QUILL
Quarterly Reports

May 2022 – July 2022

CONFIDENTIAL (up to August 2025)

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QUILL Quarterly Report

May 2022 – July 2022

Name:	Haris Amir		
Supervisor(s):	Professor John Holbrey		
Position:	Postgraduate PhD		
Start date:	October 2020	**Anticipated end date:**	September 2024
Funding body:	ESPRC/UKRI		

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

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/N-chelators for ionic liquid applications have been designed and investigated.

The viscosity of $[P_{66614}]^+$ based ILs are recorded at various temperatures and discussed how the size of the boron anions are responsible for the viscosity. When having a second look at the NMR of the alkali salts synthesised. A small yet significant impurity was identified in majority of the boron salts. A method to purify these salts was developed and the purity of the salts, after purification was confirmed by multinuclear NMR spectroscopy, before investigations in areas where high levels of purity play a significant role. The boron anions of interest are shown in Figure 1.

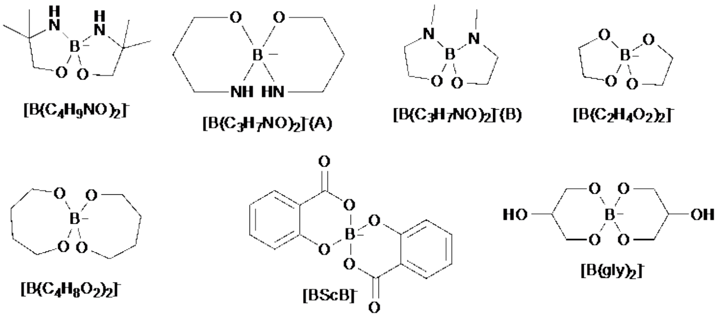

Figure 1 - Borate anions of interest

Purification of alkali salts

Once the characterisation of these ionic liquids was complete, it was decided to investigate if these novel boron anions have potential application in electro- and photo- chemistry. This meant that the salts needed to be extremely pure before being used in electrochemistry as the purity of the electrolytes plays a significant role in the flow of electrons. The purity of the salts was checked by examination of the NMR spectra of the alkali salts synthesised. It was found that, after initial synthesis, all the salts contained the same impurity that was showing up in the ^{13}C NMR.

Figure 2 shows the two peaks that should not be present in the ^{13}C spectra for these salts. It is expected that these peaks are a result of a side reaction that results in the boron anion decomposing to a 3-coordinate boron compound. As well as some of the starting material may have reacted with the base present.

A purification step was developed which involved stirring the salt in acetonitrile at 60˚C for one hour and then filtering the powder and washing with cold ethanol. Figure 3 shows the result of the purification step as the peaks observed in figure 2 are no longer present after purification was carried out. The ^{1}H NMR could not be overlapped as different solvents were chosen when preparing the sample. Highlighted in figure 4A are the impurities seen in the ^{1}H NMR, there is also a signal which is likely due to water, the presence of water could have caused some of these impurities to arise. When purified figure 4B shows the unidentified peaks are no longer present and only the expected peaks are observed. This suggests that the purification step was successful, this was repeated for all the salts. This was done so that all the samples can be investigated in electro- and photo- chemistry.

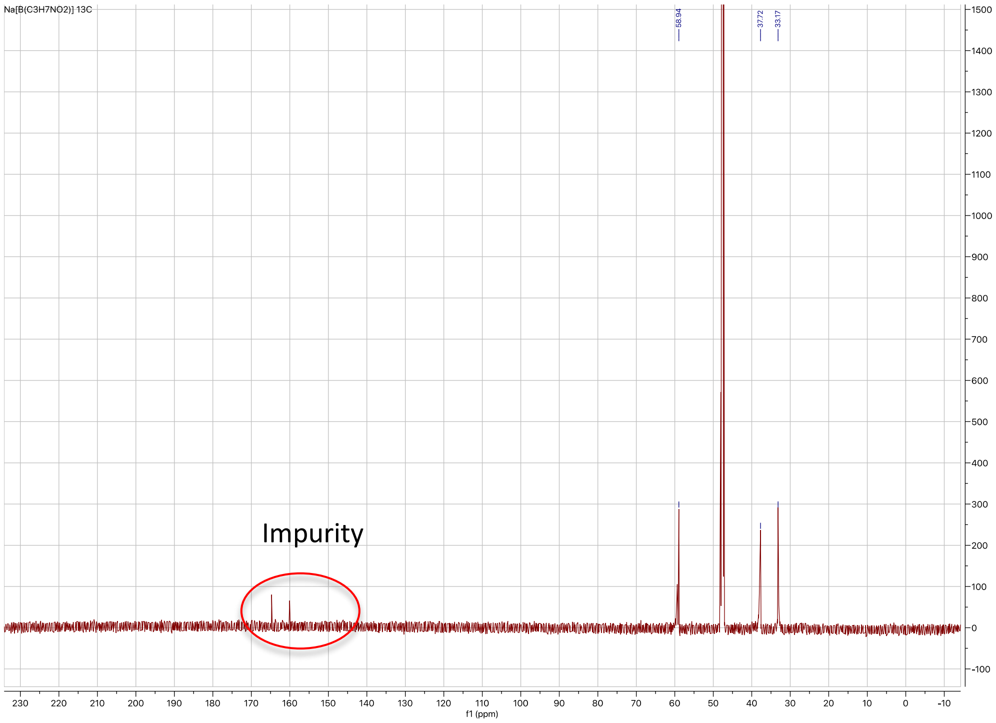

Figure 2 - ^{13}C NMR spectrum of impure $Na[B(C_3H_7NO)_2]$ in methanol-d.

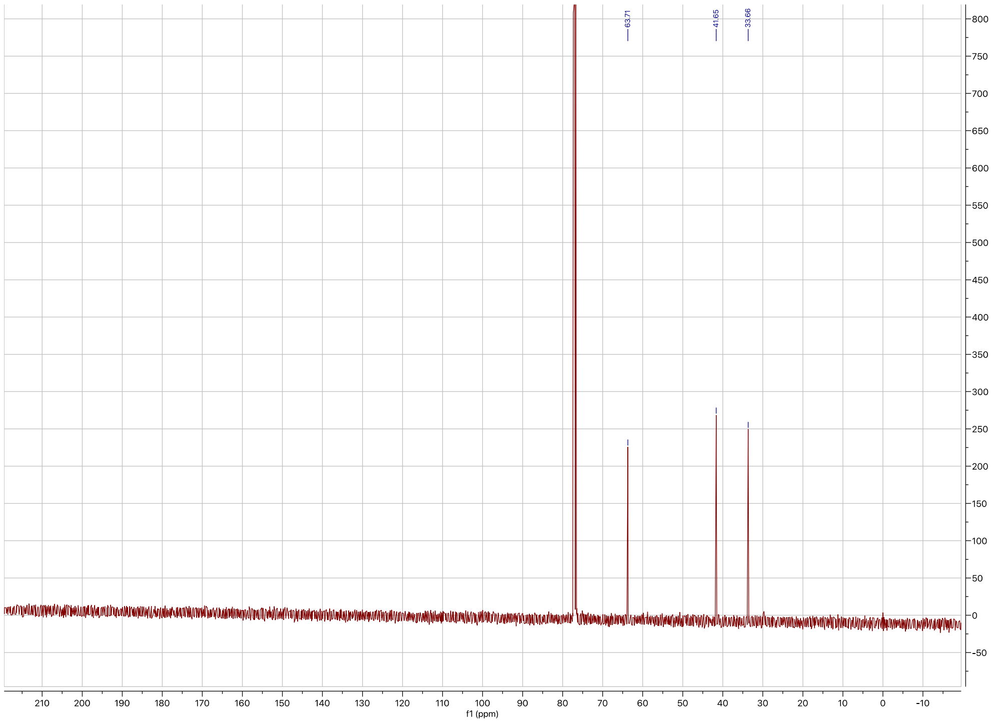

Figure 3 - ^{13}C NMR spectrum of purified $Na[B(C_3H_7NO)_2]$ in $CDCl_3$.

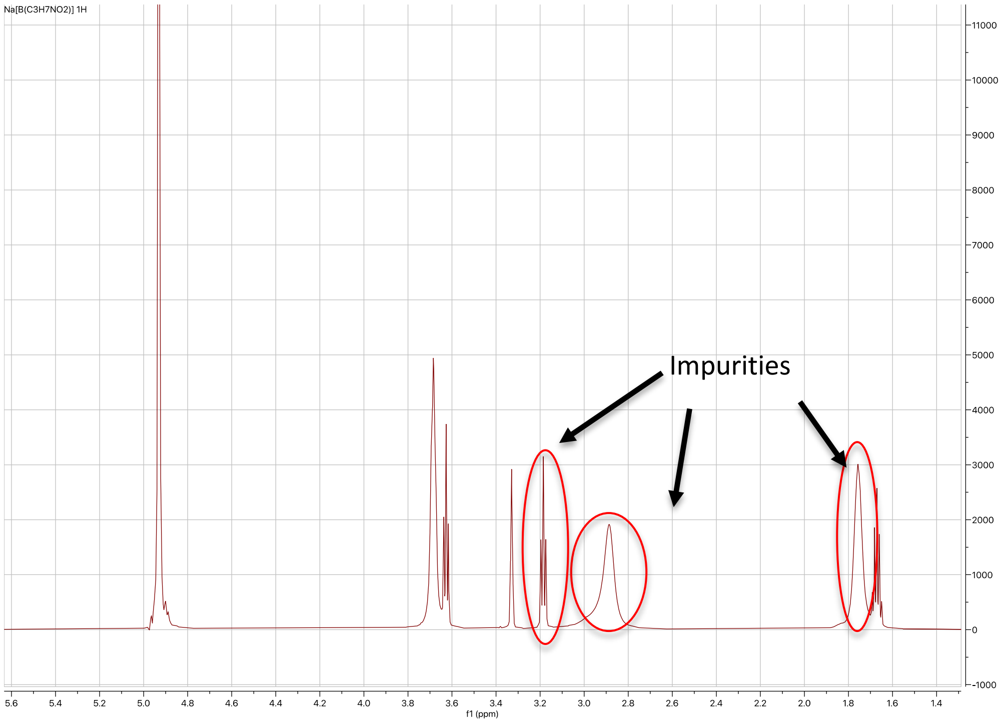

Figure 4A - ^{1}H NMR spectrum of impure $Na[B(C_3H_7NO)_2]$ in methanol-d.

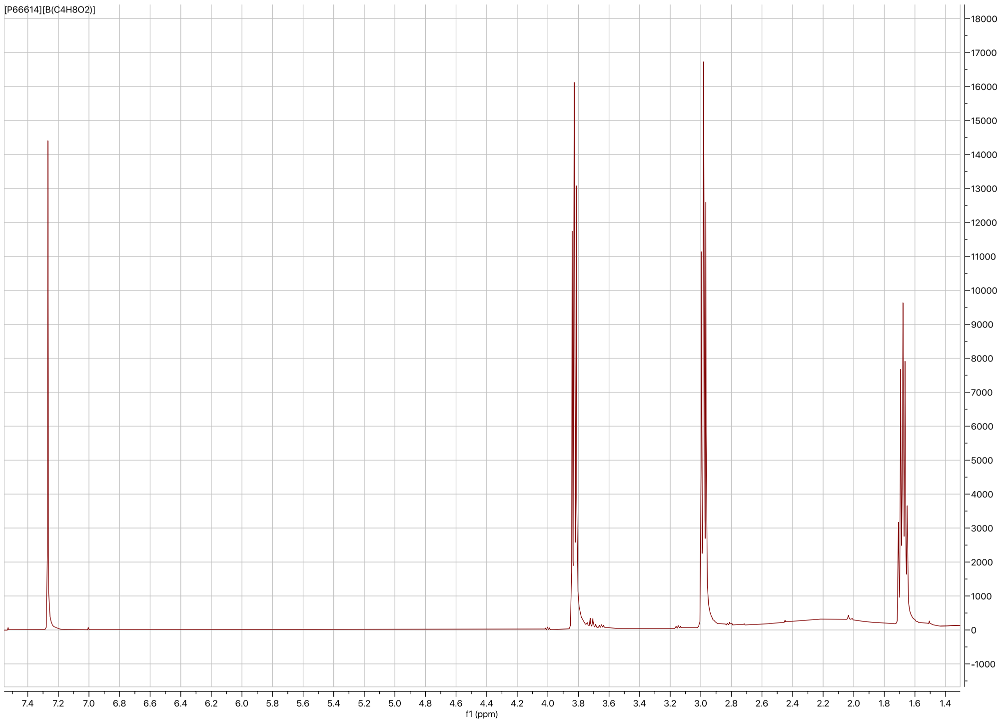

Figure 4B - ^{1}H NMR spectrum of purified Na[B(C_3H_7NO)$_2$] in $CDCl_3$.

Viscosity of [P_{66614}]$^+$ based ILs

The viscosities of the phosphonium based ILs was measured over the temperature range 20-60 °C using a rheometer MCR 302e. Viscosity was the last physical parameter that needed to be measured when describing ILs containing these borate anions. It is expected that as temperature increases the viscosity of the IL will decrease. Viscosity is proportional to the surface attraction forces between the molecules, in this context it is the attraction forces between the phosphonium cation and borate anions. Figure 5 shows the viscosity of the phosphonium based ILs, they all show the viscosity decreases as the temperature increases. This is because at higher temperatures the molecules have a greater thermal energy and are more easily able to overcome the attractive forces that bind them together. It can also be interpretated from the graph that the larger anions show an overall lower viscosity, this could be because the larger anions and cations are further apart when compared to the smaller anions such as Cl^- and [B(C_3H_7NO)$_2$]$^-$. This results in the attractive forces between the molecules to be weaker in strength, which results in a lower viscosity. There doesn't seem to be a significant different to what the boron centre is bonded to, if that is nitrogen or oxygen, rather the viscosity depends on how strong the attractive forces are between the particles. Future work will be to investigate if there is a difference in the viscosity if only nitrogen bonded boron anions are used.

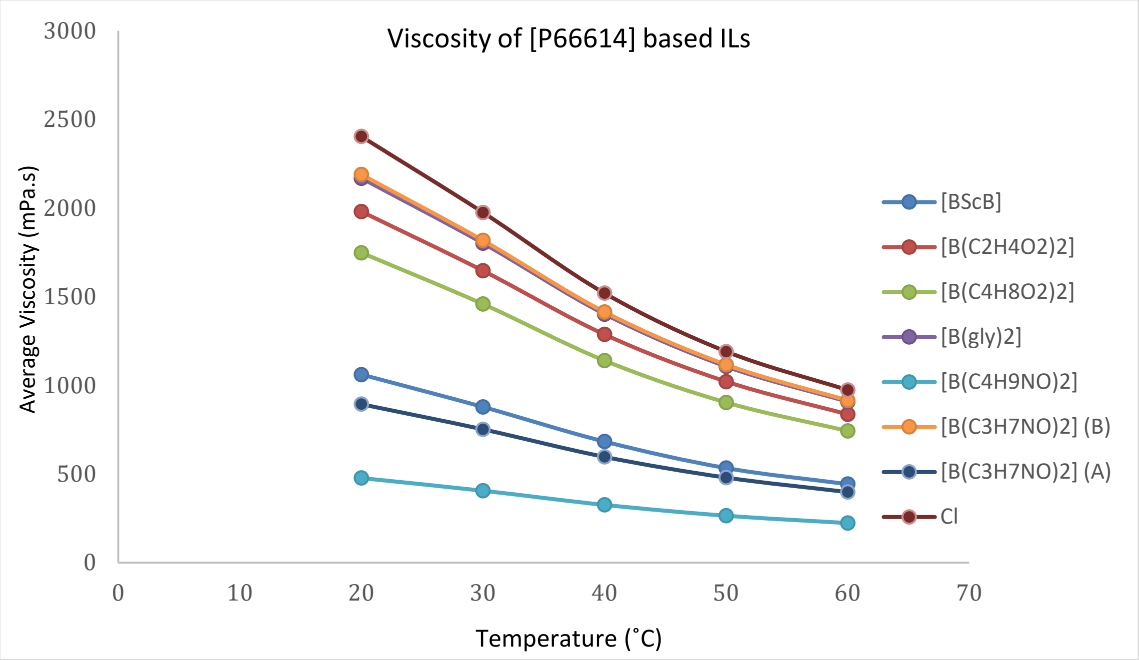

Figure 5 - Viscosity of [P_{66614}] based ILs

QUILL Quarterly Report

May 2022 – July 2022

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:**	30st September 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 technologies for the treatment of saline process water with the initial objective of selective sulfate removal from highly competitive aqueous streams. Extraction of hydrophilic oxyanions from aqueous solutions is an important industrial challenge across many sectors, from acid mine drainage to nuclear waste remediation, nuclear medicine, and general water treatment to address compliance with total discharge limits. Previously examined was the applicability of hydrophobic ionic liquid media for liquid-liquid extraction of sulfate from non-competitive aqueous solutions.

