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QUILL
Quarterly Reports

February - April 2023

CONFIDENTIAL (up to May 2026)

Contents

QUILL Quarterly Report

February 2023 – April 2023

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.

As B-O bonds are known to be labile and moisture sensitive, it was worth investigating the stability of the newly developed functionalised borate anions in water and recording an NMR over time. Some well-known borate anions (Na[BOB]) have shown to be promising electrolyte additives for lithium/sodium ion batteries, as a preliminary study cyclic voltammetry was recorded on each of the salts to gain an understanding on their electrochemical windows.

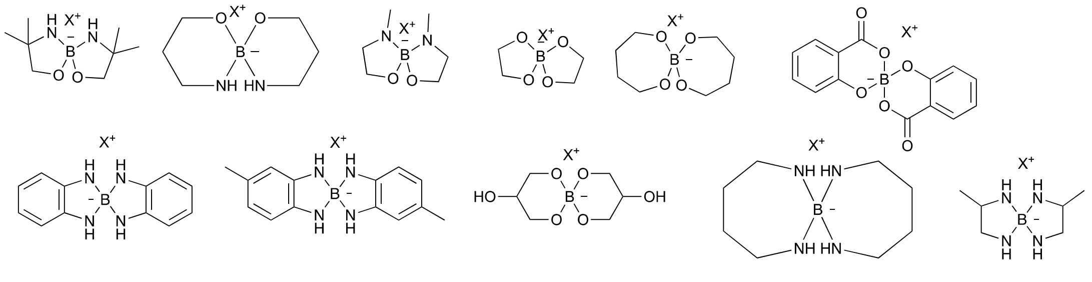

X = Li, Na

Figure 1 - Novel borate anions synthesised

Stability of borate anions

As it is known B-O bonds are labile and easily break in the presence of moisture, this limits the application of B-O chelated borate anions. The introduction of nitrogen chelated borate anions was not before investigated therefore, it was worth investigated if nitrogen chelated borate anions are less labile. Each borate salt (shown in figure 1) was dissolved in D_2O and multinuclear NMR spectra recorded over a period of time. The ^{11}B NMR was of most significant interest as the ⍰ shift is sensitive to the presence of either 4 coordinate boron, indicating presence of anions, or 3 coordinate boron (neutral species). If there are 4-

coordinate species, the ^{11}B NMR signal falls below 10 ppm whereas, for 3-coordinate species the ^{11}B NMR signal occurs between 20-18 ppm.

Results from these hydrolysis tests are shown in figures 2-4 and show the relative stability of the different borate anions in heavy water (D_2O). For $[BScB]^-$ (oxo-coorination at boron) shown in figure 2, the expected instability of the the 4-coordinate orthoborate anion to hydrolysis is apparent with immediate formation fo 3-coordinate species. After one week, a mixture of 3- and 4-coordinate borates are present with the 3-coordinate being observable as the most prominent species. When one or two oxygens of the ligands are replaced with nitrogen donors, the stability of the anion improves and no hydrolysis was observed after one week for the mixed N/O-donor borate in figure 3. However, after two weeks there was complete conversion from 4-coordinate species to 3-coordinate boron species. This suggests that the introduction of nitrogen does slow down the rate of hydrolysis, replacing all the oxygens for nitrogen's does show significant stability of the 4-coordinate borate anion (figure 4). The ^{11}B NMR shows no formation of the undesired 3-coordinate borate species, this suggests that N- chelated borate anions are significantly less labile and have greater stability in water than compared to O- chelated borate anions.

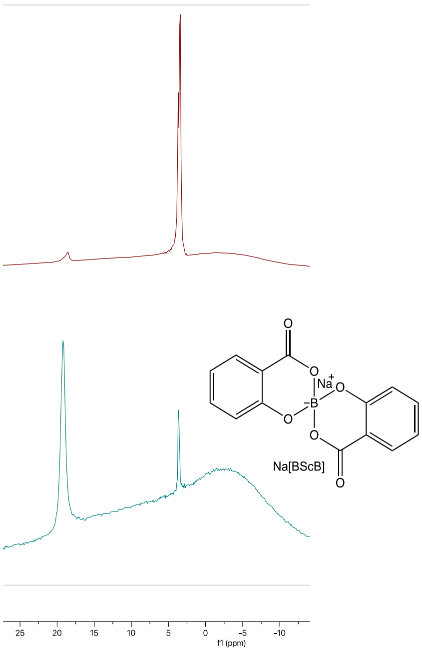


Figure 2 - ^{11}B NMR of Na[BScB] in D_2O initial run (top), after a week (bottom)

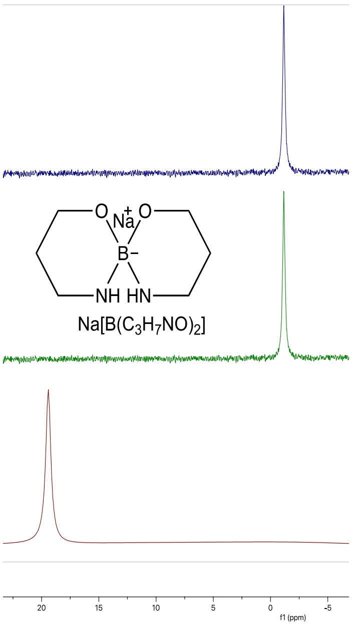


Figure 3 - ^{11}B NMR Na[B(C_3H_7NO)$_2$] in D_2O initial run (top), after one week (middle), and after two weeks (bottom)

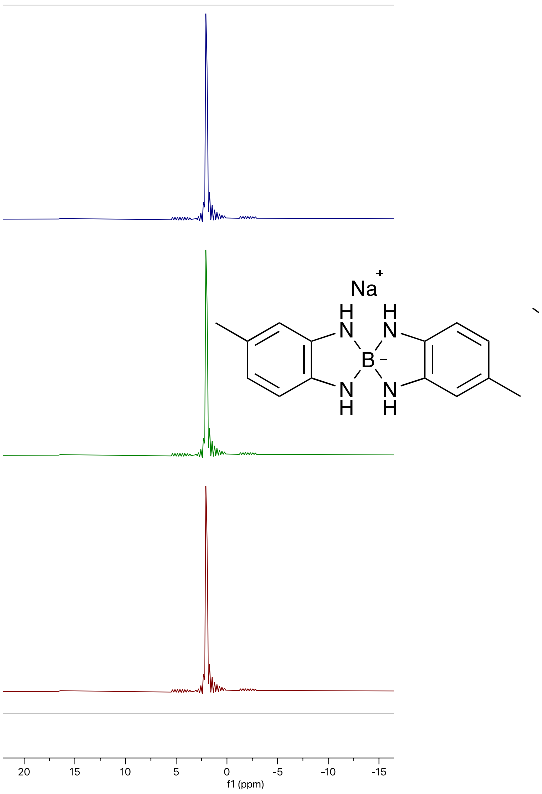


Figure 4 - ^{11}B NMR Na[B($C_7H_8N_2$)$_2$] in D_2O initial run (top), after a week (middle), after 2 weeks (bottom)

Electrochemical window examined by cyclic voltametry

Borate anions have been studied as supporting electrolytes for sodium/lithium-ion batteries, most commonly using Na[BOB] due to its promising electrochemical characteristics. The electrochemical stability of the novel borate salts shown in figure 1 was investigated using cyclic voltammetry in acetonitrile solution using a standard 3 electrode cell. Figure 5 shows the preliminary screening results.

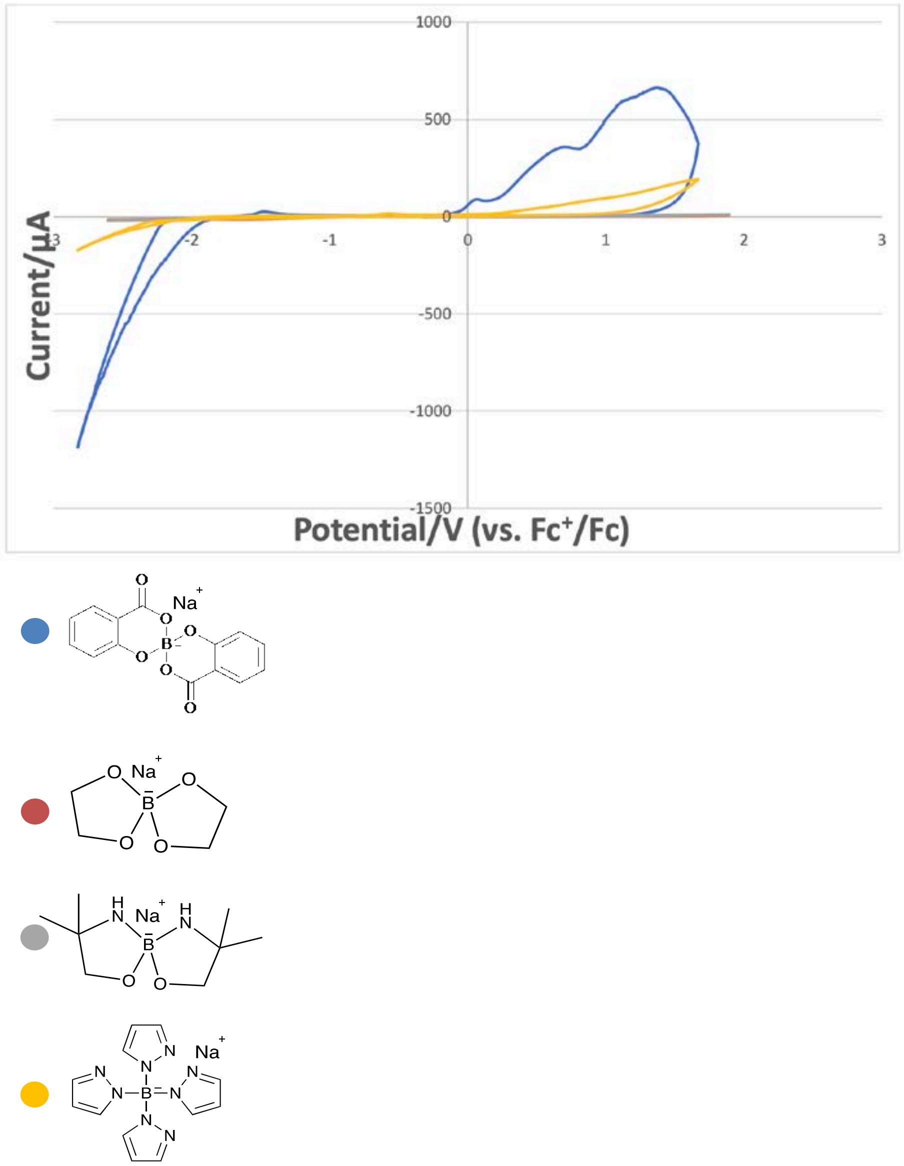


Figure 5 - CV of borate anions (as sodium salts) in acetonitrile

Lithium-ion batteries work around 4 V while acetonitrile is only stable to about 2 V, this means that the salts should be stable between +2 and -2V if they are to be investigated for Na/Li ion batteries.[1] Figure 5 shows that sodium bis(salicylato)borate, investigated as a benchmark has multiple oxidation peaks suggesting that the sample may be impure and the anion is not particularly stable under the CV experimental conditions. The same anion shows no reduction peak suggesting that what is being oxidised is not reversible, making the anion impractical for batteries. The remaining anions, particularly those with N-donor environments at boron, shows no significant oxidation or reduction peak suggesting that the anions are stable up to +2V.

Future work will be to continue to carry out electrochemical studies on these borate salts such as conductivity, charge/discharge cycles. Synthesis of non-chelated borate anions will also be carried out to investigate their chemical and physical properties. A paper, describing the synthesis and characterisation of novel ionic liquids containing these N-donor borate anions is in draft.

References

1. Mogensen R., *et al*., *ACS Appl. Energy Mater.,* 2020, **3**, 5, 4974–4982.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Dominic Burns		
Supervisor(s):	Prof John Holbrey, Prof Gosia Swadzba-Kwasny and Dr Hye-Kyung Timken		
Position:	PhD Student		
Start date:	1st October 2019	**Anticipated end date:**	31st May 2023
Funding body:	EPSRC		

Recycle and Reuse of Process Water Through Sulfate Removal: Developing an Ionic Liquid Technology for Selective Anion Recognition and Extraction

Background

This is an EPSRC industrial CASE project in collaboration with Chevron, to explore liquid technologies for the treatment of saline process water with the initial objective of selective sulfate removal from highly competitive aqueous streams. Initial work began by characterising a series of long chain tetraalkyl ammonium and phosphonium chlorides with functionalities that mimic solid ion-exchange resins and that are shown to extract sulfate via an ion-exchange (IX) mechanism. The main driving force for this process is the electrostatic attraction of sulfate towards the cationic centre however, when chloride is already present in the aqueous phase this blocks the exchange process reducing the extraction significantly. Building on this, it has also been shown before that the addition of weak anion receptors can enhance the removal of sulfate by chelation.

Lastly, I have also been working with Chevron on a CO2 capture project using ionic liquids since July 2022 however, the details of this work cannot be disclosed at this time.

Objective of this work

Main objective of this work is to develop a strategy for the selective removal of aqueous sulfate from competitive waste-water streams. A secondary objective is now the use of ionic liquids for CO_2 capture.

