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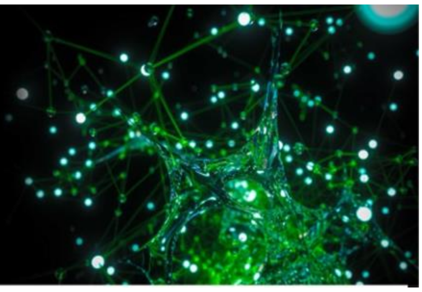

QUILL
Quarterly Reports

August 2022 – October 2022

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Contents

QUILL Quarterly Report

August 2022 – October 2022

Name:	Haris Amir		
Supervisor(s):	Prof John Holbrey		
Position:	PhD Student		
Start date:	10/01/2020	**Anticipated end date:**	09/30/2024
Funding body:	ESPRC/UKRI		

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

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 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.

After synthesis, characterisation and investigation of the library of O/N-chelated borate anions formulated as ionic liquids described previously, borate anions containing N-coordinated groups have been investigated, building on the known tetrakis(1-imidazoly)borate, to explore whether this and related functional anions are suitable for translation into ionic liquids. It has been suggested, based on density functional calculations that azolium poly(azolyl)borate ionic liquids might be effective media for reversible capture of SO_2, although the target ionic liquids are not known *ex silico*.[1] From the borate anions described in the theoretical screening study, four were chosen for synthesis and evaluation for potential to form ionic liquids and for to gas solubility. The heterocycles targeted for use to form 4-coordinate borate anions are shown in Figure 1.

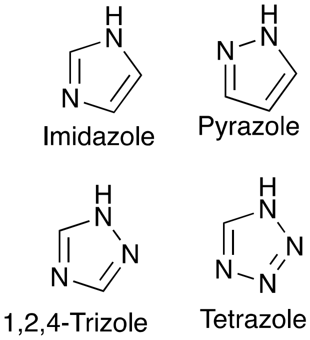
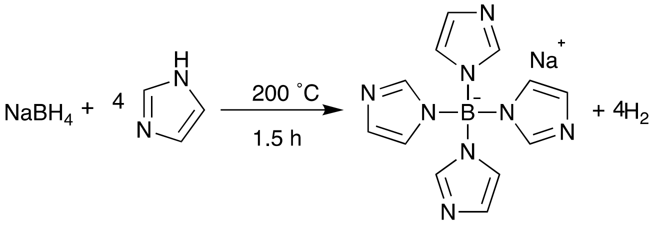


Figure 1 - The structures of the heterocycles chosen to synthesise borate anions

Sodium tetrakis(1-imidazoly)borate, Na[B(Im)$_4$] was successfully synthesised using the method described by Hamilton *et al*[2] as shown in Scheme 1.



Scheme 1 - Reaction scheme for the synthesis of Na[B(Im)$_4$]

After 1.5 h, the reaction is allowed to cool, washed with acetone and the crude product is recrystallised from ethanol. However, while the reaction was being cooled needle like crystals were formed at the neck of the round bottom flask. An aerial view of the crystals can be seen in Figure 2. Initially it was thought the crystals are of the starting material imidazole and not the desired product. An NMR of the crystals can be seen in Figure 3.

Figure 2 - An aerial view of the crystals formed.

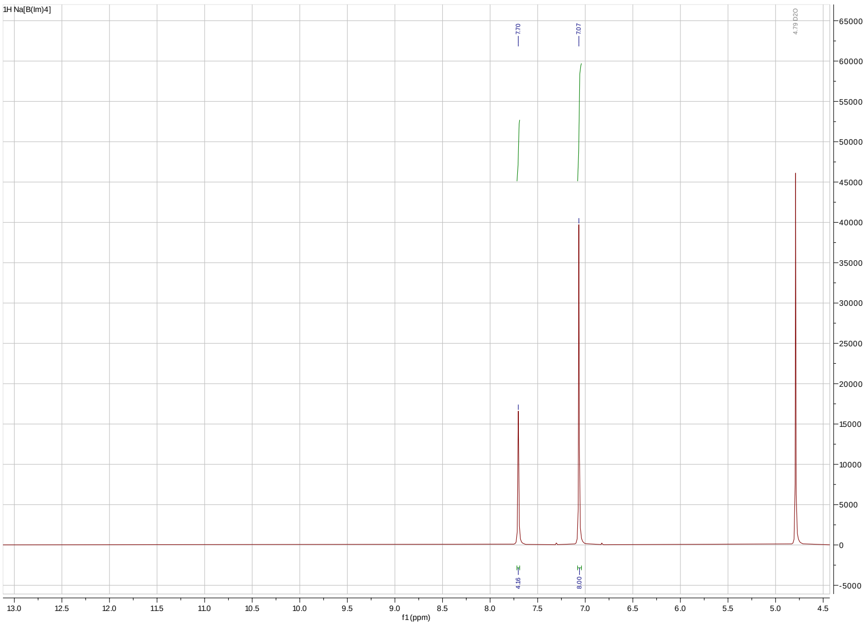


Figure 3 - ^{1}H NMR of crystals from reaction between NaBH$_4$ and imidazole in D$_2$O

The ^{1}H NMR shows no presence of N-H bond which normally has a broad singlet around 12 ppm, this alone does not confirm the crystals are the desired Na[B(Im)$_4$]. A ^{11}B NMR is required to confirm the existence of 4-coordinated boron species. A sample of the crystals have been submitted for mass spectroscopy, if the crystals are in fact Na[B(Im)$_4$] a peak of 279 m/z should be observed in the mass spectrum. A more efficient approach would be to determine the melting point of the crystals as imidazole has a melting point of 90 ˚C therefore, it would be an indication if the crystals are just starting materials.

The reaction described in Scheme 1 was repeated using pyrazole instead, the same observation was seen when the reaction was being allowed to cool Figure 4 shows the ^{1}H NMR of the crystals. There was no peak which showed the existence of the N-H bond which is expected to be around 13 ppm. Similar to the proposed Na[B(Im)$_4$] crystals, a sample of the crystals that are expected to be Na[B(pyr)] was submitted for mass spectroscopy. The melting point of pyrazole is 67 ˚C so as before determining the melting point of the crystals would help identify if the crystals are starting material or the desired product.

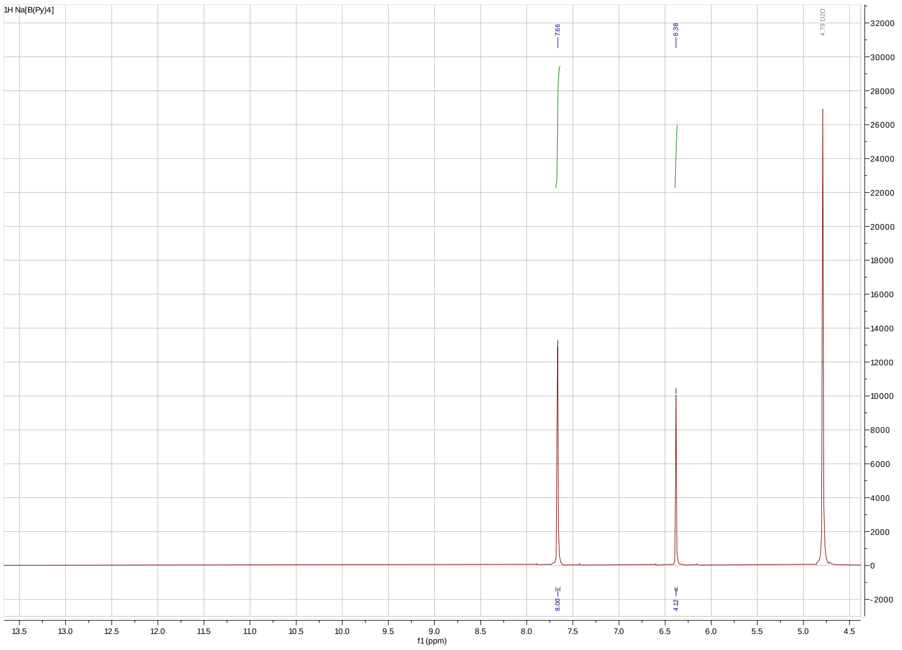


Figure 4 - ^{1}H NMR of crystals from reaction between $NaBH_4$ and pyrazole in D_2O

The future work will involve synthesising the borate anions with the remaining heterocycles shown in figure 1 using the method described in scheme 1. Once the desired borate anions have been synthesised, the next step would be to ion exchange with tetrabutylphosphonium chloride, [P_{4444}]Cl to obtain phosphonium based ionic liquids. This is so the thermodynamic properties of the borate anions can be investigated *via* thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). There will also be attempts to grow crystals of these ionic liquids for single crystal XRD to obtain a detailed information of the lattice and unit cell of the different boron anions.

