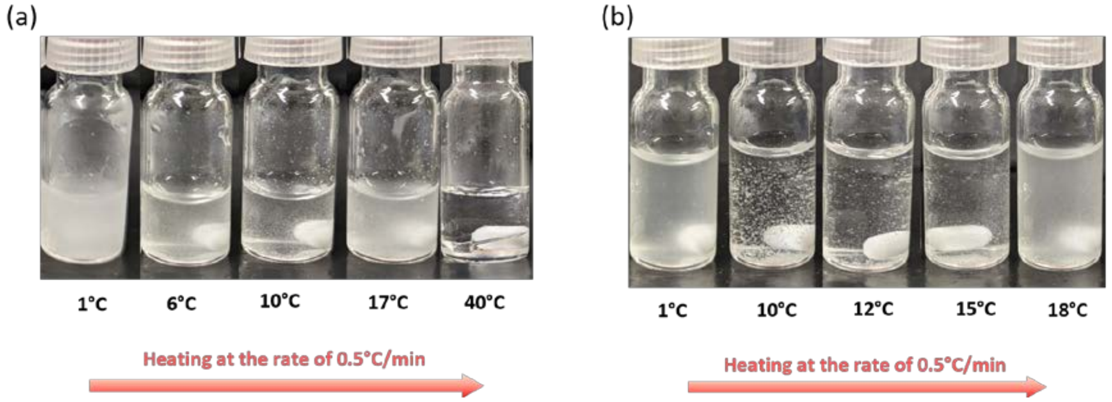
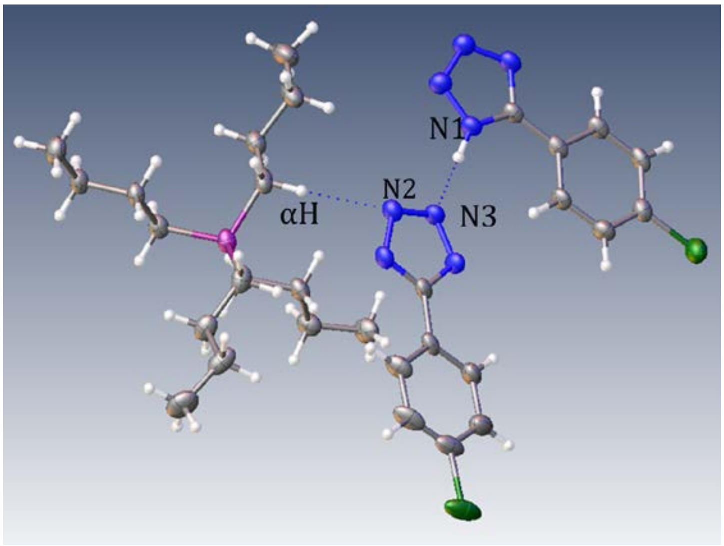
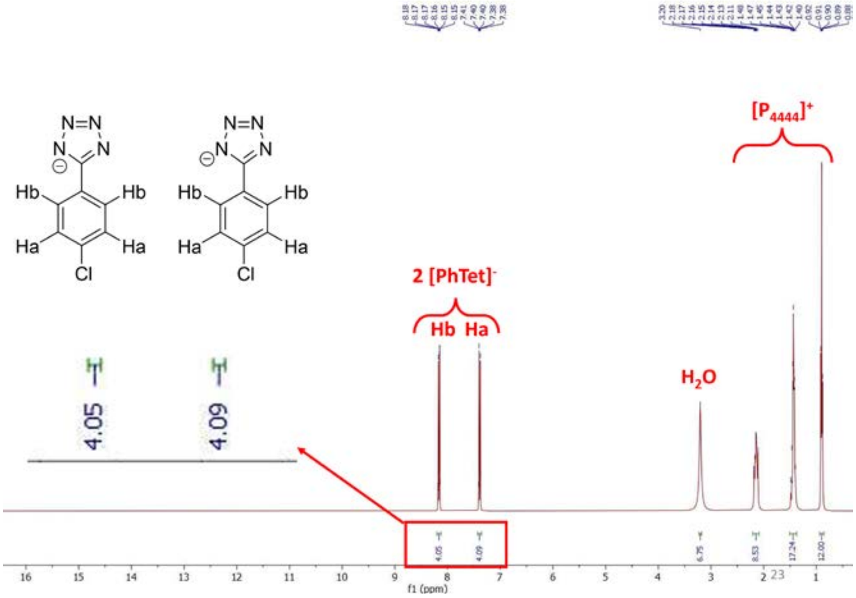


Figure 1 (a) - 14.13wt% of $[P_{4444}][2CH_3Ph\text{-}Tet]$/H2O on a heating cycle. Droplets dispersed in the solution is observed at increasing temperatures (10 °C) which becomes cloudy at higher temperatures until phase separation at 40 °C; **(b)** 11.72wt% of $[P_{4444}][4CH_3Ph\text{-}Tet]$/H2O on a heating cycle. Solution is cloudy initially at 1 °C, on heating solids appear (10 °C) dispersed in the solution which turns into small droplets (12 °C) that further become cloudy on increasing temperatures until phase separation (not shown)

2. Crystal structure from 55.33wt% $[P_{4444}][4ClPhTet]/H_2O$ showing 1 cation-anion pair : H-bond between αH-N2 and 1 protonated 5- phenyltetrazole : H-bond between NH of the tetrazole and N3 of the tetrazolate anion.



3. ^{1}H-NMR of the crystals from 55.33wt% $[P_{4444}][4ClPhTet]/H_2O$ in $CDCl_3$ showing two anion-like species in the crystal.



Conclusions and future work

1. Formation of non-stoichiometric species during crystal formation reported,
2. Undefined cloud point regions need to be investigated more,
3. Drafting a paper on the results so far on anionic functionalisation and LCST,
4. Repeating results for dicationic ionic liquid-water systems.

QUILL Quarterly Report

November 2023 – January 2024

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate & Prof Peter Nockemann		
Position:	PhD student		
Start date:	1st October 2021	**Anticipated end date:**	31st March 2025
Funding body:	Department for the Economy		

Design and Development of an Effective and Interconnected Smart Fire Suppression System for Lithium-ion Batteries in Electric Vehicles

Background

As many countries around the world begin to implement their plans to ban the sale of new petrol and diesel vehicles in the coming decades, there is a clear shift occurring towards electrification of transportation. However, there are several challenges that should be addressed if mass adoption of these vehicles is to be successful. Chiefly among which are the needs to extend range and improve battery safety. Depending on the sources used it can be argued that EVs do have a good battery safety record and the number of electric vehicle fires that occur are relatively low. Tesla's 2020 vehicle safety report claims that one of their vehicles is almost ten times less likely to be involved in a vehicle fire, than the average vehicle on the road in America per mile driven, based on data from the national Fire Protection Association and US Department of Transportation. Contrary to this, in London in 2019 based on data from the London Fire Brigade the incident rate when adjusted for the number of EVs and IC vehicles on the road is more than twice as high for EVs. Regardless of the exact frequency, when these cells are provoked it can often initiate thermal runaway, meaning that it is extremely difficult to extinguish as well as having the potential to burn both hotter and longer than a typical IC vehicle fire. The primary concern is of course for the safety of the occupants of the vehicle and the potential danger to their health. Additionally, an EV has the potential to ignite in scenarios where it may initially go unnoticed, usually if an IC vehicle ignites it will do so in use as this is when the highest temperatures are experienced. EVs on the other hand can ignite under a wider range of circumstances such as when charging. This means that the thermal runaway process may go unnoticed for some time as well as likely being close to a home or garage, causing significant property damage.

An additional concern surrounding the adoption of EVs is the level of media attention that EV fires receive. Despite being relatively infrequent especially due to the low total market share, the negative publicity generated hinders the adoption of these vehicles. As well as causing the loss of resources that were originally carbon intensive to produce.

Objective of this work

The ultimate goal is to develop a fire suppression and thermal management system that can be realistically employed in a vehicle. This work may only achieve a step in this development for such a suppression system. It is vital to consider that such a system must be compatible with thermal management systems, as the implementation of a fire suppression system without an appropriate thermal management system essentially renders the vehicle useless. This means that a vehicle has the ability to keep the cells within its pack in the optimal temperature range, promoting longevity. As well as having a sufficient suppression system that is capable of preventing the propagation of thermal runaway between cells in the event of a fault or road traffic collision.

Progress to date

Throughout the last quarter the primary focus has shifted from the writing of a literature review to the development of more complex 3D COMSOL thermal runaway chemical kinetics models that will underpin the modelling work to come in this project and supersedes the MATLAB modelling to date. This was very successful as the results obtained replicate that of literature very well. Additionally, the other main components that would be necessary to assemble a larger more complete model were also attempted including conduction, convection and radiation models. The focus has now switched to developing a rig that can be used to validate the fundamentals of the COMSOL model. This will take the form of lower power tests that don’t require a specialist facility.

Conclusions and future work

The review paper will require a few more revisions after internal review before hopefully being submitted to a journal in the coming months. Focus will remain on the rig development at present.

QUILL Quarterly Report

November 2023 – January 2024

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny & Prof John Holbrey		
Position:	PhD student		
Start date:	01/09/21	**Anticipated end date:**	30/06/25
Funding body:	Engineering and Physical Sciences Research Council (EPSRC)		

Valorisation of Waste Polyolefin Plastics Using Lewis Acidic Ionic Liquids

Background

Waste polyalphaolefin plastic can be processed using pyrolysis to produce a mixture containing a wide distribution of alphaolefin/paraffin products. This mixture can be used to generate waxes, a higher value product and a low value naphtha fraction. Using the naphtha fraction from the waste polyolefin pyrolysis (C8-C20) and a Lewis acidic ionic liquid, the oligomerisation of 1-olefins to base oil is performed. The resulting base oil should have key physical properties to that of synthetic Group IV base oils including high viscosity index (>120) combined with low kinematic viscosities (Kv_{100} = 4 cSt or 6 cSt). Producing both waxes and base oil increases the overall economic feasibility of the process which adopting a circular economy cradle to cradle approach.

Borenium ionic liquids with the general formula $[BCl_2(L)][Al_2Cl_7]$ (L = pyridine or picoline) and liquid coordination complexes based on $AlCl_3$, L-$AlCl_3$ (L = Urea or $P_{888}O$) are selected as they have high Lewis acidities and synthesised from readily available and chemicals.

Using waste polyalphaolefin plastic as a feedstock poses challenges as it highly contaminated. The recycled feedstock must be purified before oligomerisation is performed. Additives and liquid-liquid extraction are selected based on the ability to remove impurities and analysed by XRF and ^{13}C NMR.

Objective of this work

In this project, the goal is to convert 1-olefins in the naphtha fraction to lubricant base oil using liquid coordination complexes and borenium ionic liquids. The analysis of product distributions (by SimDist GC) and physical parameters are then compared to the industry standard. Before the oligomerisation can take place the impurities in the feedstock must first be removed. Without the removal of impurities, the liquid coordination complexes and borenium ionic liquids fail to oligomerise 1-olefins. This is an area of focus on this project to find sustainable method to remove impurities.

Progress to date

The reactions have been conducted using the light, heavy, and crude fractions of waste polyolefin plastic. The results revealed a competition between hydrocarbon cracking and oligomerisation of the feedstock, arising from the balance between endothermic C-C cleavage and exothermic bond formation. The reaction conditions, such as the composition of the starting feedstock and catalytic loading, determine the selectivity towards hydrocarbon cracking or oligomerisation, as depicted in Figures 1-3.