Objective of this work

The main goal of this work is the selective removal of sulfate from sea water with a lesser emphasis on removal of sulfate from other competitive aqueous streams. A secondary goal of the research is to develop methods for the removal of toxic or valuable oxyanions of interest from water streams such as naphthenic acids, phosphates ($[H_xPO_4]^{y-}$), nitrate ($[NO_3]^-$), bromate ($[BrO_3]^-$), arsenates ($[H_xAsO_4]^{y-}$), pertechnetate ($[TcO_4]^-$), chromate ($[CrO_4]^-$) and selenate ($[SeO_4]^{2-}$).

Progress to date

Not much progress has been made on this project since the last quarterly report for various reasons such as preparing for the EUChemsil 2022 conference during early June, my annual progress review at the end of June and then beginning an industry placement with Chevron at their Richmond facility in California at the start of July. Unfortunately, this work is all under NDA and so cannot be discussed.

On the sulfate side [P1888]Cl has successfully been synthesised, characterised and tested for sulfate removal similar to the other ILs. While [P1888]Cl form much more persistent emulsions than the ammonium, it appears that whether the cation is ammonium or phosphonium has no effect on the sulfate removal, and that a methyl group is equivalent to an acidic proton as shown in figure 1.

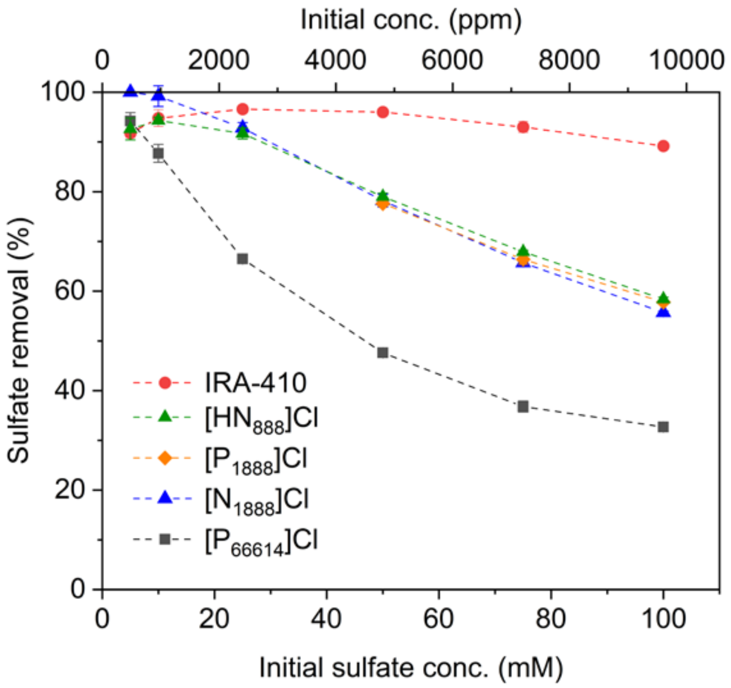

Figure 1 - Sulfate removal upon contacting 6 mL aqueous phase with 3 mL of water saturated IL.

Conclusions and future work

To summarise the electrostatic attraction is the main driving force for the IX extraction of sulfate with activity being similar to common IX resins ie. Selective for divalent anions from low ionic strength solutions and monovalent anions from high ionic strength solutions.

Future work to conclude this approach includes synthesis of a trioctylammonium IL with an ethanol side chain similar to what is seen in the IX resins. What may also be worth trying is the use of dicationic ILs or mixed ILs with a fatty acid anion to co-extraction of sulfate with divalent magnesium or calcium[1].

References

1. D. Parmentier, T. Vander Hoogerstraete, S. J. Metz, K. Binnemans and M. C. Kroon, Selective Extraction of Metals from Chloride Solutions with the Tetraoctylphosphonium Oleate Ionic Liquid, *Ind. Eng. Chem. Res.*, 2015, **54**, 5149–5158.

QUILL Quarterly Report

May 2022 – July 2022

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

Battery Thermal Management & Algorithmic 3D Temperature Control

Background

Due to recent efforts to combat climate change, electric vehicles have become a key focus of the automotive industry. One major challenge of this technology is thermal management of lithium-ion cells within the vehicle, as the performance and safety of the battery is dependent on keeping these temperatures within an optimal window of 15-30 C. As cells become larger and more powerful, the temperature differences observed across the volume of the cell increase. Therefore, a more complex method for temperature control is required for optimal safety and performance

Objective of this work

This work aims to develop a method of accurately predicting cell temperatures within a vehicle in order to provide a better battery management system

Progress to date

- Numerical model developed
- Machine learning identified as a more efficient prediction method if enough data can be collected to ensure accuracy
- Machine learning models developed
- Testing of machine learning models for electrical predictions to provide a whole battery model

Conclusions and future work

The machine learning methods used for improving voltage and SOC prediction were found to be successful. Preliminary work on this was presented at a poster session at AABC Europe 2022 conference.

This work will be completed and written up for publication.

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May 2022 – July 2022

Name:	Oisin Hamill		
Supervisor(s):	Dr Nancy Artioli and Dr Alex Goguet		
Position:	PhD		
Start date:	October 2019	**Anticipated end date:**	March 2023
Funding body:	Johnson Matthey		

Mechanism Understanding of NOx storage, release and reduction on Pt/doped ceria catalysts

Background

Due to strengthening emission legislations in Europe, North America and the rest of the world, there is a need for further optimisation of existing emission after-treatment catalytic converters for automotive applications. New legislations focus primarily of NO_X abatement and consequently the exhaust emissions of lean-burn gasoline and diesel vehicles. After treatments systems must utilise new technologies to reduce this that offer low temperature activation and high stability.

High surface area ceria is successfully employed as an excellent support of metals (Pd, Rh, Pt, etc.) in commercial catalytic systems for the oxidations of carbon monoxide and propane and automotive emission control. Ceria is a unique material with a rich and complex chemistry. It possesses high oxygen storage capacity (OSC), a unique redox property by the cycle of Ce^{4+}/Ce^{3+} redox pairs and it can be further enhanced through using dopants. Platinum supported on ceria can show enhanced NO_X storage at low temperature, as reported in the literature, together with an improved carbon monoxide/hydrocarbon light off.

Ceria supported catalysts, in general, do not operate efficiently at low temperatures and therefore must be modified in order to overcome this problem. For this reason, addition of enhancing materials is currently being considered in detail. This addition of a material that increases the performance of an already functional catalyst is called doping. The main function of this dopant is to allow the catalyst to function outside of the normal working temperature range and operating conditions to increase catalyst efficiency.

It has been proposed that the dopants, such as rare-earth and transition metal oxides, increase the concentration of surface vacancies which affect the ionic conductivity, oxygen mobility and oxygen storage capacity of the ceria. It can be speculated that all these properties are responsible for the enhanced oxidation activity by promoting oxygen diffusion and formation of more "reactive oxygen" species. Furthermore, the oxygen species play a role in the mechanism of the reaction, favouring the NO_X storage.

Additionally, presence of dopants can reportedly modify the platinum reducibility and platinum-ceria interaction, allowing more readily activation during rich purge.

This project aims to better understand the NO_X storage mechanism on the doped materials and give new insights into the activation/lean deactivation mechanisms in the presence of different dopants.

Objective of this work

The main objective considered in this project is to improve the understanding of the NO_X storage mechanism, together with the mechanism of rich purge on ceria supported platinum. We aim to gain a deeper knowledge of the rich activation and lean deactivation mechanisms as well as determine the structure of the active sites under reaction conditions. We look to develop a method to differentiate between active species and spectator species through transient methods. We will also strive to develop a global kinetic model for the reaction and all involved species. This will enable the determination of the relative importance of different reactions within the catalyst bed as well as a measurement of the exact gas compositional conditions present during the reactions. With this approach in depth information relevant to mechanistic understanding and reaction engineering application will be obtained.

Progress to date

- Pt-Sm-Al catalyst group activation testing complete for comparison to dopant affect seen on Pt-Ce group.
- Proposal accepted for ex-situ study of Pt-Sm-Al BAG call in Diamond Light Source.
- NAM27 conference attended and work to date presented on Sm dopant families.

Conclusions and future work

- Characterisation paper to be completed and submitted.
- XPS study to be completed on Sm-Al to relook at the Sm region.
- Dispersion measurements.
- EXFAS characterisations on Sm-Al to be completed and processed.
- NSC test focusing on selectivity during reduction.
- Raman spectroscopy in JM Sonning Common to be completed.
- ESRF beamline proposal to look at K-edge energies of catalyst (in-situ and ex-situ) to be submitted.

QUILL Quarterly Report

May 2022 – July 2022

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

Background

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

The RFB design has not changed much since their inception in the 20th century (e.g. vanadium RFBs were invented in 1986 at the University of New South Wales, Australia). The electrodes are still typically made using graphite bipolar plates and carbon felt materials. Carbon materials are used because they are a good conductor of electricity. Skyllas-Kazacos *et al* (2013) also emphasise that carbon is electrochemically stable at both positive and negative ends for all-vanadium RFBs, unlike metals and polyaniline materials which were also explored. However, using graphite and carbon felts limit the design freedom, and must be kept in mechanical compression to ensure electric contact between elements. 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 into 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. Not much research is available on graphene composites for SLA, but it may offer improved graphene dispersion compared to FDM.

Objective of this work

To develop existing nanocomposite research to produce 3D-printable RFB electrodes using FDM and SLA technologies.

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 finding the right graphene nanocomposite. 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 material and method to produce high electrical conductivity and excellent graphene dispersion.

After entering the laboratory in July, I have produced various graphene nanocomposites by mixing graphene nanoplatelets (GNPs) with resin and polymerising it using the SLA 3D-printer. However, the GNPs mixed with resin had a high a viscosity which caused print problems. Furthermore, the resulting composites had high GNP agglomeration and low electrical conductivity, due to poor compatibility of GNP with polymer.

Conclusions and future work

To improve the compatibility of GNPs with acrylate-based resin, I aim to synthesise oxidised graphene which is more compatible due to polarity. I will also develop my own UV-curing resin for use with SLA 3D-printing by mixing monomers and a photo-initiator. This method should improve graphene dispersion and reduce resin viscosity, enabling highly conductive composites to be 3D-printed. I will then move onto the second work package which focuses on the 3D-electrode design.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey and Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	October 2021	**Anticipated end date:**	October 2024
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 substituted 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

Three N-alkyl-acridinium salts and N-protonated heterocyclic ionic liquids had been successfully synthesised and characterised as precursors for FLP studies. The 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 which contrasts with the reported poor [2], and limiting solubility of N-methylacridinium salts in organic solvents. The H_2 experiments 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). The NMR measurements are still challenging due to current low concentrations of FLP components in the protic IL solvent, and method development is required to overcome these challenges. We have decided that we will use an internal standard whilst carrying out the ^1H NMR quantification experiments. Additionally, we have halted our investigation into how our Intrinsic IL FLP system behaves when exposed to H_2, as we have decided it is pivotal that we collect more thermal experimental data about the FLP system. We are collecting this data via DSC analysis. Our reasoning to thoroughly probe the FLP thermal properties is in order to produce a phase diagram of our FLP system and if we can. We believe that by having comprehensive information about the thermal system it will help in optimising the reaction conditions to have more definite H_2 activation experimental conditions. We have also started to collect XRD data for the N-alklylated acridinium salts. The earlier proposed work to generate N-alkyl-dicyanopyridinium cations, as analogues of the $[N\text{-}Ac]^+$ has recently been started and we are currently in the early stages of the synthesis. The Conference that was mentioned in the last report, was attended and I received a Best Poster award for ILs. I also had my Differentiation report to write and prepare for in June and it went well, as I passed it. Also the meeting gave me many new research points of investigation.

Conclusions and future work

I hope to soon have in-dept knowledge about the thermal behaviour of the FLP components of the system and that this data will provide more information on deducing definite H_2 activation experimental conditions and also produce the Phase diagram. Additionally, once this data is analysed thoroughly and once we have definite conditions for the H_2 interaction with the Intrinsic IL FLP system and quantitative data obtained, we then hope to publish our data. To conclude, we will continue to synthesis and analyse the N-alkyl-dicyanopyridiniums and hopefully fill in the gaps in the research we have collected so far.

References

1. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.,* 2010, 49, 46–76.
2. E. R. Clark and M. J. Ingleson, *Angew. Chem., Int. Ed.*, 2014, 53, 11306–11309.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	2nd year PhD student		
Start date:	April 2021	**Anticipated end date:**	April 2024
Funding body:	Tezpur University/QUB joint PhD scholarship		

LCST Phase Behaviour of Substituted Tetrabutylphosphonium 5-Phenyltetrazolate/Aqueous Mixtures

Background

In the previous report, studies on the phase behaviour for [P4444][2-OH-PhTet] was carried out and its comparison with that of [P4444][Sal] was made. Preliminary synthesis of a dicationic ionic liquid was carried out. This report further extends into the synthesis, characterisation and testing the phase behaviours of the prepared dicationic ionic liquids and one sulfonate ionic liquid.

Objective of this work

The ultimate aim of this work is to understand and explain the lower critical solubility temperature (LCST) phase behaviour of some ionic liquids, to know the boundaries and frame a methodology for synthesising such ionic liquids that can behave as a potential draw solute to be used in the forward osmosis process for sea water desalination. In this process, a range of ionic liquids with the tetrazole moiety will be synthesised, tested, and compared with the existing ones, based on the type of anion or cation chosen, that can affect the phase behaviours.

Progress to date

1. The prepared dicationic ionic liquid, 1,5-pentanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) was studied for its phase behaviour (LLE behaviour) using the instrument crystal16. It was observed that for all the compositions from 0.01 until 0.8, biphase was formed both during the heating and cooling periods in the cycle indicating an increased hydrophobicity with the size of the alkyl group on the linker chain between the two cations.

2. Synthesis of a dicationic ionic liquid, 1,6-hexanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) for testing its phase behaviour: 8.3 mmol of already prepared 1,6-hexanediyl-bis(tri-n-butyl phosphonium)dibromide was dissolved in sodium tetrazolate solution in water and was allowed to stir for 2 hours (until phase separation) at a temperature of 60 degrees.