Progress to date

As I am in the last few month of my PhD it is time to wrap up. Most of my effort is now being split between finishing the last of the ionic liquid chlorides for liquid-liquid anion exchange, this ionic liquid has a ethyl hydroxy functionality that mimics the functionality found in strongly basic type II resins. A schematic of the synthetic route is shown in figure 1. A pervious approach to this IL involving direct alkylation of trioctlyamine as the HCl salt with ethylene oxide in the resulted in over alkylation where 50% of the final product had a PEG 1 chain and 25% of the product had a PEG 3 chain. This material will also be characterised and assessed but a different approach was needed to make [N_{2OH888}]Cl reliably. The new route is shown in figure 1 and has been successfully synthesised and characterisation and sulfate extractions are currently underway.

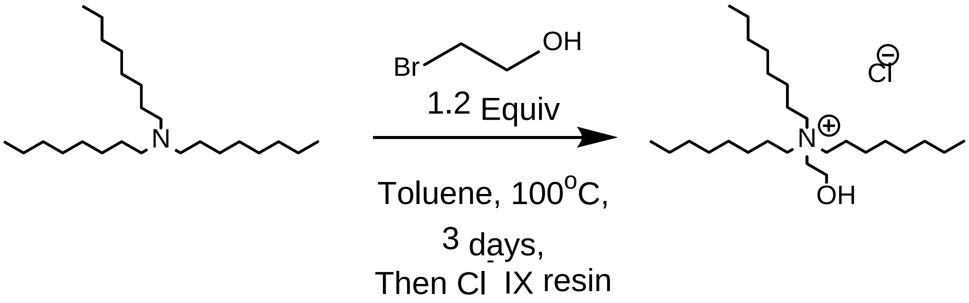


Figure 1 - Synthetic route to the ionic liquid [N_{2OH888}]Cl.

All the above is required to finish Chapter 1 of my thesis and a first paper. Chapter 2 will lead directly on from this and involves the addition of simple anion receptors into the ionic liquids to enhance the IX process. The structures of these receptors is shown in figure 3.

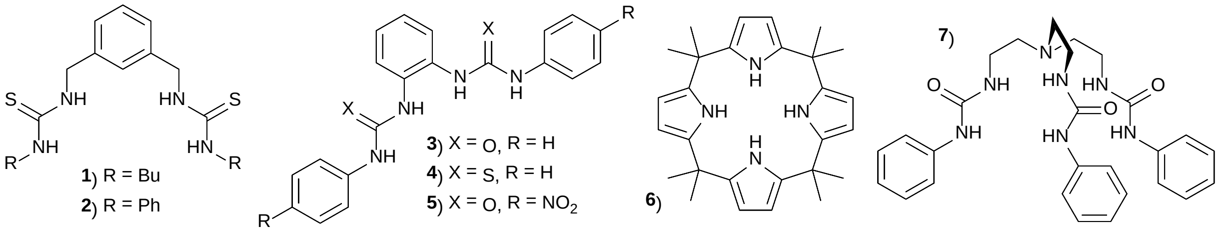


Figure 2 - Structures of the anion receptors used to enhance the ion-exchange process for sulfate removal described above.

To date all the receptors have been synthesised and current work involves adding them to Aliquat 336 to improve the IX process. Two binding studies also need to be done for each receptor to quantify the binding affinity for sulfate and chloride. Preliminary studies have shown that in DMSO, the receptors bind stronger to chloride yet they still improve the sulfate removal and so it is hypothesised that the opposite is true in the ionic liquid phase, that is, that the receptor binds sulfate stronger than chloride so a binding study in an ionic liquid phase has been devised but is currently on hold until Chapter 1 and 3 are finished. Attempts to crystalise sulfate with the above receptors so far has yielded few results due to the weak binding and the solubility of the receptor and the sulfate salt must be roughly equal in the solvent system or else one will crystalise on its own. Two single crystal X-ray diffraction structures have been isolated to date and are shown in figures 4 and 5.

Conclusions and future work

Future work: finish my PhD. Need to complete this last ionic liquid chloride that will complete my data set for a paper on sulfate removal and the first chapter of my thesis. Finishing chapter 2 and hopefully a second paper will involve a lot of anion binding studies and desperate crystallisation attempts. Chapter 3 will be on the CO2 capture project.

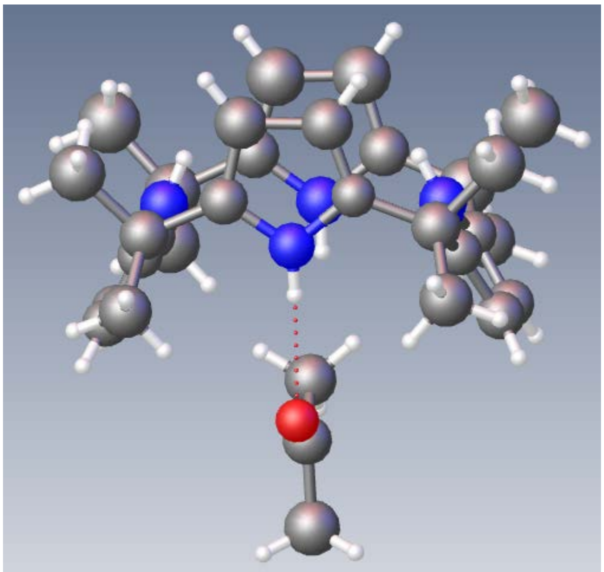
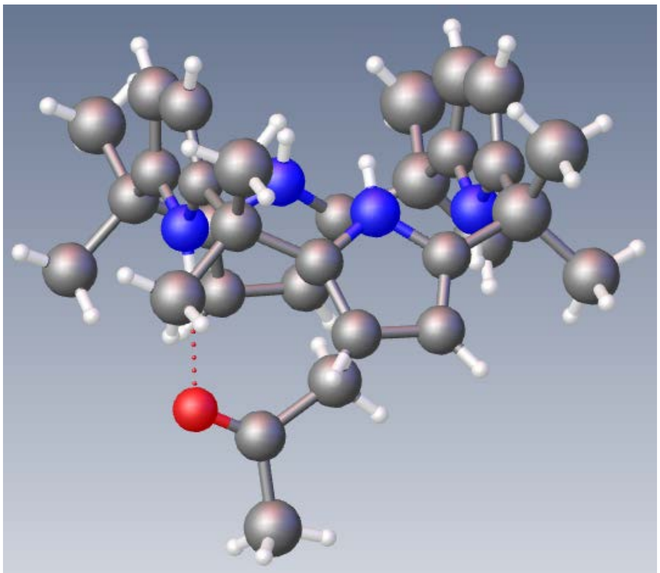


Figure 3 - SC-XRD structure of receptor **6** co-crystalising with the acetone solvent that it was grown in.



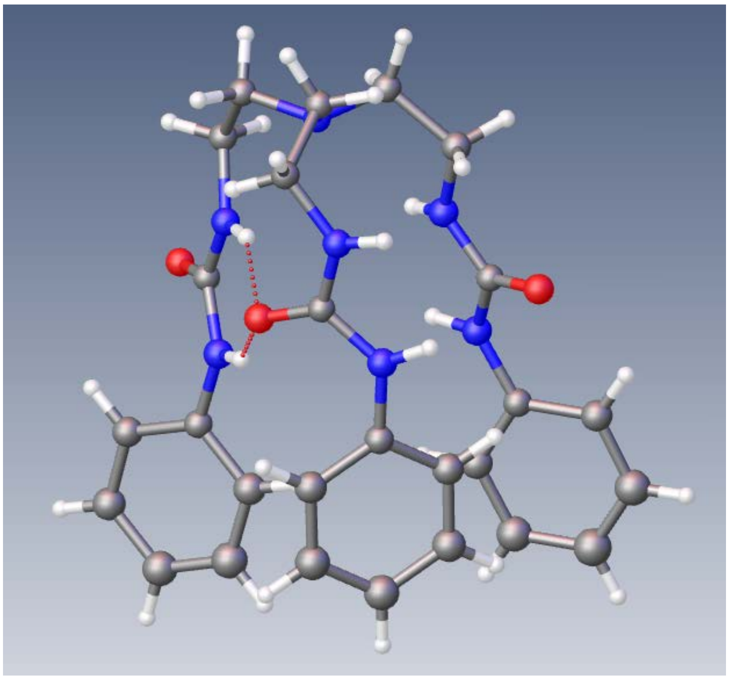


Figure 4 - SC-XRD structure of receptor **7** crystalising on its own from a DMSO-ether solvent system.

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February 2023 – April 2023

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

The following post-graduate training programmes have been completed:

- "How to read critically and take good notes" by Fabiana McCracken at Queen’s University.
-"Training on Pure and the Research Portal " by Rebecca Clarke at Queen’s University.

- Academic writing courses by Rachael O'Neill at Queen’s University. (8 weeks)

A literature review was completed and presented to Prof Nockemann. Structure of the literature review:

1. Ionic liquids
2. Ionic liquids for inorganic synthesis
3. Molecular magnets
4. Synthesis of Molecular Magnets
5. Ionic liquids for the synthesis of MMs
6. Magnetic Ionic Liquids (MILs)
7. Characterisation of MMs

Conclusions and future work

In the week starting 22 May, I will carry out the initial review presentation for my research project.

After completing this stage, I will start the initial experiments that we have planned. These experiments will be the first steps to synthesise boron-containing ionic liquids that are suitable as linkers in the synthesis of MMs.

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Feb 2023 – Apr 2023

Name:	Andrew Forde		
Supervisor(s):	Dr Stephen Glover and Prof Peter Nockemann		
Position:	PhD student		
Start date:	3rd June 2019	**Anticipated end date:**	30th June 2023
Funding body:	EPSRC		

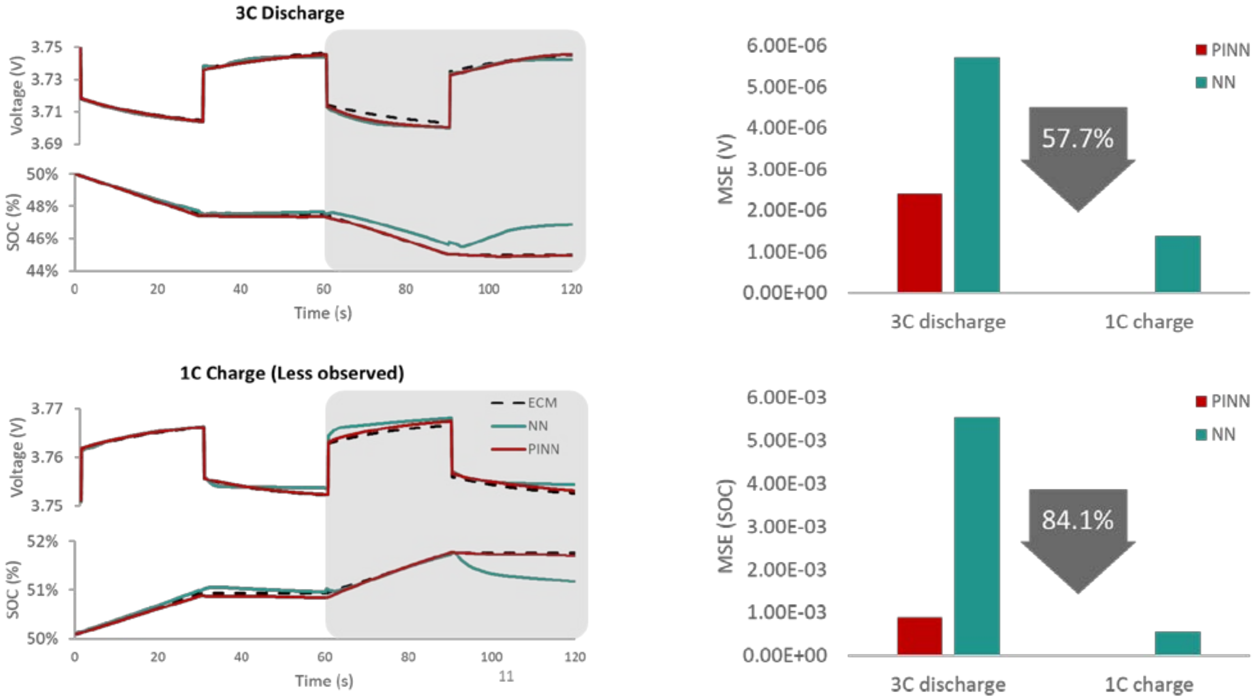
Battery Thermal Management & Algorithmic 3D Temperature Control

Background

A physics-informed neural network (PINN) for electrical battery predictions has been developed. This allows use of machine learning as an efficient method for voltage and SOC prediction while bringing added benefits over use of a standard neural network. PINNs require less data to train, are more interpretable, and generally perform better with unseen data as they are trained to obey governing equations

This work is being presented at the JSAE Spring 2023 conference, which compares the performance of the developed PINN against an equivalent standard neural network when given a very limited training dataset (256 samples).

These results show improvement on the predicted voltage and SOC when the networks were given 60 seconds of various pulse discharge cycles, along with one charge cycle. As shown, the PINN outperforms the standard network in the training region (t<60) with smoother



responses to changing current. However, in the unseen region, this gap in performance is exaggerated further, especially for SOC predictions

By adding known behaviours to the loss function (theoretical gradients of V and SOC at each time step), the PINN reduces mean-squared error compared to the vanilla neural network by an average of 57.7% for voltage prediction and 84.1% for SOC prediction.

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February 2023 – April 2023

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

3D-Printable Redox Flow Battery Electrodes

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, 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, 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.