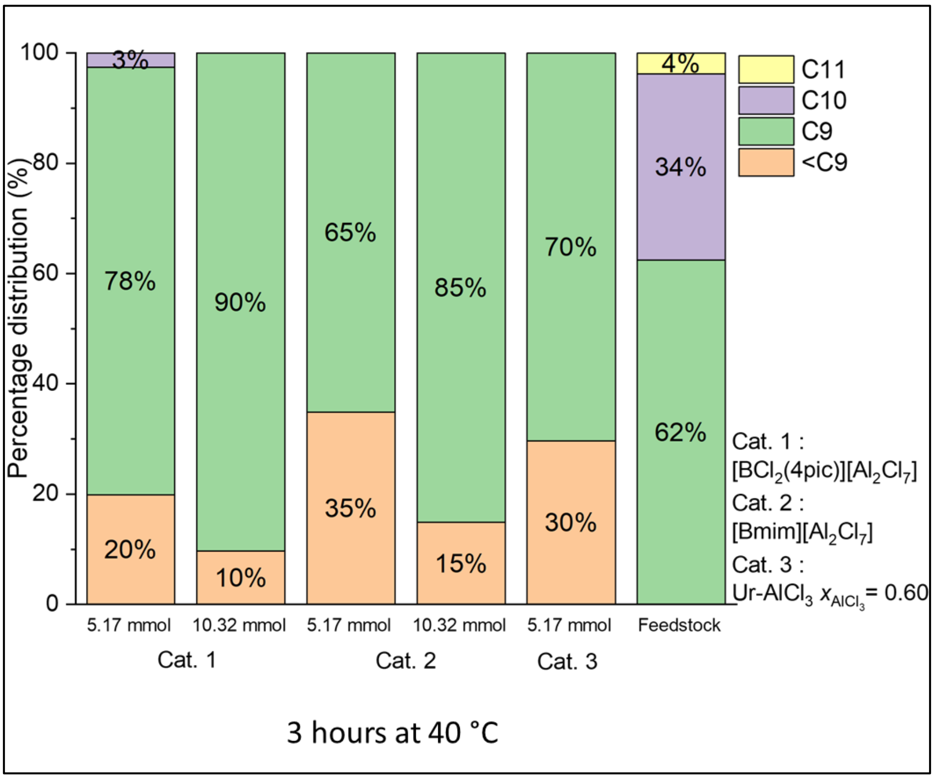


Figure 1 - Light feedstock: C9-C11

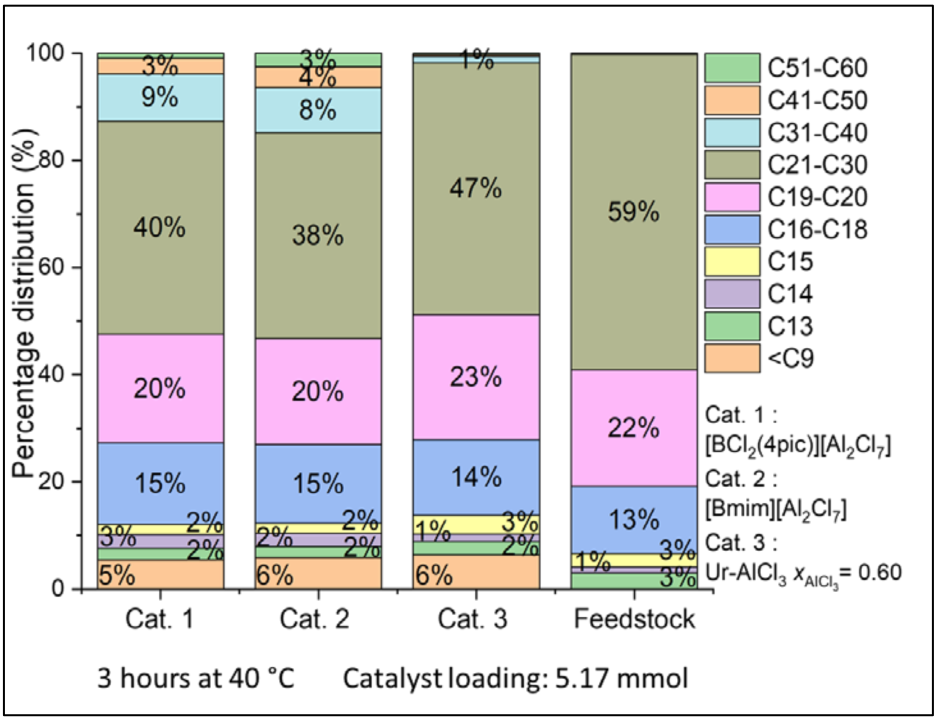
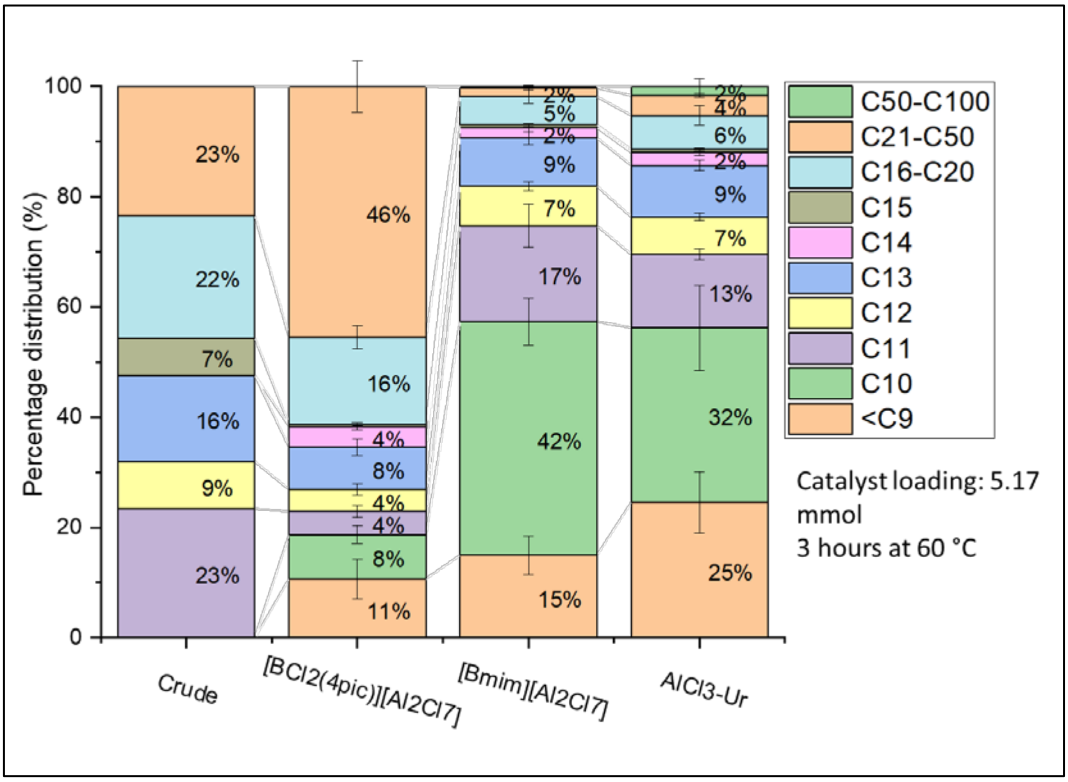


Figure 2 - Heavy feedstock: C13-C60



Catalyst loading: 5.17 mmol
3 hours at 60 °C

Figure 3 - Crude feedstock: C13-C100

After completing these reactions, the decision has been made to transition to a different plastic polymer, such as poly(ethylene) terephthalate, along with a Bronsted acidic ionic liquid for depolymerisation.

Additionally, I have been involved in a side project following the research of Dr. Novia Malviya on new chloride-free borenium ionic liquids and the calculation of the Gutmann acceptor number. I have successfully synthesised six ionic liquids and characterised them using NMR spectroscopy.

Conclusions and future work

Currently, the methodology utilising Lewis acidic ionic liquids is not the correct approach for converting waste polyolefin plastic. However, from this research, several key findings have been discovered. The quality of the batch of plastic is crucial for a reaction to occur using Lewis acidic ionic liquids, and a simple pre-washing step before pyrolysis can reduce impurities. The composition of the feedstock is highly selective in achieving hydrocarbon cracking or oligomerisation, which is also controlled by the composition of the ionic liquid and catalyst loading. The feedstock is also unsuitable for alkylation reactions with 1-decene, which previous experiments have shown these specific ionic liquids excel at with benzene and 1-decene.

The next step in plastic research is to depolymerise PET using Brønsted acidic ionic liquids with a microwave monowave reactor. In the other research synthesis of chloride-free borenium ionic liquid, the next step is to successfully calculate the Gutmann acceptor number and send samples to collaborators to test the catalytic ability of these ionic liquids.

QUILL Quarterly Report

August 2023 – October 2023

Name:	Kerri McKeever		
Supervisor(s):	Prof Gosia Swadzba-Kwasny & Prof John Holbrey		
Position:	PhD Candidate		
Start date:	14/08/2023	**Anticipated end date:**	13/08/2026
Funding body:	DfE CAST, Diamond and ISIS		

Boron and Frustrated Lewis Pairs in Supported Ionic Liquid Phases: An Interdisciplinary Study of New Metal-Free Catalysts

Background

An emerging alternative for transition metal catalysis is using Lewis acidic boranes in Frustrated Lewis pairs. Frustrated Lewis pairs (FLPs) are compounds which contain a Lewis acid and base (eg. boron/phosphine) that are either electronically or sterically hindered, preventing formation of the classical adduct, instead, in solvent they form an encounter complex in which the acid and base remain weakly associated, with the HOMO of the base and LUMO of the acid left free for reactivity with a third molecule. This unique behaviour allows for the activation of H_2 and other small molecules (eg. CO2, N2), meaning they are capable of conducting metal-free catalysis and a possible alternative to transition metals.

Analytical techniques involving X-rays and neutron scattering, including operando studies are well established for transition metal catalysis, however, the same cannot be said for boron compounds, which face a number of different challenges for example: boron is a light element and its K-edge is in the soft X-ray regime, thus for XAS studies, a vacuum is required, yet for FLP hydrogenation reactions a H_2 atmosphere is needed preventing investigation by standard methods. In this project, this will be mitigated by using ionic liquids which have a negligible vapor pressure and can be studied under high vacuum. Another challenge is the bubbling of gas through a liquid in operando studies, to overcome this we will be using supported ionic liquid phases (SILPs), where the film of an ionic liquid is supported on a porous solid. X-ray Raman spectroscopy will also be used to study boron- based FLPs, a new hard x-ray technique that can study the bulk structure of low Z materials. For neutron scattering, ^{10}B (ca 19% of natural B) absorbs neutrons well and provides poor scattering data, so isotopically pure boron compounds will be used. Additionally, DISSOLVE, a new alternative to EPSR will be used to model the experimental data.

Objective of this work

This project aims to expand the understanding and knowledge of FLP chemistry to hopefully be a viable alternative to transition metal catalysts and develop analytical techniques such as x-rays and neutron scattering to study light elements, specifically boron and overcome the challenges which accompany that. Additionally, to expand the knowledge and expertise of XRS at Diamond and in the UK, as it becomes an increasingly popular technique.

Progress to date

During November and December I continued to work on the deuteration experiments I was working on previously: [d_8-P_{66614}][NTf_2] and [d_3-C_1mim][NTf_2] , which I completed, then analyse thoroughly using NMR and mass spectroscopy, and sent them to our collaborators for further analysis. Deuterations are very important for neutron scattering as it provides multiple sets of data for the same sample, so that you can compare.

In January, I spent time synthesising samples for the beamtime at B07 at Diamond Light Source, Didcot, including BcatBu and a few ionic liquids, along with Emma who helped to make some compounds as well. I then joined Beth Murray and Prof. Gosia Swadzba-Kwasny for this beamtime which lasted from the 17th to 20th January. This experiment involved studying many different boron-based compounds using soft x-rays and comparing them to the XRS data of the same compounds which was captured in February 2023 at the European Synchrotron Radiation Facility (ESRF), as well as comparing to simulations. This work will also allow for *operando* measurements later in this project.

After returning from this trip from Diamond, I began analysing the captured data and I am continuing to do so, as well as continuing to analyse the data from X-ray Raman Spectroscopy (XRS), using python, as mentioned above, which is a new technique which uses hard x-rays to study low Z materials. I travelled to Diamond Light Source early to spend a few days with Dr. Luke Higgins to discuss this data analysis. The purpose of this is to remove the background so that you can compare the graph produced for different compounds.

Furthermore, I prepared and delivered a presentation at the group meeting on the background of my project, what I have done so far and my next steps for the future, as this was my first presentation it took some time to prepare and create diagrams.

Additionally, with my initial progress review (IPR) scheduled for February, I started to prepare my report and presentation for this.

During this quarter, I also completed a fire safety induction and a respirator mask fitting, as well as continuing to receive training on how to use the various lab equipment as I am still new to my PhD for example, I learned how to use the XRF machine. Subsequently, I helped in the big school-wide lab clear out to dispose of old chemicals, (older than 10 years old) and update the inventory.

Conclusions and future work

In conclusion, in this quarter, I have continued to familiarise with my project and learning the equipment and laboratory procedures. I completed two deuteration experiments and made a trip to Diamond Light Source to conduct a soft x-rays experiment, and subsequently have started to analyse the data captured from this experiment.

Going forward, I will be going to the ESRF in February with colleagues from Diamond Light Source to help with their experiment and reanalyse a compound from our previous experiment here. Additionally, I am preparing for my IPR and the upcoming QUILL meeting.

QUILL Quarterly Report

November 2023 – January 2024

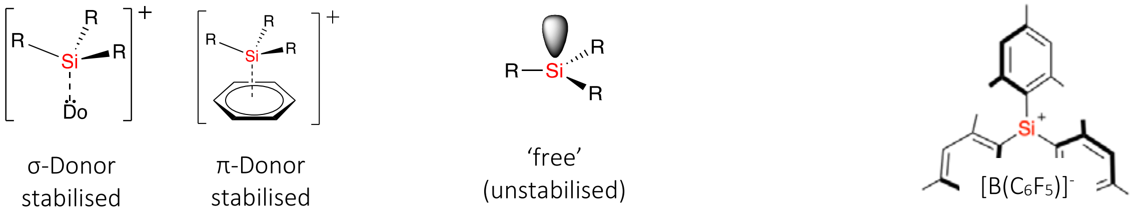
Name:	Shannon McLaughlin		
Supervisor(s):	Professor Gosia *Swadźba*-Kwaśny		
Position:	PhD Student (3rd year)		
Start date:	October 2020	**Anticipated end date:**	September 2024
Funding body:	Department for the Economy (DoE)		

Ionic Liquids Based on Silicon Cations

Background

The chemistry of Lewis acidic main group cations is of increasing importance, as metal-free catalysis gains interest of the scientific community. One of the longest-standing challenges in main group synthetic chemistry has been the preparation of tricoordinate, tetravalent silicon cations in the condensed phase. Silylium ions are extremely Lewis acidic and have a high electrophilicity, oxophilicity and fluorophilicity, affording unique transformations that cannot be performed by traditional metal catalysts. Recently, synthetic methods to generate stable silylium cations have become more accessible and more effective.