References

1. H. Tang, and D. Lu, ChemPhysChem., 2015., **16**., 2854-2860.
2. H. B. Hamilton, A. K. Kelly, W. Malasi, and J. C. Ziegler, Inorg. Chem., 2003, **42**, 9, 3067–3073.

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August 2022 – October 2022

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

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

Background

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

Lastly, I have also been working with Chevron on CO_2 capture with ionic liquids although the details of this work cannot be disclosed at this time as we intend to patent the technology.

Conclusions and future work

So far the results suggest that electrostatics dominate the sulfate removal as ILs with either one sterically short group (either methyl or just a proton) all perform broadly similar with significantly better sulfate removal than $[P_{66614}]Cl$ which only has larger alkyl chains. It is proposed that the ability for sulfate to closely approach the positive centre of cations and therefore maximise the electrostatic attraction when a single short chain is present enhances ion pairing and extraction. The figures below summarise the effect of aqueous sulfate and chloride concentration as well as the effect of the phase-volume ratio. Currently one more IL needs to synthesised and characterised before this can all be written up into a paper.

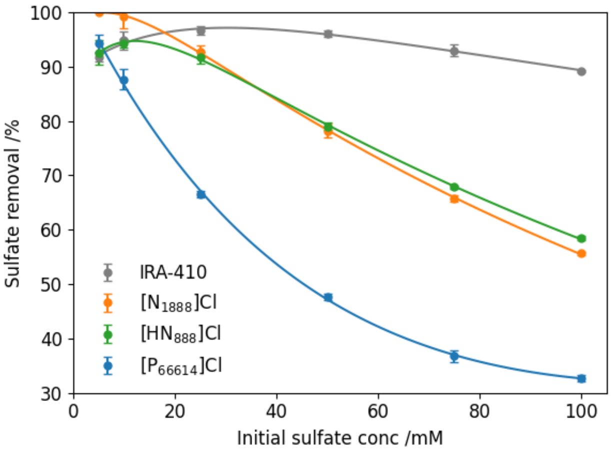

Figure 1 - Sulfate removal from aqueous solutions using various ILs with Amberlite IRA-410 as a comparison

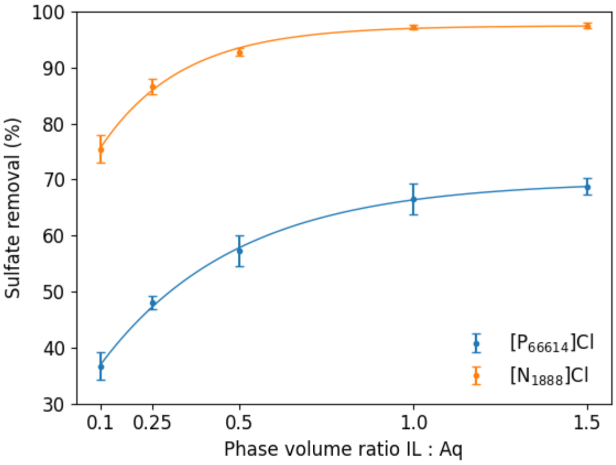

Figure 2 - Effect of phase volume ratio on the extraction of sulfate from a 27.1 mM sodium sulfate solution (a non-competitive model sea water solution).

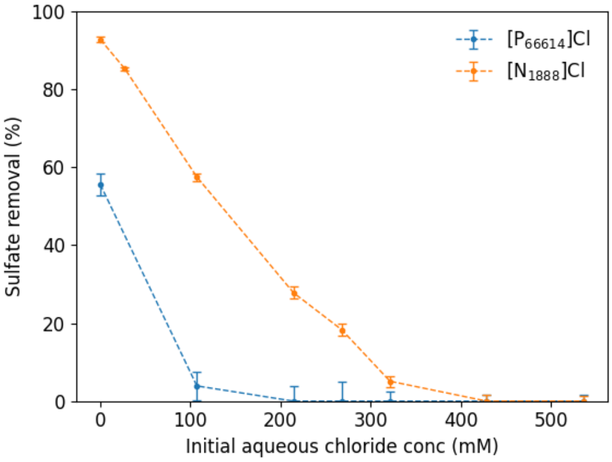

Figure 3 - Effect of competitive chloride in the aqueous phase inhibiting the sulfate removal from a 27.1 mM solution up to 550 mM chloride representing standard sea water concentration.

Future work involves the synthesis of an additional IL that mimics the functionality found in type II strongly basic anion exchange resins to complete the data set for a paper. Then focus can be shifted to competing the research on the addition of anion receptors into the ILs for a second paper.

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Name:	Oisin Hamill		
Supervisor(s):	Dr Nancy Artioli and Dr Alex Goguet		
Position:	PhD Student		
Start date:	01/10/2019	**Anticipated end date:**	30/03/2023
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

- STEM/EELS Studies completed @ JM.
- Raman Spectroscopy (in-situ and ex-situ) completed @ JM.
- Draft of Thesis Chapter 1 (Sm-Ce / Sm-Al paper) completed.
- Thesis layout presented & confirmed.
- Writing up started.

Conclusions and future work

- Sm-Ce lean deactivation tests on 1%Pt catalysts TBC.
- Nd & Pr dopant activation cyclic tests on 0, 0.25 & 1 wt.% Pt TBC.
- BAG call to be attended at Harwell 9-11th Dec 22.
- EXAFS / XANES conclusions to be closed out.

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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). Electrodes are still typically made using carbon felt as these have good electrical conductivity, electrochemical activity, and are mechanically and chemically stable. However, using carbon felt as an electrode material limits cell design and is associated with a high interphase electrical resistance. Additionally, for flow-over electrode designs, flow channels must be machined into graphite plates which is complex and expensive. 3D-printable electrodes may offer a greater design freedom where, for example, flow channels can be printed as part of the design, and porous and solid elements can be combined.

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

Objective of this work

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

Progress to date

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

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

Conclusions and future work

Future work will build on the experimental work undertaken so far exploring SLA 3D printing and will also explore FDM 3D printing routes. Functionalisation of graphene such as by using a silane coupling agent or ionic liquids will be explored as this has been shown to improve dispersion and electrical conductivity of 3D-printed nanocomposites. After creating a viable 3D-printable electrode material, the focus will be on manufacturing different 3D-electrode structures and testing in RFB test cells (e.g., flow-through, flow-across, and multi-stack systems).