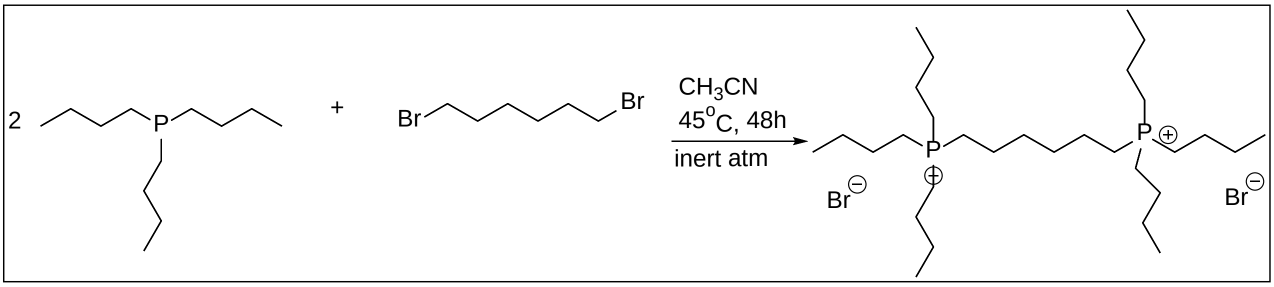


Figure 1 - Synthesis of 1,6-hexanediyl-bis(tri-n-butylphosphonium)dibromide

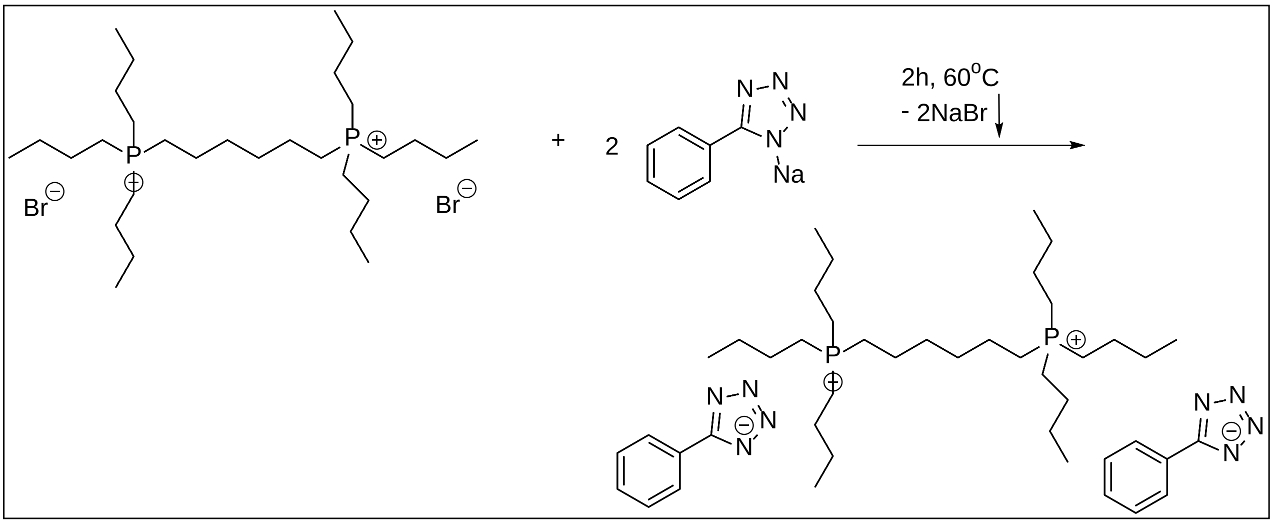


Figure 2 - Synthesis of the dicationic ionic liquid, 1,6-hexanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate).

3. The prepared dicationic ionic liquid, 1,6-hexanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) was studied for its phase behaviour (LLE behaviour) using the instrument crystal16. It was seen that the composition mass fractions from 0.02 to 0.7 of the dicationic ionic liquid, 1,6-hexanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) with water showed turbidity formation from a clear homogenous phase, while heating the liquid-liquid mixtures from 6°C to 70°C. A steady increase in the cloud point temperature was observed from 0.1 until 0.65 mass fraction of 27, however, for compositions higher than 0.65, a transparent single phase and no clear biphase was noticed on further increasing the temperatures up to 90°C, thus reaching the limiting point. On the lower concentration end, it was evident that there was a slight increase in the cloud point for compositions below 0.03 which further increased drastically for 0.02 of ionic liquid/water mixtures until reaching a limiting value near 0.01 of the mixture (Figure 15) indicating another shift in the critical temperature to below 10°C with critical compositions containing very high compositions of water (> 90 wt% of water).

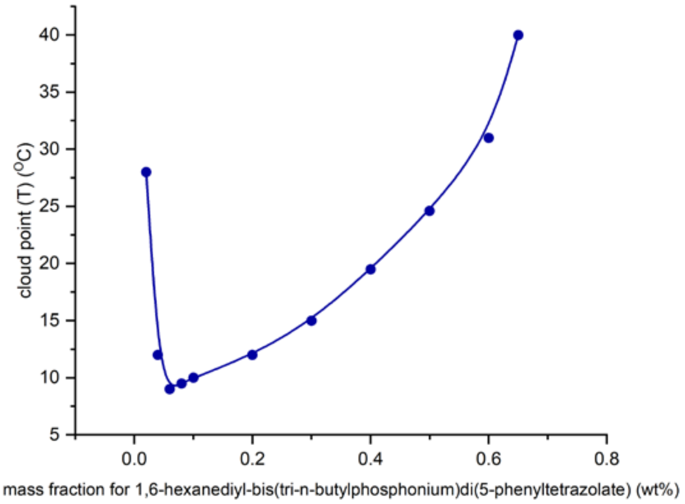


Figure 3 - Temperature-composition phase diagram for mass fraction of the dicationic ionic liquid.

4. Participated in the 28th EUCHEMSIL conference in Greece, from 5th to 10th June 2022 by presenting a poster titled, “LCST behaviour of functionalized tetrabutylphosphonium phenyl tetrazolate/aqueous mixtures”.

5. Synthesis of a dicationic ionic liquid, 1,8-octanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) for testing its phase behaviour: 9.8g of already prepared 1,6-hexanediyl-bis(tri-n-butyl phosphonium)dibromide was dissolved in sodium tetrazolate solution in water and was allowed to stir for 2 hours (until phase separation) at a temperature of 60 degrees.

6. The prepared dicationic ionic liquid, 1,8-octanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) was studied for its phase behaviour (LLE behaviour) using the instrument crystal16. It was observed that for all the compositions biphase was formed both during the heating and cooling periods in the cycle.

7. Appeared for the second milestone, differentiation on the 29th of June 2022.

Conclusions and future work

1. Synthesis of ionic liquids and LCST behaviour of them in water has been initiated and study of systems containing (i) anion modification and (ii) cation modification, both demonstrating how critical temperature and hydrophilicity can be modified.

2. Preliminary studies on the effect of salinity on critical temperature has been carried out.

3. Systematic screening of the substituted phenyltetrazoles will be carried out for their LLE behaviour of the corresponding prepared ionic liquids (monocationic and dicationic).

4. Cation-development: cations other than tetrabutylphosphonium will be developed and studied for their effect on LLE behaviour in terms of critical points, hydrophilicity index, etc

5. Assessment of the ‘pre-requisites’ for an IL to behave as an efficient draw solute for FO, like the osmotic pressure, viscosity, and development of strategies to implement these within materials (for example, addition of hydrophilic groups to enhance water flux, etc) along with measuring the water osmotic pressures.

6. Screening of the LLE behaviour with water using COSMOtherm will be carried out.

QUILL Quarterly Report

May 2022 – July 2022

Name:	David McAreavey		
Supervisor(s):	Dr Stephen Glover, Dr Oana Istrate and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	October 2021	**Anticipated end date:**	October 2024
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 an IC vehicle will ignite 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

In the most recent quarter, the project passed through the differentiation gateway requiring both a project write-up, presentation and Q&A session with a panel. As such the amount of modelling and number of additional outputs achieved was reduced in comparison to the period pervious, as more time was dedicated to writeup and consolidation of the work already completed. A small number of additional simulations were run looking at the effect of PCMs on the thermal management. These have highlighted some concerns surrounding the negative effect the low thermal conductivity can have on thermal management of the system. In an ideal scenario there should be harmony between the function of thermal management and runaway prevention, without one being detrimental to the other. As such the scope of the project has been widened to also consider liquid gas PCMs, this is not to say that solid liquid PCMs have been ruled out entirely, there are still a number of other simulations to be run to fully evaluate this avenue. This will include other materials such as phase change composites as well as other initiation types, such as cell puncture and physical abuse, with the majority of the simulations to date having used thermal abuse ignition which is among the most violent initiation types.

After completion of differentiation the focus was shifted to looking at addressing the feedback provided. The primary addition to the project the panel wanted to see was the inclusion of chemical kinetics in the modelling being undertaken. This would be as a means of ensuring that the heat generation of the cells under abuse conditions were accurately modelled, as well as making sure the project contained the required depth to be worthy of a doctorate at its completion. To date the modelling had used the temperature profiles from literature, and so these profiles were not coupled to the rate of reaction, which is reliant on the temperature meaning it was not a perfect representation of the physical event. In an ideal scenario the heat generated by both the trigger cell and any subsequent cell that exhibits heat generation, would include a mechanism by which the rate of heat generated by thermal decomposition reaction, would be influenced by the rate of reaction and in turn the heat being conducted into it from its surroundings. The difficulty occurs from the fact that its awkward to include this mechanism in the trigger cell, as it will be highly dependent on the initiation type. At present a working knowledge of the current state of the art is being developed in the area of chemical kinetics modelling, but the exact method by which this will be applied is still unclear. The majority of the literature reviewed to date has used experimental work in the form of either ARC or DSC results, that mean the modelling constants required can be calculated or estimated which is not currently an option for this project. As such the modelling will likely have to be built upon the constants or modelling efforts of others in the field that have already been validated.

Conclusions and future work

The project passed through the differentiation gateway with the project graded as a level one. There is additional modelling to be carried out to conclusively decide if the project should follow the avenue of solid liquid PCMs or potentially liquid gas PCMs. The modelling of liquid gas PCMs will require additional model development to include the heat rejection modes. Additionally, before this stage the model requires the development of a mechanism to best model the effect on the reaction rate based on the heat being generated and rejected from the system. This will have to be weighed up against the time demand of implementing it along with it being adequately well proven.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Sam McCalmont		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Margarida Costa Gomes		
Position:	PhD Student		
Start date:	January 2020	**Anticipated end date:**	June 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 chemisorbents based on measurement of gas solubility and partitioning from model industrial gas stream compositions and conditions

Progress to date

During the last three months, among my studies I have had the opportunity to complete a research visit to ENS de Lyon as part of collaboration with Prof Margarida Costa Gomes. Apart of this trip was to increase my skill set using different techniques involving the use of calorimetry, which allows for the change in heat of a system to be monitored.

This trip started the initial research into the project to study the effect of mixing ionic liquids. Calorimetry would determine if the mixing of the ionic liquids is favourable or non-favourable and determine if this would help explain what potential the mixing of ionic liquids would have for ethylene and ethane solubility and the separation of the gases. The ionic liquids apart of this mixture are butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ([$C_4{}^4$CNPy][NTf_2])

and 1-butyl-4-imidiazolium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Im][NTf_2]$). Also, during these last three months, I had the opportunity to attend EuChemsil 2022, and progress with other work in QUB.

From what has been learnt so far is that the use of the cyanopyridinium has not improved stronger interactions being involved as possibly thought. The interactions between the gases and the ionic liquid have focused on physisorption interactions. In theory, there was two modes of association proposed for ethylene. The inclusion of the cyanide group promoting the separation (in favour for ethylene) and in the addition of the cyanide group acting as an electron withdrawing group to the pyridinium ring to help promote affinity for electron rich π systems.[3,4]

Mixture of ionic liquids (mixture of protic ionic liquids for 1-ethylimidazolium nitrate and propylamine nitrate for example) has been tested for ethylene and ethane absorption, and the mixture has shown to increase the selectivity towards ethylene compared to that of using the individual ionic liquids.[5] In the same article, silver is also incorporated into the mixture of ionic liquids to increase the selectivity towards ethylene.

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 main experimental plan was using calorimetry to determine the enthalpy of mixing between the $[C_4{}^4CNPy][NTf_2]$ and $[C_4C_1Im][NTf_2]$ to determine if favourable or unfavourable mixing of the ionic liquid occurs. In terms of what was completed in the research visit was initial physical properties such as density (figure 1) and viscosity (figure 2) of different compositions of the mixture. Figure 1 shows the range of densities from the more viscous $[C_4{}^4CNPy][NTf_2]$ to the less viscous $[C_4C_1Im][NTf_2]$.

The densities of the mixed $[C_4{}^4CNPy][NTf_2]$ and $[C_4C_1Im][NTf_2]$ can then be used to determine the excess molar volume. This can show if the mixture expands, or contracts compared to what is expected ideally. In terms of the viscosity, the cyanopyridinium ionic liquid is more viscous than that of $[C_4C_1Im][NTf_2]$. Both ionic liquids contain a butyl alkyl chain and share a common anion. From this, the pyridinium ring with the nitrile group attached produces strong electrostatic attraction (the nitrile group being a strong electron withdrawing group, creating strong dipole-dipole interactions) than that of the imidazolium ring system.