Conclusions and future work

Future work is to analyse different graphite modification techniques and produce nanocomposites from these. I then aim to undertake CV and EIS experiments using a potentiostat, with the aim of seeing if graphite oxidation impacts electrochemical activity of the electrode material. Other future work is to turn nanocomposites into filament that can be printed using fused deposition modelling (FDM). A review paper on flow-over vs flow-through cell architectures is also planned for the next few months.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey and Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	1 October 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

Four *N*-alkyl-acridinium salts and *N*-protonated heterocyclic ionic liquids as precursors for FLP studies have been successfully synthesised and characterised. *N*-Alkylacridinium *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. The H_2 screening experiments, initiated previously are still under detailed investigation. Addition of low pressure gaseous H_2 to [R-Ac][Tf_2N]/[H-lut][Tf_2N]/lutidine mixtures results in the generation of proton NMR signals that can be assigned to formation of the hydro-acridine molecular adduct (addition of a hydride) and collapse of the lutidine signals into bulk IL H-lutidinium cations (protonation). Since the last Report, we have decided that using headspace GC is not the best way to analyse our results. The results that we were seeing via ^1H NMR spectra pre/post activation, are much more informative than those from GC. The main problem that was encountered whilst using headspace GC was that the response – as a method to quantify the H_2 uptake - was nowhere near as sensitive as that observed using ^1H NMR and required extensive method development and recalibration to be effective. Additionally, the GC response to H_2 uptake as a function of time over days was negligible in conflict with the evolution of new signals observed by ^1H NMR spectroscopy which indicated that FLP activation of H_2 was occurring. On the contrary, we probably should have anticipated these results, as headspace GC is extremely difficult to use, especially when manual injections is the method of placing the sample on the column. We are planning on purchasing an autosampler, but in the meantime we need to explore alternative avenues if we aim to quantify the uptake efficiency of H_2 by the [Me-Ac][NTf_2] /2,6-lutidine system. Currently, we are revising the results previously attained by TGA and DSC analyses and have changed the DSC method to ensure that there are not more thermal events occurring within the IL mixtures. We also have selected a range of imines to be used to probe the IL-FLP systems capcity for catalytic result of imines to amines. We also have attained results for the reversibility of H_2 capture by the intrinsic IL FLP system and also for the dehydrogenation of the synthetically made hydrogenation products. For the past three months I have also supervised a European intern student and during this time I have been able to juggle two aspects of this research. As well as the work mentioned above, ongoing investigations are being conducted to synthesise a range of 3,5-dicyanopyridine analogues. 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]. However, through recent discussions we have decided that this class of alkylated 3,5-dicyanopyridines should have a good, innate ability to act as IL based charge transfer materials, as previous work on cyanopyridinium IL work within the group was successful in establishing a new class of charge transfer materials [4]. However, this is proving difficult, as there is not much reported within the literature on these species.

Conclusions and future work

We will carry out our substrate reactions with the [Me-Ac][NTf_2]/2,6-lutidine IL system in the very near future, once we finalise the thermal nature of the system. Additionally, we hope to come up with a plan once we have carried out these reduction reactions to probe the fluorescent nature of the system, as we are not entirely sure if light has a role to play in the hydrogenation reactions of these species. Additionally, ongoing work is being undertaken in the exploration and the synthesis of the 3,5-dicyanopyridine ILs.

References

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4. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, W. M. Reichert, K. R. Seddon and S. J. Teat, *New J. Chem.,* 2008, 1953-1967.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2024
Funding body:	TU-QUB joint PhD scholarship		

LCST Behaviour in 5-Phenyltetrazolate Based Ionic Liquids

Background

In the previous report, the synthesis of different mono- and dicationic phenyltetrazolate ionic liquids of ammonium and phosphoniums was undertaken. The goal was to investigate how changes in temperature affect their phase behaviours. Additionally, a variety of functionalized 5-phenyltetrazolate ionic liquids of phosphoniums were synthesized to examine the impact of different substituents on the phase behaviours of IL-water mixtures. Preliminary attempts to deuterate the tetrabutylphosphonium bromide salt using a previously reported procedure were also made.

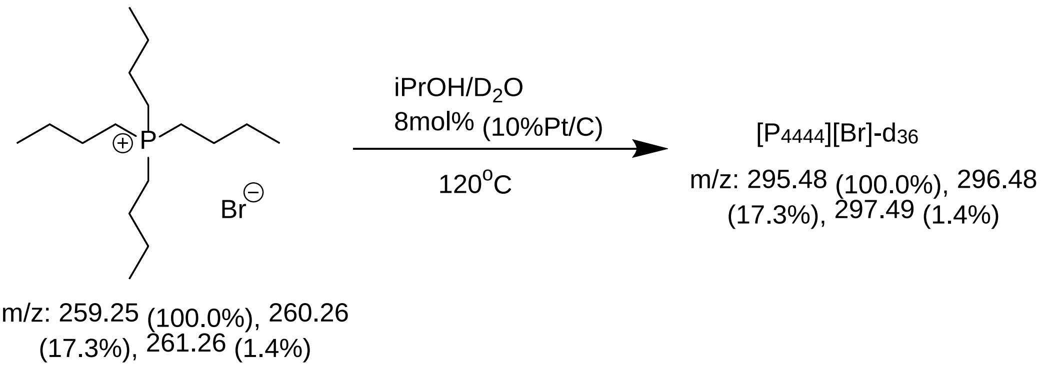
Objective of this work

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. Deuteration of tetrabutylphosphonium bromide:

   Deuteration of this phosphonium salt was attempted using a reported procedure from Sajikia et.al.[1] wherein, the group tried deuterating a series of long chain fatty acids implementing a mixed solvent system of D2O/iPrOH using a 10% Pt/C catalyst in a sealed pressure vessel. This method was opted due to the ease of access of the reagents used and deuteration under the absence of any external hydrogen source. The method however is limited to hydrocarbons without the presence of a cationic centre and therefore various optimisations were carried out in terms of substrate concentration, catalyst loading, temperature conditions, substrate-to-solvent ratio, etc., to obtain the desired product.
   The reaction scheme is shown here,



The method involved an in-situ generation of hydrogen source from the isopropanol that gets activated by the catalyst to form acetone during the process.
The product obtained after extraction and purification, however, yielded a 2.7% conversion into its deuterated form after running the reaction for 24hours. This was analysed using mass spectrometry. Furthermore, the same product was reused for a second batch of the reaction in the microwave with a fresh batch of solvent and catalyst system for another 24hours, which gave a 5.5% conversion into the deuterated form. This was repeated multiple times up to 120hours that yielded a conversion of 17 hydrogens into deuterium from the original substrate.

However, considering the hydrogens adjacent to the phosphonium centre do not get deuterated as reported[2] by the same group, a conversion rate of 60% was achieved at the end of 5 days. This on the other hand could not be utilised to make the deuterated ionic liquid due to less amount of the end product formed.

Synthesis on a larger sale using the autoclave pressure reactor is underway.

2. Analysis of deuteration using mass spectrometry:

   The m/z value of the protonated tetrabutylphosphonium bromide is 259.25 (100%), 260.26 (17.3%), 261.26 (1.4%) and that of the complete deuterated one is 295.48 (100%), 296.48 (100%), 297.49 (1.4%). This was taken as a reference to track the progress of conversion of the number of hydrogens to deuterium as a function of time. Snapshots of the obtained MS results are shown below for reference.

3. Neutron scattering experiments at ISIS-Muon Source were carried out on ionic liquid, tetrabutylphosphonium (protonated) with 5-phenyltetrazolate (deuterated) in water and deuterium oxide mixtures at different temperatures that are above and below the LCST of the original ionic liquid.

4. Presented a poster and talk on the QUILL-IAB meeting held on April 2023

5. Presented a poster on the 9th International congress on Ionic liquids (COIL-9) held in Lyon, France from 24th to 28th April 2023.

6. Received an RSC travel grant and Emily Sarah Montgomery Travel scholarship to attend the international conference.

7. Preliminary studies on understanding the eutectic properties in SAT-urea derivative mixtures were undertaken.

Mass spectrometry results:

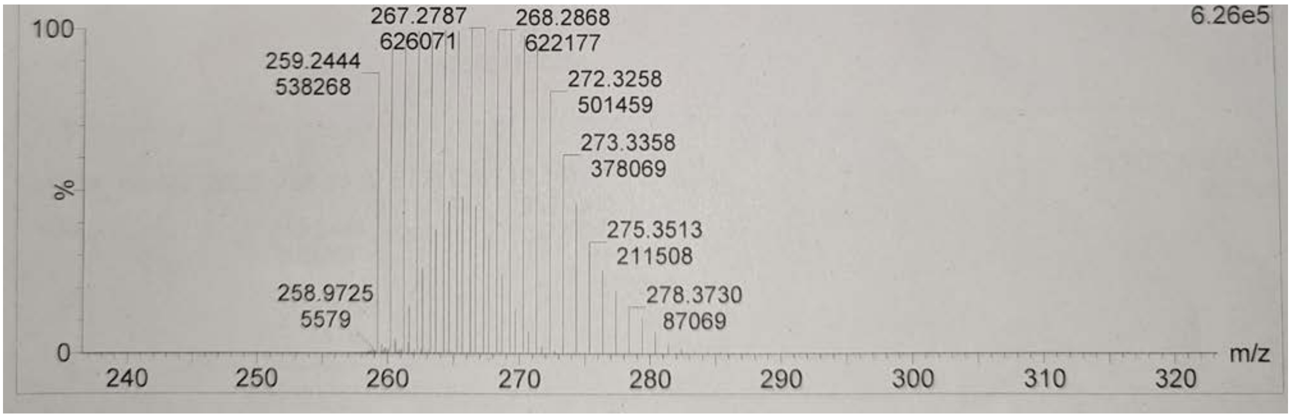


Figure 1 - m/z 267.27 (100%) after 72h

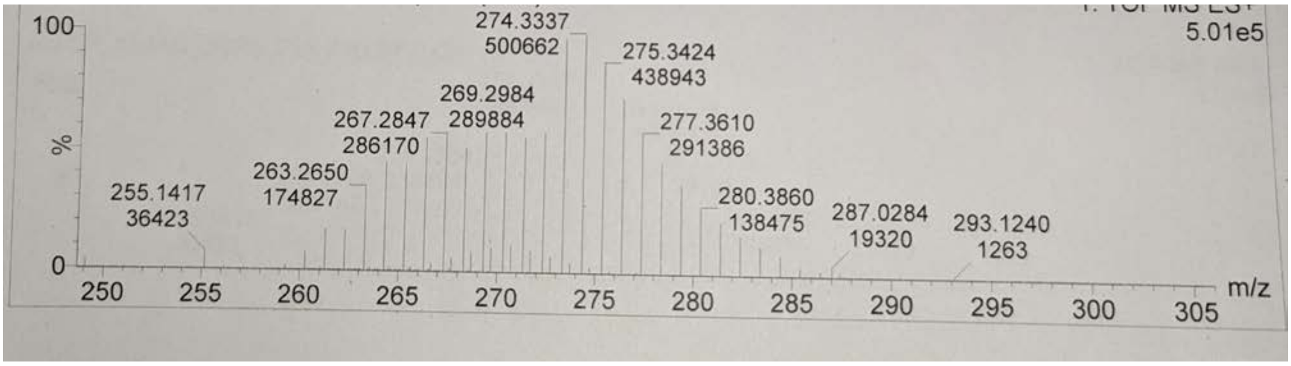


Figure 2 - m/z 274.33 (100%) after 96h

Future work:

1. Complete the studies on SAT-urea mixtures, experiments on liquid cell,
2. Complete COSMO-RS simulation studies to understand liquid-liquid equilibrium behaviour in the IL/water systems and correlate with experimental results,
3. Complete a set of isothermal micro-calorimetry experiments planned in ENS de Lyon with collaborations, on the IL/water systems,
4. Prepare the ILs for their crystallographic studies to understand the phase behaviour,
5. Draft a publication based on these results.

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QUILL Quarterly Report

February 2023 – April 2023

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate and 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, due to the nature of these thermal events they 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 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

Since January the primary focus of the work conducted has been on producing simulation outputs that would form the basis of a conference paper for JSAE 2023 Spring Congress. Several different simulations were conducted including looking at a range of different cells spacings when indirect liquid cooling and a pure paraffin were applied between the cells. A very clear increase in the peak temperature of the neighbouring cells is observed as the cell spacing is reduced, additionally simulations were run with varying thermal conductivity of the PCM applied. At lower thermal conductivities there is clearly an isolating effect to the heat generated but as the thermal conductivity is increased which ultimately benefits the thermal management a reduction in performance of the thermal runaway propagation prevention was clearly conveyed.

Furthermore, calculations were undertaken to estimate the weight impact of the cell spacing deemed necessary from the simulations conducted. By plotting energy consumption against the vehicle weight for a number of vehicles within the one platform a relationship between weight and efficiency could be derived. This then means an estimate of the range impact could be made based on the inclusion of PCMs within these battery packs. It was shown that for a cell spacing of 3mm a range impact of between two and four percent could be expected.

Conclusions and future work

Simulations have been conducted to produce a conference paper based on the work so far and this has been submitted to JSAE 2023 Spring congress. The main focus of this paper is the weight, volume and mass implications of these PCM systems.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Sam McCalmont		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Margarida Costa Gomes		
Position:	PhD student		
Start date:	Jan 2020	**Anticipated end date:**	July 2023
Funding body:	EPSRC Doctoral Training Partnership		

Chemisorbent Materials for Olefin and Paraffin Separation

Background

Separation of light olefins from their paraffin counterparts have been described as one of the seven chemical separations to change the world.[1] Global annual production of light olefins exceeds 200 million tons, about 30 kg for each person on the planet. The current method for their separation is cryogenic distillation, one of the most energy-intensive processes in the industry. Alternative methods can focus on the olefin being selectively captured either through a physical interaction (physisorption) or chemical reaction (chemisorption).