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Name:	Aloisia King		
Supervisor(s):	Prof John Holbrey and Prof Małgorzata Swadźba-Kwaśny		
Position:	PhD student		
Start date:	01 October 2021	**Anticipated end date:**	March 2024
Funding body:	EPSRC		

Intrinsic FLP Systems in Ionic Liquids

Background

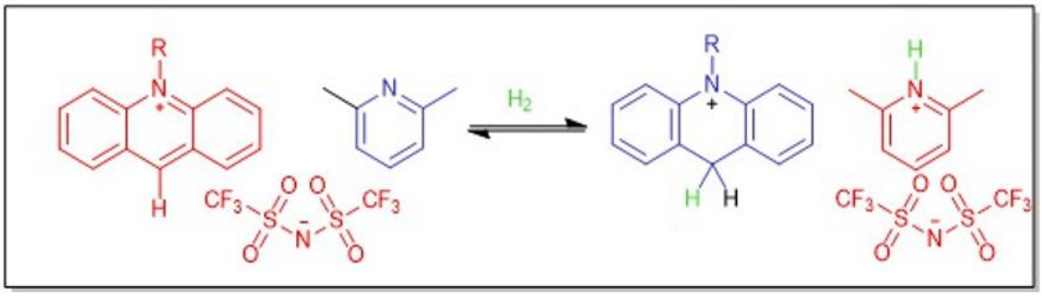
Frustrated Lewis acid/base pairs (FLPs) are potential metal-free alternatives to platinum group metal catalysts and have been shown to activate hydrogen for hydrogenation chemistry [1]. Typical examples of FLPs that have been studied are combinations of a sterically hindered bulky phosphine Lewis base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

Objective of this work

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

Progress to date

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. Since the last Report we have conducted a thorough investigation into the thermal properties of the system- both sides of the equilibrium were investigated. We constructed the phase diagrams for the system through DSC analysis. Additionally, from this thermal analysis we have deduced that the acridinium salt/lutidine acid-base pairs form an ionic liquid FLP and that these ionic liquid characteristics are retained in the corresponding protonated H-lutidinium salt/dihydroacridine mixture, which will give us the potential to tune and optimise hydrogen activation by shifting the equilibrium shown in Scheme 1.



Scheme 1 - Intrinsically IL FLP activation of H_2 through heterolytic cleavage at an N-alkylacridinium cation/lutidine FLP forming N-alkyl-9,10-dihydroacridine and H-lutidinium cation, retaining an IL+base environment across the reaction profile.

Also, since the last report I have obtained training on Shimadzu GC-2030 manual injection with TCD detector and the associated LabSolutions software, from Mason technologies. This training was pivotal for the progression of the research, as I needed a method to quantify the H_2 uptake by the FLP systems. Over the next few months the plan is to familiarise myself with the machine so we can get the final few results we need to publish the paper.

Additionally, since the last report I have began writing my first Scientific paper to report on the research gathered over the past year, with the plan to submit to the Journal in late December/ early January. We plan to initially report our findings on the simple Intrinsic IL FLP system and hence, compare the H_2 activation in the other Intrinsically IL FLPs that we have synthesised. I am also preparing to go and present this work at the MSILDG Christmas meeting on the 19th of December in London. I mentioned previously too that we were working on developing another range of molecules with the potential to act as our LA in our Intrinsic IL FLPs and I have been investigating these Dicyano-pyridines too. I have successfully synthesised Pyridine-3,5-carboxilic acid, Pyridine-3,5-dicarboxamide, Pyridine-3,5-dicarboxylate, diethyl pyridine-3,5-dicarboxylate,Pyridine-3,5-dicarbonitrile and 1,4-Dihydropyridine-3,5-dicarbonitrile. These molecules are all precursors to the final desired Methyl pyridine-3,5-dicarbonitrile [Tf_2N], Ethyl pyridine-3,5-dicarbonitrile [Tf_2N], Propyl pyridine-3,5-dicarbonitrile [Tf_2N], Butyl pyridine-3,5-dicarbonitrile [Tf_2N] and the Benzyl pyridine-3,5-dicarbonitrile [Tf_2N]. I have began to investigate the synthesis of the first anion and method development is underway.

Conclusions and future work

As mentioned, we plan to submit our work to be considered for publishing late December/ early January. We will gather the final results we need and run another set of H_2 experiments, quantifying the systems interaction with H_2 via the Shimadzu GC-2030 manual injection machine. Also, the plan is to continue developing the additional acridinium anions and cyanopyridine anions.

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.

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August 2022 – October 2022

Name:	Sanskrita Madhukailya		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	2nd year PhD student		
Start date:	19th April 2021	**Anticipated end date:**	20th 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 phase behaviour for diphosphonium ionic liquids, namely, 1,5-pentanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate), 1,6-hexanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) and 1,8-octanediyl-bis(tri-n-butylphosphonium)di(5-phenyltetrazolate) were carried out. This report further extends into the synthesis , characterisation and testing the phase behaviours of some corresponding ammonium ionic liquids.

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. Synthesis of ammonium ionic liquids of the type [N_{444n}][PhTet], where n= 4,5,6,8 and [N_{6666}][PhTet]: Firstly, tributylamine for the former and trihexylamine for the latter, and 1-bromoalkane, depending on the length of the alkyl chain in the cation of the ionic liquid was mixed in the ration 1:1 in acetonitrile as a solvent for 24-30 hours at 50-60 degree Celcius. The tetraalkylammonium bromide salt was obtained by extraction with hexane. This was subjected to anion exchange with sodium 5-phenyltetrazolate to obtain the desired ammonium ionic liquid.

2. Synthesis of dicationic ionic liquid, 1,8-octanediyl-bis(tri-n-butylammonium)di(5-phenyltetrazolate) for testing its phase behaviour: 22.46 mmol of already prepared 1,8-octanediyl-bis(tri-n-butyl ammonium)dibromide was dissolved in sodium 5phenyl tetrazolate solution in water and was allowed to stir for 3-4 hours at a temperature of 60 degrees.

3. The prepared dicationic ionic liquid, 1,8-octanediyl-bis(tri-n-butylammonium)di(5-phenyltetrazolate) was studied for its phase behaviour (LLE behaviour) using the instrument crystal16. It was observed that for 50wt% compositions the mixture showed biphase during the heating and a single on cooling below 15 degrees Celcius.

4. Participated in the CCE PGR Research Day in September by presenting a poster and won the 'Best Poster' award for the same.

5. Participated in the QUILL IAB meeting in September by presenting a poster and giving an oral presentation on the works done so far. Received the 'Runner-up Presentation' prize for the same.

Conclusions and future work

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

2. 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

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

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

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

Background

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

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

Objective of this work

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

Progress to date

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.

This has led to fundamental models being developed in excel based on the system of equations and inputs outlined in literature. While these initial models helped to verify the function of the equations in a finite difference model, due to the extreme temperature gradients produced due to the runaway reactions a very small timestep is required to ensure the stability of the model. Therefore, to allow for an adequately short timestep the model was recreated in MATLAB. As a result of the sensitivity of the models along with the lack of consistency across input values it has so far proven difficult to reproduce the results provided in literature with a satisfactory level of accuracy. This process is still ongoing.

Conclusions and future work

Progress has been made on replicating previous work but the data and clarity of the available literature has made progress slower than ideal. A baseline model needs to be completed and verified using literature before it can be diversified into the range of different areas and scenarios that are needed in this project.

QUILL Quarterly Report

August 2022 – October 2022

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

Chemisorbent Materials for Olefin and Paraffin Separation

Background

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

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

Objective of this work

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

Progress to date

In summary, for the last few months of the PhD program, the time has been divided between two main projects. Both papers focus on the use of nitrile groups in ionic liquids as their inclusion has shown to increase the separation potential of ethylene and ethane, why this exactly is, is not known.[3] One will be focusing on nitrile groups in the anion of the ionic liquid (paper A) and one will focus on the nitrile groups present in the cation (paper B). Paper B will include the study of mixtures of different salts (inorganic/organic) to study the influence of the mixing for the solubility of ethylene and ultimately the separation. This is where the work completed in Lyon will be added to. This paper may include the work involving ionic liquids plus metal salts will be added keeping in theme with the mixtures.