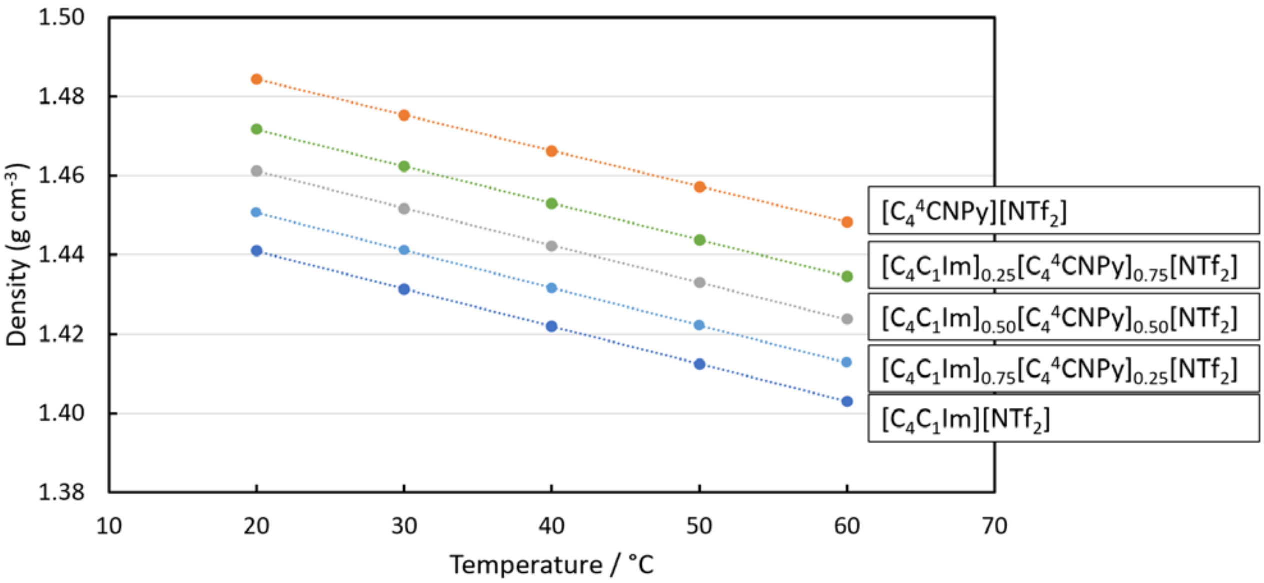


Figure 1 - The densities of the pure $[C_4{}^4CNPy][NTf_2]$ and $[C_4C_1Im][NTf_2]$, and their mixtures at different compositions in terms of mole fraction between temperatures of 20 °C and 60 °C. ($[C_4C_1Im]_x[C_4{}^4CNPy]_{(1-x)}[NTf_2]$)

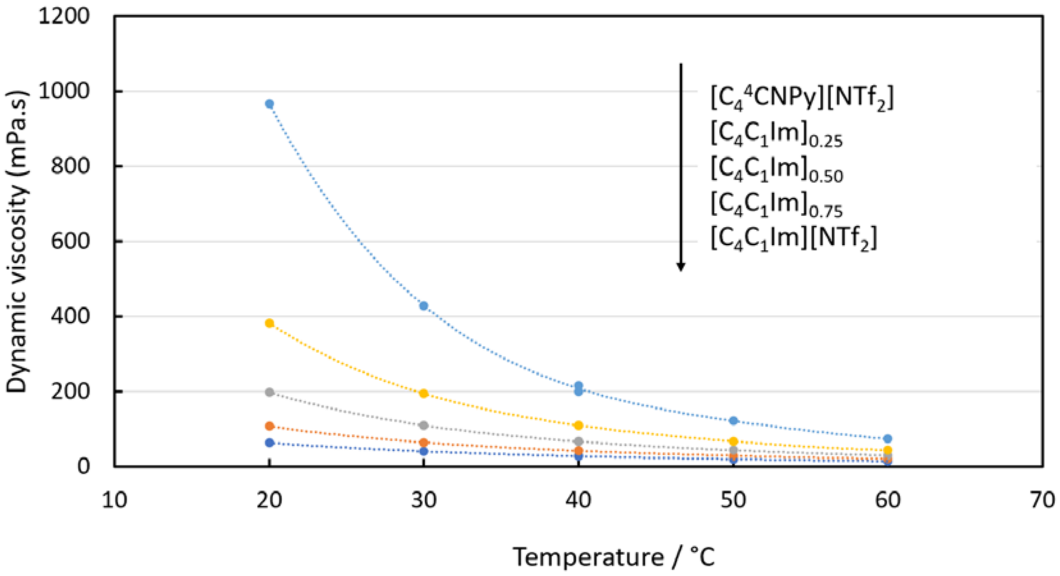


Figure 2 - The viscosity of the pure $[C_4{}^4CNPy][NTf_2]$ and $[C_4C_1Im][NTf_2]$, and their mixtures at different compositions in terms of mole fraction between temperatures of 20 °C and 60 °C. ($[C_4C_1Im]_x[C_4{}^4CNPy]_{(1-x)}[NTf_2]$)

During the initial findings, the excess molar volume of the mixture increased (the mixture expanded from what was expected from ideality). This would indicate an increase possibility in more free volume available. This in turn could possibly increase volume for more gas to be absorbed and indicate no favourable interactions between the two ionic liquids. The enthalpy of mixing produces a positive enthalpy value indicating that external energy is required for the mixing of the ionic liquids (*i.e.* entropy). The enthalpy of mixing of the ionic liquids is close to the ideal system (low values of enthalpy of mixing).

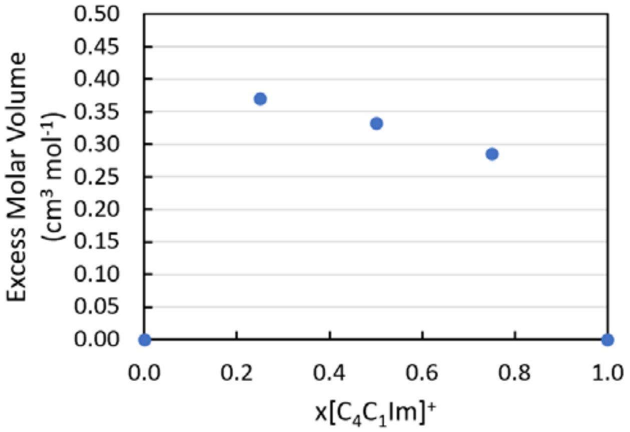


Figure 3 - The excess molar volume of calculated at different compositions of $[C_4{}^4CNPy][NTf_2]$ and $[C_4C_1Im][NTf_2]$ ($[C_4C_1Im]_x[C_4{}^4CNPy]_{(1-x)}[NTf_2]$)

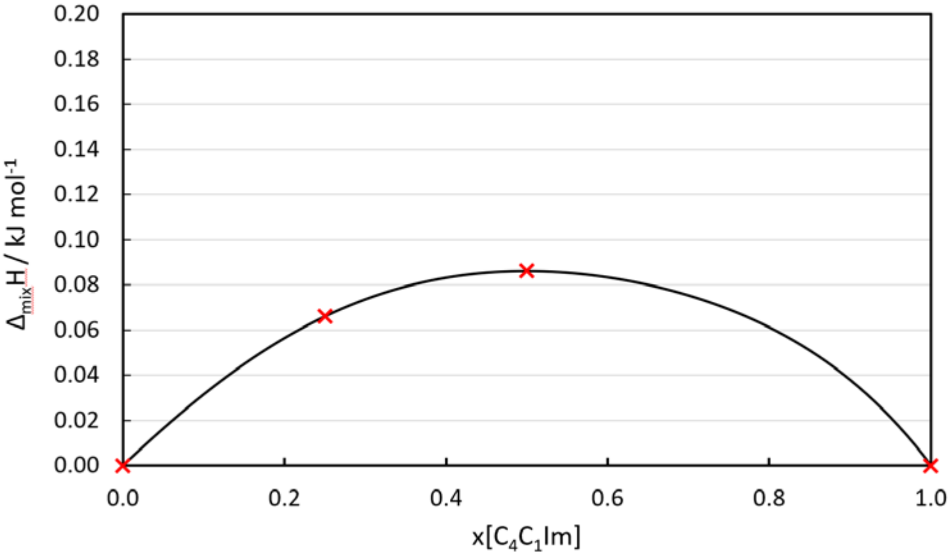


Figure 4 - The excess enthalpy of mixing of $[C_4C_1Im]_x[C_4{}^4CNPy]_{(1-x)}[NTf_2]$. The red crosses represent compositions tested.

In relation to other work completed, June was occupied mostly with the attendance of Euchemsil 2022 and preparation for the visit to ENS Lyon. In terms of other work completed over the last three months, further investigation into trying different materials for the ethylene and ethane uptake to understand a potentially more favourable material for preferential solubility of ethylene. One material that was investigated was the use of adiponitrile. Adiponitrile is butyl chain with nitrile groups at both ends of the molecule ($(CH_2)_4(CN)_2$). The purpose of this test is to see if what is seen in terms of the ionic liquids for ethylene and ethane uptake (*i.e.* alkyl chains for solubility of the gases and nitrile groups for the separation potential) can be reciprocated, and see if the trends can be seen in other non-ionic liquids. What has been seen so far in figure 5 (only ethylene tests completed) is that ethylene solubility is similar to the test standard of $[C_4C_1Im][NTf_2]$. This would bring benefits such as no requirement for the synthesis of ionic liquids and decrease the cost of manufacture. What is still required is the ethane tests, and going into the future investigate the potential mixing of the adiponitrile with ionic liquids, and also similar molecules to adiponitrile.

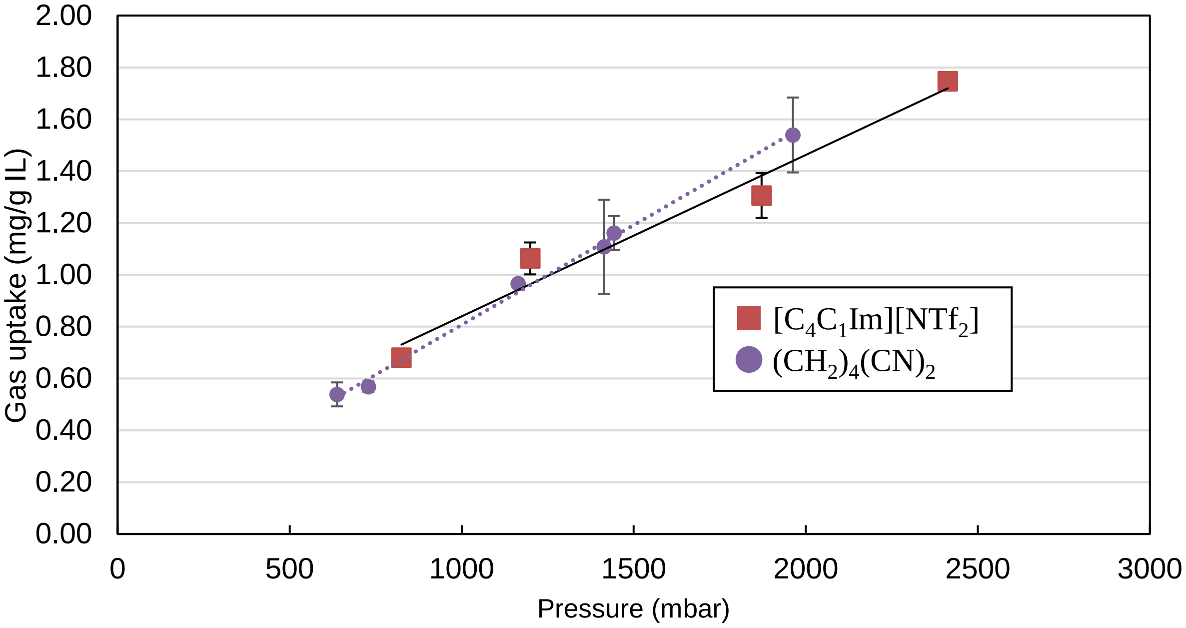


Figure 5 - The uptake of ethylene for $[C_4C_1Im][NTf_2]$ and adiponitrile $(CH_2)_4(CN)_2$.

An analogue of ionic liquids are also being investigated, and that is low melting mixtures/deep eutectic solvents (DES) (figure 6). One DES tested to date is that of TOPO (trioctylphosphine oxide):$FeCl_3$, and what was found before was the uptake of ethylene was greater in this DES than that of the standard $[C_4C_1Im][NTf_2]$. However, what was interesting was if the iron was having an effect or if it was the inclusion of TOPO (long alkyl chains, known to have influence on the solubility of ethylene and ethane). A second DES tested was TOPO:Lev (levulinic acid), and what has been found so far is the ethylene solubility is greater than that of TOPO: $FeCl_3$ (and in turn $[C_4C_1Im][NTf_2]$), perhaps suggesting the iron centre had no favourable impact on the solubility of ethylene. Tests are still on going.

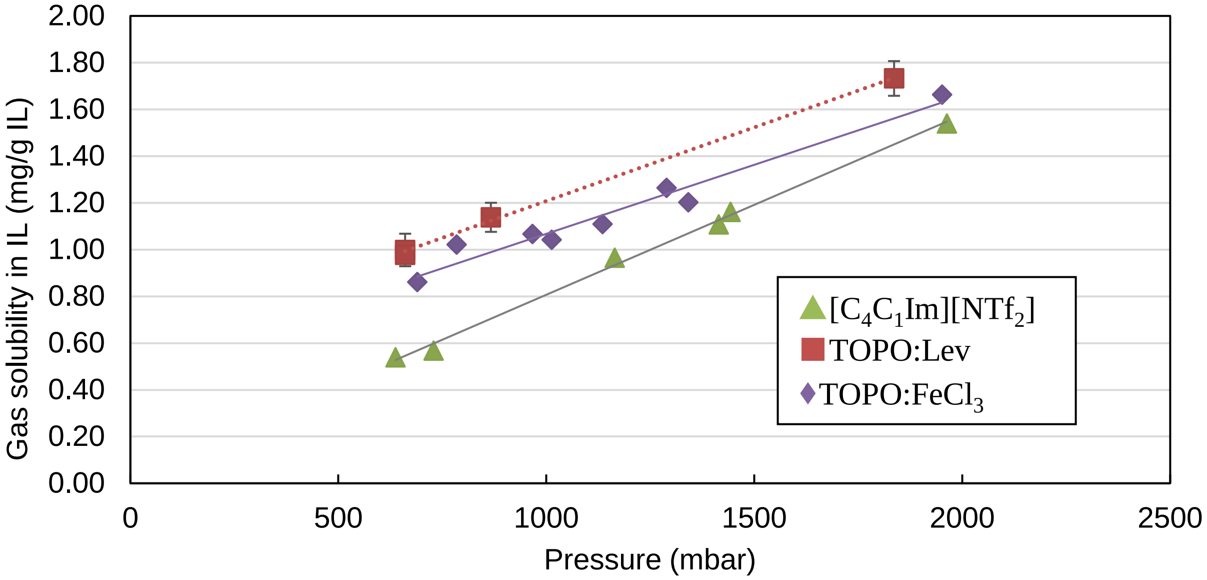


Figure 6 - The ethylene uptake of ethylene for [C_4C_1Im][NTf_2], TOPO:Lev and TOPO:$FeCl_3$

Conclusions and future work

In terms of the mixture of ionic liquids, the solubility of ethylene and ethane will be determined in the different compositions of [$C_4{}^4$CNPy][NTf_2] and [C_4C_1Im][NTf_2] and to determine if there is any trend, at all between, the excess molar volume and enthalpy of mixing, and that of the solubility. Low mixing mixtures / deep eutectic solvents will also be investigated further, and with introducing metal salts into these DES (to see if any preferential solubility compared to that of the IL studies) to see if any chemisorption can be detected for ethylene and ethane.

References

1. D. S. Sholl and R. P. Lively, *Nature*, 2016, 532, 435–437.
2. L. Moura, C. C. Santini and M. F. Costa Gomes, *Oil Gas Sci. Technol. – Rev. d'IFP Energies Nouv.*, 2016, **71**, 23.
3. L. Moura, W. Darwich, C. C. Santini and M. F. Costa Gomes, *Chem. Eng. J.*, 2015, **280**, 755–762.
4. C. Hardacre, J. D. Holbrey, C. L. Mullan, M. Nieuwenhuyzen, T. G. A. Youngs, D. T. Bowron and S. J. Teat, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1842–1853.
5. M. Xu, B. Jiang, H. Dou, N. Yang, X. Xiao, X. Tantai, Y. Sun and L. Zhang, *J. Memb. Sci.,* 2021, 639, 119773

QUILL Quarterly Report

May 2022 – July 2022

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadzba-Kwasny and Prof John Holbrey		
Position:	PhD student		
Start date:	September 2021	**Anticipated end date:**	October 2024
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. (Fig 1.)

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.

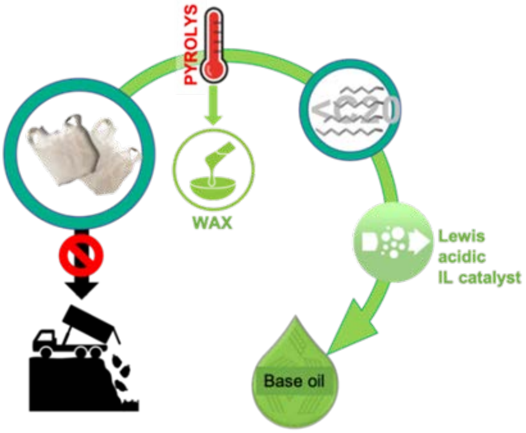


Figure 1 - Circular economy cradle to cradle approach

Objective of this work

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

Progress to date

The removal of impurities has been the focus to date by using additives and liquid-liquid extraction followed by analyses by XRF. The additive (10 wt %) and feedstock (5 g) was added to a vial and stirred overnight. Water was then added, and the aqueous layer removed, and the top layer analysed by XRF. The results were compared to the untreated feedstock to analyse which additive achieved the best results.