Silylium ions can be categorised as either stabilised or 'free' (Figure 1a). As they are highly reactive, silicon cations are commonly found as species which are stabilised, whereas 'free' silicon cations are extremely rare. The first ever 'free' silylium cation to be isolated was the trimesitylsilylium cation ($(Mes)_3Si^+$) illustrated in Figure 1b.[1] Silylium ions are usually quite a reactive species but the bulky mesityl groups in compound **1** help to shield the silicon centre from attack by large nucleophiles. These steric interactions also prevent the silylium ion reacting with the solvent and the product alkene making it much more stable. The tridurylsilylium cation ($(duryl)Si^+$)[2] was later isolated along with the related species $(C_6Me_5)_3Si^+$.[3] Till date these three compounds are the only examples of 'free' species whose structures have been confirmed by X-ray crystallography.



1

Figure 1 - a) Example structures of stabilised and unstabilised silylium ions b) Structure of 'free' trimesitylsilylium cation

Objective

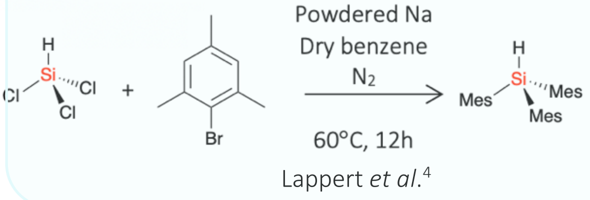
This work reports on the first-ever attempt to prepare and characterise silylium ionic liquids. The first goal of this project is to synthesise the 'free' trimesitylsilylium cation illustrated in Figure 1b.

Progress to date

Synthesis of trimesitylsilane:

Trimesitylsilane was synthesised following the method described by Lappert *et al.*[4] 0.74 g of trimesitylsilane was synthesised (white crystals shown in Figure 2). A second batch of trimesitylsilylium was synthesised to increase the yield. ^1H, ^{13}C and ^{29}Si NMR spectra for trimesitylsilane were recorded. Peaks observed matched exactly to literature values in all NMR spectra.

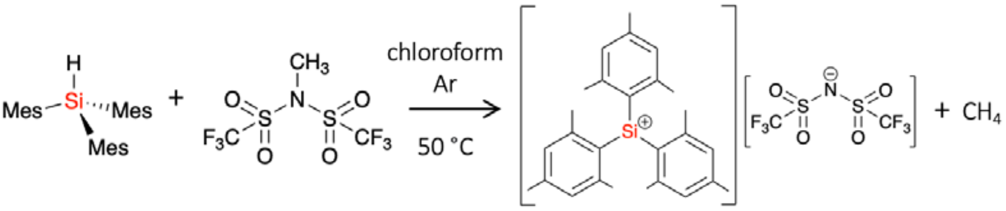
Scheme 1: Synthesis of trimesitylsilane.



Synthes

Figure 2 - White crystals of trimesitylsilane, first batch (left) and second batch (right)

Scheme 2 - Synthesis of $[Si(Mes)_3][NTf_2]$



The synthetic route, illustrated in Scheme 2, was conducted using air-sensitive techniques to generate trimesitylsilylium bis[(trifluoromethyl)sulfonyl]imide (bistriflimide), $[Si(Mes)_3][NTf_2]$. The trimesitylsilane starting material was synthesised following the method described previously by Lappert *et al.*[4] Trimesitylsilane was reacted with *n*-methyl bis[(trifluoromethyl)sulfonyl]imide ($Me[NTf_2]$) and refluxed under argon in chloroform at 50 °C. The progress of the reaction was monitored using ^{1}H, ^{13}C and ^{29}Si NMR. The product was purified until there was no trimesitylsilane present in the NMRs. A stacked ^{29}Si NMR spectra of trimesitylsilane and $[Si(Mes)_3][NTf_2]$ is shown in Figure 3. Tertiary silylium ions have silicon NMR shifts in the between 40 and 120 ppm whereas 'free' silylium ions have silicon NMR shifts greater than 200 ppm.[1] The silicon peak for $[Si(Mes)_3][NTf_2]$ appears at approximately -44 ppm. This signal does not fall in the region expected for a 'free' silylium ion which suggests that not all the trimesitylsilane has reacted.

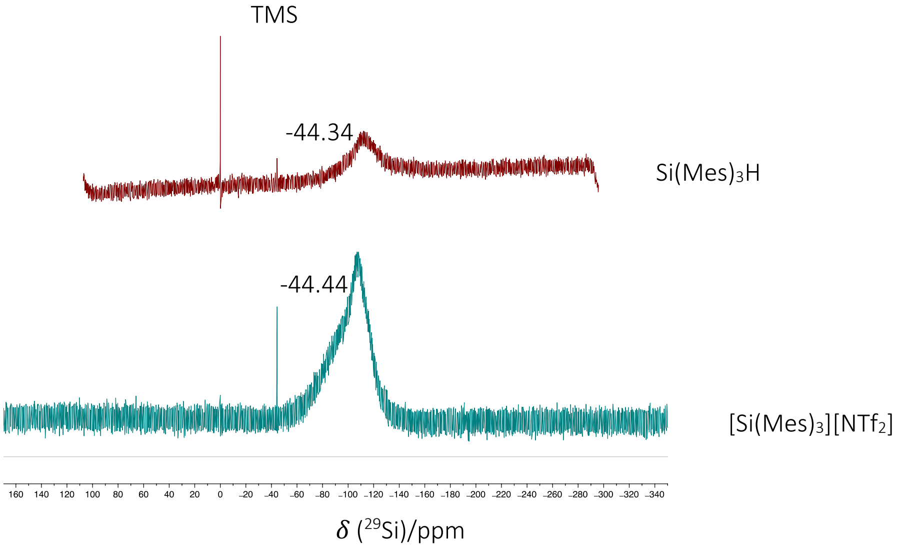


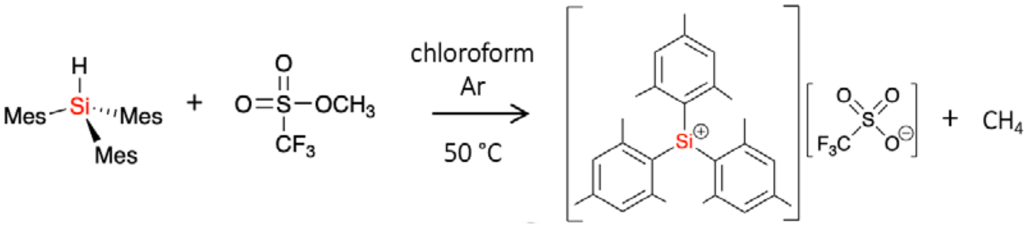
Figure 3 - Stacked ^{29}Si NMR spectra of $Si(Mes)_3^+$ containing compounds

Characteristic Studies:

The crystals of $[Si(Mes)_3][NTf_2]$ obtained from the reaction in Scheme 2 were previously characterised using multiple analytical techniques, including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and single crystal X-ray diffraction (XRD). These characterisation studies were repeated with samples being prepared in a glovebox and air-sensitive techniques utilised when possible, for example, closed pan TGA.

Synthesis of $[Si(Mes)_3][OTf]$:

Scheme 3 - Synthesis of $[Si(Mes)_3][OTf]$



The synthetic route, illustrated in Scheme 3, was proposed to generate trimesitylsilylium trifluoromethanesulfonate (triflate), $[Si(Mes)_3][OTf]$. The trimesitylsilane starting material will be reacted with methyl trifluoromethanesulfonate (Me[OTf]) and refluxed under argon in chloroform at 50 °C. The progress of the reaction was monitored using ^{1}H, ^{13}C and ^{29}Si NMR.

Conclusions and future work:

A complete characterisation study of the compound formed *via* the reaction shown in Scheme 3 will be conducted to determine if $[Si(Mes)_3][OTf]$ has been successfully synthesised. TGA and DSC curves have already been obtained using air-sensitive techniques. The stacked TGA and DSC curves of all the $Si(Mes)_3^+$ containing compounds are shown in Figure 4 and Figure 5, respectively.

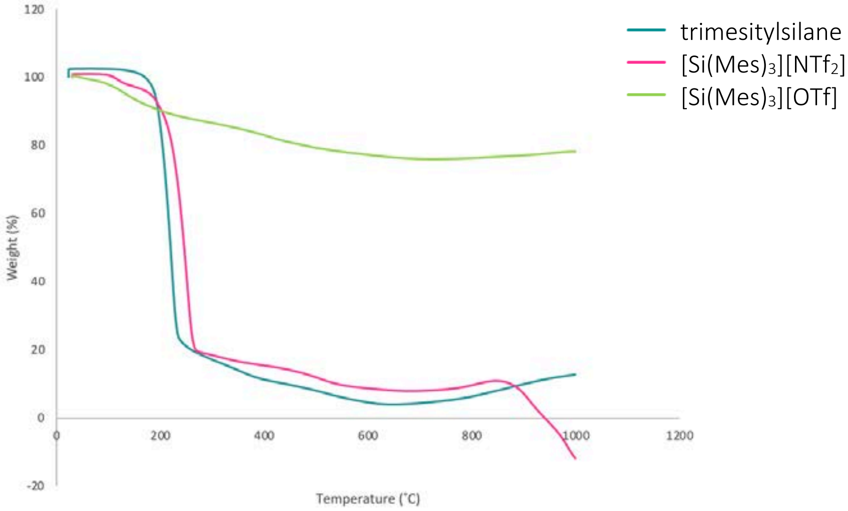


Figure 4 - Stacked TGA curve of $Si(Mes)_3^+$ containing compounds

In the TGA curve of $[Si(Mes)_3][NTf_2]$ decomposition of the compound begins around 180 ˚C. After heating this sample to 1100 ˚C there is still approximately 40 % of the compound remaining by weight. This suggests that the product does not fully decompose and instead turns to char. Similarly, in the TGA curve of $[Si(Mes)_3][OTf]$ decomposition begins around 136 ˚C. After heating this sample to 1000 ˚C there is still approximately 70 % of the compound remaining by weight. A potential explanation for this could be formation of a glassy carbon type material but further characterisation studies will need to be conducted to confirm this.

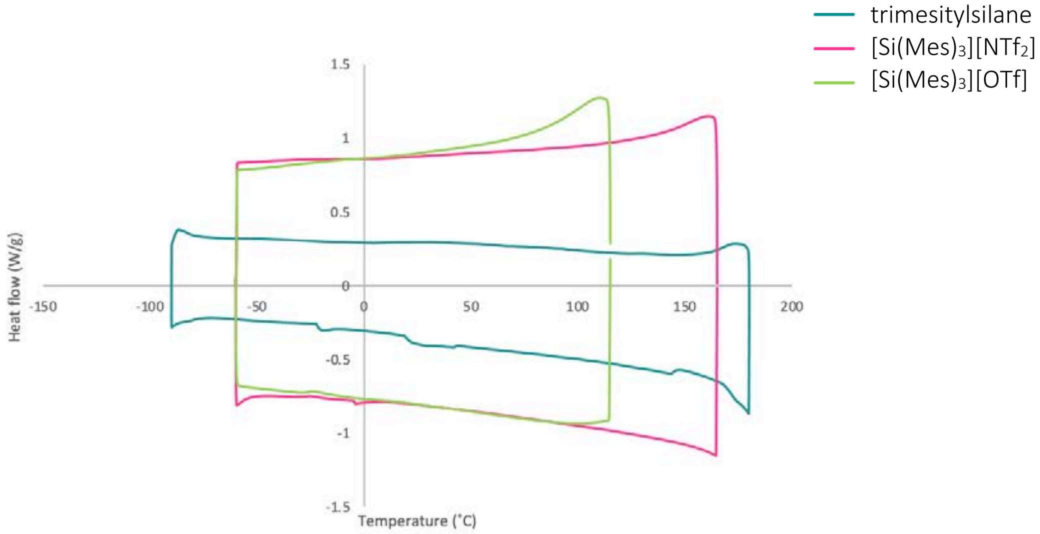
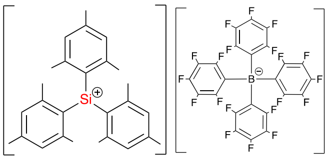
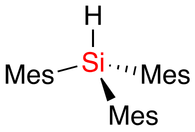
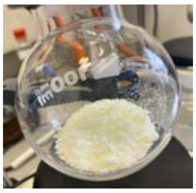
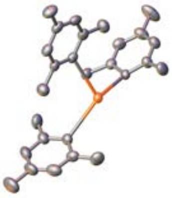
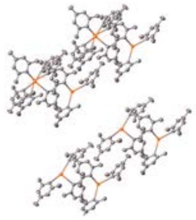
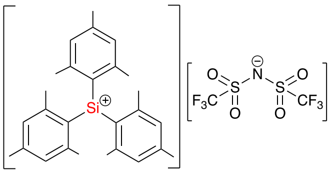
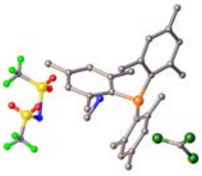
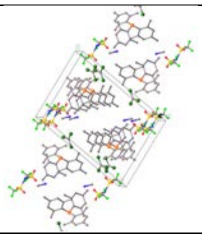
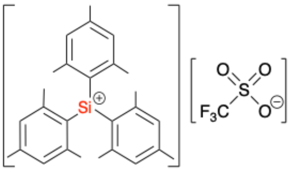


Figure 5 - Stacked DSC curve of Si(Mes)$_3^+$ containing compounds

In the DSC curve of [Si(Mes)$_3$][NTf$_2$] there are two glass transitions at -4 ˚C and -24 ˚C whereas the DSC curve for [Si(Mes)$_3$][OTf] shows a single glass transition at -22 ˚C.