One class of alternative sorbents are ionic liquids (ILs). However, so far, IL physisorbents have not demonstrated sufficient efficiency in either selectivity or capacity to compete with current technologies.[2] Complexation of ethylene through its double bond with silver and copper ions has been used in the literature for chemical separation of olefins and paraffins. However, other components of raw gas feeds, such as acetylene, can react with the silver and become explosive. This has prevented the uptake of these materials into large scale processes.

Objective of this work

To develop and test new chemisorbent materials for the separation of light olefins and paraffins; to achieve high capacity combined with selectivity for the selected materials. To investigate, and rationalise, selectivity and capacities of chemisorbent based on measurement of gas solubility and partitioning from model industrial gas stream compositions and conditions.

Progress to date

In summary, for the last few months of the PhD program, the time has been divided between two main projects. Both papers focus on the use of nitrile groups in ionic liquids as their inclusion has shown to increase the separation potential of ethylene and ethane, why this exactly is, is not known.[3] One paper will be focusing on nitrile groups in the anion of the ionic liquid (paper A) and the second paper focuses on the nitrile groups present in the cation (paper B). Paper B will include the study of mixtures of different salts (inorganic/organic) to study the influence of the mixing in the solubility of ethylene and ultimately the separation. This paper may include the work involving ionic liquids plus metal salts which will be added keeping in theme with the mixtures. For both paper A and B, molecular dynamic studies are being investigated by a collaboration project within the School of Mathematics and Physics in Queen's University Belfast.

Paper A:
This paper will focus on including the nitrile functional group in the anion while keeping a constant cation. The common cation chosen will be $[C_4C_1Im]^+$ cation. The anions chosen (increasing order of nitrile group content) are thiocyanate $[SCN]^-$, dicyanamide $[DCA]^-$, tricyanomethanide $[TCM]^-$, and tetracyanoborate $[TCB]^-$. The solubility of ethylene and ethane in the ionic liquids have been determined so far *via* the screening method. All three ionic liquids present lower absorption capacity for the uptake of ethane and ethylene than $[C_4C_1Im][NTf_2]$, matching the literature data on nitrile based ionic liquids as noted before. These ionic liquids are now being brought to the gas solubility system. A possible source for the tetracyanoborate ionic liquid has been found *via* a collaboration made in COIL9 conference.

Paper B:
The following cyanopyridinium ionic liquids will be included in this paper. The butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^4CNPy][NTf_2]$) and butyl-3-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^3CNPy][NTf_2]$), and a 50:50% molar mixture of butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^4CNPy][NTf_2]$) : 1-butyl-4-imidiazolium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Im][NTf_2]$) are currently being studied for ethylene and ethane solubility. The purpose of using the mixture is to promote the use of the $[C_4C_1Im][NTf_2]$ as a dilutant and perhaps promoting the solubility of ethylene and ethane. This could perhaps promote more physisorption to occur, or perhaps allow for the stronger interactions to occur around the $[C_4{}^4CNPy]^+$ when it is in a more free environment. The raw solubility data has been collected for each of the materials above. The data is being analysed and so far, shows the general trend with other physisorbent based ionic liquids. Within figure 1 this can be seen when compared with $[C_4C_1Im][NTf_2]$. If stronger interactions were expected, the solubility of ethylene in $[C_4{}^4CNPy][NTf_2]$ and $[C_4{}^3CNPy][NTf_2]$ would be increased compared to that of the purely physisorbent $[C_4C_1Im][NTf_2]$.

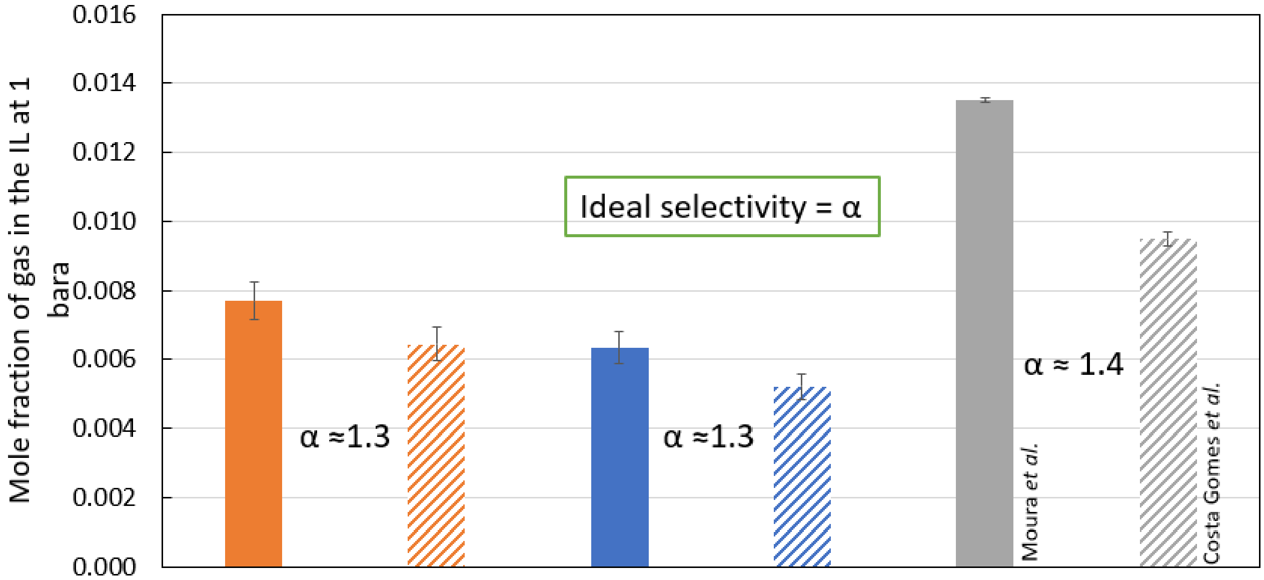

Figure 1 - Mole fraction of ethylene and ethane at 1 bara in three different ionic liquids. Left (orange) $[C_4{}^4CNPy][NTf_2]$, middle (blue) $[C_4{}^3CNPy][NTf_2]$ and previously reported data on the right for $[C_4C_1Im][NTf_2]$ as a reference.[4,5] The ideal selectivity towards ethylene also reported.

Paper C:
Title: “Insights into the absorption of hydrocarbon gases in phosphorous-containing ionic liquids”. The paper has been accepted to the Journal of Physical Chemistry B and now has been published.

Conclusions and future work

For both papers, the characterisation and solubility data are being collected, and will be collected during the last months of the PhD project. During this coming quarter, the groundwork for paper B papers will be finalised. The thesis will also become the main focus.

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QUILL Quarterly Report

November 2022 – January 2023

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadzba-Kwasny and Prof John Holbrey		
Position:	PhD student		
Start date:	01/09/21	**Anticipated end date:**	01/09/24
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

In the previous report we discussed that the new batch of feedstock contained less impurities than the previous batch of feedstock. Reactions with LCCs and borenium ionic liquid and two distributions of feedstock, a light feedstock and a heavy feedstock show competition between cracking and oligomerisation reaction. The balance between the endothermic cleavage vs the exothermic reaction can explain the results. The results show high sensitivity toward feedstock catalyst and reaction parameters.

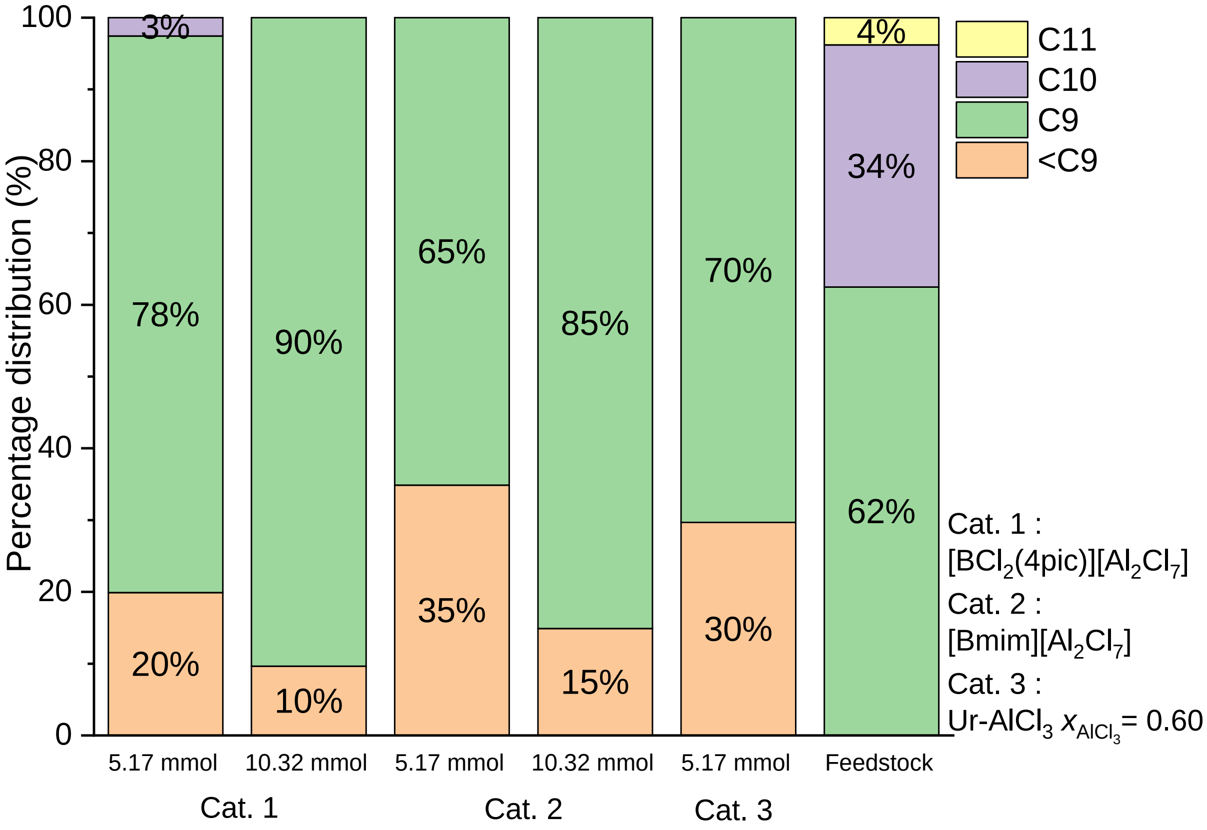


Figure 1 - C9-C11 light feedstock results

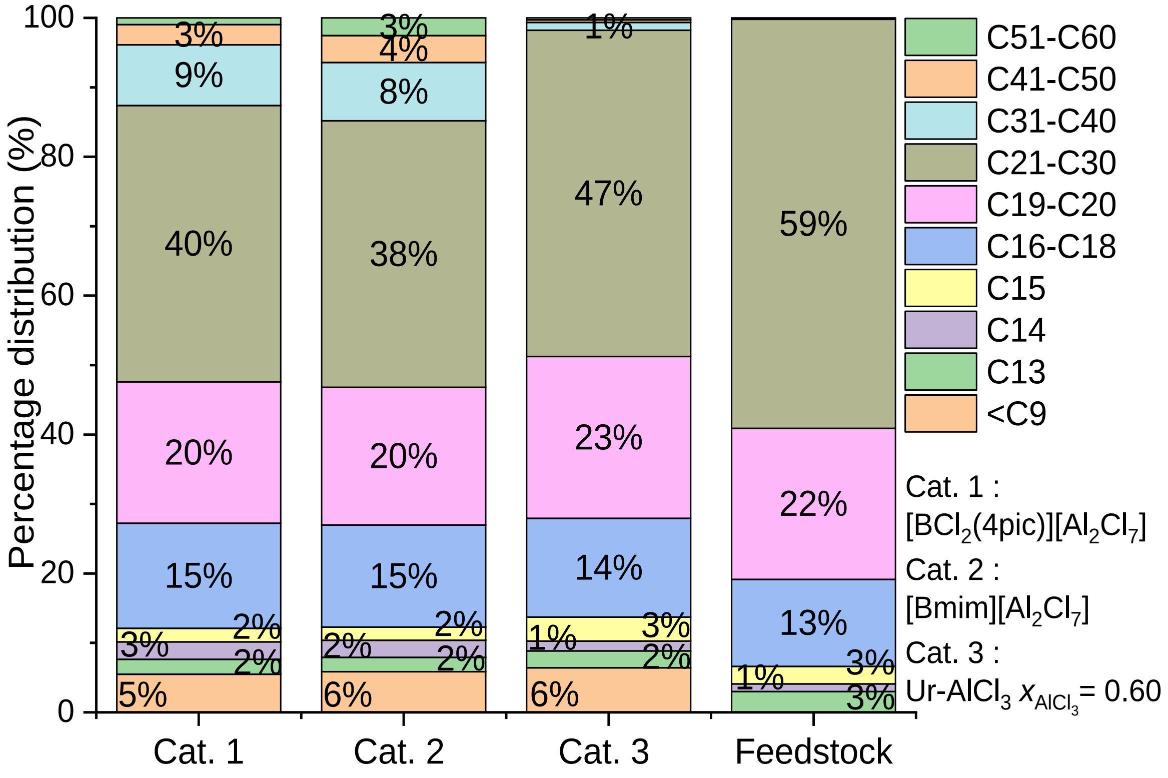


Figure 2 - C9-C20 heavy feedstock results

Conclusions and future work

After much discussion and limited success with the recycled waste plastic feedstock we have decided to move on from this area of research and move toward model systems and new ionic liquids. The model reactions include oligomerisation of 1-decene, Friedel-crafts alkylation with benzene and 1-decene and the diel alders reaction.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Anne McGrogan		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD student		
Start date:	01/10/2019	**Anticipated end date:**	31/06/2023
Funding body:	EPSRC		