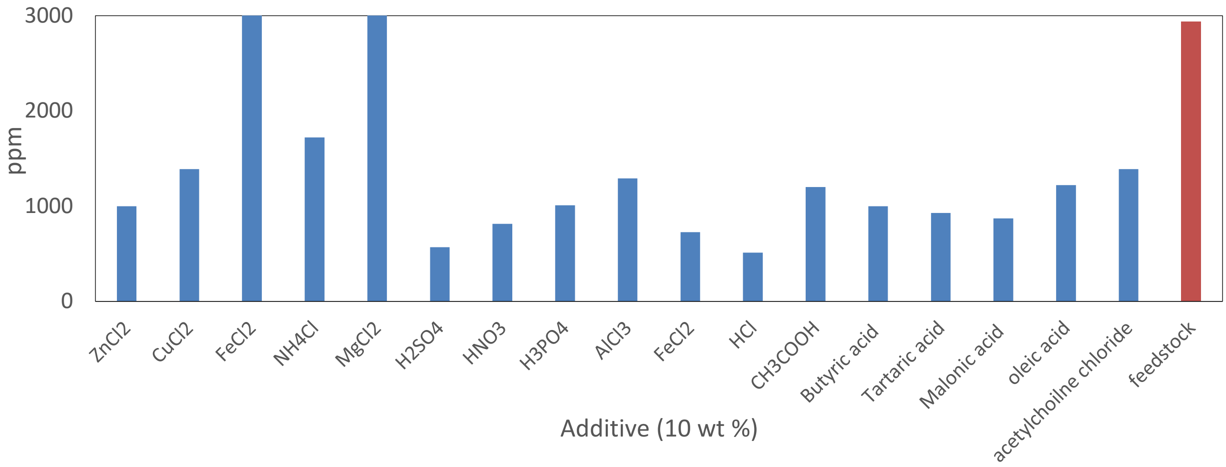


Figure 2 - Removal of Si

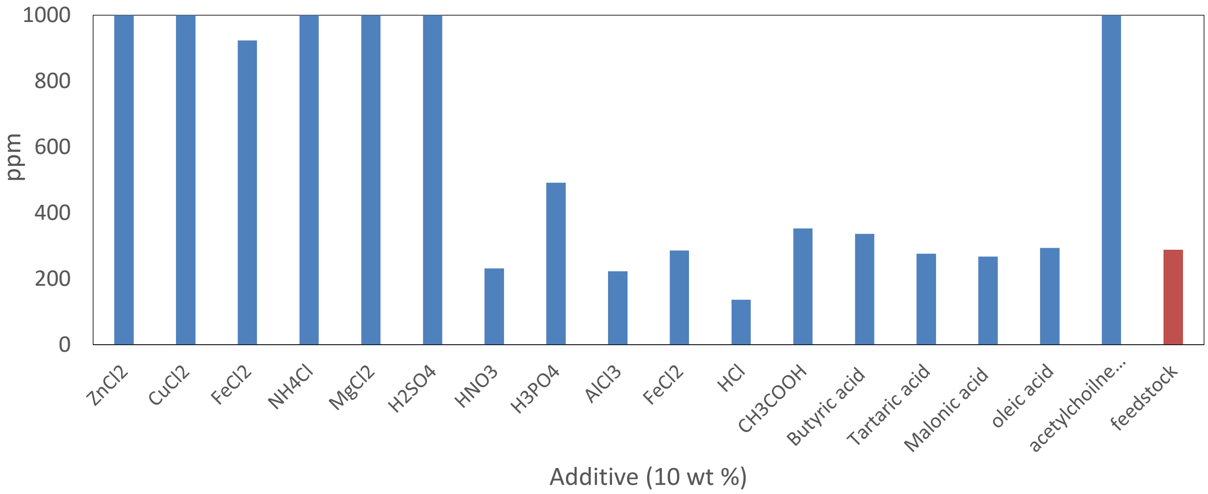


Figure 3 - Removal of S

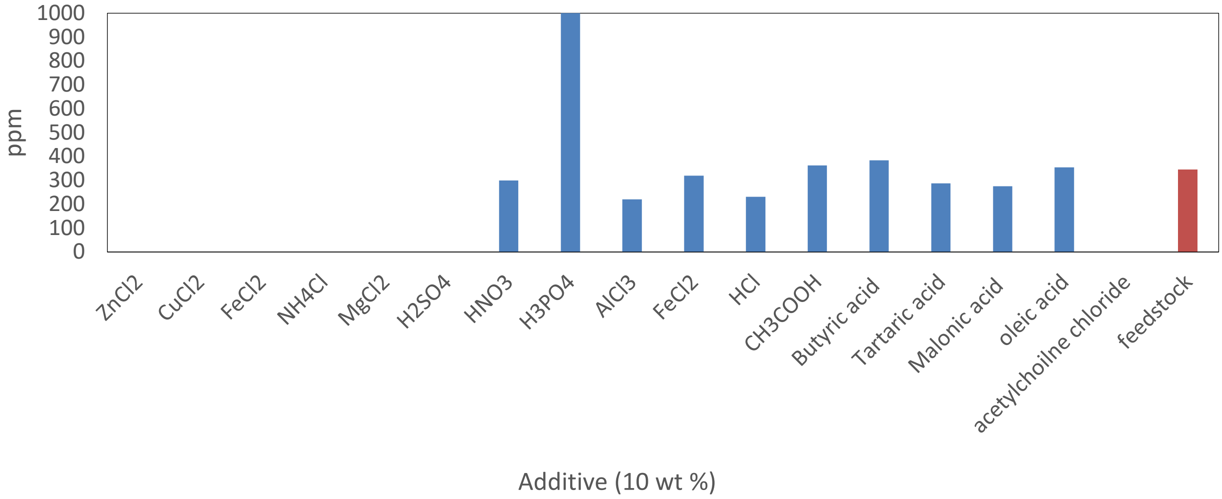


Figure 4 - Removal of P

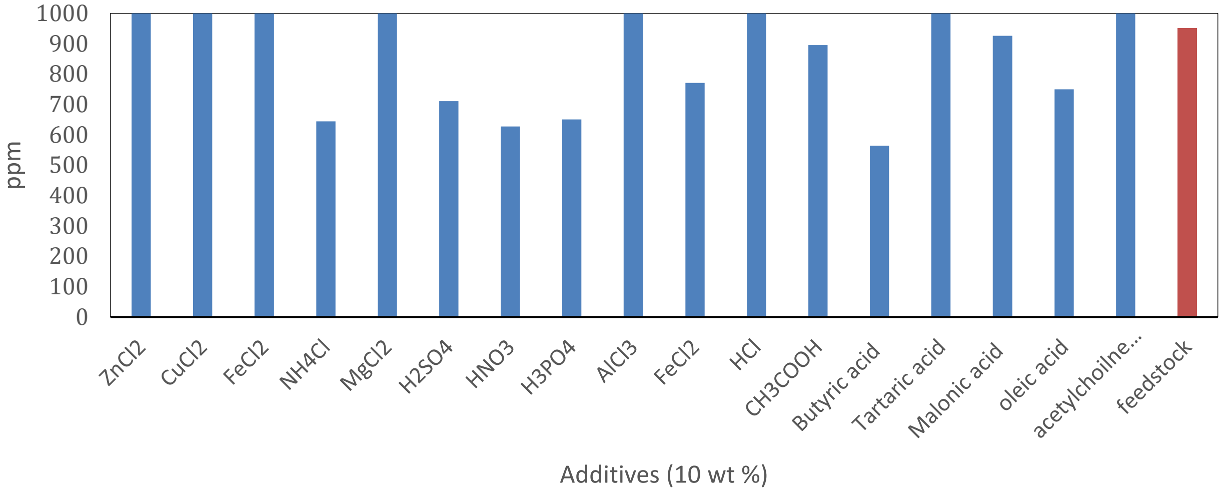


Figure 5 - Removal of Cl

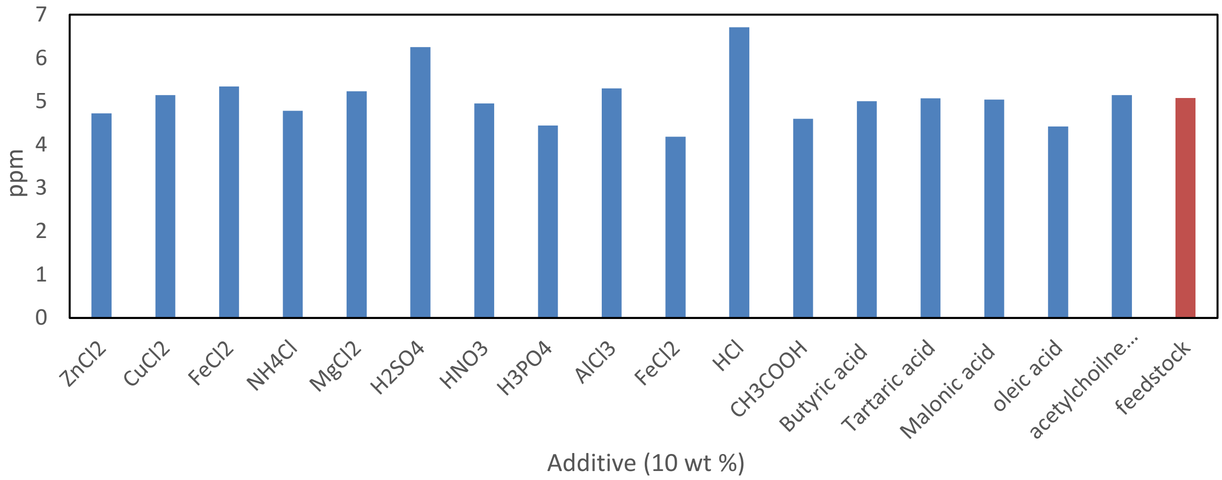


Figure 6 - Removal of Br

Conclusions and future work

The results show that a multistep approach is needed as additives such as $ZnCl_2$ removes phosphorus impurities however increases sulfur impurities, while HCl removes sulfur impurities. There is no change in bromine or chlorine impurities. The next step is to optimise a method to remove impurities with the best performing additives and include several washings to produce a pH neutral feedstock. Once this is complete, liquid coordination complexes and borenium ionic liquids catalyst will be used for the oligomerisation of the feedstock.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Anne McGrogan		
Supervisor(s):	Professor Gosia Swadźba-Kwaśny		
Position:	PhD Student		
Start date:	October 2019	**Anticipated end date:**	June 2023
Funding body:	EPSRC		

Liquid-Liquid Transition in Phosphonium Ionic Liquids

Background

This project was a collaboration with Zaneta Wojnarowska from University of Silesia, Katowice. The work investigates first-order liquid-liquid transition (LLT) in a series of ionic liquids containing trihexyl(tetradecyl)phosphonium cation $[P_{66614}]^+$ and anions of different sizes and shapes, providing an insight into the structure-property relationships governing LLT. My involvement in this work was the synthesis of some ionic liquids. $[P_{66614}][NTf_2]$ exhibits a clear LLT and this ionic liquid was selected to study its liquid structure above and below LLT by neutron scattering. This work will describe the synthesis of deuterated $[P_{66614}][NTf_2]$ and its liquid structure by neuron scattering and analysis of the data using DISSOLVE software.

When isotropic liquid is cooled below its melting point, it either crystallises, or enters a metastable supercooled state, which turns into a non-equilibrium amorphous phase (glass). However, a few single-component materials exhibit yet another behaviour, undergoing a first-order liquid-liquid transition (LLT). LLTs separate fluids of different local structures, density and thermodynamic properties. They have been detected in various media, from atomic elements (sulfur, phosphorus,[1] silicon,[2,3] carbon[4]) to molten oxides.[5,6,7] Only four room temperature molecular liquids exhibit LLT: water,[8,9] triphenyl phosphate,[10,11,12] *n*-butanol[10] and D-mannitol.[13] Nevertheless, LLT in these systems remains controversial, since it occurs in the supercooled state capable of cold crystallisation.[14] Furthermore, very little is known about the effect of molecular packing on LLT, except for a few simple cases.[15,16] Consequently, critical factors inducing such a transition are unclear. The first evidence of LLT in aprotic ionic liquids (ILs) was reported in 2021 for trihexyl(tetradecyl)phosphonium tetrahydroborate, $[P_{666,14}][BH_4]$.[17] Upon the transition, the IL was reported to undergo enhanced ordering of the alkyl chains in the nonpolar domains, as inferred from calorimetric, XRD and IR spectroscopy data. This work inspired our own systematic investigation into LLTs in $[P_{66614}]^+$ ionic liquids based on six anions: $[BF_4]^-$, $[SCN]^-$, $[TAU]^-$, $[TFSI]^-$ $[BOB]^-$ and $[TCM]^-$. $[P_{66614}][BF_4]$ crystallised from supercooled melt, $[P_{66614}][BOB]$ underwent a glass transition, and the four remaining samples exhibited LLT in a differential scanning calorimetry (DSC) experiment. In addition to calorimetric proof of LLT *via* DSC, the phase change was detected by the measurement of conductivity relaxation times, both under isobaric cooling and under isothermal compression up to 500 MPa. This work has been published in *Nature Commun.*[18]

The next stage of this work is to synthesise deuterated [P_{66614}][NTf_2] to study its structure by neutron scattering. Neutron diffraction is a highly effective technique for observing structures in the liquid state. Hydrogen/deuterium substitution is a crucial and very powerful tool in neutron diffractionexperiments. While X-ray scattering of each atom is dependent on the atomic number (Z), inneutron scattering the incident beam interacts with the nucleus of the atoms. Owing to the differences in the sign of the coherent scattering between 1H and 2H (-3.74 fm and 6.67 fm), the comparison of the data recorded from the isotopically substituted systems is a very useful tool in computer simulations.[19] Furthermore, although 1H scatters best, it provides a lot of inelastic scattering which detracts from overall data quality. Therefore, for neutron scattering measurements, it is most beneficial to study both protiated and deuterated analogues of the species of interest, in addition to equimolar mixtures for best data quality.

Objective of this work

To synthesise deuterated [P_{66614}][NTf_2] and to study its liquid structure above and below LLT by neutron scattering using DISSOLVE software.

Progress to date

Synthesis of deuterated [P_{66614}][NTf_2]

The protiated [P_{66614}][NTf_2] was studied by neutron scattering at the ISIS neutron and muon source at the Rutherford Appleton Laboratory, Oxfordshire in May. I have also been trying out different methods of synthesising the deuterated version as detailed below.

Firstly, the direct deuteration of [P_{66614}]$^+$ was attempted:

5 g of $P_{66614}Cl$, with 0.5 g NaOH and 0.25 g Pt/C and 50 ml D_2O was added to a 100 mL parr reactor body (made of Hastelloy c276) and after sealing, the reactor was charged with a pressure of nitrogen (40-50 bar). The reactor was then heated to 180 ^oC using the Parr heating mantle and stirred (using the mechanical stirrer) at 600 RPM for 3 days. Four subsequent cycles with fresh D_2O were performed. After cooling the reactor to room temperature, the mixture was filtered through Celite to remove the catalyst, which was further washed with methanol. ^1H, ^2D, ^{13}C and ^{31}P NMR was recorded. Mass spec showed that 8 hydrogens (four P–CH_2 protons) of the 68 were deuterated.