Table summarises the data obtained **Table 1 -** for the Si(Mes)$_3^+$ containing compounds synthesised. Information from literature is included for comparison.

Comparison of Si(Mes)$_3^+$ containing compounds.

Compound	Structure	Appearance	Crystal Structure	Unit Cell	δ ^{29}Si (ppm)
[Si(Mes)$_3$][B(C$_6$F$_5$)$_4$] (from literature)		oil or liquid clathrate[1]	*	*	225.5[1]
trimesitylsilane Si(Mes)$_3$H					-44.34
[Si(Mes)$_3$][NTf$_2$]					-44.44
[Si(Mes)$_3$][OTf]		dark brown solid	?	?	?

* No literature data available

In the trimesitylsilane crystal structure the two mesityl groups lay flat along the plane of the silicon centre and the third mesityl group sticks out of the plane to help minimise steric hindrance. The silicon atoms also keep the centre of the unit cell unoccupied to lower the lattice energy of the crystal. I expect that this space in the unit cell will be filled with anions when this compound is used as a starting material to synthesise new ionic liquids. The [Si(Mes)$_3$][NTf$_2$] crystal structure has a primitive unit cell, consisting of alternate sheets of two cations in the centre with anions on either side. This repeating pattern is likely held together by strong intermolecular forces. The chloroform present in the crystal structure is likely due to some solvent molecules getting ‘caught’ within the crystal while it was growing.

The product formed *via* the reaction in scheme 3 (potential [Si(Mes)$_3$][OTf]) will be purified and recrystallised once there is no trimesitylsilane present in the NMRs. Single crystal XRD will be used to try to determine the crystal structure and a unit cell. Further characterisation studies including powder X-ray diffraction (PXRD) and mass spectrometry (MS) will also be conducted for all the compounds synthesised. PXRD will help determine whether the crystal structure is representative of the bulk of the sample. The Gutmann–Beckett method will be used to assess the Lewis acidity of species and capillary melting points will also be determined.

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3. A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, Organometallics, 2013, **32**, 4713-4722.
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QUILL Quarterly Report

November 2023 – January 2024

Name:	Beth Murray		
Supervisor(s):	Prof Małgorzata Swadźba-Kwaśny & Prof John Holbrey		
Position:	PhD student		
Start date:	October 2022	**Anticipated end date:**	October 2025
Funding body:	Department of Economy		

Inorganic Chemistry of Group 13 Elements in Sustainable Uses

Background

Between November and January, I have been working extending the research I carried out at Monash University in Melbourne, looking into liquid coordination complexes (LCCs) as electrolytes for aluminium batteries.

Regarding electrolytes for aluminium batteries, rechargeable batteries hold a crucial position in the energy management strategy of the European Union (EU). The EU acknowledges energy storage solutions as essential elements that contribute to grid flexibility and support the seamless integration of renewable energy sources into the energy system.[1] Secondary (rechargeable) batteries exhibit exceptional energy conversion efficiency, superior performance, reliability, and the ability to provide on-demand responses.[2] Presently, lithium-ion batteries are considered cutting-edge technology, however, they are plagued by high costs and flammability concerns. These batteries are widely prevalent in mobile electronic devices and are being increasingly utilized in transportation and grid applications.[1] Lithium-ion batteries offer several advantages, including high energy density, design flexibility, self-discharge, good cycle life, and low maintenance.[3] However, it is important to note that lithium has a low abundancy on Earth, which contributes to its high cost and reduces the long-term sustainability of relying heavily on the metal. Furthermore, as already mentioned elemental lithium is unstable and highly flammable.[4]

Metals from Groups 1 and 2 have been considered as substitutes for lithium (Li) in batteries, but aluminium (Al) from Group 13 appears to hold significant promise. It is abundantly available on Earth, making it a cost-effective option. Moreover, aluminium offers safe handling, the capability to exchange three redox electrons per cation, and exhibits high gravimetric and volumetric capacity.[5] One drawback of Al batteries is their limited commercialisation, primarily due to the absence of suitable electrolytes. Many attempts to commercialise Al batteries faced technical challenges, including difficulties in achieving reversible electroplating/stripping of aluminium, inadequate stability of Al-ion cells, and corrosion issues.[1] While there has been significant research on electrolytes for lithium-ion batteries, limited attention has been given to finding suitable electrolytes for Al batteries. However, ionic liquids (ILs) have emerged as a promising candidate. ILs are composed entirely of ions and often have a melting point below ambient temperature. They possess several desirable properties, including high ionic conductivity, minimal volatility, very low flammability, and excellent chemical and electrochemical stability.[3] Promising electrolytes were developed through the dissolution of aluminium salts, such as $AlCl_3$ or $Al(TFSI)_3$, in ionic liquids containing bis(trifluoromethanesulfonyl)imide ($[TFSI]^-$) or trifluoromethanesulfonate ($[OTf]^-$) anions.[6, 7] While electrolytes using ILs show promise, they also present certain challenges, such as cost. Despite the cost advantage of aluminium over lithium, the use of ionic liquids can introduce additional expenses. The organic cation, despite having a spectator role, contributes significantly to the overall cost. Secondly, one of the challenges associated with using ILs is their higher viscosity compared to organic solvents, which hampers the conductivity of Al(III). Another significant drawback is corrosion, especially in chloride-containing systems, which remains a critical issue. Lastly, there is a limited scope for optimisation when using ILs as electrolytes. The concentration of Al(III) is constrained by the solubility of the aluminium salt, and also by the potential negative effects that high salt concentration can have on the electrolyte, such as an increase in viscosity that can be detrimental to conductivity.

At this juncture, we introduce LCCs as novel analogues of ILs that have been developed specifically to address the challenges encountered with ILs in various applications. LCCs supply the demand for cost-effective analogues of ionic liquids that possess, high metal content, and adjustable environments around the metal centre. These analogues are highly sought after for applications such as metal electrodeposition,[8] Lewis acid catalysis,[9] and as electrolytes for lithium-ion batteries.[10]

Objective of this work

The primary goal of the research on liquid coordination complexes (LCCs) for aluminium battery electrolytes was initially centred around synthesising semiconductor nanoparticles through the utilisation of LCCs. This segment of work work concentrates on the use of liquid coordination complexes based on aluminium as electrolytes in aluminium-ion batteries. This research is founded on the promising potential of aluminium in batteries, attributed to its high abundance on Earth, its capability to exchange three redox electrons per cation, as well as high gravimetric and volumetric capacity.[5]

Progress to date

Regarding previous quarterly reports, work had been carried out at Monash University in Melbourne, Australia for six weeks, as part of the Macfarlane research group. In the initial stage of the research, the objective was to reproduce the literature data on the utilization of a urea-$AlCl_3$ LCC as an electrolyte in aluminium batteries. The LCC electrolyte had received considerable attention in previous publications, making it a suitable candidate for replication using a coin cell configuration. Coin cells were selected for this study due to their ability to operate with minimal electrolyte, allowing for symmetrical and full cell experiments to be conducted, although no literature had reported the use of a coin cell. **Figure 1** shows the preliminary results obtained from galvanostatic cycling test performed on symmetrical Al/Al cells, employing the urea-$AlCl_3$ electrolyte ($\chi_{AlCl_3} = 0.58$). Unfortunately, initial findings showed a high overpotential of approximately 2 V, and cell shorting, which from further investigation proved to be that the Al discs needed to be polished before use, likely due to the presence of a residual oxide layer on the surface.[11]

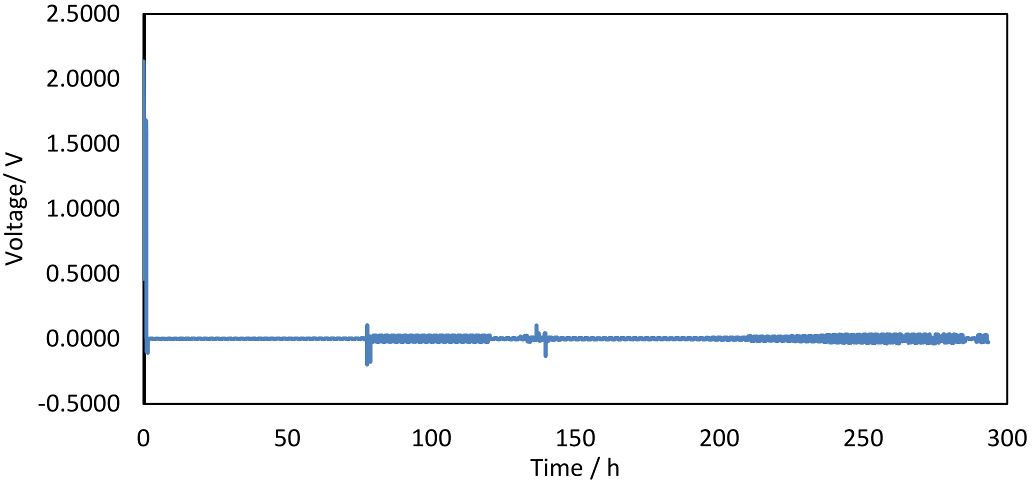

Figure 1 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte

A polishing solution was prepared by combining sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and nitric acid (HNO_3) (further details in section 5.2.2). After polishing of the Al discs, the cycling results were comparable to literature,[5] showing a lower overpotential and stable cycling (Figure 4).

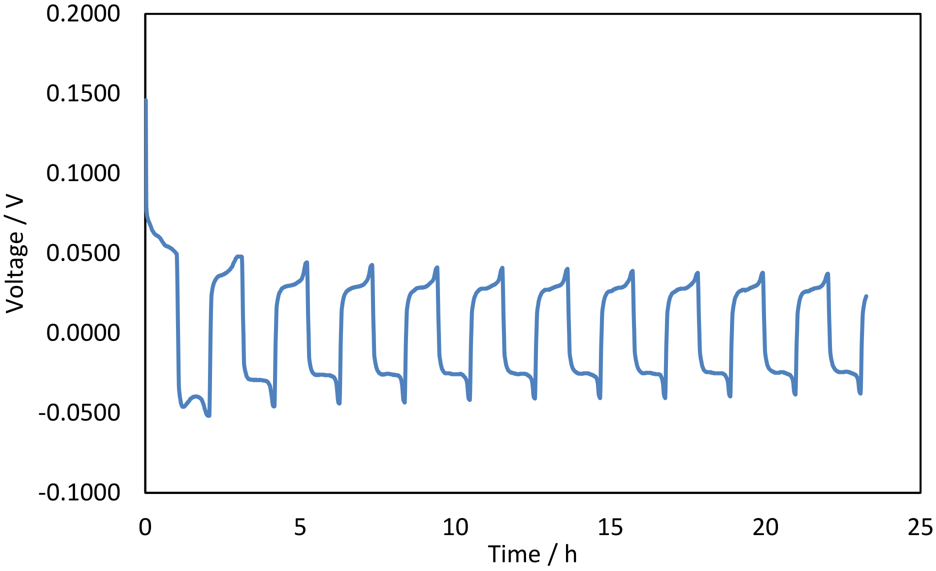

Figure 2 - Galvanostatic cycling of Al/Al symmetrical cell with urea-$AlCl_3$ electrolyte, after the Al electrodes were polished with acid

EMImCl-$AlCl_3$, a non-flammable IL that operates at room temperature, has gained significant attention as a favoured electrolyte for aluminium batteries. This IL exhibits notable attributes, including high ionic conductivity, exceptional thermal stability, chemical stability, and electrochemical stability.[12] In 2016, Sun *et al.* conducted a study investigating the impact of incorporating various common solvents, such as acetone, acetonitrile, tetrahydrofuran (THF), toluene, and dichloromethane (DCM), into the EMImCl-$AlCl_3$ IL. Cyclic voltammetry (CV) was employed as a screening method to assess the impact of solvents on the electrochemical activity of the solution. This technique was utilized to determine whether the interaction between the IL and a solvent induces significant changes in the electrochemical behaviour. interestingly, certain solvents like tetrahydrofuran (THF) and acetonitrile were found to negatively affect the performance of the electrolyte. In contrast, the addition of DCM and toluene not only sustained the deposition and stripping of aluminium effectively but also resulted in a notable improvement in current density. Specifically, the current density was enhanced by 13% with the addition of toluene and 10% with the addition of DCM, surpassing the performance achieved with the pure IL.[13] The urea-$AlCl_3$ is known to be a less effective electrolyte than EMImCl-$AlCl_3$, due to its higher viscosity and lower ionic conductivity.[14] In an attempt to explore similar effects observed in the EMImCl-AlCl3 system, we opted to incorporate DCM and toluene into the urea-AlCl3 LCC, to assess if such addition could enhance the performance of the electrolyte in any manner. Unfortunately results showed an equimolar blend of urea-AlCl3 and DCM led to a substantial increase in overpotential compared to the LCC electrolyte without DCM (**Figure 3**).