Paper A:

This paper will focus on including the nitrile functional group in the anion while keeping a constant cation. The common cation chosen will be $[C_4C_1Im]^+$ cation. The anions chosen (increasing order of nitrile group) are thiocyanate $[SCN]^-$, dicyanamide $[DCA]^-$, tricyanomethanide $[TCM]^-$, and tetracyanoborate $[TCB]^-$. The first three anions have been collected, but the tetracyanoborate has been difficult to source the correct amount due to the rarity of the anion and expense of the salt. The solubility of the ethylene and ethane in the ionic liquids will be tested in the new year, and the characterisation data is being collected currently.

Paper B:

The cyanopyridinium ionic liquids will be included in this paper. The butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^4CNPy][NTf_2]$) and butyl-3-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^3CNPy][NTf_2]$), and a 50:50% molar mixture of butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^4CNPy][NTf_2]$) : 1-butyl-4-imidiazolium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Im][NTf_2]$) are currently being studied for ethylene and ethane solubility. The isothermal titration nanocalorimetry data of mixing different compositions of butyl-4-cyanopyridinium bis(trifluoromethylsulfonyl)imide ($[C_4{}^4CNPy][NTf_2]$) : 1-butyl-4-imidiazolium bis(trifluoromethylsulfonyl)imide ($[C_4C_1Im][NTf_2]$) have been collected and this was collected during the research visit in Lyon will be added to this paper (as described during the last quarterly report). A summary from this work showed that the enthalpy of mixing of the two ionic liquids was only slightly positive, suggesting that the ionic liquids mixed ideally with no new interaction between them. Work conducted before involving the mixing of metal salts and $[C_4C_1Im][NTf_2]$ using the screening method will be included in this section (this data again described before during a previous quarterly report).

Conclusions and future work

For both papers, the characterisation and solubility data are being collected, and will be collected during the last months of the PhD project. During this coming quarter, the groundwork for both papers will be written, and the data and results will be added as they are ready.

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QUILL Quarterly Report

August 2022 – October 2022

Name:	Emma McCrea		
Supervisor(s):	Prof Małgorzata Swadzba-Kwasny and Prof John Holbrey		
Position:	PhD Student		
Start date:	01/09/21	**Anticipated end date:**	01/09/24
Funding body:	Engineering and Physical Sciences Research Council (EPSRC)		

Valorisation of Waste Polyolefin Plastics Using Lewis Acidic Ionic Liquids

Background

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

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

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

Objective of this work

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

Progress to date

In the previous report, the removal of impurities was reported using additives and liquid-liquid extraction. The level of elemental impurities was measured using NEX QC+ QuantEZ XRF with FP analysis application. This application use template modelling without the use of a standard calibration curve. It was found that this method of measuring elemental impurities produced inconsistencies when repeating measurements. As a result, the data produced by FP analysis can not be replicated.

To combat this problem, EMP analysis with a calibration curve was produced with XRF standards to analyse the samples. This method removes the modelling component of the analysis and is directly compared to the calibration curve. This removes the inconsistencies in the results.

Analysis of impurities was also carried out by ^{1}H NMR, the was no change in the level of impurities before and after the additives and liquid-liquid extraction. (Fig 1)

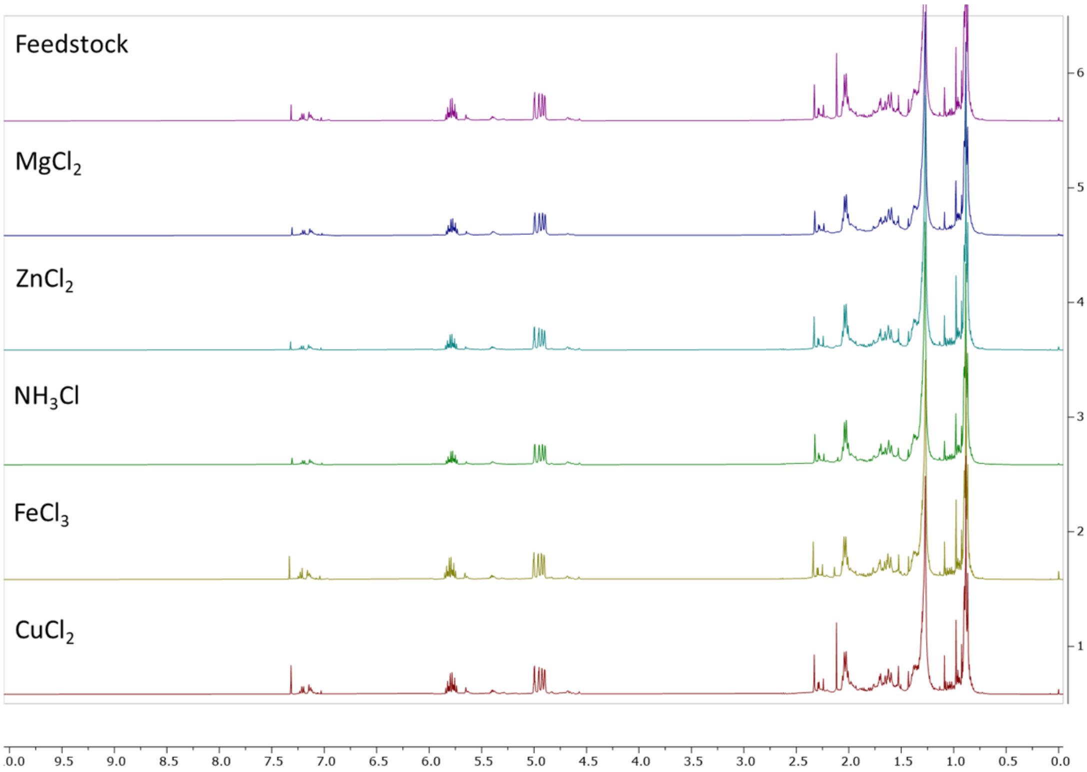


Figure 1 - ^{1}H NMR analysis of impurities

The impurity removal method described above failed to remove the impurities below a level that enabled the liquid coordination complex and borenium ionic liquid catalyst to perform oligomerisation as seen in the SimDis GC. (Fig 2 and 3) The distribution of hydrocarbons remained the same after addition of catalyst and no oligomerisation products were formed suggesting that the impurities inhibited the catalyst.