Structure of Bistriflimide Ionic Liquids

Background

The basic liquid state structure of ionic liquids (ILs) is dominated by columbic interactions and comprise of alternating shells of anions and cations. Understanding the arrangement of ions in ILs is crucial as many of their properties and applications are directly related to their structure. Neutron diffraction and Monte Carlo simulation methods are effective techniques to help elucidate the structure of liquids and explain their behaviour.[1,2] Neutron diffraction has been used to determine the structure of a wide range of liquid systems, from water[2,3] and organic solvents[4–6] to more complex systems including ionic liquids[7–9] as well as investigating the interactions between ionic liquids and solute molecules.[10]

The most common ILs are composed of nitrogen or phosphorous, which are the focus of this work. These are combined with the bis(trifluoromethanesulfonyl)amide anion which is one of the most widely used anions and there has been multiple structural studies reported for ionic liquids consisting of 1-alkyl-3-methylimidazolium and bis(trifluoromethanesulfonyl) imide ions.[11–14] Early MD simulations showed that their structure is characterised by nanostructure formation.[15–18] At first, it was thought that this was due to the aggregation of alkyl chains of sufficient length, while the polar regions (e.g. imidazolium ring and anions) were distributed homogeneously. However, an atomistic simulation then suggested that there is also aggregation of these polar domains which exists alongside the non-polar domains of the alkyl chains.[19]

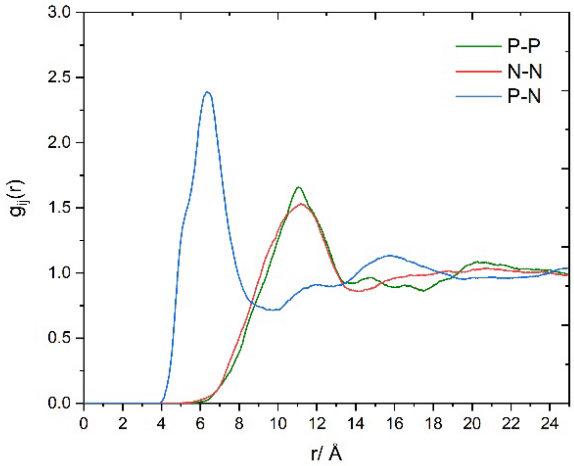
Tetraalkylphosphonium-based ionic liquids are of interest as they have relatively high thermal and electrochemical stability, making them attractive options for energy storage applications (e.g., batteries and supercapacitors).[20–22] There has been several studies on the structure of ionic liquids based on the [P_{66614}] cation.[23–28] Gontrani *et al.*[23] studied the tetradecyltrihexylphosphonium chloride IL using X-ray scattering and MD simulations and reported that the structure is dominated by strong cation-anion interactions and by the existence of nanoscale segregation, similar to imidazolium-based ILs. The strong ion pairing, in particular for tetraalkylphosphonium halides, has been related to their low degree of ionicity. This has led to these liquids, in the most extreme case, being described as liquid ion pairs: an interesting intermediate between true molecular solvents and true ionic liquids as described by MacFarlane *et. al.*[29] The Walden plot showed significantly lower conductivity for [P_{66614}][Cl] than would be expected given the viscosity. These findings can be rationalised since the chloride anion is very small, it can get close to the positively charged phosphonium centre and form strong interactions. In fact, the long cation alkyl chains can effectively align and trap the chloride anion. The situation is different when we consider a bulkier anion such as bis(trifluoromethylsulfonylimide) (NTf_2), we see that [P_{66614}][NTf_2] has higher ionicity as the bulky anion can not get close to the phosphorus atom and does not form liquid ion pairs.[29] Specific to the trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide ionic liquid, [P_{66614}][NTf_2], X-ray scattering and molecular dynamics (MD) simulation studies investigating the structure and dynamics of this IL have been reported by Liu and co-workers[26] and Margulis group.[24,25,30]

Objective of this work

The aim of this work is to analyse the structure of three ionic liquids by neutron scattering using Dissolve software and compare to MD and x-ray scattering results. The three ionic liquids are: 1-ethyl-3-methylimidazolium bistriflimide [C_2mim][NTf_2], 1-decyl-3-methylimidazolium bistriflimide [C_{10}mim][NTf_2] and trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide ionic liquid, [P_{66614}][NTf_2].

Progress to date

I am currently analysing the neutron scattering results using Dissolve software for the three ILs. There has been good correlation of the results with MD and x-ray scattering. The most important information can be extracted from the radial distribution functions. In particular, we compare the behaviour between the charged species. For [P_{66614}][NTf_2], the phosphorus of [P_{66614}] and the nitrogen of [NTf_2] are the most charged atoms of the ionic liquid and are considered to be the most central atoms of the molecules. Figure 1 shows the radial distribution functions calculated at 298 K for the cation-cation, cation-anion and anion-anion correlations. The cation-anion distributions are explored further, and Figure 1 shows the interactions between the P atom and the S and O atom of the anion, in addition to the N atom correlation.



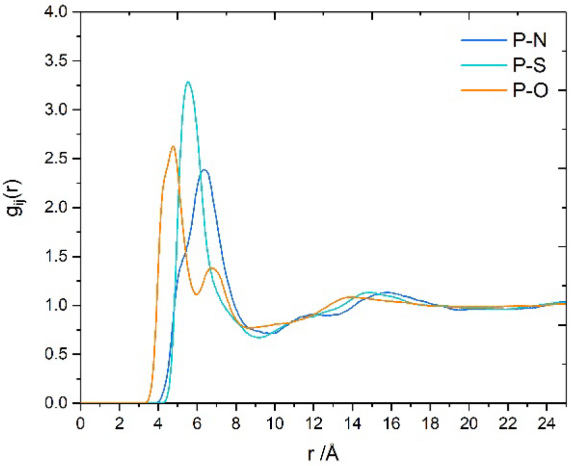


Figure 1 - Radial distribution functions for top: the cation-cation (P-P) distribution (green line), anion-anion (N-N) distribution (red line) and cation-anion (P-N) distribution (blue line) and bottom: cation-anion RDFs of P of P_{66614} and nitrogen (blue), sulfur (turquoise) and oxygen (orange) of the NTf_2 anion.

The P-N *g(r)* indicates a strong interaction between the oppositely charged species, with the main peak centred at ~6 Å accompanied by a slight shoulder at ~5 Å. Calculation of the coordination number shows that each cation is surrounded by about three anions in the first coordination shell, in agreement with MD studies by Liu and co-workers.[26] It has been reported that hydrogen bonding can occur between the anions and the protons alpha to the phosphorus (HP) in the cation. Therefore, these specific atom interactions were investigated (Figure 2).[31,26] It is evident that there is a strong interaction between the HP atoms in P_{66614} and O atom in NTf_2 at a distance of 2.7 Å, indicating the possible formation of hydrogen bonds. These results are in agreement with previous MD studies by Liu and co-workers.[26]

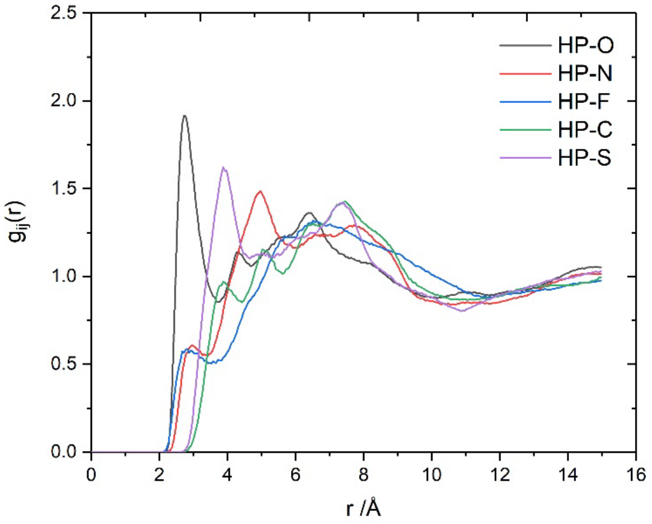


Figure 2 - Radial distribution functions between the HP atoms of the cation and the different atoms of the anion.

Conclusions and future work

The models of the three ILs show good agreement between experimental and simulated data. Further analysis has shown good correlation to previous MD and x-ray scattering results. Future work involves testing the robustness of these models by starting from three different sets of potentials and seeing if the models converge on the same outcome.

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QUILL Quarterly Report

February 2022 – April 2023

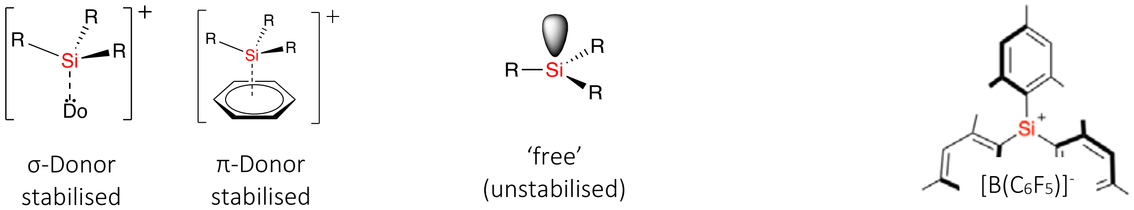
Name:	Shannon McLaughlin		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD student (3rd year)		
Start date:	October 2020	**Anticipated end date:**	December 2023
Funding body:	Department for the Economy (DoE)		

Lewis Superacidic 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.

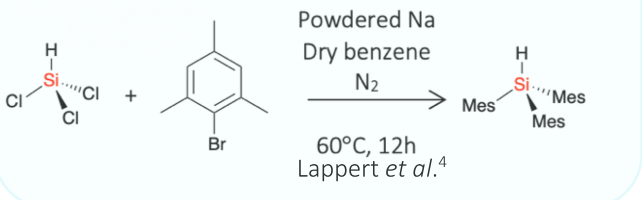
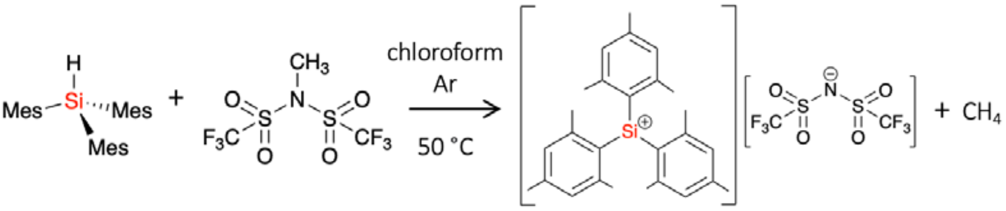


Figure 2 -White crystals of trimesitylsilane, first batch (left) and second batch (right).

Synthesis of [Si(Mes)$_3$][NTf$_2$]:

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.

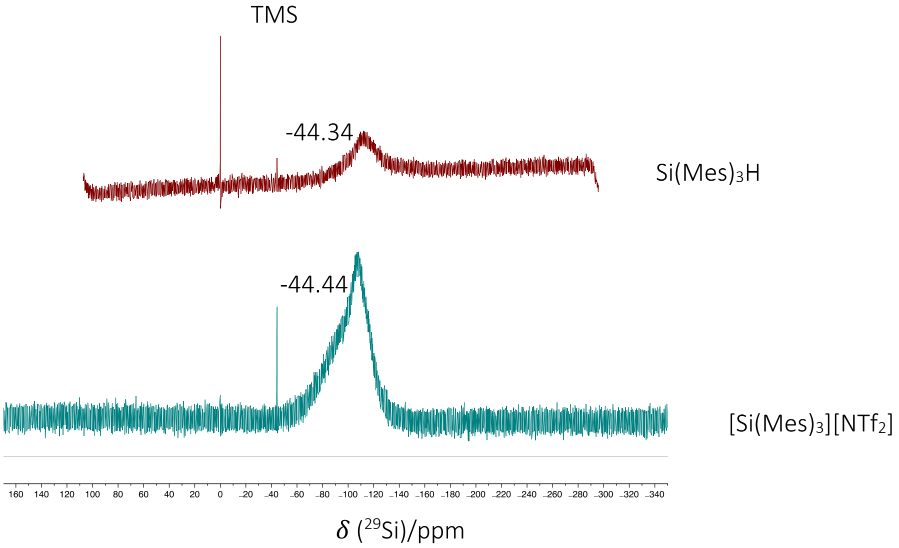


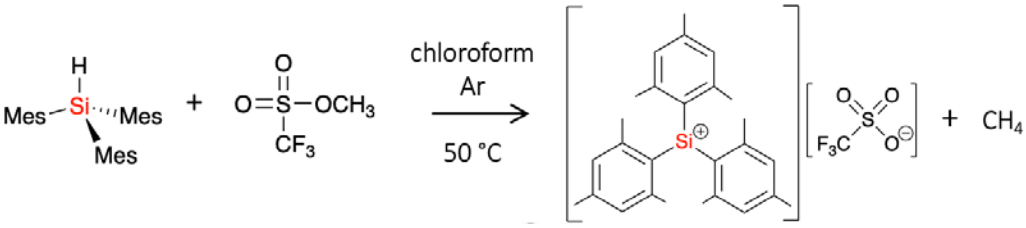
Figure 3 - Stacked ^{29}Si NMR spectra of Si(Mes)$_3^+$ containing compounds.

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.