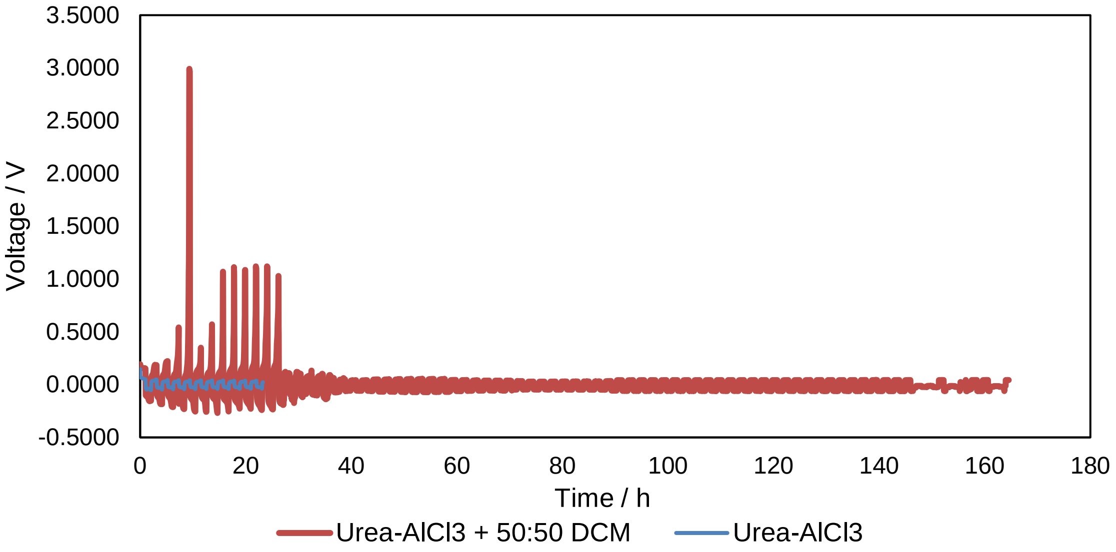

Figure 3 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ electrolyte with the addition of equimolar amounts of DCM

The urea-$AlCl_3$ electrolyte was also studied with the addition of toluene (50% w/w) to explore the possibility of further enhancing the system. Symmetrical Al/Al cycling demonstrates promising outcomes, with the electrolyte performing well, particularly at higher current rates (**Figure 4**). This is a promising outcome, as to date no literature has reported on a urea-$AlCl_3$ electrolyte with the addition of toluene. While this initial progress is encouraging, further investigations are required to assess whether this system is a viable option for Al-ion batteries. These upcoming studies will encompass physical characterisations like viscosity, but the focus will primarily be on ionic conductivity. Additionally, I intend to experiment with different w/w% of toluene added to determine the optimal conditions.

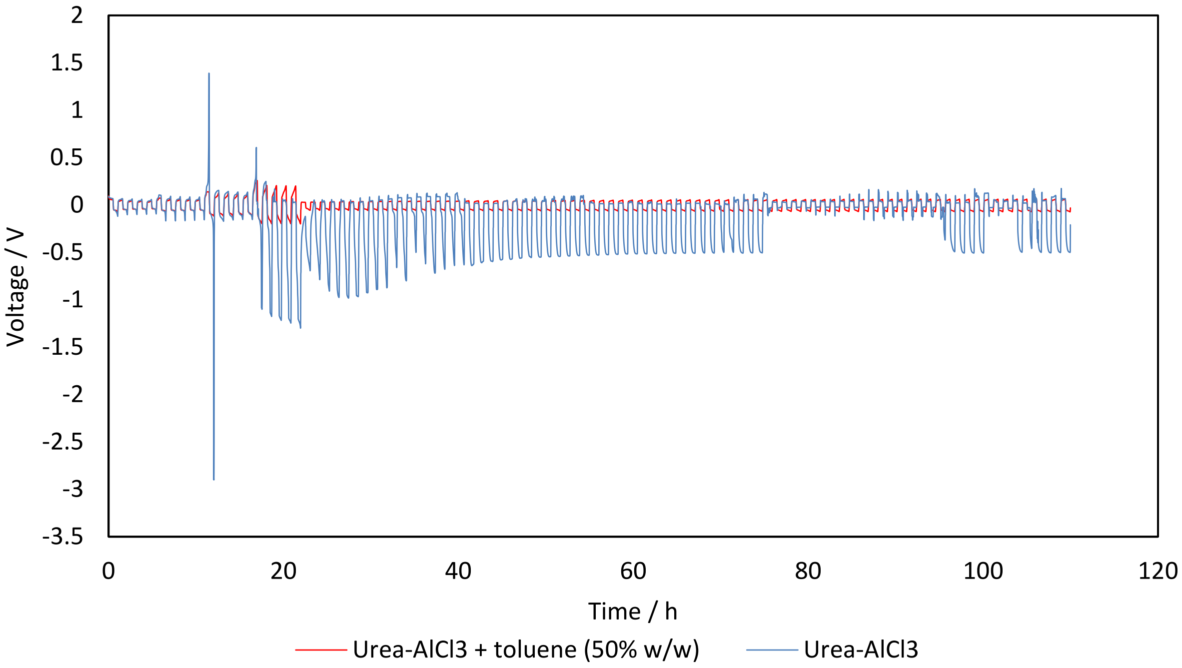

Figure 4 - Comparison of symmetrical Al/Al cycling with urea-$AlCl_3$ electrolyte and urea-$AlCl_3$ with the addition of toluene (50% w/w)

As mentioned earlier, a coin cell configuration was utilized for all the studies due to the restricted supply of materials needed for preparing the electrolyte. This setup proved to be satisfactory for the Al/Al symmetrical cycling experiments. However, challenges arose when transitioning to a full cell configuration. A full cell configuration was made using a graphite cathode. The cyclic voltammetry (CV) results from the urea-$AlCl_3$ cell showed a trace similar to that reported in literature,[15] however, with an additional oxidation peak around 1.3 V (Figure?). To identify the nature of the additional peak, several coin cells with different independent variables were tested. One of these coin cells ran without a graphite electrode but only the carbon fiber paper support, and the peak was still observed. This result indicates that the graphite electrode was not the cause of this side reaction. Next, a coin cell experiment was conducted without the entire graphite cathode and support. In this test, the electrolyte was in direct contact with the stainless steel coin cell. Surprisingly, the oxidation peak remained present, implying that a side reaction might be occurring between the urea-AlCl3 electrolyte and the stainless steel coin cell. To conclusively confirm our speculation, a final test was conducted using a coin cell with an aluminium triflate ($Al(OTf)_3$) in diglyme electrolyte. This test showed no oxidation peak at 1.3 V, providing further evidence that the reaction occurs between the urea-AlCl3 electrolyte and the stainless steel coin cell. This is likely attributed to corrosion issues associated with chloride electrolytes,[16] as it interacts with the coin cell.

To investigate the impact of toluene on the urea-$AlCl_3$ LCC, speciation studies, which include Raman and NMR were conducted on both the pure LCC, the LCC containing toluene and neat toluene. **Figure 5** shows the comparison of each Raman spectra, clearly showing the addition of toluene affects the structure of the neat LCC. The peaks labelled from the urea-AlCl3 spectra correspond to different aluminium species. When toluene is added the peaks disappear, signalling that the Al-Cl and Al-O bonds are broken. Interestingly, the Raman spectra of the LCC with varying amounts of toluene (25%-75%) exhibited no discernible differences. This observation suggests that even small quantities of toluene can disrupt the structure, and the added quantity does not have a distinguishable effect.

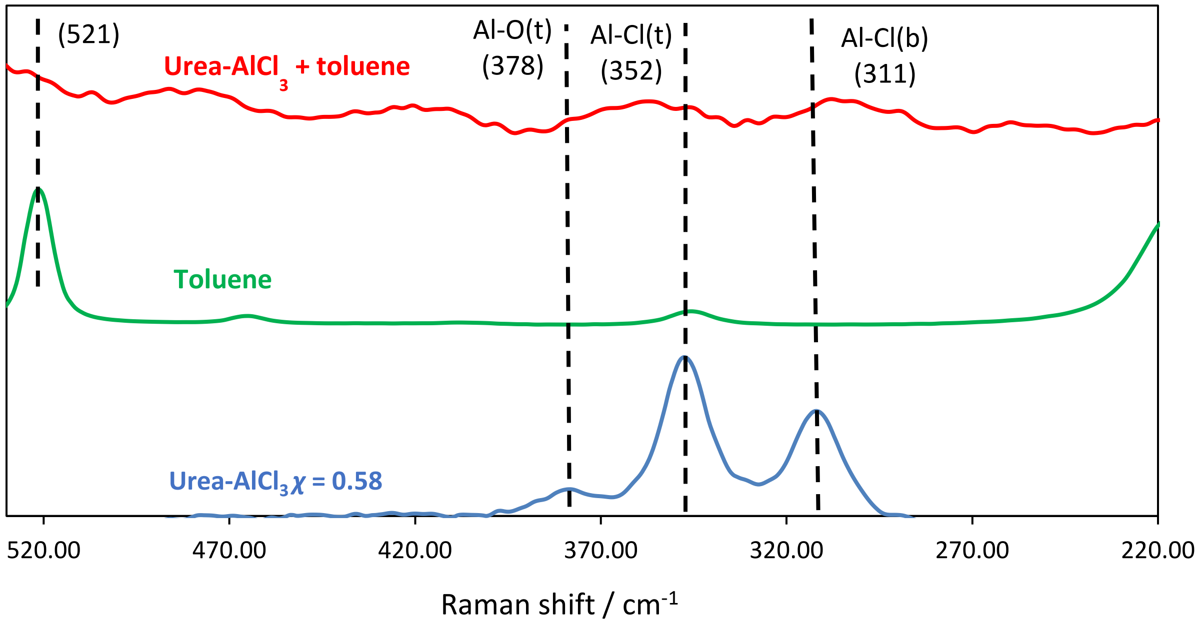

Figure 5 - Comparison of the Raman spectra for urea-AlCl3 LCC, urea-$AlCl_3$ LCC with toluene and neat toluene

Figure 6 shows the ^{1}H NMR spectra for urea-$AlCl_3$ with toluene (25%, 50% and 75%), neat urea-$AlCl_3$ and neat toluene. The neat toluene NMR has a cluster of peaks from 6.5-6.8 ppm, corresponding to the aromatic protons, and the singlet at 1.75 ppm corresponds to the three protons of the CH_3 group. It can be seen from the spectra that the CH_3 peak is still present when toluene is mixed with the LCC at all three ratios. This suggests that $AlCl_3$ didn't extract a proton from the CH_3 group to form a carbocation. All peaks shift more upfield, due to an increased electron density.