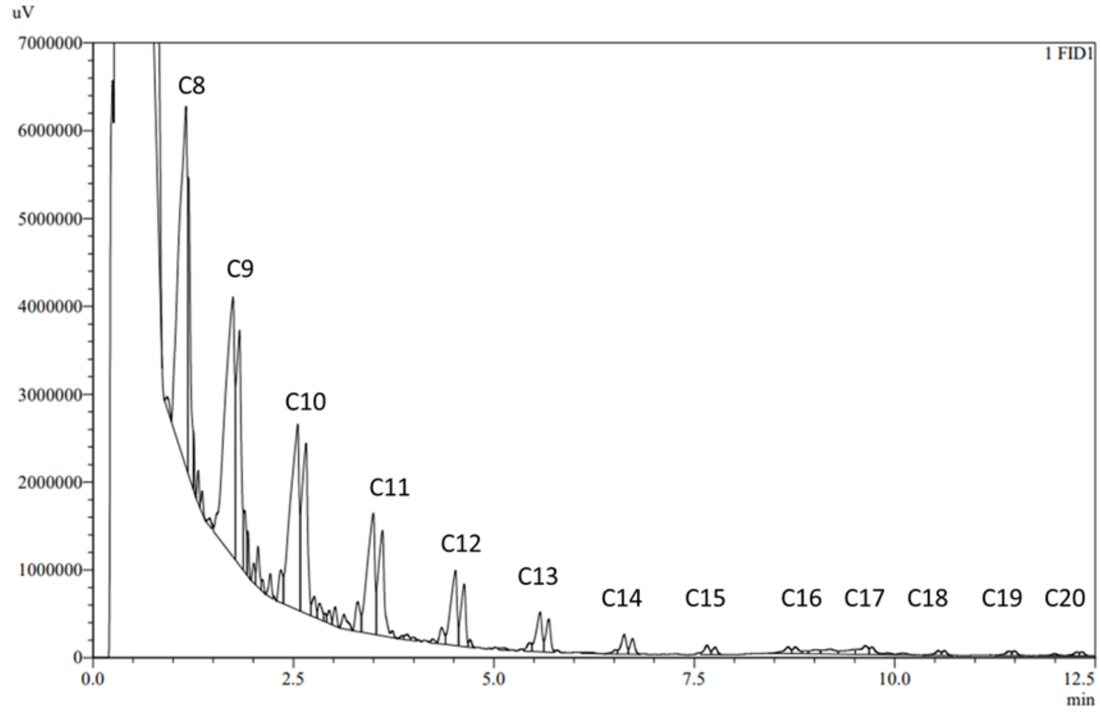


Figure 2 - Distribution of hydrocarbons before addition of catalyst

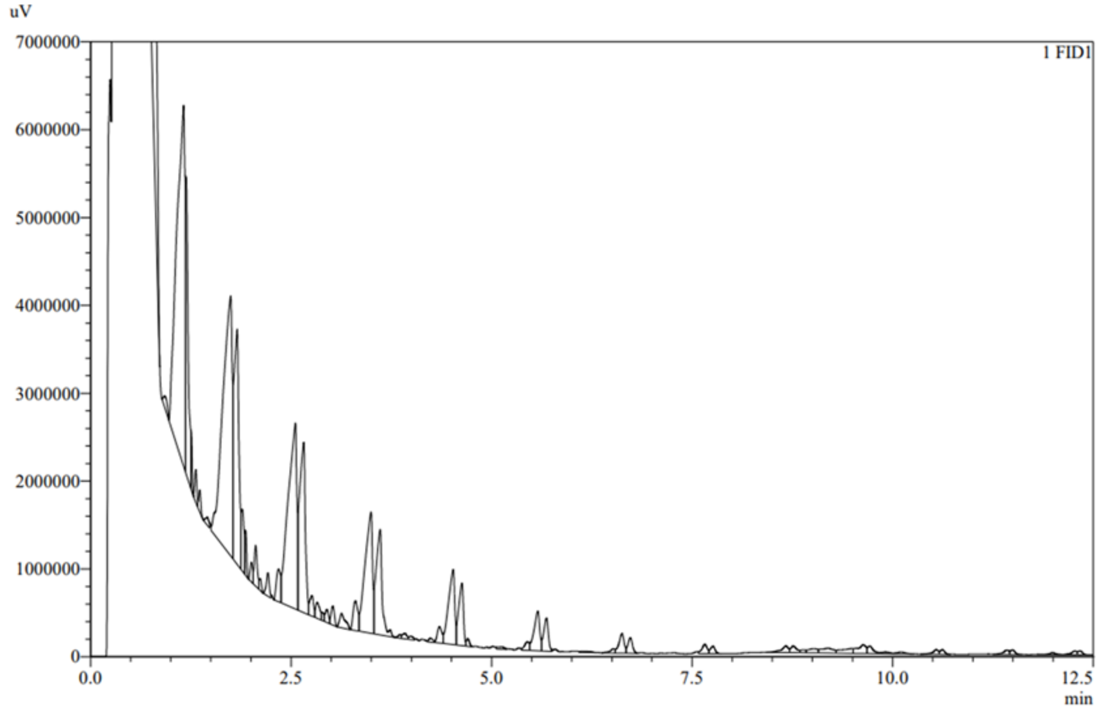


Figure 3 - Distribution of hydrocarbons after addition of catalyst

Deep eutectic solvents had been found to extract impurities from model diesel fuel.[1] The deep eutectic solvents where prepared and equal volumes of DES and feedstock were added and stirred overnight.

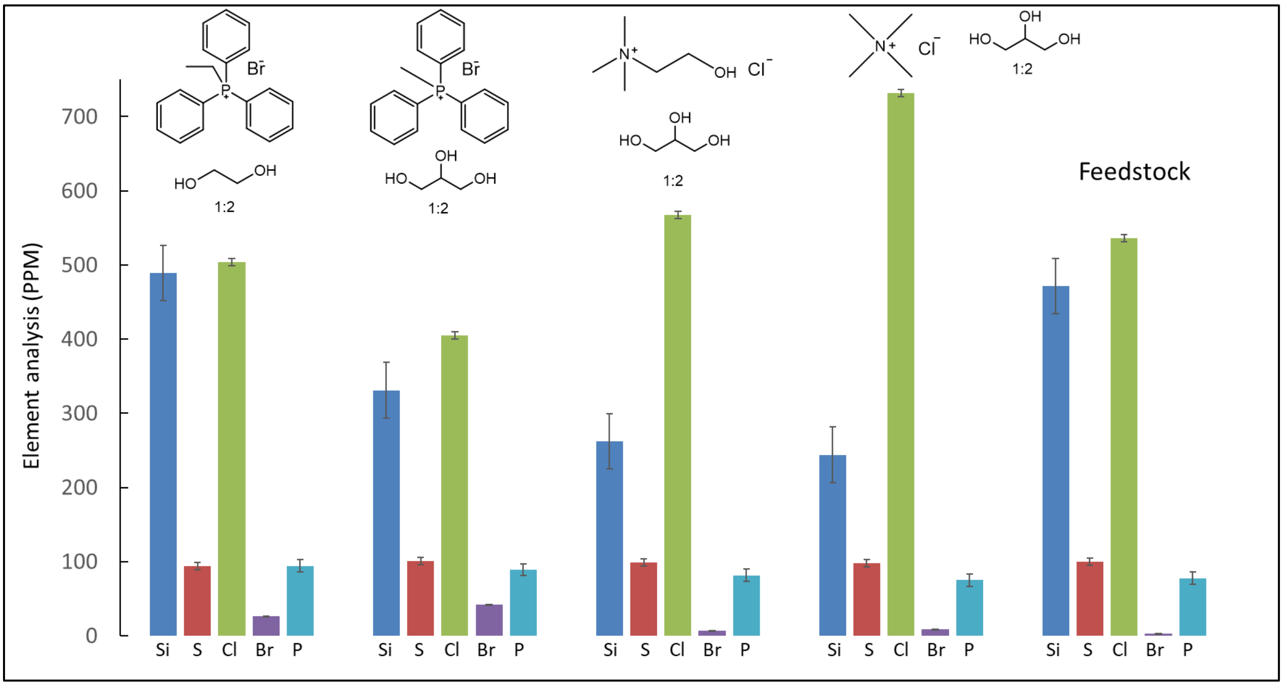


Figure 4 -. Elemental analysis of impurities using DES extraction

Using deep eutectic solvents to remove impurities from the feedstock decreased Si impurities however it increased other elemental impurities and aromatic impurities remained when analysed by ^{1}H NMR. This suggests that an alternative method to remove impurities is required.

Conclusions and future

The high levels of impurities in this batch of recycled polyolefin plastic have posed a significant challenge and the source of the impurities is unknown. A new batch of washed LDPE was obtained with the analysis and oligomerisation of this batch is the focus of my future work. The analysis by XRF, ^{1}H and ^{13}C NMR, GC-MS and SimDist GC will be obtained to characterise and establish the level of impurities. Oligomerisation of the feedstock with liquid coordination complexes and borenium ionic liquids with the characterisation of product distribution by SimDist GC.