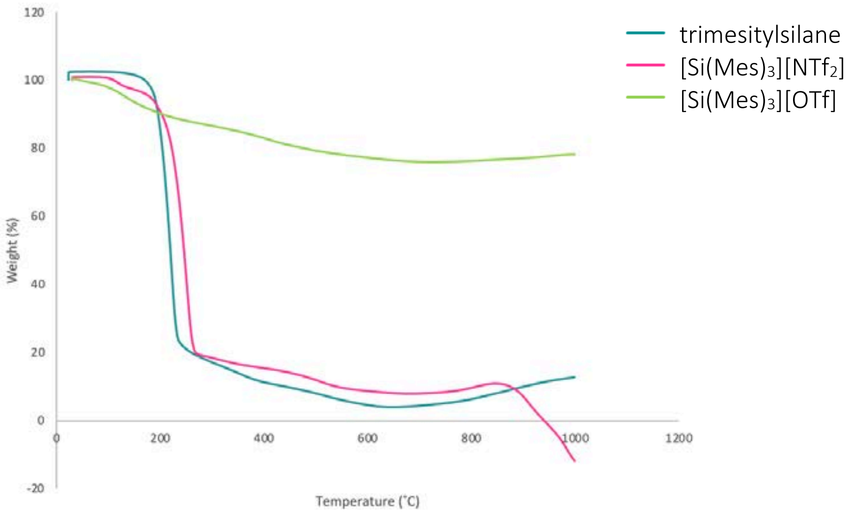
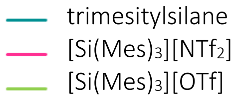


Figure 4 - Stacked TGA curve of Si(Mes)$_3^+$ containing compounds.

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.



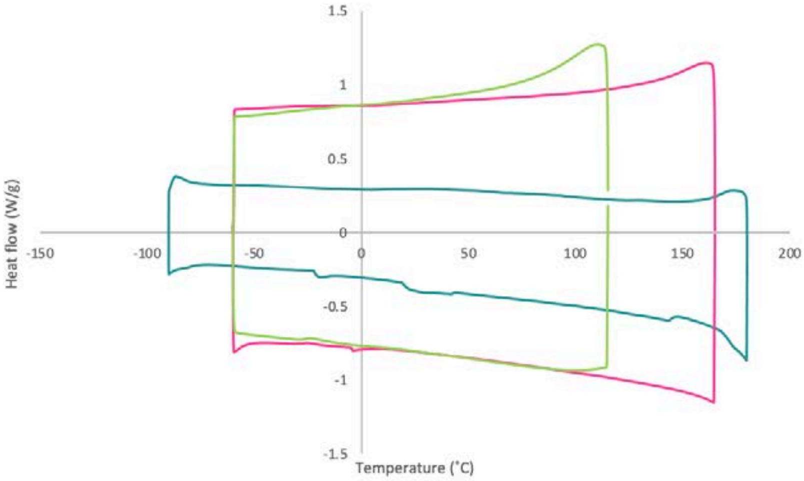
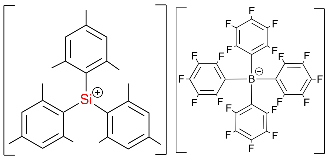
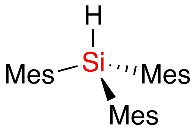
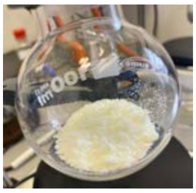
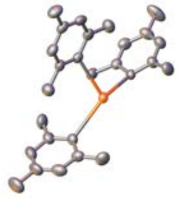
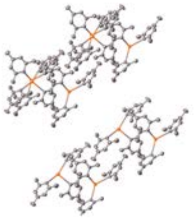
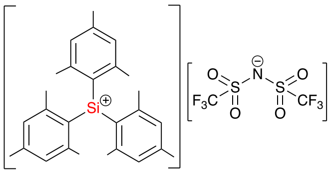
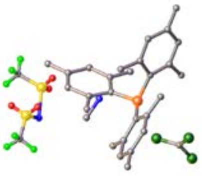
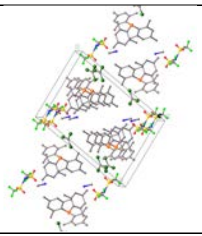
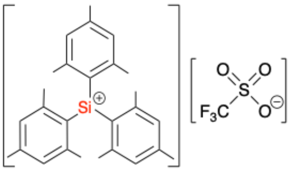


Figure 5 - Stacked DSC curve of Si(Mes)$_3^+$ containing compounds.

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

Table 1 - 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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QUILL Quarterly Report

February 2023 – April 2023

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

Liquid Coordination Complexes for the Synthesis of Semiconductor Nanoparticles

Background

My current work is based on the continuation of my MChem project, that focuses on the recovery of gallium metal from the zinc manufacturing industry, specifically zinc leachate solution, using hydrophobic deep eutectic solvents (DESs).

Global demand for gallium has rapidly increased over the past two decades, due to its applications in electronic devices. Challenges in its supply are exasperated by the lack of gallium ore, with this metal being recovered as a secondary element from mine tailings of other metal industries, chiefly aluminium, although recovery from zinc mine tailings is also potentially possible.[1] Finally, gallium supply is endangered by geopolitical consideration, with the majority being supplied by China (80%).[2]

As mentioned, this work focuses on the separation of gallium from zinc leachate solution, due to in Northern Ireland, this route of recovery being of great interest, on account of Europe's largest zinc mine being located in County Meath, Ireland.[3]

Hydrophobic DESs are based on the knowledge of hydrophobic ionic liquids and share similar characteristics such as long alkyl chains to promote hydrophobicity, however, are deemed less challenging and cheaper to prepare.[4] Previous literature on hydrophobic deep eutectic solvents (DESs) present hydrogen bond acceptor (HBA) molecules in combination with hydrogen bond donor (HBD) molecules, such as a carboxylic acid. A HBA molecule of great interest is trioctylphosphine oxide (TOPO), due to its application as a metal extractant in industry,[5] as well as its long alkyl chains which promote hydrophobicity. Although TOPO is used in aqueous organic liquid-liquid extractions, a major limitation to the process is its low solubility in hydrocarbon solvents, such as kerosene,[6] which are the chosen solvents for industrial extraction processes. By incorporating TOPO into a DES, it allows for large amounts of the phosphine molecule to be concentrated in the liquid form.

Objective of this work

The aim of this work is to explore hydrophobic DESs as a possible route for the extraction and recovery of gallium from the zinc manufacturing industry. Our strategy relies on the use of hydrophobic DESs as cost-effective, bifunctional solvents for the extraction of gallium. The overall aim is to find a system that results in the optimum amount of gallium being recovered, along with high gallium selectivity over competitive metals in the simulated zinc leachate.

Once I have completed all laboratory work on gallium separations and whilst continuing to write a paper for publication, I plan to also start on the nanoparticle section of my work. For this part of my project the aim is to develop new liquid coordination complexes (LCCs) and investigate them as precursors for the synthesis of semiconductor nanoparticles. This will include the studying the electrochemistry of Al LCCs and their applications as electrolytes, the synthesis and spectroscopic characterisation of firstly Ga/In selenide nanoparticles, before looking at ternary LCCs as precursors for nanoparticle synthesis.

Progress to date

We have developed a family of DESs based on trioctylphosphine oxide (TOPO), in combination with a selection of benign and inexpensive small organic molecules, that can act as cooperative complexing agents and/or reducing agents. These mixtures are then tested for the extraction and recovery of gallium from a simulated zinc leachate solution, where small (36 ppm) quantities of gallium are present, accompanied by very large quantities of other metals.

Initially, energy dispersive x-ray fluorescence (ED-XRF) had been used to determine the metal concentration of the aqueous phase pre-extraction, post-extraction and post-metal stripping. This was done by preparing several multi-metal stock solutions in 6M HCl, with decreasing metal concentration, allowing a calibration curve for each metal present in the zinc leachate to be created by empirical analysis (EMP) on ED-XRF. After several months of furthering my knowledge on this method, the decision has now been made to use XRF as a screening technique for results, before using inductively coupled plasma optical emission spectroscopy (ICP-OES) for accurately determining the metal concentration in the aqueous phase. Due to aluminium being one of the metals usually co-extracted and stripped alongside gallium, it is important to be able to accurately determine the amount of aluminium recovered from the zinc leachate solution. This is crucial in being able to calculate separation factors and demonstrate the selectivity of the system. One of the drawbacks of ED-XRF analysis is the difficulty in measuring lighter elements, such as aluminium, as its fluorescence struggles to reach the detector, making it difficult for the instrument to accurately determine how much of the element is present.

A TOPO:malonic acid system ($\chi_{TOPO} = 0.60$) has been shown to successfully extract, and recover gallium from a zinc leachate solution (16.5 ppm). A drawback of this system, however, is low selectivity towards gallium with aluminium, iron and copper also being recovered. Further systems have been tested with the aim of improving selectivity, including a TOPO:erythorbic acid ($\chi_{TOPO} = 0.68$) eutectic. This system resulted in higher gallium selectivity, due to preventing the recovery of copper in the stripped aqueous phase; speculated to be a result of Cu(II) being reduced to Cu(I),[7] therefore, chemically dissimilar from Ga(III).[8] Figure 1 shows a process flow diagram of how DESs are used to recover metals from a model zinc leachate feedstock solution.

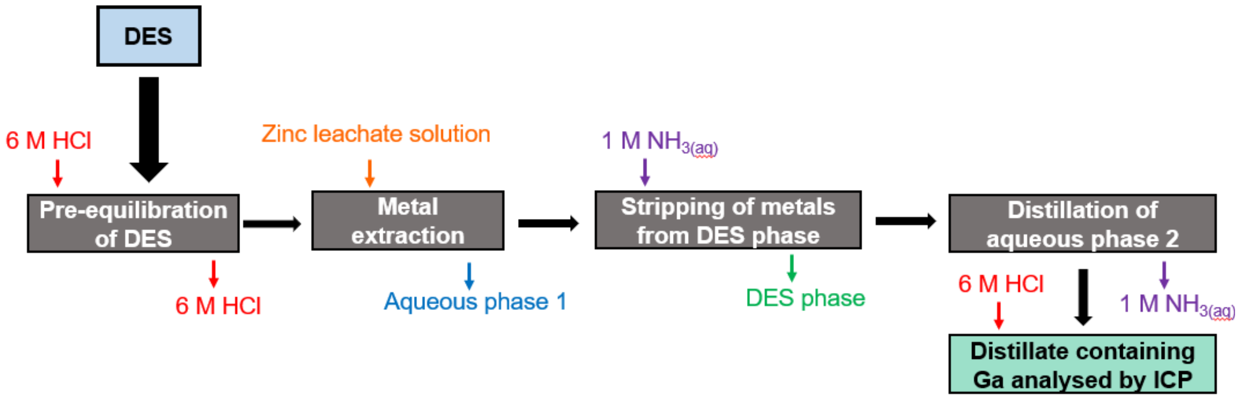

Figure 1 - Flow diagram showing the process of how gallium is extracted and recovered from a simulated zinc leachate solution using a DES.

The latest development in this work has been the addition of a small concentration of ascorbic acid (0.15 mol dm^{-3}) to the TOPO:malonic acid system ($\chi_{TOPO} = 0.60$). Ascorbic acid (vitamin C) is a known natural reducing agent,[9] that has the potential to reduce Fe^{3+} to Fe^{2+} and/or Cu^{2+} to Cu^{+}.[10] By reducing iron and copper, it is speculated both metals are converted into less easily recovered versions and thus susceptible to co-stripping. As gallium is most likely present in the form of the tetrahedral $[GaCl_4]^-$ species in 6 M HCl solution,[11] by reducing iron to its +2 oxidation state, and copper to its +1 state, this will result in their tetrahedral ionic radii being more dissimilar to Ga^{3+} tetrahedral ionic radii. The ionic radii of these ions are shown in Table 1. The amount of gallium also recovered is a lot greater when ascorbic acid is added to the system in comparison to when ascorbic acid is absent (27.5 ppm and 8.4 ppm respectively).

Table 1 - Tetrahedral ionic radii of gallium, iron and copper ions.[8, 12]

Metal ion	Tetrahedral ionic radii / Å
Ga^{3+}	0.47
Fe^{3+}	0.49
Fe^{2+}	0.63
Cu^{2+}	0.57
Cu^{+}	0.60

Table 2 shows the average distribution ratio (D_M) for the metals recovered from the eutectic phase and their corresponding separation factors (β), for the TOPO:malonic acid ($\chi_{TOPO} = 0.60$) system and the TOPO:malonic acid ($\chi_{TOPO} = 0.60$) system with the addition of ascorbic acid. As the experiments were run in duplicate, the average values are shown.

Table 2 - Average distribution ratios and separation factors for metals in aqueous stripped phase.

System	Metal	D_M	β
TOPO:malonic acid	Al	0.002	115.233
	Cu	0.237	0.706
	Fe	0.120	1.333
	Ga	0.162	1
	In	0	Unmeasurably high
	Zn	0	Unmeasurably high
TOPO:malonic acid + ascorbic acid	Al	0.002	224.677
	Cu	0.161	3.508
	Fe	0.271	2.15
	Ga	0.559	1
	In	0	Unmeasurably high
	Zn	0.001	643.948

The separation factors of aluminium, copper and iron are shown in Figure 2 for both systems. The results obtained show how with the addition of ascorbic acid the separation factors of the three metals improves, with a large improvement visible for aluminium. Although difficult to see in the bar chart, from Table 2 it can be seen the separation factors for both copper and iron also improve.