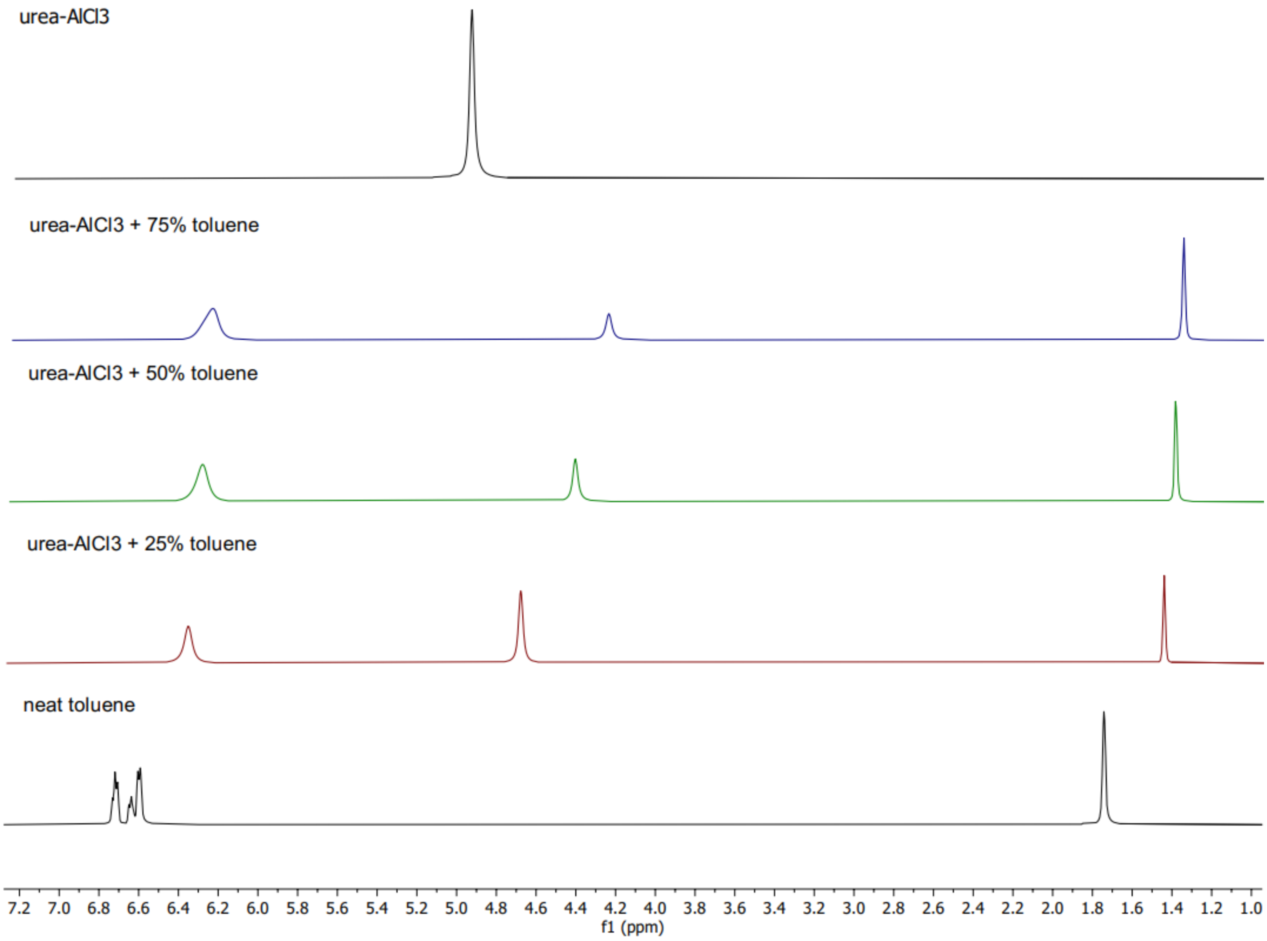

Figure 6 - ^{1}H NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary)

Figure 7 shows the ^{13}C NMR NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. From the spectra it can be seen that all toluene peaks are present, therefore, the structure of toluene is unaltered when mixed with urea-$AlCl_3$. The one carbon peak of urea is also retained when mixed with toluene.

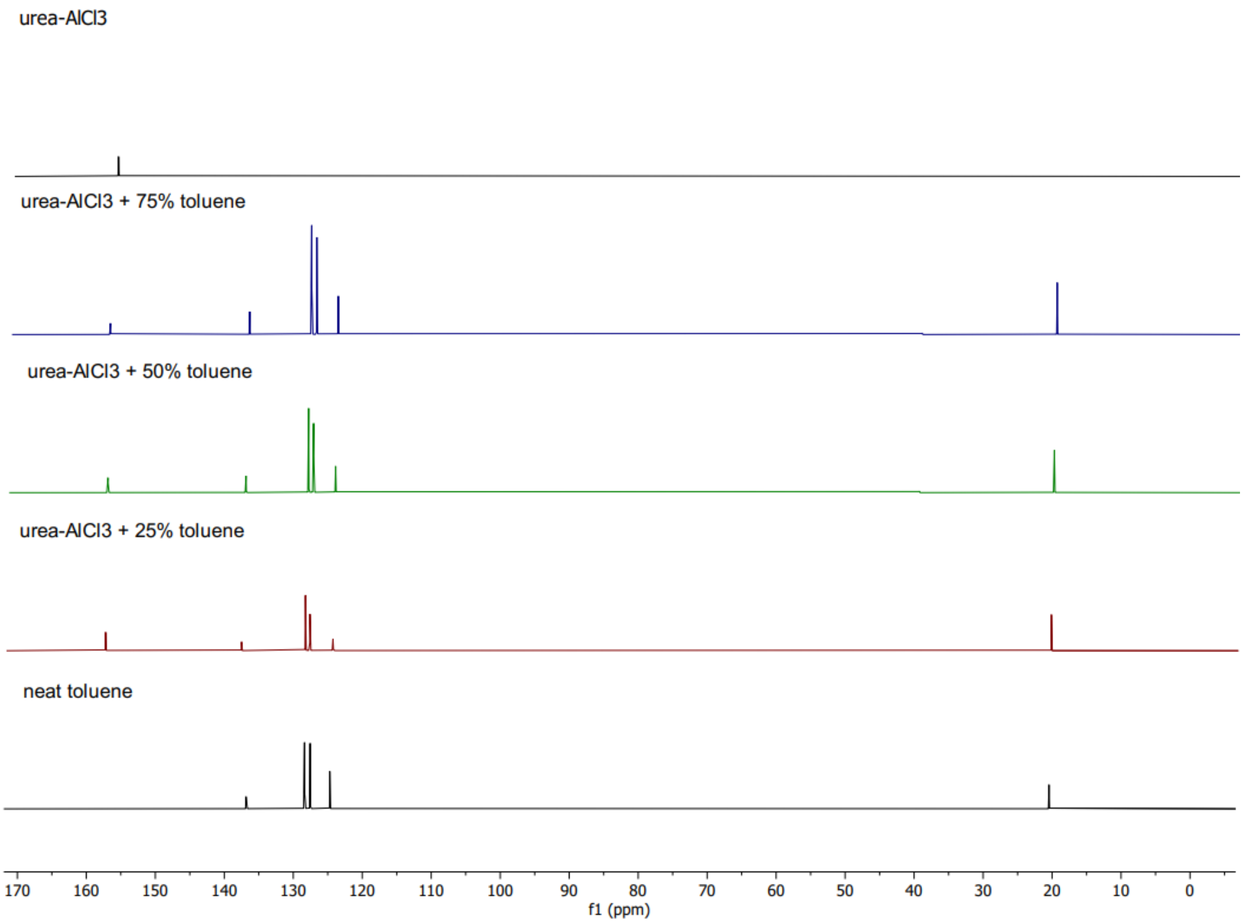

Figure 7 - ^{13}C NMR comparison of urea-$AlCl_3$ with toluene (25%, 50% and 75%) with neat urea-$AlCl_3$ and neat toluene. NMR solvent: d_6-DMSO (capillary)

Conclusions and future work

The literature findings on the use of urea-AlCl3 (χ_{AlCl_3} = 0.58) as an electrolyte for Al batteries were successfully reproduced using a coin cell configuration. Galvanostatic symmetrical cycling demonstrated stable performance once the aluminium electrodes were polished with an acid mixture to ensure the elimination of any residual oxide layer on their surfaces.
TOPO-$AlCl_3$ (χ_{AlCl_3} = 0.60) exhibited intriguing outcomes as an electrolyte, including high stability. However, its potential use as a battery electrolyte is likely hindered due to the size of the ligand, as it is not expected to function effectively as a charge carrier.

Continuing with the research on the urea-$AlCl_3$ electrolyte, additional investigations involved examining the impact of additives, such as DCM and toluene, on the electrolyte's performance. Unexpectedly, the addition of DCM had a detrimental effect on the galvanostatic symmetrical cycling, as results show high overpotentials. However, the addition of toluene yielded much more promising results, as the electrolyte performed well, showing good stability at much higher current rates.

This study has also revealed that coin cells are unsuitable for this research due to the corrosive nature of chloride electrolytes. The CV results indicated that an oxidation reaction was taking place between the urea-$AlCl_3$ electrolyte and the stainless steel of the coin cell, necessitating the search for an alternative cell option. Our collaborators at Monash University have undertaken efforts on an alternative cell, currently in the testing phase as a laminated pouch cell.

Brief speciation studies using Raman and NMR techniques have offered valuable insights into the impact of toluene on the urea-$AlCl_3$ LCC. This exploration aims to elucidate the reasons behind the improved performance of the electrolyte with the addition of toluene. Additional investigations, such as ^{27}Al NMR studies, and further review of relevant literature, are required to comprehend the impact of toluene on the system.

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QUILL Quarterly Report

November 2023 – January 2023

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey & Dr Leila Moura		
Position:	PhD student		
Start date:	01/10/2019	**Anticipated end date:**	27/03/2025
Funding body:	Self-funded		

Use Ionic Liquids That Exhibit LCST (Lower Critical Solution Temperature) Behaviour as Draw Fluids for Water Treatment, Desalination and Separation

Background

New Ionic liquid materials have been recently developed that exhibit lower critical solubility temperature (LCST) behaviour with water. That is, they are miscible at a low temperature and split into two aqueous phases on heating beyond a critical temperature. Such materials have the potential to be used as draw fluids for forward osmosis (FO) water desalination using low grade energy to address the global challenge to provide clean, accessible drinking water to all the world's populations. In this research , new ionic liquids will be investigated as advanced fluids for forward osmosis water treatment. This offers opportunities to advance less energy intensive alternative to conventional reverse osmosis as a solution to the global challenge of providing potable water in regions of low availability.

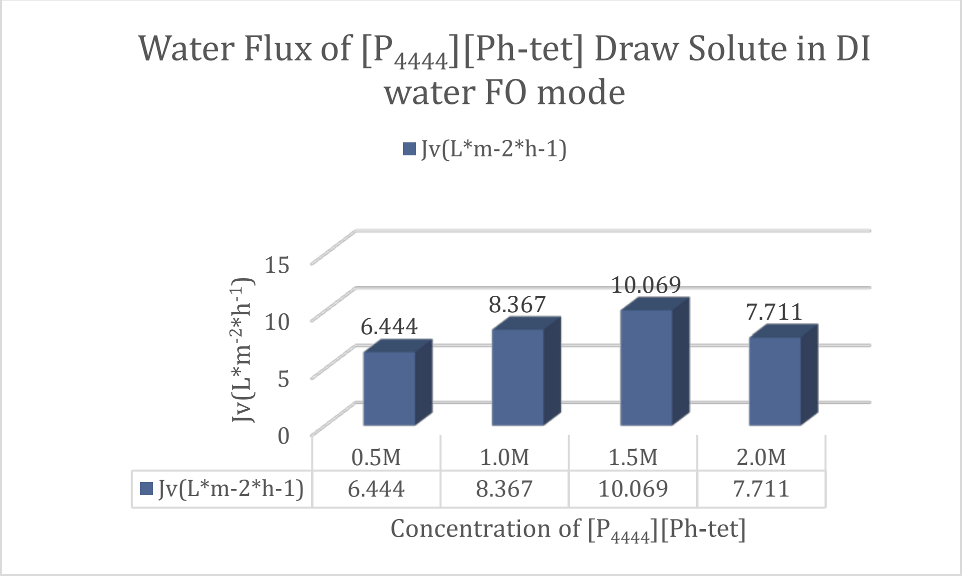
Objective of this work

My research program in the use of ionic liquids as potential draw fluids for FO water treatment includes:

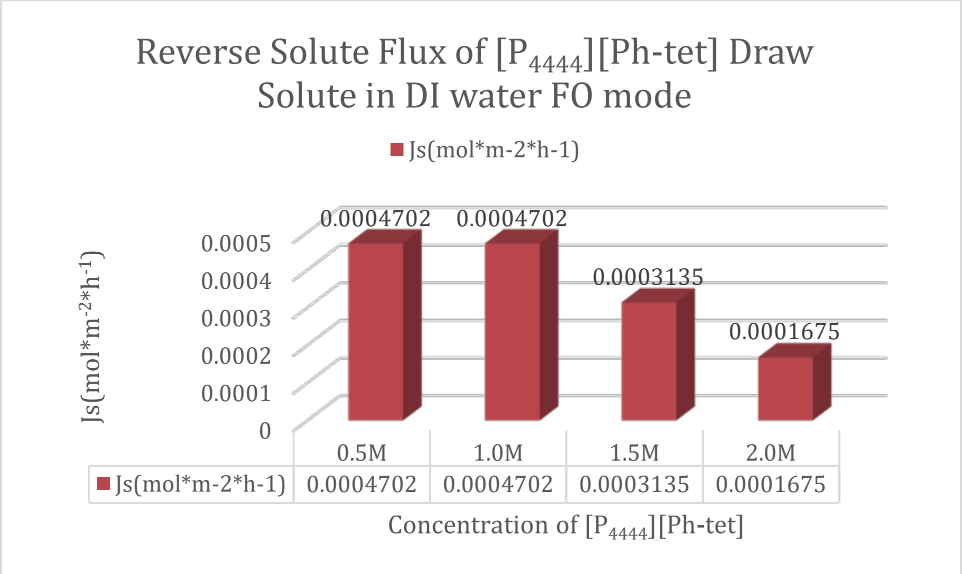
1. Preparation of appropriate model tetrabutylphosphonium/ammonium ionic liquids
2. Characterisation of aqueous/ionic liquid phase behaviour as a function of aqueous component salinity, pH, temperature and to draw structure-performance relationships with the ionic liquid cation/anion components
3. Develop a FO membrane cell system to test and evaluate draw fluid characteristics and parameters of selected systems
4. Optimize ionic liquid to use as draw fluid, developing a proof-of-concept ionic liquid-based FO desalination demonstrator for benchmarking
5. Examine the applicability of these draw fluids to water-processing of a range of feeds and product streams (desalination, waste concentration, biomass dewatering)
6. Measure the energy consumption and compare with typical method of water treatment