QUILL Quarterly Report

August 2022 – October 2022

Name:	Anne McGrogan		
Supervisor(s):	Prof Gosia Swadzba-Kwasny		
Position:	PhD Student		
Start date:	01/10/2019	**Anticipated end date:**	31/03/2023
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.

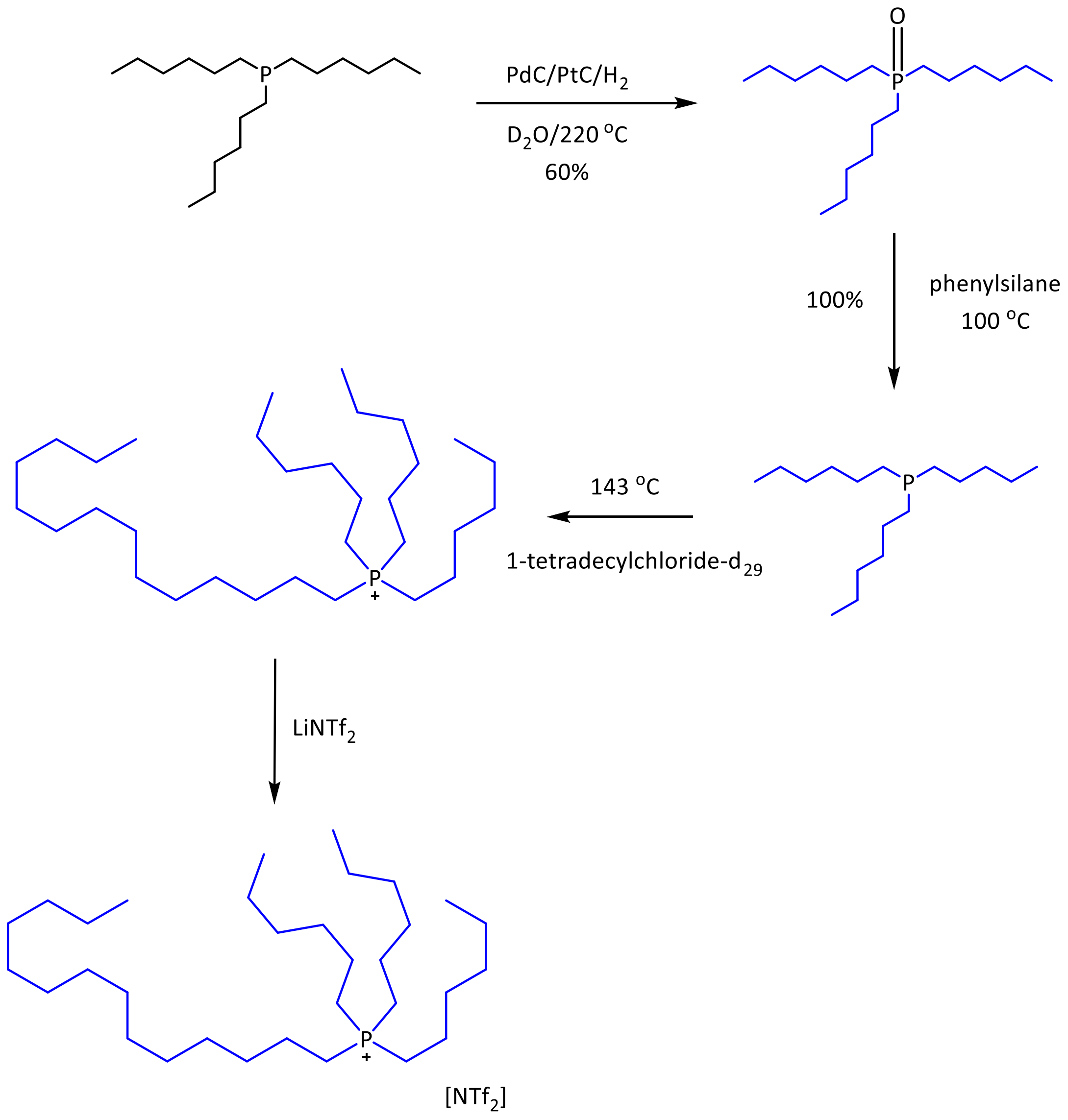
Progress to date

The synthesis of deuterated $[P_{66614}][NTf_2]$ is reported, following a procedure adapted from Rob Atkin *et al.*[20]

Synthesis of 1-tetradecylchloride-d_{29}

Tetradecanol was synthesised at the Deuteration Facility at ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory in Oxfordshire, UK.

13.93 g (0.117 mol) of thionyl chloride was placed in a 2-necked flask equipped with condenser and pressure equalising dropping funnel, which were both fitted with calcium chloride guard tubes. 9.5 g of tetradecanol-d_{29} was placed in the pressure equalising dropping funnel and added slowly with stirring. Evolution of heat and SO_2 evolved. When all the alcohol was added, the mixture was refluxed for 3 hours. The excess of thionyl chloride was then distilled (78-80 °C), and the crude 1-tetradecylchloride at 98 °C and 0.5 mbar. This was then washed with D_2O, 10% sodium carbonate solution and twice with D_2O. Then, dried with anhydrous calcium chloride and distilled again.



Scheme 1 - Synthesis of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide-d$_{68}$

Deuteration of trihexyphosphine oxide-d$_{39}$

A mixture of trihexylphosphine (3.5 g, 0.00987 mol), 10% Pt/C catalyst (0.75 g), and 10% Pd/C catalyst (0.75 g) in D_2O (65 mL) was stirred under N_2 bubbling for 2 min followed by H_2 bubbling for 2 min at room temperature. The reaction mixture was heated at 220 °C for 1 day. After cooling, the reaction mixture was diluted with dichloromethane, filtered through Celite, washed with dichloromethane and then the aqueous phase was extracted with dichloromethane (3 x 50 mL). The combined extracts were dried over $MgSO_4$ and then evaporated to give deuterated trihexylphosphine oxide-d$_{39}$ as a white solid (1.7 g, 49% yield).

Synthesis of deuterated trihexylphosphine-d$_{39}$

A solution of trihexylphosphine oxide-d$_{39}$ (4.5 g, 0.0149 mmol) in phenylsilane (6 mL) was heated to 100 °C under argon overnight. The reaction was monitored by ^{31}P NMR in degassed $CDCl_3$ through the disappearance of the starting material peak at 50.8 ppm and the appearance of trihexylphosphine peak at -33.65 ppm.

Phenylsilane was removed under reduced pressure to give pale yellow residue, which is used in the next step without further purification.

Synthesis of deuterated trihexyltetradecylphosphine chloride-d_{68}

Trihexylphosphine-d_{39} (4.5 g, 0.0127 mol) and tetradecylchloride-d_{29} (4.32 g, 0.0165 mol) neat were heated to 140 °C in a sealed tube in the glovebox. The temperature was maintained at 143 ºC for 24 hrs. The progress of the reaction was monitored by ^{31}P NMR spectroscopy in $CDCl_3$ (^{31}P peak at at -33.65 ppm disappeared to give a peak at 32 ppm.

Synthesis of deuterated trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide-d_{68}

Trihexyl(tetradecyl)phosphonium chloride $[P_{666,14}][Cl]$ (0.010 mol eq.) was dissolved in hexane and Li[TFSI] was dissolved in D_2O, combined in a round-bottomed flask, and left to react (1 h, RT, 600 rpm). The organic layer was separated and washed with D_2O. Hexane was removed and the ionic liquid was dried under high vacuum (12 h, 70 °C, 10^{-2} mbar).