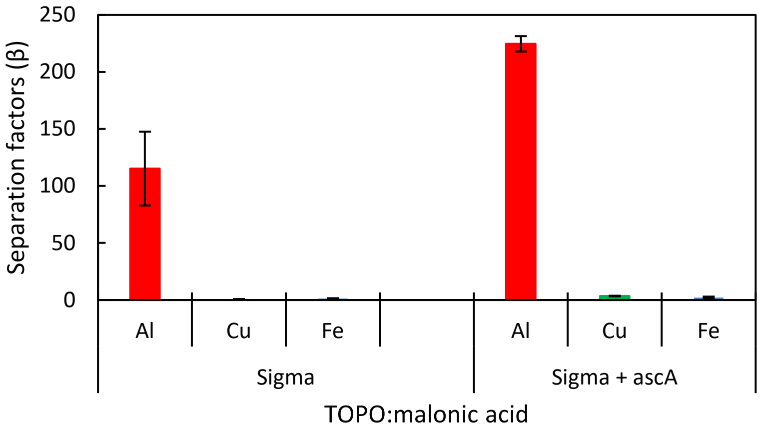

Figure 2 - Comparison of the separation factors of metals for the TOPO:malonic acid system ($\chi_{TOPO} = 0.60$) without and containing ascorbic acid.

Conclusions and future work

From this work good progress has been made regarding the recovery of gallium from a simulated zinc leachate solution, however, there is still a comprehensive amount of future work that could be carried out.

Firstly, the identification of eutectic mixtures was completed in the screening study of various HBDs in combination with TOPO. This allowed for the eutectic mixtures to be scaled up and tested as extractants for gallium from a simulated zinc leachate solution. Although in the extraction study, the eutectic systems in this work showed high metal coextraction, therefore, demonstrating low selectivity towards gallium, the benefits of these systems are later highlighted in the metal stripping studies. Both TOPO:malonic acid (χ_{TOPO} = 0.60), and TOPO:erythorbic acid (χ_{TOPO} = 0.68) systems have been shown to successfully recover gallium from a simulated zinc leachate solution. It has also been shown that the addition of a low concentration of ascorbic acid (0.15 mol dm^{-3}) to the TOPO:malonic acid system (χ_{TOPO} = 0.60) improves the selectivity of the system, by reducing the amount of iron and copper also recovered alongside gallium, whilst remaining to give high gallium selectivity over aluminium, indium and zinc. At this moment I speculate this is due to the reducing properties of ascorbic acid, however, further studies will need to be carried out to confirm this speculation.

This leads on to my future work, which includes x-ray absorption studies on four liquid samples, corresponding to four stages in the gallium recovery process: 1. the zinc leachate solution before contact with the DES (aqueous), 2. the DES phase after contact with the zinc leachate solution, 3. the DES after the metals are recovered from it, and 4. the final aqueous phase after the metals are recovered from the DES phase. By completing these studies, I hope to gather information on the chemical environment of the metals present in the process of recovering gallium from the simulated zinc leachate solution, and therefore, determine the changes that occur to the metal ions present in the zinc leachate solution throughout the process. The speciation, coordination geometry and oxidation state of the metals will be critical to understand the roles TOPO, malonic acid and ascorbic acid play in the process of recovering gallium from a simulated zinc leachate solution. This will allow for rationalisation as to why the process of gallium recovery, using a TOPO:malonic acid system, is optimised with the addition of ascorbic acid.

Further future work also includes continuing more studies on gallium recovery using DESs, which will be necessary for publication. These studies will involve altering the concentration of ascorbic acid added to the DES, to see if there is an optimum concentration that allows for better selectivity, as well as testing the recyclability of the eutectic system, as this is a common topic within hydrometallurgy research. Another objective I plan to achieve in this work is improving the selectivity of the system in the final aqueous phase, as this phase includes only gallium alongside the competitive metal iron. A route I plan to investigate to separate the iron and gallium is by using oxalic acid, with the aim of oxalic acid forming a precipitate with the iron present in the aqueous phase,[13] therefore, allowing easy separation by filtration to obtain a gallium pure aqueous phase.

In addition to the gallium recovery work, I am also going to attend Monash University in Melbourne for six weeks throughout May and June, to complete work on the electrochemistry of liquid coordination complexes (LCCs), specifically aluminium LCC electrolytes. As well as this, I plan to carry out some electrodeposition studies on my final aqueous phase obtained in the gallium separation work, with the aim of separating the iron and gallium from each other, as an alternative option to oxalic acid precipitation with iron.

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QUILL Quarterly Report

November 2022 – January 2023

Name:	Liam O'Connor		
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Funding body:	Department for the Economy		

3D-Printed Polymer Graphene Nanocomposites for Biosensor Applications

Background

A polymer strain sensor works on the principle that the electrical conductivity is proportional to the mechanical strain applied. Thus far, literature has focused on the prosthetic using feedback from pressure sensors in the fingertip to give feedback to the user. One of the limitations of using this pressure sensor is that it can only distinguish objects within the surface area of the sensors, which is 15 mm2. A solution to the limitation of pressure sensors is to develop a strain-dependent electrically conducting material and coat the outer material of the prosthetic. An important feature of the material used to manufacture a prosthetic arm is that it needs to be 3D printable. 3D printing of the prosthetic arm is required because there is no standard size for a person's arm. The materials being investigated are thermoplastic polyurethane (TPU) because of its strong hysteresis response to mechanical strain, nylon-11 (PA11) because of its piezoelectric properties, and graphene nanoplatelets (GNP) because it is shown to increase the electrical conductivity of other piezoelectric polymers, such as polyvinylidene fluoride (PVDF) at 25 wt.% (weight per cent)

Objective of this work

The work aims to develop a strain-dependent electrically conducting material that can be used as a strain sensor and be FDM 3D printed. This will be done by determining the optimal graphene for the manufacturing of TPU/GNP filaments, determining the optimal graphene loading for the manufacturing of PA11/GNP filaments, determining the optimal graphene loading for the manufacturing of TPU/PA11/GNP filaments, and determining the optimal manufacturing layering for TPU/PA11/GNP filaments.

Progress to date

Majority of the SEM images have been gathered. The piezoelectric properties have also been evaluated showing that the Nylon with 10 wt. % showed the greatest increase in piezoelectric properties.

Conclusions and future work

The TPU/PA11/GNP blend is ductile, like the TPU/GNP composite. It has an electrical percolation threshold like the PA11/GNP composite. PA11/GNP composite at 10wt. % showed an electric response to mechanical strain applied whereas the blended composite did not show any electric response to mechanical strain.

The next stage is to focus on the writing up of the thesis and publishing papers based around the work. Also to 3D print the blend and evaluate the mechanical and electromechanical properties.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Scott Place		
Supervisor(s):	Dr Paul Kavanagh (Primary) and Dr Mark Muldoon (Secondary)		
Position:	PhD student (4th Year)		
Start date:	Oct 2019	**Anticipated end date:**	Sep 2023
Funding body:	EPSRC		

Molecular Electrocatalysts for Energy and Electrosynthetic Applications

Background

This project focuses on the nitroxide radical molecule, TEMPO, and its derivates, their electrokinetic properties, and their applications in energy storage, energy generation, and electrosynthetic applications. TEMPO-like molecules can be electrochemically oxidised at an electrode surface to an active oxoammonium form, which can then react with substrates in a chemical redox reaction, which regenerates them to their nitroxide (or hydroxide, when protons are present) form. These reactions follow the well-established EC' (electrochemical-chemical) two-step reaction profile, studied extensively by Savéant and co-workers and Dempsey and co-workers, among others.

Electrolysis for organic synthesis is gaining popularity in the literature as a low-waste and simple procedure for converting a number of substrates to their corresponding products. TEMPO and its derivatives are an example of chemicals that can be used as electrocatalysts for oxidation reactions, where direct electrochemical oxidation of the substrate may be too energy intensive.

Objective of this work

The aim of this work is to use TEMPO and its derivatives as a case-study for the application of combined electroanalytical techniques for use in synthetic organic chemistry. Since electrochemistry and organic chemistry are typically divergent paths from an early stage in most chemist's careers, there is a language-barrier of sorts between the two fields. Here we aim to show how electroanalytical techniques can be used to benchmark electrocatalyst performance, highlighting key considerations to take during the analysis.

Progress to date

In my previous report, I detailed recent findings indicating the incompatibility of an organic solvent based reaction medium for the electrochemical oxidation of alcohols using TEMPO nitroxide radicals. In that report, I discussed how we were investigating the use of aqueous media for this reaction, using a pH 10 carbonate buffer solvent system to investigate our catalysts.

Since then, we have discovered that the pH 10 carbonate buffer solvent system lends itself to the overoxidation of benzyl alcohol to benzoic acid for different derivatives of TEMPO that we aim to investigate. This makes direct rational comparisons of the catalysts difficult in terms of their kinetics, as some of them are performing a different reaction. We have since discovered that the counter reaction plays an important role in the deactivation of the catalyst / destruction of aldehyde product. We have returned to an organic medium and transitioned to an H-cell electrochemical setup using a membrane, as opposed to the undivided single-compartment cell we were using before. This appears to have improved the performance of our alcohol oxidation significantly, seemingly selectively producing the aldehyde product at relatively high conversions. Recent challenges have involved achieving high mass balances in our product mixtures and we have spent a significant amount of time investigating the potential causes of this loss, including searching for side-reactions, membrane crossover, reactant/product evaporation, and adsorption effects of the carbon felt electrodes.

The new H-cell setup shows more promise for practical synthesis for our reaction, though does come with its own further challenges. The implementation of a membrane and significantly increased interelectrode distance is raising the overall cell voltage to very high levels, driving up power requirements for the reaction and causing issues with our electroanalytical equipment. We are currently investigating potential solutions to this issue, including scaling down our reaction to more manageable levels, testing different membrane materials, and working with the glassblowers to design bespoke glassware that will allow us to make use of our potentiostats more fully.

Conclusions and future work

This quarter has been busy with troubleshooting to ensure the best possible setup for quality electroanalysis. We are nearing a suitable reaction setup and aim to generate comparable catalyst performance data in the near future, before writing up this study and submitting for publication.

Following this, we will be investigating the use of controlled-current potentiometry as a method for rational design of electrosynthesis procedures. Current methods for selection of reaction conditions appear to be mostly trial and error, but we believe the use of electroanalysis may allow us to guide better-informed and more time-efficient decisions.

QUILL Quarterly Report

February 2023 – April 2023

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD student		
Start date:	1st October 2019	**Anticipated end date:**	1st October 2023
Funding body:	Self funding		

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

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

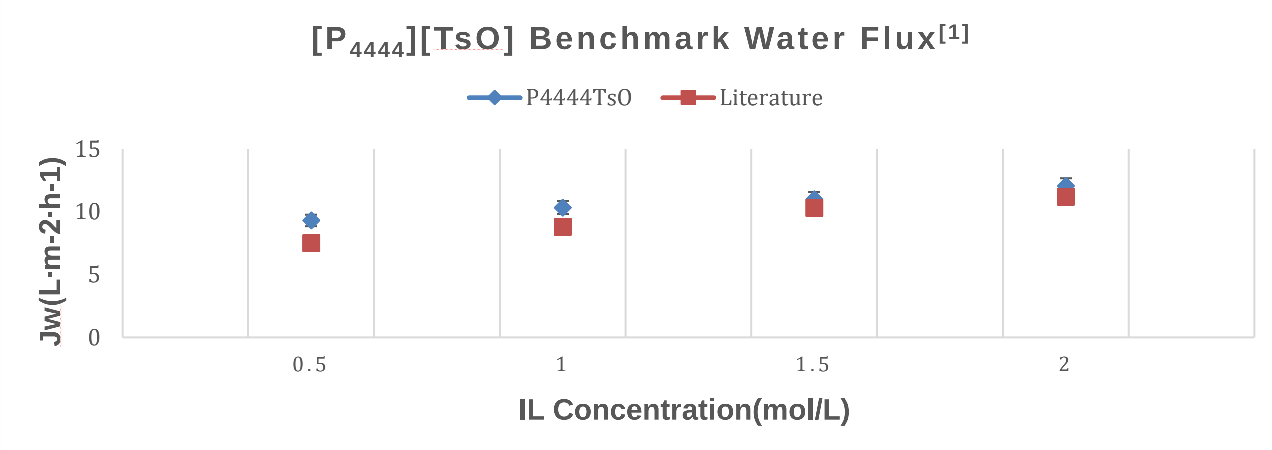
My research program in the use of ionic liquids as potential draw fluids for FO water treatment includes:

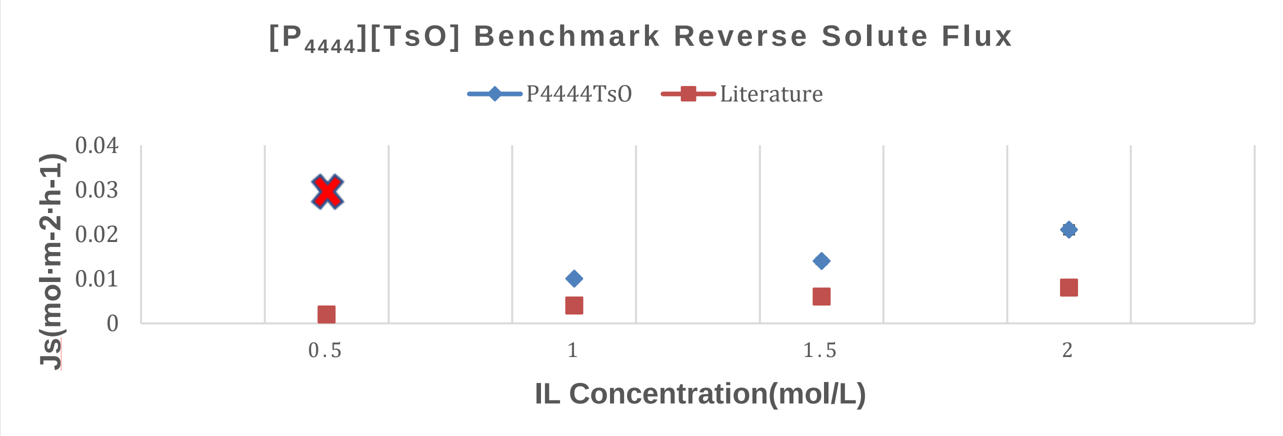
1. Preparation of appropriate model tetrabutylphosphonium/ammonium ionic liquids.
2. Characterisation of aqueous/ionic liquid phase behaviour as a function of aqueous component salinity, pH, temperature and to draw structure-performance relationships with the ionic liquid cation/anion components .
3. 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.