As this was not a sufficient level of deuteration, another method was attempted starting from PCl_3 and the deuterated alcohols.

Method from PCl_3:

Firstly, deuterated hexanol and tetradecanol were converted to the chlorides.

$P_{66614}Cl$: Magnesium turnings (0.54 g, 1.2 eq.) was transferred into an oven-dried two-necked round-bottomed flask (100 cm^3) equipped with a reflux condenser with argon gas inlet, a septum and a stirring bar. Then, anhydrous diethyl ether (10 cm^3) was added, followed by a crystal of iodine, and the flask was heated to 30 °C. Subsequently, a small portion of 1-chlorohexane (2.5 g, 1 eq.) was added dropwise. After approximately 50% was added, a spontaneous reaction ensued as evidenced by the disappearance of the yellow iodine colour, the appearance of a grey colour in the reaction solution, and the commencement of gentle refluxing. The remainder of the solution was added and the reaction was allowed to proceed (35 °C, overnight), before being cooled back to room temperature.

In another oven-dried two-necked round-bottomed flask (100 cm^3), equipped with a stirring bar and connected to an argon Schlenk line, phosphorus trichloride (0.51 g, 12.35 mmol), with lithium bromide (0.03 g, 1.24 mmol) and copper(I) iodide (0.07 g, 1.24 mmol) were added to degassed, dry diethyl ether (15 cm^3). The flask was placed on a heater stirrer equipped with an acetone-dry ice bath (-78 °C), and the mixture was allowed to cool with vigorous stirring.

The solution of the Grignard reagent was transferred *via* a cannula filter into the PCl_3 solution, and stirred at -78 °C. The dry ice-acetone bath was then removed, and the reaction mixture was brought to ambient temperature and left to react for a further 2 h with vigorous stirring on reaching this temperature. The solvent was removed under reduced pressure (25 °C, 10^{-2} bar) and the product was dissolved in pentane (25 cm^3). Degassed water (25 cm^3) was subsequently added, and the flask was vigorously shaken by hand, the organic layer was removed *via* cannula transfer into an oven dried flask (100 cm^3) and again washed with degassed water (25.0 cm^3). This was transferred *via* cannula into an oven dried flask (100 cm^3). Finally, the organic phase was dried using sodium sulfate and the liquid phase was transferred *via* cannula filtration into an oven dried flask (100 cm^3). The solvent was removed under reduced pressure in an ice bath (0 °C, 10^{-2} bar), to give a colourless liquid.

The next step was the alkylation to form $P_{66614}Cl$. 1-chlorotetradecane (1.3 eq.) was added to the flask in acetonitrile and heated to reflux (60 °C) under argon for 2 weeks. Analysis ongoing.

Conclusions and future work

Future work involves completing the synthesis and attending beamtime to study the structure of deuterated and partially deuterated $[P_{66614}][NTf_2]$. Then, analysis of the data using DISSOLVE software.

References

1. Y. Katayama, T. Mizutani, W. Utsumi and O. Shimomura, 2000, **403**, 1998–2001.
2. V. V. Vasisht and S. Sastry, *Adv. Chem. Phys.*, 2013, **152**, 463–517.
3. D. J. Superconductivity, R. D. M. Dekker, N. York, I. Saika-voivod, P. H. Poole and F. Sciortino, 2001, **412**, 1–4.
4. J. N. Glosli and F. H. Ree, *Phys. Rev. Lett.*, 1999, **82**, 4659–4662.
5. W. Xu, M. T. Sandor, Y. Yu, H. B. Ke, H. P. Zhang, M. Z. Li, W. H. Wang, L. Liu and Y. Wu, *Nat. Commun.*, 2015, **6**, 1–9.
6. G. N. Greaves, M. C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox, Q. Vu Van, O. Majérus, C. J. Benmore, R. Weber, C. M. Martin and L. Hennet, *Science (80-.).*, 2008, **322**, 566–570.
7. S. Wei, F. Yang, J. Bednarcik, I. Kaban, O. Shuleshova, A. Meyer and R. Busch, *Nat. Commun.*
8. C. A. Angell and P. D. Bennett, *J. Am. Chem. Soc.*, 1982, **104**, 6304–6309.
9. I. Kaori, M. CT and C. Angell, *Nature*, 1999, **398**, 492–495.
10. R. Kurita and H. Tanaka, *J. Phys. Condens. Matter*,
11. R. Kurita and H. Tanaka, *Science (80-.).*, 2004, **306**, 845–848.
12. M. Kobayashi and H. Tanaka, *Nat. Commun.*, 2016, **7**, 1–8.
13. M. Zhu, J. Q. Wang, J. H. Perepezko and L. Yu, *J. Chem. Phys.*, , DOI:10.1063/1.4922543.
14. H. Tanaka, *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000,

62, 6968–6976.

15. Q. S. Zeng, Y. Ding, W. L. Mao, W. Yang, S. V. Sinogeikin, J. Shu, H. K. Mao and J. Z. Jiang, *Phys. Rev. Lett.*, 2010, **104**, 1–4.
16. L. Liu, S. H. Chen, A. Faraone, C. W. Yen and C. Y. Mou, *Phys. Rev. Lett.*, 2005, **95**, 1–4.
17. M. A. Harris, T. Kinsey, D. V. Wagle, G. A. Baker and J. Sangoro, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**, 1–6.
18. Z. Wojnarowska, S. Cheng, B. Yao, M. Swadzba-Kwasny, S. McLaughlin, A. McGrogan, Y. Delavoux and M. Paluch, *Nat. Commun.*, 2022, **13**, 1–10.
19. V. F. Sears, *Neutron News*, 1992, **3**, 26–37.

QUILL Quarterly Report

May 2022 – July 2022

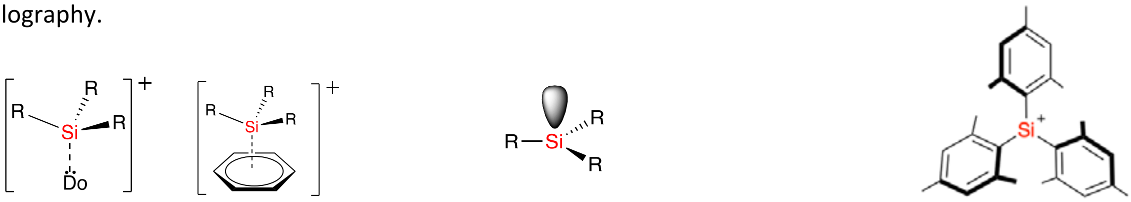
Name:	Shannon McLaughlin		
Supervisor(s):	Professor Gosia Swadźba-Kwaśny		
Position:	PhD Student (2nd year)		
Start date:	October 2020	**Anticipated end date:**	July 2024
Funding body:	Department for the Economy		

Thinking Inside the (Glove)Box: Lewis Superacidic Ionic Liquids Based on Main Group 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.



σ-Donor stabilised

π-Donor stabilised

'free' (unstabilised)

$[B(C_6F_5)]^-$

1

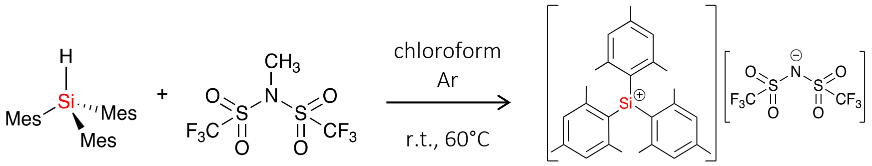
Figure 1 - a) Example structures of stabilised and unstabilised silylium ions. b) Structure of 'free' trimesitylsilylium cation.

Objective:

This work reports on the first-ever attempt to prepare and characterise silylium ionic liquids.

Alternative Synthetic Route:

Scheme 2 - Synthesis of trimesitylsilylium bis(trifluoromethanesulfonyl)imide $[(Mes)_3Si][NTf_2]$.



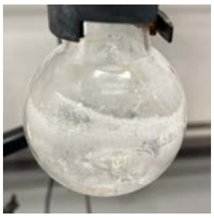


Figure 3 - $[(Mes)_3Si][NTf_2]$ crystals.

A novel synthetic route, illustrated in Scheme 2, was prosed to generate trimesitylsilylium bis(trifluoromethanesulfonyl)imide [$(Mes)_3Si$][NTf_2] (Figure 3). The trimesitylsilane starting material was synthesised following the method described previously by Lappert *et al.*[4] Trimesitylsilane was allowed to react with n-methyl bis[(trifluoromethyl)sulfonyl]imide (Me[NTf_2]) in chloroform and the resulting mixture was set to reflux at 50°C under argon for two days. The solvent was removed *via* rotary evaporation which left a pale-yellow viscous liquid. ^1H, ^{13}C and ^{29}Si NMRs of this liquid were ran in $CDCl_3$. The ^1H NMR (Figure 4) showed a peak at 5.78 ppm which confirmed that there was still some unreacted trimesitylsilane remaining. This peak is due to the hydrogen bonded directly to the silicon centre in trimesitylsilane, this signal should disappear once all the starting material has been converted to chlorotrimesitylsilane. This mixture was then dissolved in acetonitrile solvent and the solution was set to reflux at 60°C for a further 2 days. The new solvent was chosen due to its higher boiling point. This allowed the mixture to be refluxed at a higher temperature and helped drive the reaction to completion. When the new solvent was removed *via* rotary evaporation white crystals formed suggesting that an adduct had formed with the acetonitrile. ^1H, ^{13}C and ^{29}Si NMRs of these crystals were recorded in $CDCl_3$. NMRs confirmed the successful synthesis of trimesitylsilylium bis(trifluoromethanesulfonyl)imide [$(Mes)_3Si$][NTf_2].

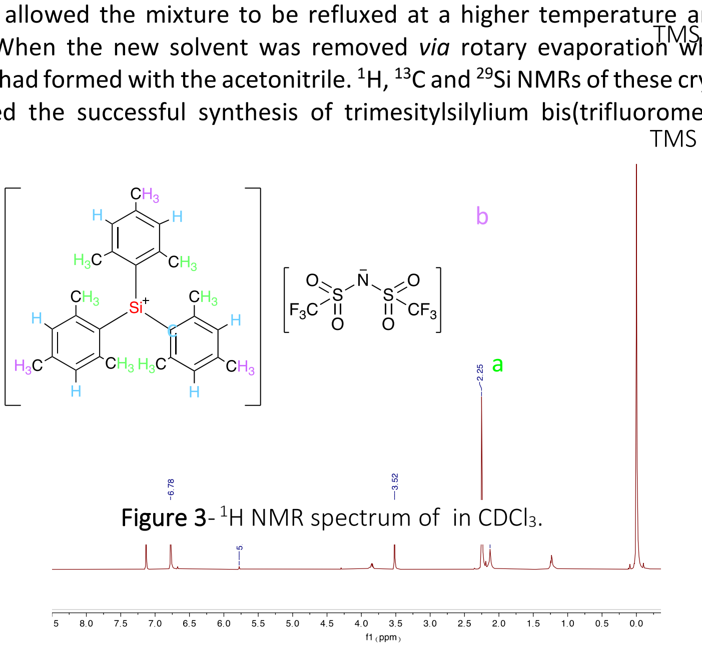


Figure 3- ^1H NMR spectrum of in $CDCl_3$.

Characteristic Studies:

The crystals of [$(Mes)_3Si$][NTf_2] obtained from the reaction in Scheme 2 were characterised using multiple analytical techniques, including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and single crystal x-ray diffraction (XRD).

Single Crystal X-ray Diffraction:

Variable temperature single crystal XRD was also used to help gain an insight into how the cations and anions pack together within the crystal structure. The unit and crystal structure cell are illustrated in Figure 5a and Figure 5b, respectively. The crystal 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.

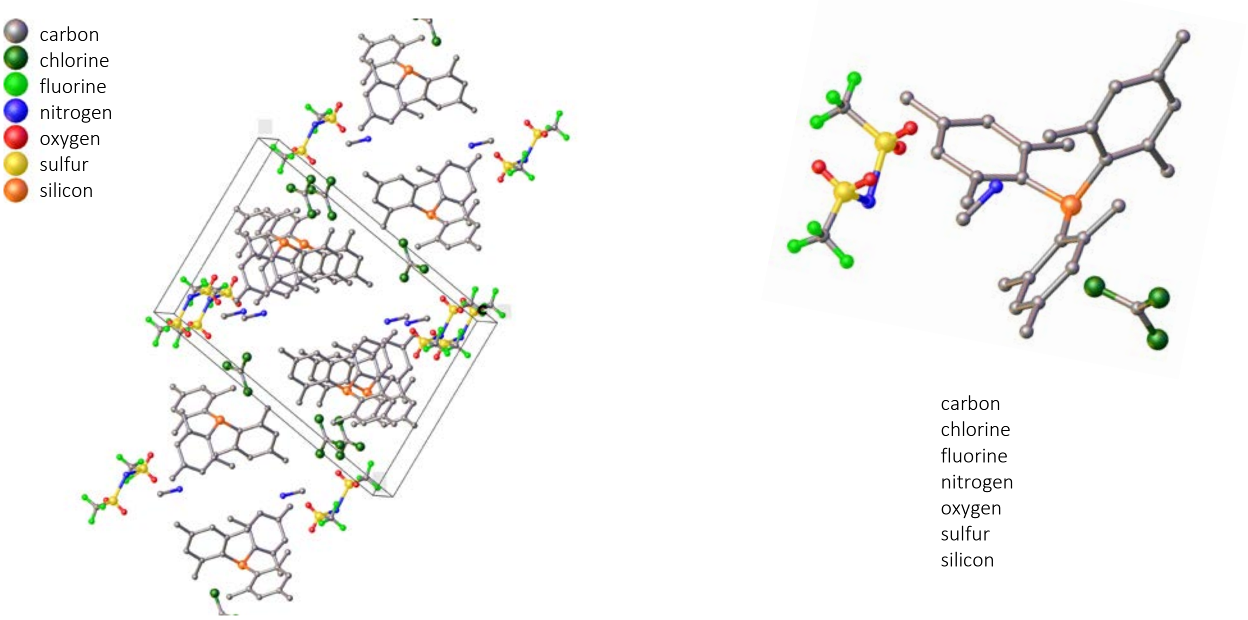


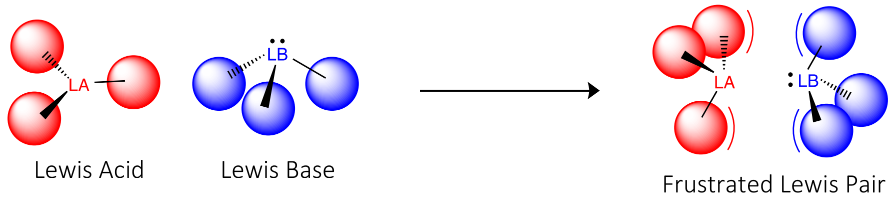
Figure 5- a) Unit cell of [$Si(Mes)_3$][NTf_2]. b) Crystal structure of [$Si(Mes)_3$][NTf_2].

Frustrated Lewis Pairs:

Background:

A Lewis acid is a chemical species that contains an empty orbital which is capable of accepting a pair of electrons from a Lewis base to form a Lewis adduct.[5] Frustrated Lewis pairs (FLPs) are compounds or mixtures containing a Lewis acid and a Lewis base that cannot combine to form a classical adduct due to steric hindrance (Scheme 3).[6-8] The close proximity of these free Lewis acidic and Lewis basic sites gives rise to interesting reactivity.