Progress to date

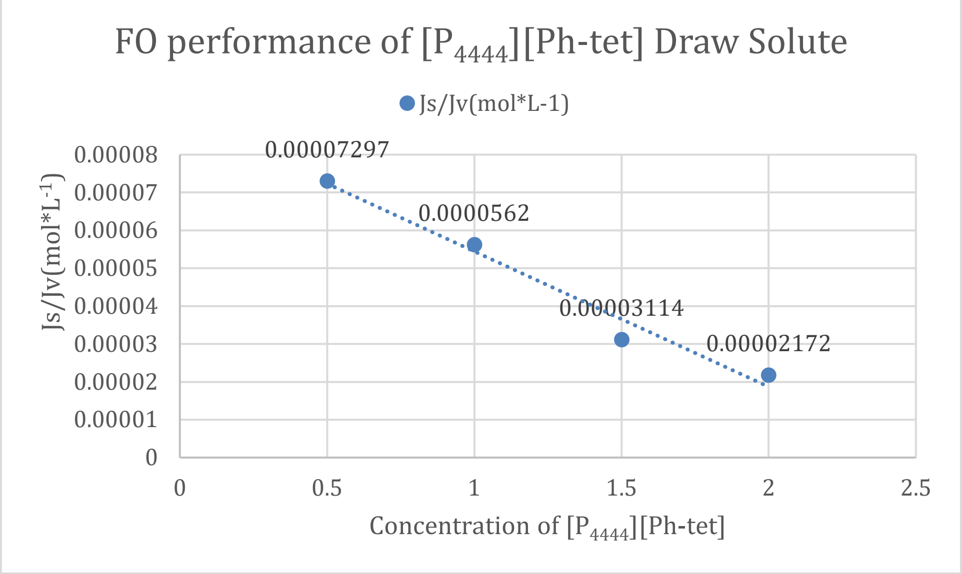
LCST-type draw solute material $[P_{4444}]$[Ph-tet][1] has been tested in our Forward Osmosis performance test system(System is benchmarked by $[P_{4444}]$[TsO][2]) and run 5 times under FO mode(Membrane active layer face to Feed Solution)to delete the error.



Water Flux of $[P_{4444}][Ph\text{-}tet]$ Draw Solute in DI water FO mode



Reverse Solute Flux of $[P_{4444}][Ph\text{-}tet]$ Draw Solute in DI water FO mode



FO performance of $[P_{4444}][Ph\text{-}tet]$ Draw Solute

Conclusions and future work

In the analysis of $[P_{4444}]$[Ph-tet] as a draw solute in forward osmosis processes, an anticipated increase in both water flux (Jv) and solute flux (Js) trends is observed, attributed primarily to the enhanced driving force. This enhancement stems from a significant chemical gradient, which subsequently elevates the osmotic pressure differential between the feed solution and the draw solution. However, a slight decrement in these trends is noted at a 2.0M concentration, which can be rationalized by the propensity of the large molecular size of $[P_{4444}]$[Ph-tet] to induce a dilutive external concentration polarization, particularly on the draw solute side, and is exacerbated in conditions of increased viscosity.

The empirical data for $[P_{4444}]$[Ph-tet] exhibit water flux values that are on par with other ionic liquid (IL) draw solutes, yet fall short when compared to traditional inorganic draw solutes, such as NaCl[3] and NH_3-CO_2[4] solutions. Despite the adverse effect of its larger molecular size on water flux, this characteristic concurrently offers a significant advantage in terms of solute flux (Js). The increase in molecular size notably reduces membrane diffusivity and curtails back transport through the Thin-Film Composite Forward Osmosis (TFC-FO) membrane, enhancing the efficiency of solute retention.

Moreover, the ratio of solute flux to water flux (Js/Jv) for $[P_{4444}]$[TsO] exceeds that of a wide range of both inorganic and organic draw solutes, highlighting its superior capability in minimizing the solute loss to reverse flux per unit volume of permeated water. Nonetheless, it is observed that certain IL draw solutes, such as $[P_{4444}]$TMBS[5], demonstrate superior performance compared to our material. This observation underscores the necessity for optimization of our material, specifically through the modification of the chemical group of the anion, with the objective of achieving higher water flux, reduced reverse solute flux, and lower viscosity.

Our next plan is to test $[P_{4444}]$[Ph-tet] under PRO mode(Membrane active layer face to Draw Solute) both in DI water and Model Seawater. Samples will be run for 5 times to delete error.

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QUILL Quarterly Report

November 2023 – January 2024

Name:	Michael Sweeney		
Supervisor(s):	Dr Leila Moura & Prof John Holbrey		
Position:	PhD Student		
Start date:	Oct 2023	**Anticipated end date:**	Oct 2026
Funding body:	CAST Award (DfE & Chevron)		

CO_2 Capture from Commercial Flue Gas Process Streams

Background

The removal of CO_2 from flue gas is crucial to curbing greenhouse gas emissions into the atmosphere. As the effects of climate change begin to set in across the global, governments across the world have come together and agreed to reduce emissions, setting themselves targets and new maximum emission limits.[1–4] Industry will need to optimise or develop technologies to prevent the atmospheric escape of CO_2 generated by industrial processes accounting for around 21% of emissions.[3] The current industrial standard using amine scrubbers is energy intensive and has other drawbacks regarding recycling and corrosion.[5] Our goal is to develop new processes that have potential industrial application and outperform the current standard.

The current industrial benchmark for carbon dioxide capture (CO_2) from flue gas streams are amine scrubbers. There are many drawbacks to the current standard from corrosivity, solvent loss and a high energy requirement for desorption of the CO_2. There has been much research into the use of different amines and blending different amines together to mitigate some of these drawbacks.[6]

Among some of the widely applied amines are monoethanolamide (MEA)[7] a primary amine, methyldiethanolamine (MDEA) a secondary amine and piperazine (PZ) a cyclic amine.[6] The structures are shown in Figure 3. While exact mixtures vary by company the amine that is applied the most often in blends MEA.[7] It is commercially available and as it is quite viscous water is added to lower the viscosity with the final solution being roughly MEA 30% wt.[8,9] This however increases the energy input required for desorption as the solution has to be heated to 100-120^{0}C to release the CO_2,[9] the increase in energy comes from the high specific heat capacity of water.

Different attempts have been employed in reducing the amount of water with other solvents and added organic solvents to mitigate the shortcomings of the water system. While this helped decrease the energy input viscosity problems persisted.[10]

There are other drawbacks such as degradation of the amine solution as the amine solution eventually breaks down to form corrosive byproducts, incurring additional cleaning costs. MEA is used as the industrial benchmark over other amines for its low cost and effectiveness. MEA captures CO_2 through chemisorption, it binds the CO_2 to form the carbamate byproduct and regenerates with CO_2 release upon heating as can be seen in Figure 1. and the schematic outline of the scrubbing set up in Figure 2.

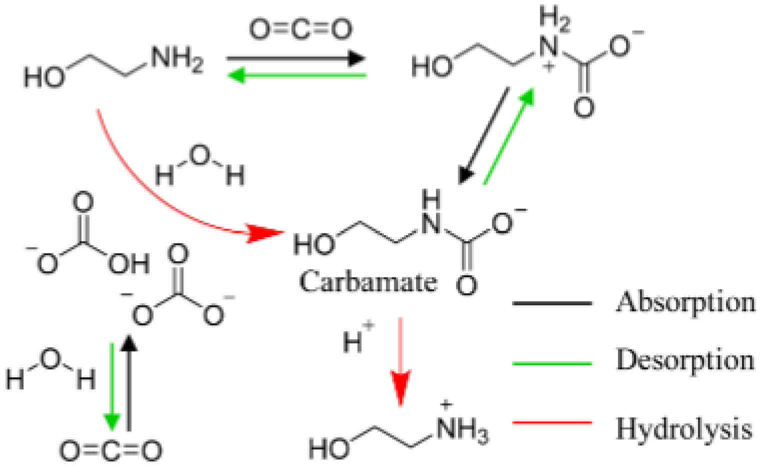

Figure 1 - Reaction pathway for MEA & CO_2[11]

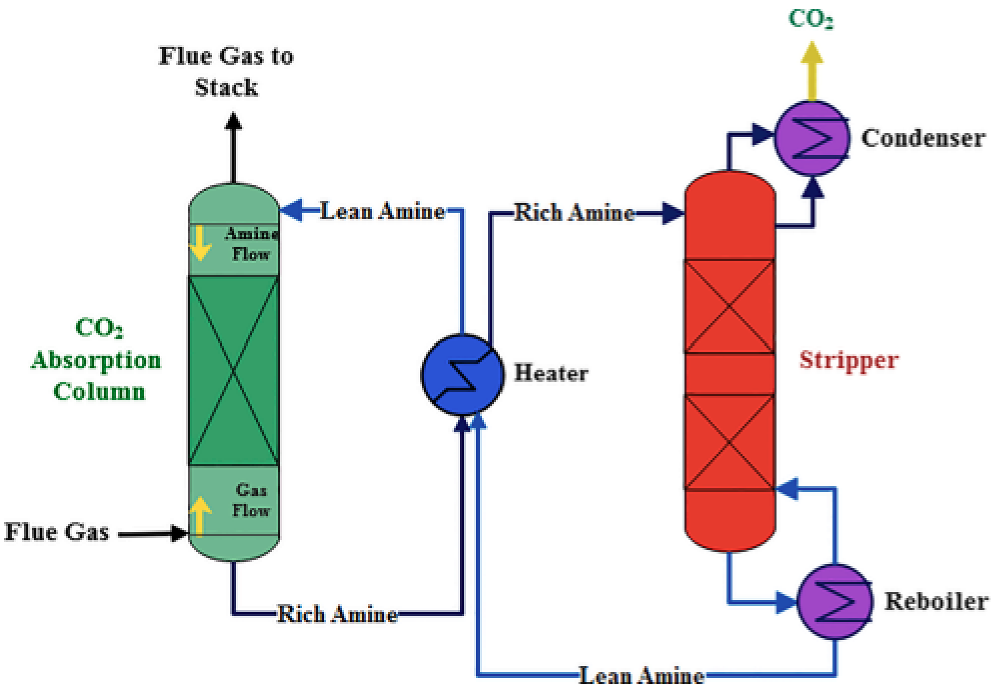

Figure 2 - Schematic diagram of a typical amine scrubbing system. Reproduced[12]

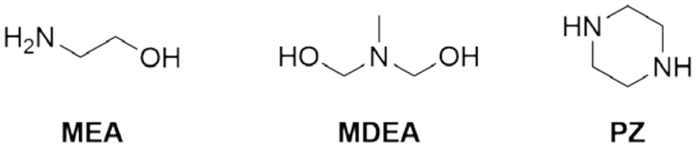

Figure 3 - Common amine structures

Objective of this work

The main objective of this project is to capture carbon dioxide (CO_2) from commercial process streams namely flue gas, using ionic liquids (ILs) or analogue materials. Flue gas is the exhaust from industrial processes from oil refinery.

Progress to date

The main part of the database consists of ILs with no additives i.e. IL/amine blends, IL/solvent blends etc. This aims to capture trends arising from past work with varying cation & anions, it records the densities of the ILs if given, water content, molecular weight (M_w), pKa of the anion, viscosity pre & post CO_2 capture, CO_2 capacity for a range of temperature and pressures, conversions from mol/mol, mol/kg, mol/g etc. mole fraction and to Henry's constant. The third part consists of a structural data of each cation & anion that is reported a standardised nomenclature and a record of appearance in previously reported research.

The initial findings of the database are;

- Large section of research conducting into trying to optimise amine scrubbers using blended solutions, different amines or adding ILs (10%wt). This has lead to reduction in regeneration energy and CO_2 capture example in Figure 3
- Formation of carbamate or carbonate/bicarbonate the main chemical reactions via chemisorption.

I began synthesising three superbasic ILs reported by Angell et al[13] to test their CO_2 capacity, tetrabutylammonium diformylamide ([TBA][DFA]), N-butyl-N-methyl pyrrolidinium diformylamide ([P14][DFA]) and N-butyl-N-methyl pyrrolidinium succinimide ([P14][Suc]) structures shown in Figure 4.