Conclusions and future work

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

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QUILL Quarterly Report

August 2022 – October 2022

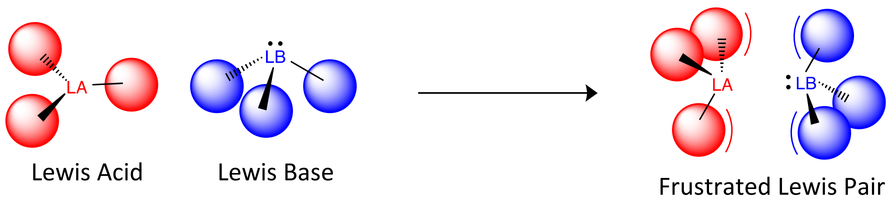
Name:	Shannon McLaughlin		
Supervisor(s):	Prof Gosia Swadźba-Kwaśny		
Position:	PhD Student (2nd year)		
Start date:	October 2020	**Anticipated end date:**	July 2024
Funding body:	Department for the Economy (DoE)		

Frustrated Lewis Pairs in Ionic Liquids

Background:

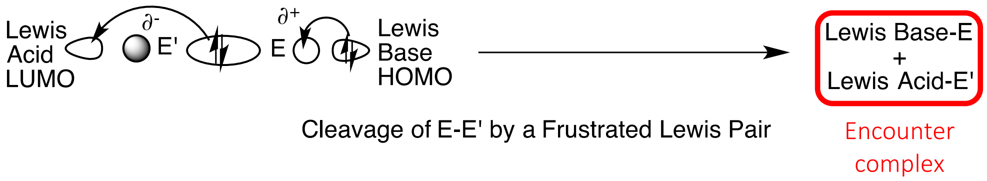
Frustrated Lewis pairs (FLPs) are compounds or mixtures containing a Lewis acid and a Lewis base that cannot combine to form a classical adduct due to steric hindrance (Scheme 1).[1-3]

Scheme 1 - Formation of a sterically hindered FLP between a Lewis Acid and a Lewis Base.



The proximity of free Lewis acidic and Lewis basic sites gives rise to very interesting reactivity. FLP chemistry has been used as a strategy to allow main group compounds to activate small molecules, including metal-free hydrogen splitting.[4] In the hydrogen activation reaction mechanism frustrated Lewis pairs undergo heterolytic splitting of dihydrogen forming a proton (H^+) and a hydride (H^-). The isolated Lewis acids and bases don't coordinate hydrogen. Hydrogen activation by FLPs follows bimolecular reaction kinetics, despite there being three different species involved. This has led to the proposition that pre-organised acid-base encounter complexes must be present in solution. Additionally, the encounter complex in the ionic liquid can be detected using proton NMR suggesting both a higher degree of association and a longer lifetime. This theory is supported by kinetic analysis and computational studies. It is thought that the ionic liquid stabilises the encounter complex through matrix isolation which may contribute to the enhanced kinetics of hydrogenation.

Scheme 2 - Representation of orbital interactions in substrate cleavage (E-E') by an FLP.



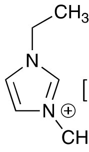
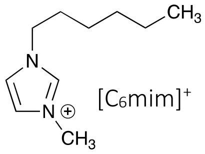
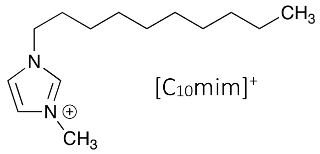
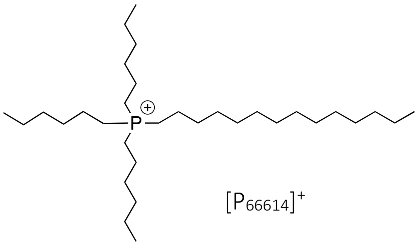
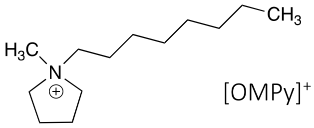
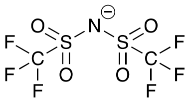
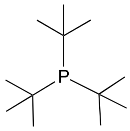
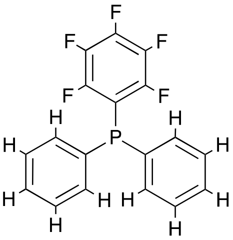
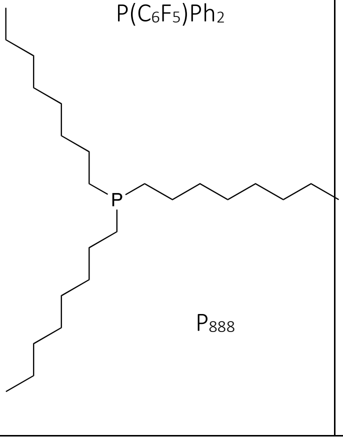
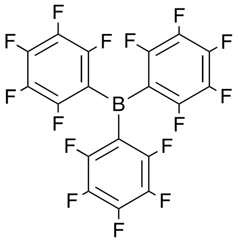
The FLP made from tri-*tert*-butylphosphine and tris(pentafluorophenyl)borane has previously been studied by the Stephan group and within QUILL. It has been shown to effectively split hydrogen in both deuterated benzene and in two ionic liquids. In both cases uptake of hydrogen by the FLP system was confirmed by the formation of a new pair of broad peaks of equal integration in the proton NMR spectrum. This demonstrated the ability of this FLP to split hydrogen in the ionic liquid medium, despite the very low solubility of molecular hydrogen in ionic liquids. The hydrogen is split irreversibly. In molecular solvents such as benzene the attraction is too strong, and hydrogen cannot be released at ambient pressure. In [C_{10}mim][NTf_2] hydrogen was only released under reduced pressure at 150°C but this also resulted in the decomposition of the FLP components.

This study demonstrated enhanced encounter complex formation in ionic liquids. In previous work, the presence of a weakly-associated encounter complex in the model FLP solution: tris-*tert*-butylphosphine ($P(^tBu)_3$) and tris(pentafluorophenyl)borane $B(C_6F_5)_3$ in benzene, was confirmed *via* P...B correlation analysis from neutron scattering data and Empirical Potential Structure Refinement (EPSR).[5] The low diffusivity characteristics of ionic liquids is suggested to enhance high populations of encounter complex. The FLP in the ionic liquid solution retained its ability to split hydrogen.

Objective:
Investigate various of FLP/IL and FLP-IL solutions for their ability to split hydrogen. Finally, active FLP/IL solutions have been tested for their ability to hydrogenate model organic substrates.

Progress to date:
Preparation of FLP/IL systems:
Three different phosphorus components were chosen to generate the FLPs including tri-tert-butylphosphine ($P(^tBu_3)$), trioctylphosphine (P_{888}), *and* diphenyl(pentafluorophenyl)phosphine ($P(C_6F_5)Ph_2$). These phosphorus compounds were chosen as they are all sterically hindered in different ways, either with long alkyl chains, branched groups or rings attached. This makes them attractive targets to potentially form FLPs when combined with BCF. 160 mmol solutions of these FLPs were prepared in three imidazolium based ionic liquids ([C_2mim][NTf_2], [C_6mim][NTf_2] and [C_{10}mim][NTf_2]), one phosphonium ionic liquid ([$P_{666,14}$]Cl) and one pyridinium ionic liquid ([OMPy][NTf_2]). To make up these solutions 0.0324 g (0.16 mol) of the phosphorus compound was weighed into a glass vial and 1 mL of ionic liquid/d_6-benzene was added. 0.0820 g of tris(pentafluorophenyl)borane BCF was then added and left to dissolve under stirring for 1 hour to generate a FLP. An experimental matrix showing the various combinations of frustrated Lewis pairs and ionic liquids in the FLP/IL system is illustrated in Table 1. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMRs were recorded with a d_6-DMSO capillary.

Table 1 - Experimental matrix showing the various combinations of frustrated Lewis pairs and ionic liquids in the FLP/IL systems.