Scheme 3 - Formation of a sterically hindered FLP between a Lewis Acid and a Lewis Base.



FLP chemistry has helped to develop catalysts for metal-free hydroamination of alkynes[9] as well as the reduction of organic unsaturated subrates[10] and CO_2.[11] It has been used as a strategy to allow main group compounds to activate small molecules, including metal-free hydrogen splitting.[12]

Gas sensing:

Recent studies into room temperature ionic liquids (RTILs) have shown promise as potential air stable and non-volatile electrolytes for amperometric gas sensors.[13,14] A typical amperometric gas sensor consists of three electrodes connected through an electrolyte, which is covered by a gas-permeable membrane. The gas passes through the membrane, diffuses into the electrolyte and is detected at the working end of the electrode. This is illustrated in Figure 6.[14,15] The majority of commercially available amperometric gas sensors (O_2, CO, SO_2, H_2S, NO_2, Cl_2) use conventional solvents such as acetonitrile or H_2SO_4/H_2O mixtures. These sensors have extremely short 'lifetimes' as they can't operate effectively in extremely dry or humid conditions. They cannot survive drastic temperature changes as the electrolyte dries up and the solvent must be replaced, usually within a few days or weeks. Conversely, RTILs possess negligible volatility and have a high chemical stability. This makes them ideal electrolyte media for use in gas sensors that need to operate in more extreme operating conditions (<300 °C) as there is no chance of solvent evaporation or degradation. Advantageous properties of RTILs include their intrinsic conductivity (no need for supporting electrolyte), their wide potential windows (to investigate compounds that may have been inaccessible otherwise) and in a few cases, their increased gas solubility. Current research involves the use FLP/IL systems as potential electrolyte media for hydrogen detection.

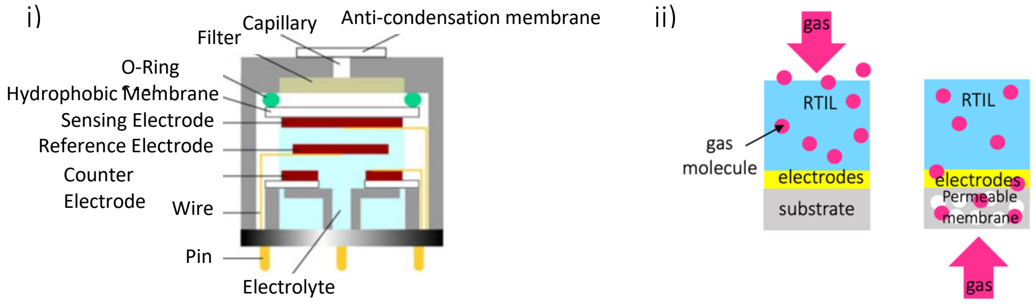


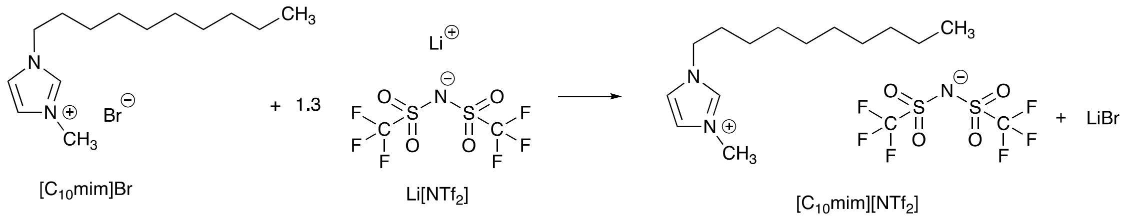
Figure 6 - Schematic diagrams of i) the structure of an amperometric gas sensor ii) diffusion of gas molecules from gas phase through IL to the electrode.

Objective:

Synthesise multiple FLP/IL to test their ability to split hydrogen. Systems which successfully activate hydrogen may have potential to be utilised as electrolyte media for amperometric gas sensors.

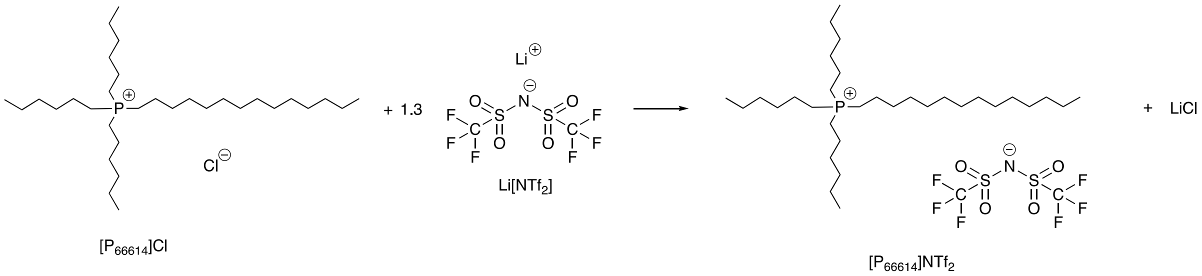
Synthesis of ionic liquids:

Scheme 4 - Synthesis of $[C_{10}mim][NTf_2]$.



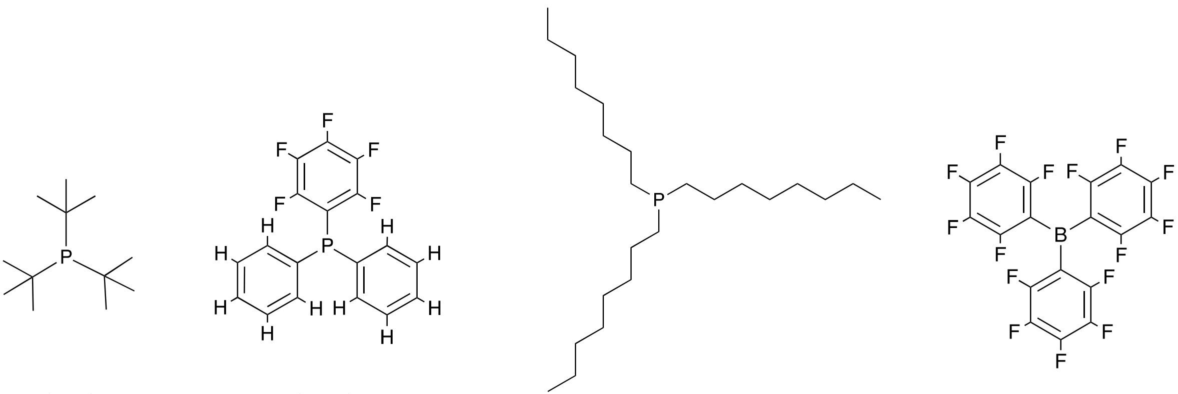
The synthesis of $[C_{10}mim][NTf_2]$ is illustrated in Scheme 4. $[C_{10}mim]Br$ (0.397 mol, 120.50 g) and $Li[NTf_2]$ (0.523 mol, 150.04 g) were separately dissolved in 400 mL of deionised water (total 800 mL) and then combined, resulting in the formation of a separate liquid phase. This was left to stir for 1 hour at room temperature. The aqueous layer was separated out and the organic layer was collected and washed. The first wash was with 100 mL of deionised water and 100 mL of dichloromethane (DCM). Fifteen subsequent washes were performed with deionised water. The solvent was removed *via* rotary evaporation at 35 °C which left a dark yellow viscous liquid. The product was dried overnight on the Schlenk line at a temperature of 70 °C. 172.59 g of $[C_{10}mim][NTf_2]$ was obtained giving a percentage yield of 86.30%.

Scheme 5 - Synthesis of $[P_{66614}][NTf_2]$.



The synthesis of $[P_{66614}][NTf_2]$ is illustrated in Scheme 5. Trihexyl(tetradecyl)phosphonium chloride $[P_{66614}]Cl$ (0.211 mol, 109.73 g) and $Li[NTf_2]$ (0.273 mol, 78.41 g) were separately dissolved in 250 mL deionised water (total 500 mL) and then combined, resulting in the formation of a separate liquid phase. This was left to stir for 1 hour at room temperature. The aqueous layer was separated out and the organic layer was collected and washed. The first wash was with 100 mL of deionised water and 100 mL of dichloromethane (DCM). Six subsequent washes were performed with deionised water (100 mL). The DCM solvent was removed *via* rotary evaporation at 35 °C and the ionic liquid was then dried overnight on the Schlenk line at 70 °C. This gave a colourless viscous liquid. 145.82 g of $[P_{66614}][NTf_2]$ was synthesised giving a percentage yield of 90.85%. ^1H, ^{13}C, ^{19}F and ^{31}P NMRs were taken of the ionic liquid in d_6-DMSO.

Future Work:
Future work will involve the synthesis and purification of 150 ml of $[C_2mim][NTf_2]$. The ionic liquids synthesised ($[C_2mim][NTf_2]$, $[C_{10}mim][NTf_2]$ and $[P_{66614}][NTf_2]$) will be used as solvents for various FLP systems to test their ability of to activate hydrogen. Deuterated benzene (d_6-benzene) will also be tested as a control solvent. Three sterically hindered phosphorus compounds, tri-*tert*-butylphosphine ($P(^tBu)_3$), trioctylphosphine (P_{888}) and diphenyl(pentafluorophenyl)phosphine ($P(C_6F_5)Ph_2$), were chosen to be investigated as potential FLP components along with tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). The structure of each compound is illustrated in Figure 7. Each phosphorus compound will be weighed into a glass vial and 1 mL of ionic liquid/d_6-benzene will be added using a syringe. 0.0820 g of $B(C_6F_5)_3$ will be added and the solution will be left to dissolve under stirring overnight. This will generate a 160 mmol solution of each FLP.



$P(tBu)_3$ $P(C_6F_5)Ph_2$ P_{888} $B(C_6F_5)_3$

Figure 7 - a) Structure of phosphorus compounds under investigation. b) Structure of tris(pentafluorophenyl)borane.

References:

1. K. C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin and J. B. Lambert, *Science.*, 2002, 297, 825–827.
2. J. B. Lambert and L. Lin, 2001, J. Org. Chem., 66, 8537–8539.
3. A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler and T. Müller, 2013, Organometallics, 32, 4713-4722.
4. M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Rivière and M. Rivière-Baudet, J. Organomet. Chem., 1980, 202, 5-12.
5. P. W. Atkins, T. L. Overton, J. P. Rourke and M. T. Weller, Shriver and Atkins' Inorganic Chemistry, Fifth Edition, 2010.
6. D. W. Stephan, J. Am. Chem. Soc., 2015.
7. D. W. Stephan and G. Erker, Angew. Chemie - Int. Ed., 2015, 54, 6400–6441.
8. D. W. Stephan, Acc. Chem. Res., 2015, 48, 306–316.
9. T. Mahdi and D. W. Stephan, Angew. Chemie - Int. Ed., 2013, 52, 12418–12421.
10. J. Lam, K. M. Szkop, E. Mosaferi and D. W. Stephan, Chem. Soc. Rev., 2019.
11. M. A. Courtemanche, M. A. Légaré, L. Maron and F. G. Fontaine, J. Am. Chem. Soc., 2014, 136, 10708–10717.
12. G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, Science, 2006, 314, 1124–1126.
13. E. I. Rogers, A. M. O'Mahony, L. Aldous and R. G. Compton, ECS Transactions, 2019, 33, 473.
14. D. S. Silvester, Current Opinion in Electrochemistry, 2019, 15, 7–17.
15. I. Cretescu, D. Lutic and L. R. Manea, in Electrochemical Sensors Technology, InTech, 2017.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Hugh O’Connor		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover and Dr Josh Bailey		
Position:	PhD Student		
Start date:	October 2019	**Anticipated end date:**	June 2023
Funding body:	EPSRC		

Redox Flow Battery Materials for Energy Storage

Background

As fossil fuel supplies dwindle and the climate change problem escalates, the need to harness renewable energy resources increases. However, these energy sources are intermittent and unpredictable, making them difficult to be used in a safe and stable power grid. For this reason, it is important that new energy storage technologies are developed which can shift energy from off-peak demand times to peak demand times. One of the most promising emerging technologies is the redox flow battery (RFB).

In RFBs, redox couples are dissolved in electrolyte solutions and stored in separate reservoir tanks. During charge and discharge these electrolytes are pumped from reservoir tanks into half cells where they react in an electrode, either consuming or generating electrons.

This working principle gives rise to a number of key advantages over other conventional battery technologies. In flow batteries, power and energy is decoupled; power is controlled by the stack effectiveness whilst energy is determined by the electrolyte stored in reservoir tanks. This makes RFBs highly customisable, allowing them to be tailored to meet a wide range of requirements. They also have a long working life; with the electrolytes stored in separate tanks, the electrodes don’t undergo complex redox reactions and experience less structural changes and strain than those found in conventional batteries. One drawback of RFBs however is their low energy density and high costs when compared to other energy storage technologies.

Improving the energy density, energy storage efficiency and sustainability could make RFBs an even more promising candidate for large scale energy storage applications. Innovative and more efficient manufacturing techniques could also potentially provide a solution in reducing inevitable costs that will occur when implementing a new energy storage technology.

One method of improving the performance of RFBs is designing better performing flow fields, manifolds and cell stack topologies resulting in a better performing cell battery.

Objective of this work

To investigate the effect of modified cell topology and stack architecture on the power density of redox flow batteries, identifying key performance influencers and improving economic viability.

Progress to date

Extensive work has been carried out into the investigation of novel cell and manifold topologies to improve cell performance. Fused Deposition Modelling (FDM) 3D-printing has been identified as a powerful tool to produce lab scale RFB test cells at an extremely low cost. At the end of the previous quarter, these findings were published in a paper for the RSC journal Sustainable energy and fuels.

This platform has been used to carry out a study investigating the effect of cell topology on flow battery performance. For the first time, cells with different geometries have been 3D-printed and directly compared to each other along with modelling results.

This platform has also facilitated the development of new novel electrolytes for low-cost energy storage and to manufacture miniaturised flow cells for micro–X-ray CT imaging in the synchrotron at diamond light source. This work has yielded interesting results into the interaction between electrolyte and different electrodes within flow battery cells. Reconstruction and processing of these images is ongoing and will be complete in the coming months.

Conclusions and future work

Experimental work investigating the performance of different cell geometries is wrapping up, with a number of non-tradition cell architectures showing promise. The data from these experiments is being analysed and further modelling work carried out. Future work will involve the development of a 3D-printed "zero-gap" flow battery cell, allowing further comparisons between different flow cell topologies.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Liam O'Connor		
Supervisor(s):	Dr O Istrate and Prof B Chen		
Position:	PhD student		
Start date:	October 2020	**Anticipated end date:**	October 2023
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

The TPU/PA11/GNP nanocomposite has been thermally and electrically characterised. Electrical characterisation has shown that the electrical percolation threshold is similar to PA11 samples. Rheologically the blended polymer nanocomposite also behaves similar to PA11 XRD and thermal analysis has shown that there is little change to the blended polymer matrix with the presence of GNPs.

Conclusions and future work

The next stage of the project is to mechanical evaluate the polymer blended nanocomposite and manufacture filaments of TPU, PA11, and TPU/PA11 mixed with graphene nanoplatelets and 3D print samples and evaluate whether or not the manufacturing process affects the mechanical and electrical properties.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Scott Place		
Supervisor(s):	Dr Paul Kavanagh (Primary) and Dr Mark Muldoon (Secondary)		
Position:	PhD Student		
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 are able to 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 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 the previous report, I detailed my ongoing work using a combination of long-term chronoamperometric (CA) studies on a larger scale and gas chromatography (GC) for analysis of catalyst stability, product conversion, and product selectivity. I pointed out that achieving reproducibility is challenging in this sort of setup due to issues such as ohmic drop and electrode passivation.