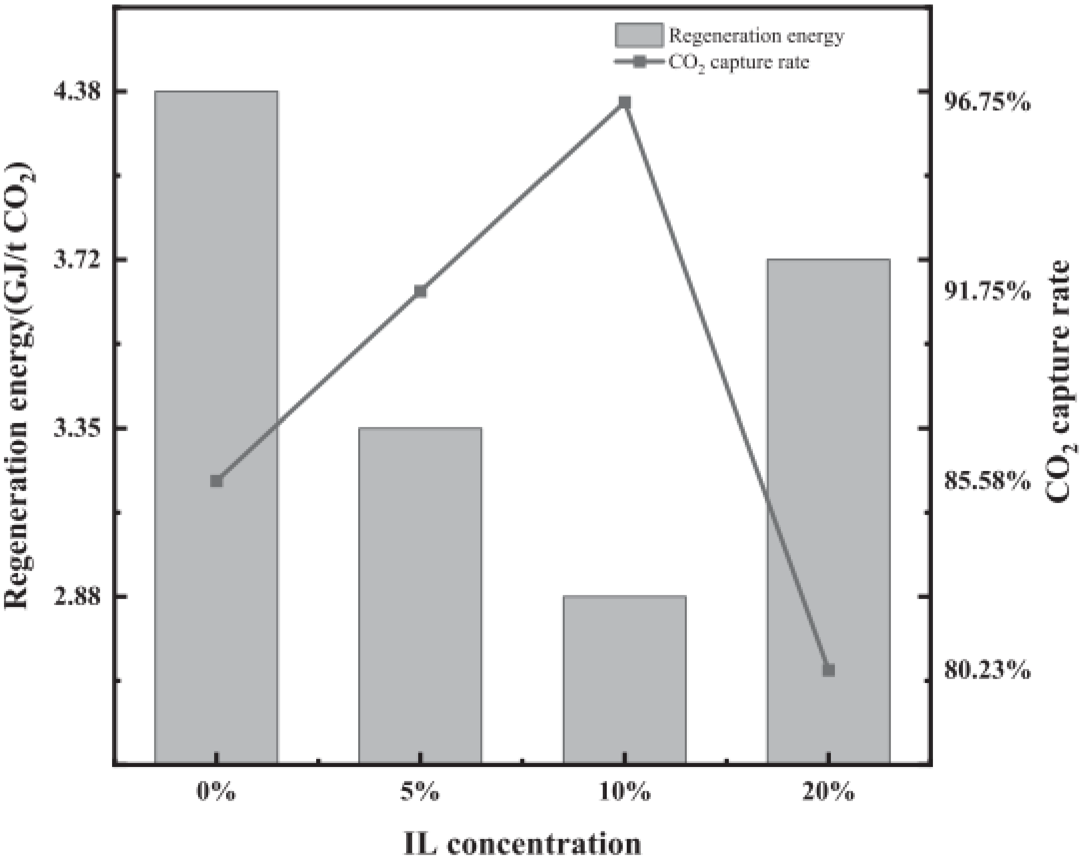

Figure 4 - Example of amine/IL blend on CO_2 capture and regeneration energy. Reproduced[10]

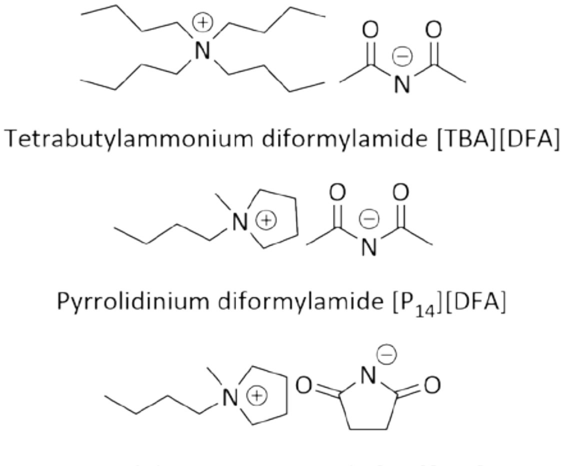

Figure 4 - Structure of ILs

Conclusions and future work

Work on the database will continue with more papers being added and updated periodically. This will allow for an insight into trend in pKa, desorption temperature, viscosity, optimal water content. Filtering of papers should be completed shortly and inputting the numerical value will begin after.

Solubility testing will begin testing the three ILs outlined above in Figure 4, measuring their water content via Karl fisher titration, testing their regeneration capacity by heating and bubble N_2 through, CO_2 capacity via GC method reported by Moura et al.[14] From this we will be able to continue the validate the methodology after benchmarking against ILs from the database and combining the insights gained from the database to design and synthesis new ILs.

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QUILL Quarterly Report

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Start date:	2020	**Anticipated end date:**	2024
Funding body:	EPSRC		

Gas Separation Technologies

Background

Biogas is a renewable and carbon neutral energy source obtained through anaerobic digestion (AD) of organic waste. Biomethane is obtained through the upgrading of biogas produced from anaerobic digesters. It consists of mainly methane and carbon dioxide with many trace compounds including hydrogen sulfide, ammonia, silioxanes, terpenes and water vapour. Biomethane must be of a purity equal to or better than that of natural gas if it to be utilised for grid injection therefore a methane purity of above 96% must be achievable from any prospective technology. Carbon dioxide should make up 2.5-4% of the remaining volume with contaminants such as sulfur and siloxanes being limited to 10 mg/m^3 and 0.1 mg/m^3 respectively. The primary focus of this research is on carbon dioxide/methane separation as these are the two major components of biogas.[1]

Currently biogas upgrading is multistep, with scrubbing used for carbon dioxide removal from the biogas stream to concentrate methane. This involves the use of liquid amines such as MEA (monoethanolamine) where carbon dioxide is captured through a chemisorption process. Regeneration of the amines requires high energy inputs in the form of steam at 100-150^{o}C to reform the initial liquid amine. Water scrubbing can also be used but this requires large amounts of water and leads to methane slip due to the lower selectivity of water compared with other technologies. Membranes offer another option for upgrading but these also suffer from a range of issues such a low throughput coupled with fouling and plasticisation. The degradation of membranes leads to issues both economically in the form of having to replace them but from an environmental standpoint it is unsustainable to continuously have to dispose of and manufacture replacement membranes. Cryogenic distillation offers a method of using nontoxic materials to produce high purity gas streams through the utilisation of low temperatures and high pressures which allows carbon dioxide to liquefy leaving a pure methane stream. However the energy cost associated with this method is massive which makes it less sustainable and exceedingly costly.[2]

It is for these reasons that we seek to create novel materials which will be more efficient, more sustainable and economically viable for biogas upgrading. Initial work will consist of the use of deep eutectic solvents in conjunction with other materials to increase their upgrading capabilities.

Work to date
Low melting mixtures (LMMs) for biogas upgrading

PO based materials were made using 2 different POs with varying chain length but identical functionality. These were combined with a variety of HBDs containing various functionalities including carboxyls, ketones and alcohols to probe the effect of varying HBD.

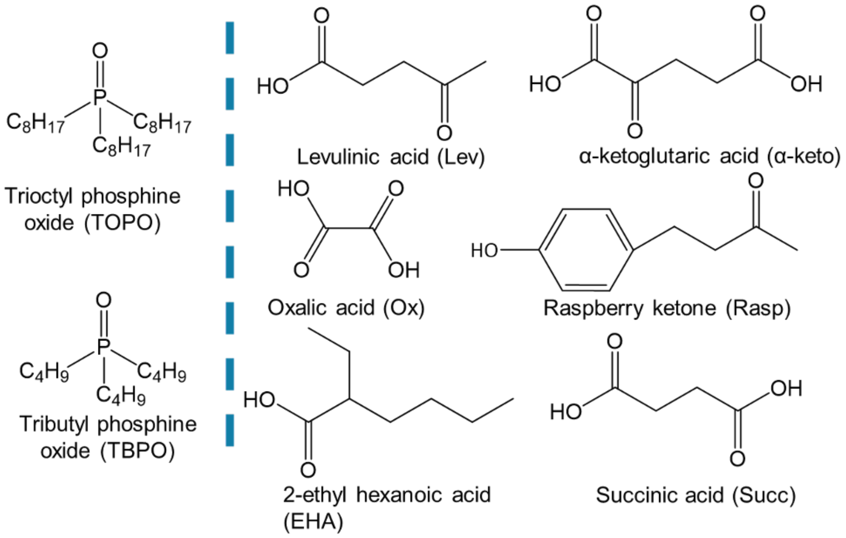

Figure 1 - Structures of phosphine oxides (left) and hydrogen bond doners(right) used to make low melting mixtures in this work.

Gas solubilities for CO_2 and CH4 can be seen below expressed in molality Henry's constants show that phosphine oxide based LMMs have CO_2 capacities superior to that of $[C_1C_6Im][NTf_2]$, which is considered to be one of the best physisorbant ILs for CO_2 uptake. Comparable capacities to industrially used sulfolane along and superior uptakes to several choline based LMMs. Ideal selectivity is also high with α being between 5.5-6.5 for LMMs tested in the gas solubility system which is considerably higher than that of industrially used sulfolane(2.2) and lower than that of $[C_1C_6Im][NTf_2]$(10.3)

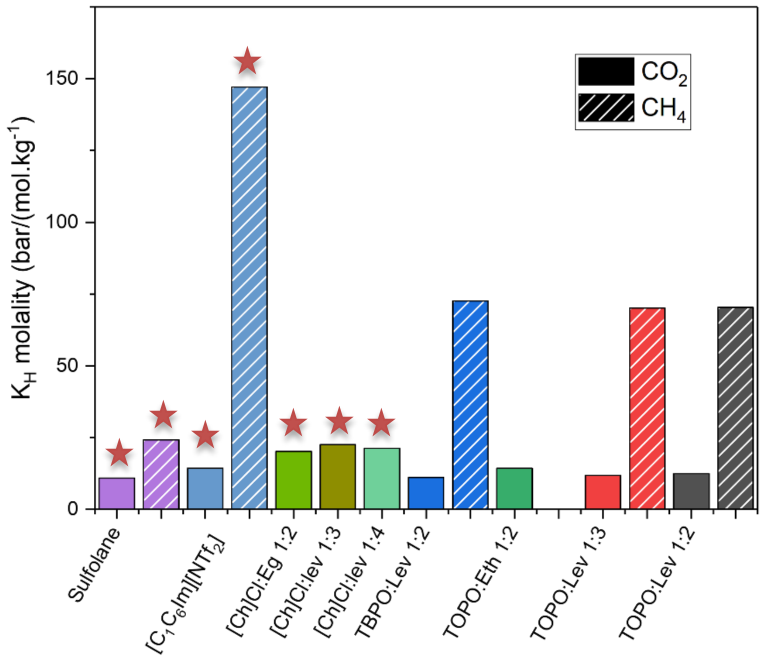

Figure 2 - Gas uptake capacities expressed in molality based henry's constants for materials tested in this work and literature sources(starred) where solid bars represent CO_2 and striped CH_4

To test the ability of these materials to remove multiple contaminants form a biogas stream we tested their partition coefficients with 33 different Volatile organic compounds limonene,D4 siloxane and Toluene(figure 3). All results showed that over 99.9% of VOC remained in the LMMs tested showing good promise for single stage multi-component removal for biogas upgrading streams.

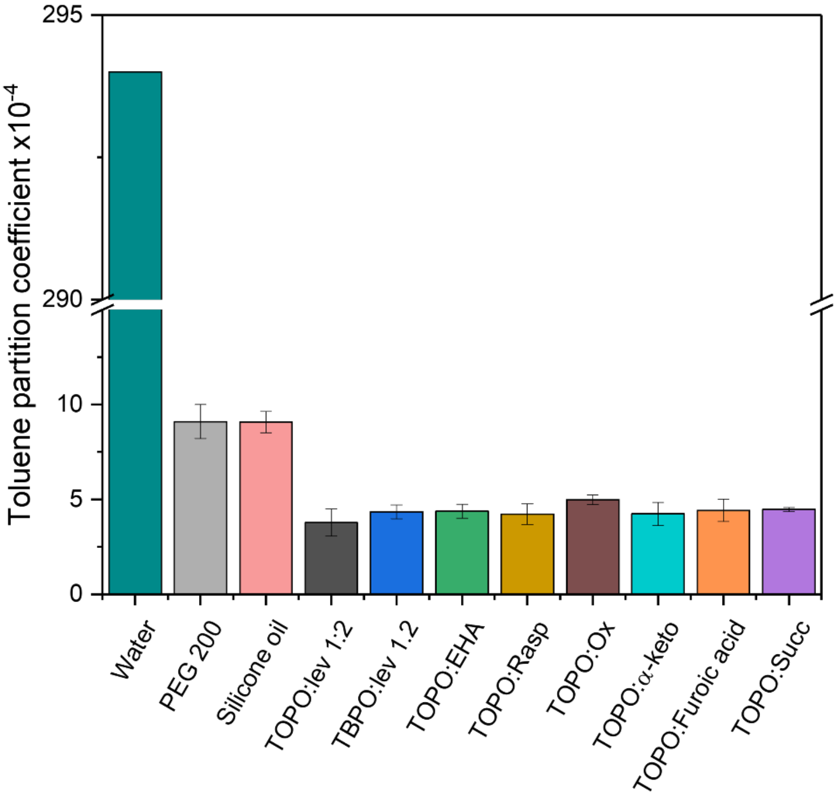

Figure 3 - Partition coefficients of toluene in various solvents tested in this work and a literature value for water obtained using similar methods

Future work

A paper is currently being written about these and other results relating to PO based LMMs for biogas upgrading. We have also recently published a paper in ACS sustainable chemistry relating to a new gas uptake screening method.

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