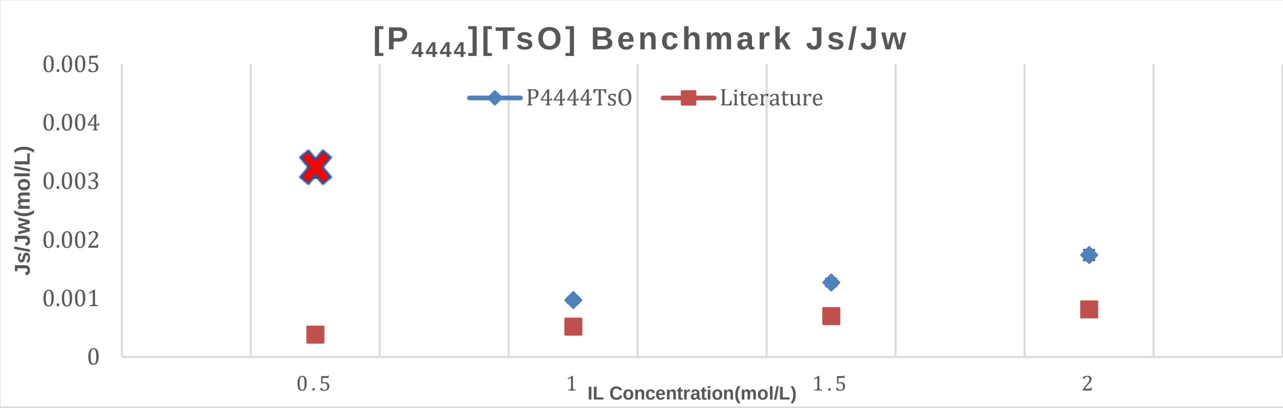
Progress to date

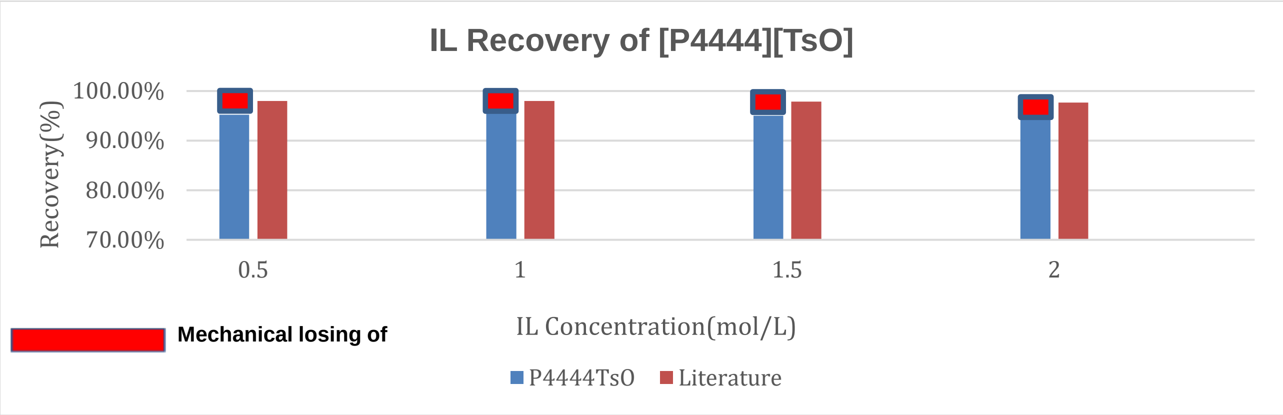
A substantial quantity of thermo-sensitive ionic liquid, including [P_{4444}][TsO] and [P_{4444}][Ph-tet], has been synthesized and fully characterized through NMR, FT-IR, and TGA analyses. We conducted two FO performance tests using the [P_{4444}][Ph-tet]/water mixture (0.5M-2.0M) and obtained a range of data. However, the benchmark experiments showed significant differences between our results and those reported in the literature.

As a result, we have completed benchmark experiments with literature to ensure the accuracy and reliability of our data output.









Benchmark experiments data using [P_{4444}][TsO] Jw, Js, Js/Jw and Ionic Liquid Recovery(0.5M-2.0M IL concentration run with TFC membrane 15L/h flow rate, 298K)

Conclusions and future work

Based on the benchmark data, we have demonstrated the capability to achieve a range of positive results on our forward osmosis test system. Additionally, the change of membrane has resulted in a decreased reverse solute flux, which benefits the forward osmosis process.

Moving forward, we plan to conduct testing of the [P_{4444}][Ph-tet]/water solution (0.5M-2.0M) in our system and compare its FO performance with literature. We will also focus on testing more LCST type IL materials to select and optimize the best one for various industrial applications. After testing these thermo-sensitive ILs, we will explore other types of draw solutes, such as switchable CO2-stimuli materials, and compare their performance to highlight the advantages of IL draw solutes.

QUILL Quarterly Report

February – April 2023

Name:	John Young		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Sophie Fourmentin		
Position:	PhD student		
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.

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^oC 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.

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

Gas screening methodology

Measurements to quantify the gas capacity and selectivity of both liquids and solids can be painstakingly slow and have a high associated cost. I have been developing a headspace GC (HS-GC) methodology to quickly screen liquid and solid sorbent materials for their gas capacity and separation ability. The screening can be performed at a range of pressures and temperatures, with a variety of pure gases and mixtures of gases. To do this I tested multiple combinations of HS-GC vials, stoppers and caps, resulting in the combination described in figure 1. The idea is to use the vials as mini equilibration vessels in which PVT based measurements can occur. These measurements are not expected to be as accurate as other methods, but we expect them to serve for screening purposes.

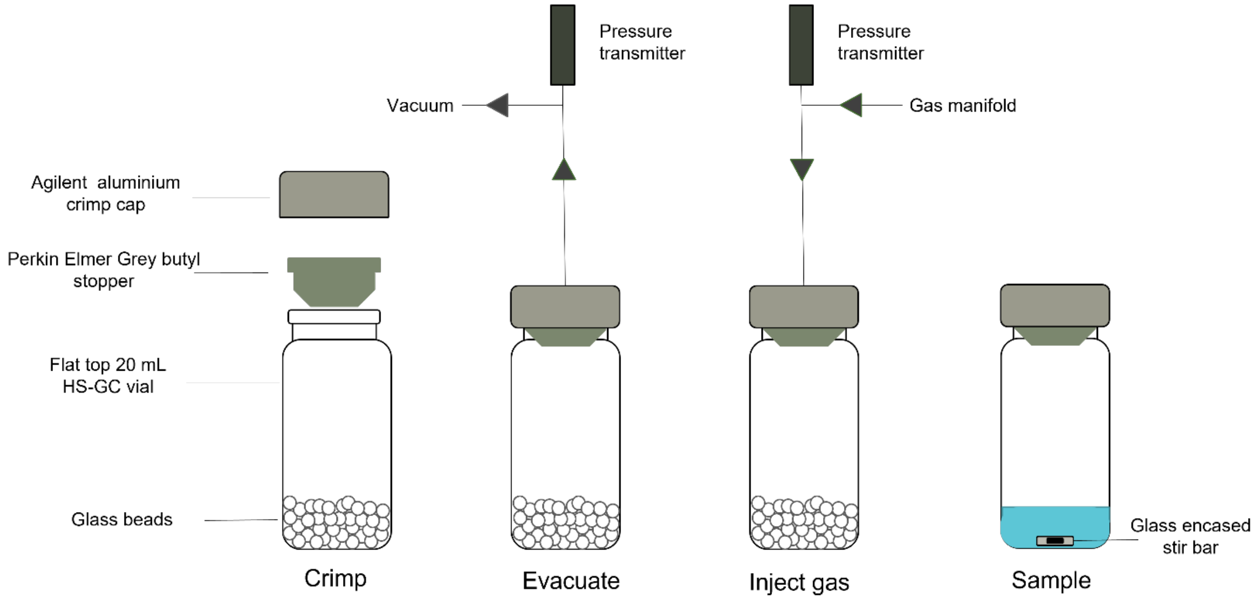


Figure 1 - Schematic of HS-GC vial preparation for calibration (glass beads) or for gas uptake measurements with sample (blue liquid)

By injecting a known "initial pressure" (quantity determined by PV calculations) of pure gas into an evacuated HS-GC vial we can compare the peak area associated with the injected gas from a calibration curve to the recorded peak area after equilibration with a known sorbent. The pressure difference in these two values equates to the gas uptake. An example can be seen below in figure 2 where a variety of CO_2 uptake isotherms of initial pressure against peak area shows that decreased peak areas can be seen in materials with a higher associated gas capacity. We have recently improved the method to allow for a triplicate of vials to be prepared in as little as 3 minutes by altering some experimental conditions.

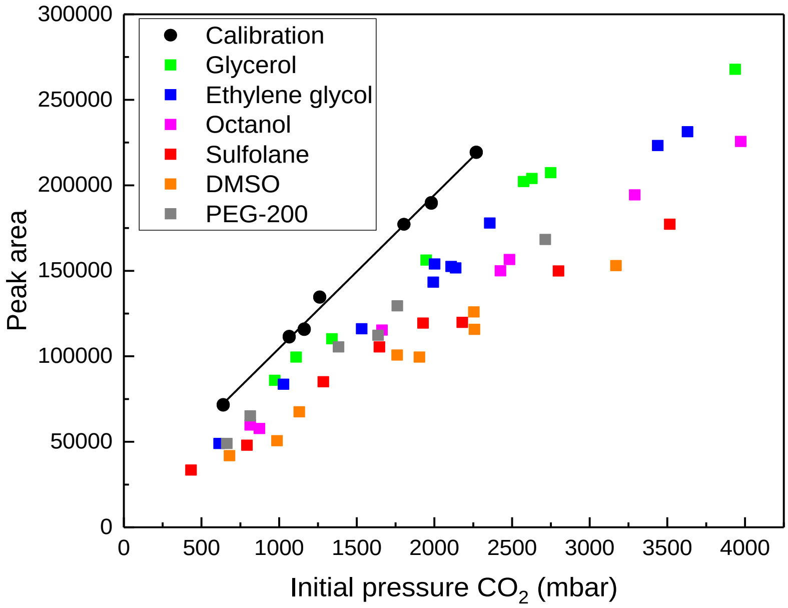


Figure 2 - Comparison of peak areas associated with different materials after equilibration with a known initial CO_2 pressure when compared to a calibration curve using glass beads[3–6]

This data was then converted to mole fraction as a function of equilibrated pressure and compared to literature data for the same materials (fig 3). It can be seen that the experimental gas capacities using this method are in good agreement with that of the literature data within the same pressure range.

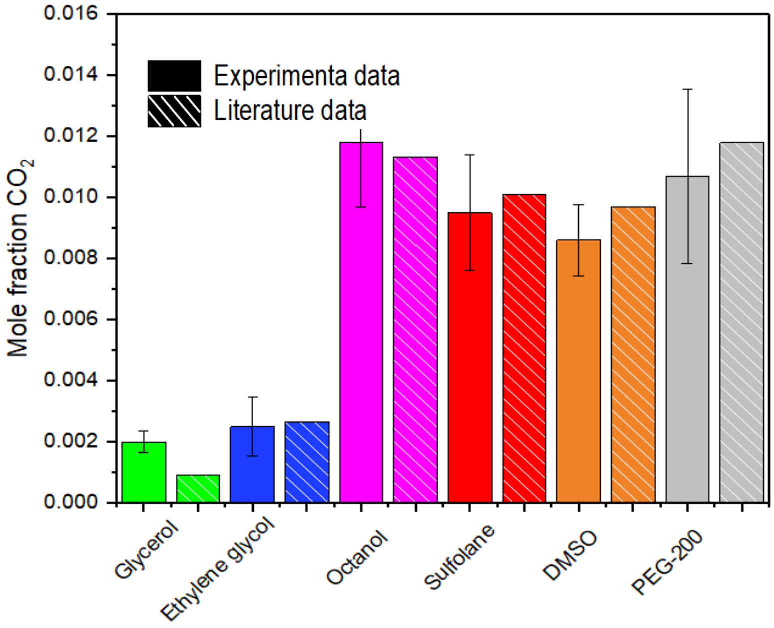


Figure 3 - Experimental uptake data of pressure against mole fraction of CO_2 obtained in this work (Solid colour) when compared with uptake data from literature sources (white stripes) showing good agreement with literature data.

Measurements like these have been carried out with CO_2, CH_4, C_2H_4 and C_2H_6 so far with both solid and liquid systems. These have also been found to yield results which compare well to that of literature. The error, accuracy and deviations from the literature data for these measurements is also being estimated.

Future work

More data must be collected and after which we will write a methodology-based paper about this work. We would also like to be able to quantify the capacity of hydrogen in various sorbents. Calibration curve and measurements with hydrogen are underway.

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