Since then, I have redesigned my electrochemical setup to determine this information on a more analytical scale. This smaller scale setup using standardised equipment and electrodes reduces variation between each run, and still allows for the use of GC to determine catalyst selectivity. Experiments are currently underway using this new, smaller setup. GC results are promising, but error is still quite high, which we are attributing to the much more dilute samples and much smaller quantities of internal standards used during GC analysis. To combat these issues, we are currently redesigning the GC method to include a greater injection volume and are using standard stock solutions for the addition of the standard to the mixture. Results from these studies should be with us by the end of the week.

Conclusions and future work

Once we have ensured that our results are reproducible and reliable, we will take some example catalysts from our line up and perform synthetic-scale experiments to demonstrate how our analysis translates to real-world performance. To do this, we will perform constant current potentiometry using graphite electrodes to produce a meaningful amount of product, before analysis using GC. This should conclude this part of the study and we will be working towards write-up for publication in the coming months.

Additionally, we have received comments relating to our previous work on the nitroxide radical polymer, PIPO, and have devised some additional experiments to include in our upcoming related publication. This will involve immobilising PIPO on a graphite support and performing a synthetic-scale constant current potentiometry experiment in aqueous medium.

We hope to wrap up both PIPO and TEMPO-derivative benchmarking studies within the next month or two. Following this, we will be moving on to using electrocatalysts in Li-air batteries for the degradation of the problematic lithium peroxide, an insulating by-product that forms during cell discharge. We have some preliminary results indicating that mediators like TEMPO may be used for this purpose, but this study is still in very early stages.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD Student		
Start date:	October 2019	**Anticipated end date:**	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

Background

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

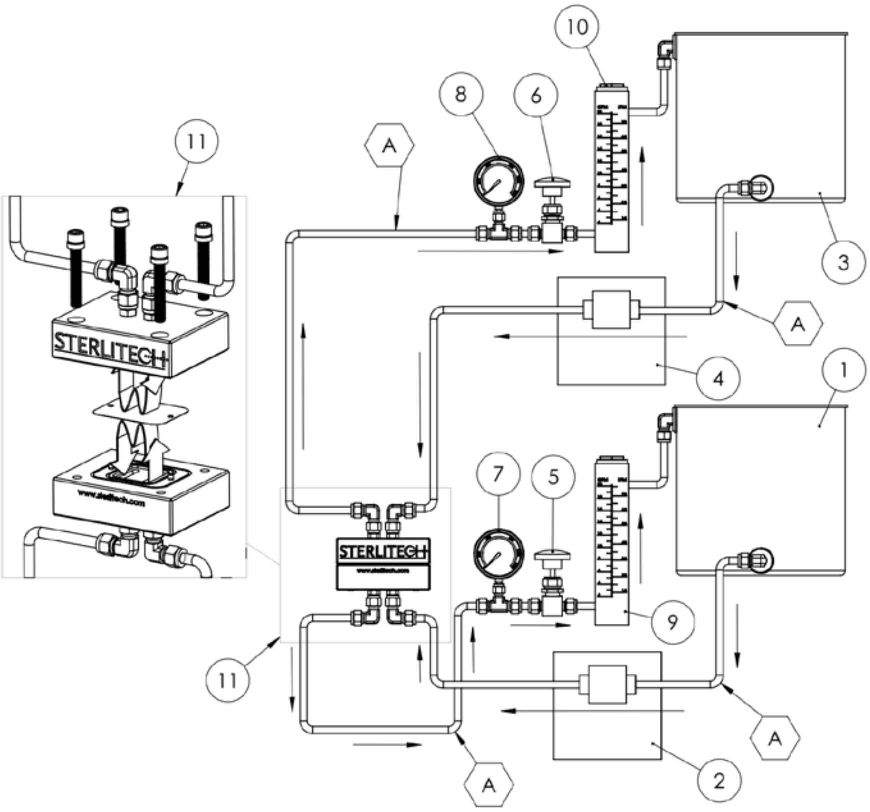
Objective of this work

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

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

Forward osmosis test system was set up and pre-tested by 2mol/L sodium chloride solution as draw solute under 8ml/min flow rate. (Tube is Tygon A-60-F) 0.2mol 51etrazolate51osphonium 5-phenyl 51etrazolate was prepared and characterized by NMR.



CF016A/ CF016SS/ CF016HAS FO FLOW DIAGRAM	
Item No.	Part Description
1	Feed Tank
2	Feed Pump
3	Draw Solution Tank
4	Draw Solution Pump
5	Concentrate Pressure Control Valve
6	Draw Solution Pressure Control Valve
7	Concentrate Pressure Gauge
8	Draw Solution Pressure Gauge
9	Concentrate Flow Meter
10	Draw Solution Flow Meter
11	CF016A-FO Cell Assembly
A	3/8" Low Pressure Tubing

Flow diagram of Forward osmosis system

Conclusions and future work

After the pre-experimentally test, the forward osmosis system was confirmed to stably run. Preliminary estimate of draw solute volume is about 300ml.

Next step is preparing a lot of materials(Firstly tetrabutylphosphonium 5-phneyl tetrazolate) for draw solute and test their IL/water system's forward osmosis performance. 4 different concentration IL/water samples(0.5, 1.0, 1.5, 2.0 mol/L concentration) will be prepared. Then their J_v,J_s and J_v/J_s will be measured and calculated by the following formula.

$$J_w=\Delta m/S_m\Delta t\rho w$$

Δm is the change in mass of the draw solution measured at time interval (Δt), ρw is the density of water, and S_m is the effective membrane area.

$$J_s=\Delta(C_tV_t)/S_m\Delta_t$$

C_t is the feed solute concentration and V_t is the feed volume. The C_t values were obtained from conductivity measurements for NaCl or from TOC analysis of the feed for ILs as draw solutes. The NaCl conductivity data were converted to Ct values through a calibration curve.

QUILL Quarterly Report

May 2022 – July 2022

Name:	Richard Woodfield		
Supervisor(s):	Dr Stephen Glover and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	June 2019	**Anticipated end date:**	May 2023
Funding body:	EPSRC		

Modelling Vanadium Redox Flow-Batteries in Transport Applications

Background

Flow batteries have received significant attention in the past years for use in grid storage applications. The decoupling of the relationship between power and energy density offers a very unique way to store energy to suit the user's particular needs. The extremely long cycle life of a flow-battery is another attractive asset, as the electrodes do not undergo cyclic stressing in the same way Li-ion and other chemistries do. Flow-batteries have received very limited attention regarding their use in transport applications. There is untapped potential in the fact that the discharged electrolyte of a flow-battery could be rapidly swapped at a traditional gas-station, where the infrastructure is already half in-place with storage tanks under the stations. With the electrolyte being entirely re-usable, the station would use an on-site flow-battery to recharge their reservoir and provide passing vehicles with opportunity to swap their electrolyte with readily charged fluid.

Objective of this work

The overall goal of the project is to identify viable electric or hybrid modes of transport that would benefit from the use of a flow-battery, given the refillable nature of the flow-battery electrolyte reservoirs. Even the applications rendered not viable will have outcomes, as the amount by which the energy density of the electrolyte would need to improve by is also providing electrolyte chemists with targets to aim for. The investigations will be carried out using software to model battery and vehicle behaviour, primarily Simulink.

Progress to date

Demonstrated the feasibility of vanadium redox flow batteries in ferry applications, where electrolyte swapping is utilised to rapidly increase the ferry charge. It was shown that, when compared to a diesel system, the vanadium redox flow battery ferry offered a similar cost per voyage while offering a threefold reduction in CO_2. This work has been published in the Journal of Energy Storage:

Electro-thermal modelling of redox flow-batteries with electrolyte swapping for an electric ferry
https://www.sciencedirect.com/science/article/pii/S2352152X22013044

Conclusions and future work

Battery testing will commence shortly which will result in data that can feed into vanadium redox flow battery models, enabling a more accurate model under dynamic scenarios, such as road transport. The main focus is now fixed on vanadium redox flow battery buses, where the project will aim to show the feasibility of various bus routes using collected GPS data. Various hybrid powertrains will be explored (VRFB/Li-ion, VRFB/PEMFC) and compared to existing buses.

QUILL Quarterly Report

February 2021 – April 2021

Name:	John Young		
Supervisor(s):	Dr Leila Moura, Prof John Holbrey and Prof Sophie Fourmentin		
Position:	PhD student		
Start date:	October 2020	**Anticipated end date:**	March 2024
Funding body:	EPSRC		

Gas Separation Technologies

Background

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

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

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

Work to date

CO_2 uptake in TOPO-based hydrophobic low melting mixtures

The screening methodology has improved since previous reports with the utilisation of our own recently repaired head-space gas chromatograph (HS-GC). This has increased the maximum screening pressure to around 3.5 bar for CO_2 and 4 bar for CH_4, extending the scope from the upper limit of 1.8 bar as described in the previous report.

Hydrophobic low melting mixtures (HLMMs) have been a major focus of my research this quarter. They have been previously synthesised in QUILL based on trioctylphosphine oxide (TOPO) combined with acid hydrogen-bond donors (Fig 1) and have substantially lower viscosity than many other reported LMMs such as choline chloride based mixtures.[3]

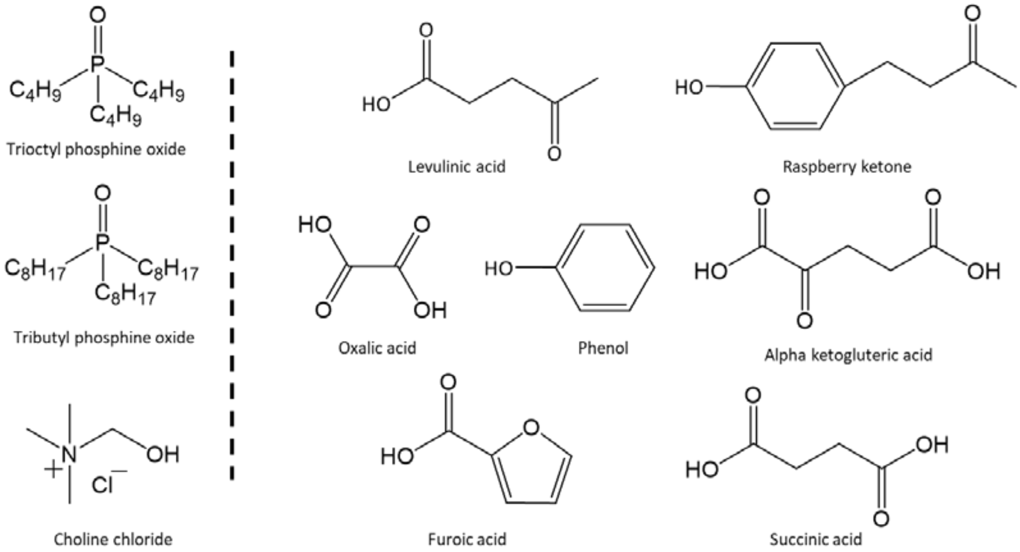


Figure 1 - Structures of hydrogen bond acceptor (left) and hydrogen bond donor (right) components of TOPO-based HLMMs used in this work

Gas uptake measurements have shown that these materials have exceptionally high CO_2 uptake when compared with other DES physisorbants such as choline chloride:levulinic acid 1:2. Highest capacities are found in the system containing levulinic acid as a HBD. Both the TOPO and the TBPO LMMs have uptake capacities comparable to that of our reference IL [BMIM][NTf_2] as can be seen in figure 2. A wide range of other HBDs have also been tested all with uptake capacities higher than that of choline chloride based LMMs. This indicated that the levulinic acid itself plays and important role in the uptake capacity of the materials as has been previously reported in choline chloride DES.[4] Gas system measurements are currently underway to confirm the uptake capacities of the most promising materials.

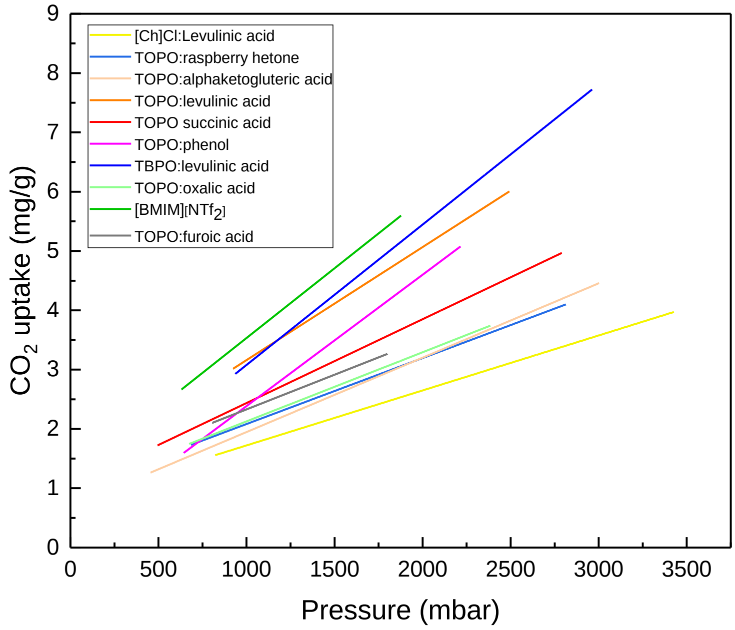


Figure 2 - Plot of CO_2 uptake in mg/g as a function of pressure in various TOPO based deep eutectic solvents using [BMIM][NTf$_2$] as a comparative standard ionic liquid

Synthesis of deuterated randomly methylated beta cyclodextrin (RAMEB)

Synthesis of Deuterated RAMEB was also carried out. This required the initial deuteration of native cyclodextrin using noble metal catalysts. This was followed by a two-step methylation initially with iodomethane-d3 and then further methylated through the use of dimethyl sulfate-d6 which was synthesised form methanol-D3 and chlorosulfonic acid. This resulted in a highly deuterated sample of RAMEB-d which was subsequently used for neutron scattering experiments. These experiments were carried out in order to investigate the liquid structure of the RAMEB:levulinic acid deep eutectic solvent along with the effect of water of the liquid structure. This could help to give information in the nature of supramolecular DES which could allow rational design of these materials with the goal of CO_2/CH_4 separation.

Future work

Gas uptake measurements will be completed using the gas system for our most promising results. This will serve to confirm the results and also confirm the accuracy of the GC methodology. This will also allow for materials to be tested at elevated temperature which is commonly carried out industrially. Once this has been completed the results will be published.

Synthesis of modified cyclodextrins will also be carried out in the hope of solubilizing them in our most promising systems. These will then be tested for VOC uptake before and after addition of modified cyclodextrins.

References

1. F. M. Baena-Moreno, M. Rodríguez-Galán, F. Vega, L. F. Vilches and B. Navarrete, *Int. J. Green Energy*, 2019, 16, 401–412.
2. M. R. Rodero, R. Ángeles, D. Marín, I. Díaz, A. Colzi, E. Posadas, R. Lebrero and R. Muñoz, in *Biogas*, Springer, 2018, pp. 239–276.
3. E. L. Byrne, R. O'Donnell, M. Gilmore, N. Artioli, J. D. Holbrey and M. Swadźba-Kwaśny, *Phys. Chem. Chem. Phys.*, 2020, 22, 24744–24763.

4. R. Ullah, M. Atilhan, B. Anaya, M. Khraisheh, G. García, A. ElKhattat, M. Tariq and S. Aparicio, *Phys. Chem. Chem. Phys.*, 2015, 17, 20941–20960.