Ionic Liquids (ILs)		**Frustrated Lewis Pairs (FLPs)**	
Cations	**Anion**	**Lewis Acids**	**Lewis Base**
Imidazolium  $[C_2mim]^+$  $[C_6mim]^+$  $[C_{10}mim]^+$ Phosphonium  $[P_{66614}]^+$ Pyridinium  $[OMPy]^+$	bistriflimide  $[NTf_2]^-$	 $P(^tBu)_3$  $P(C_6F_5)Ph_2$  P_{888}	tris(pentafluorophenyl) borane  BCF

Hydrogen Splitting using FLPs:

A novel NMR tube has been designed with a wider neck allowing a septum to be attached and two needles connected. Hydrogen is bubbled through the FLP in the ionic liquid directly in the NMR tube. This unique design will hopefully improve contact between the hydrogen and the ionic liquid as well as encouraging gas transfer. A preliminary study of the FLP made from $P(^tBu)_3$ and BCF in $[C_2mim][NTf_2]$ was conducted to test the hydrogenation setup. Pure hydrogen was bubbled through the FLP solution for 3 hours at a rate of 2 ml/min. As expected, uptake of hydrogen was confirmed by the formation of a new pair of broad peaks of equal integration in the proton NMR spectrum.

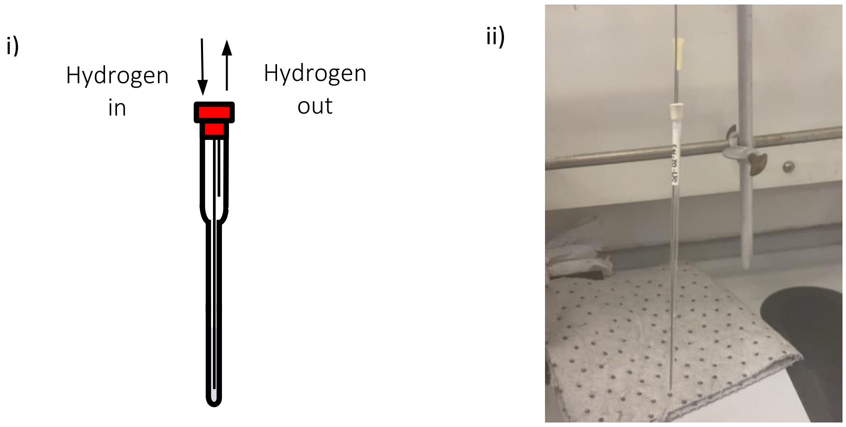


Figure 1 - i) Diagram of initial hydrogen bubbling set up. ii) Photo of current hydrogen bubbling set up using a gas rig.

Pure hydrogen was bubbled through the FLP solution for 12 hours at a rate of 2 ml/min. In all cases uptake of hydrogen by the FLP system was confirmed by the formation of a new pair of broad peaks of equal integration in the proton NMR spectra. This demonstrated that the new FLP made from trioctylphosphine was able to successfully split hydrogen in both imidazolium ionic liquids.

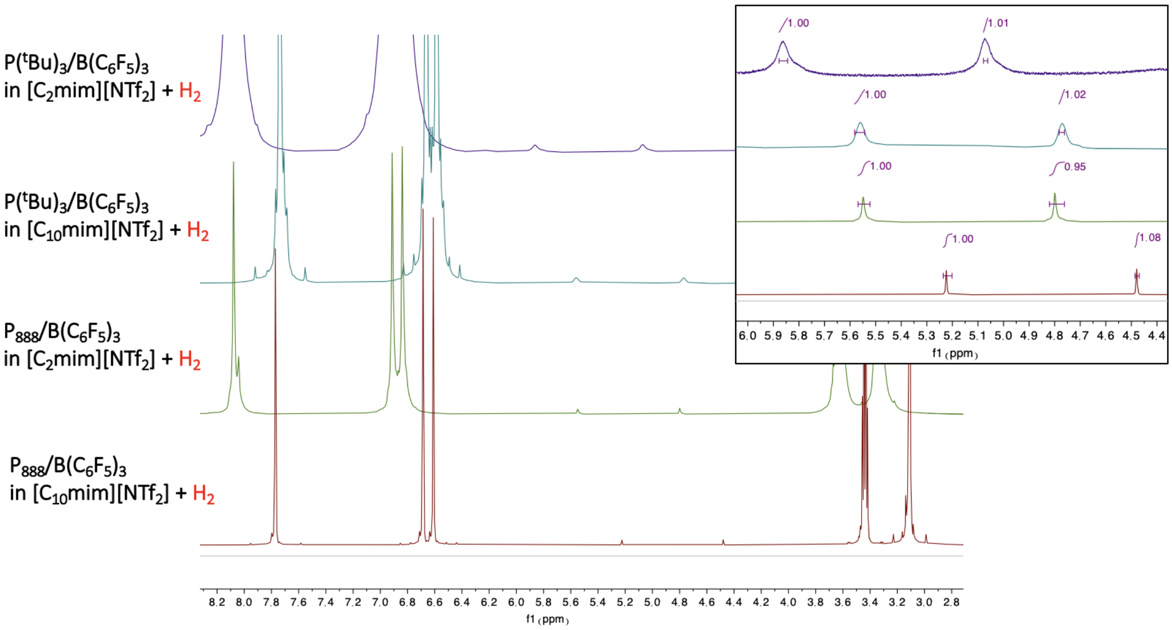
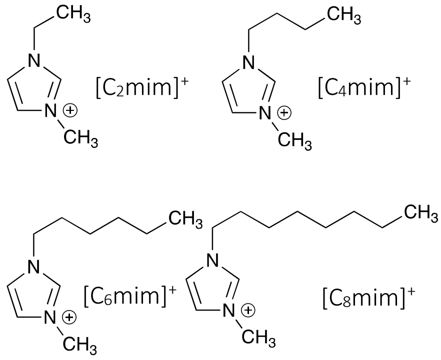
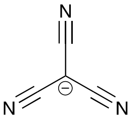
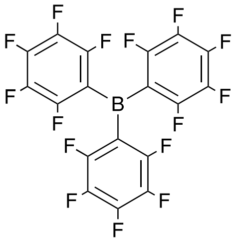
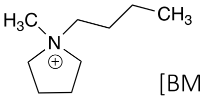


Figure 2 - Stacked ^1H NMRs of FLP/IL systems after bubbling with H_2 for 12 hours.

Preparation of FLP-IL systems:

Lewis acidic ionic liquids with Lewis basic ligands on the boron centre were studied as neat IL-FLP systems. 160 mmol solutions were prepared in four imidazolium ionic liquids ($[C_2mim][TCM]$, $[C_4mim][TCM]$, $[C_6mim][TCM]$ and $[C_8mim][TCM]$ and one pyridinium ionic liquid ([BMPy][NTf$_2$]). To make up these solutions 0.0820 g of tris(pentafluorophenyl)borane (BCF) was weighed into a glass vial and 1 mL of ionic liquid was added. The solution was and left to dissolve under stirring for 1 hour to generate a FLP. An experimental matrix showing the various combinations of frustrated Lewis pairs and ionic liquids in the FLP/IL system is illustrated in Table 2. ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMRs were recorded with a d$_6$-DMSO capillary.

Table 2 - Experimental matrix showing the various combinations of frustrated Lewis pairs and ionic liquids in the FLP/IL systems.

Ionic Liquids (ILs)		**Lewis Base**
Cations	**Anion**	
Imidazolium  [C$_2$mim]$^+$ [C$_4$mim]$^+$ [C$_6$mim]$^+$ [C$_8$mim]$^+$	tricyanomethanide  TCM	tris(pentafluorophenyl) borane  BCF
Pyridinium  [BMPy]$^+$		

Results and conclusions:

FLP/IL Systems:

I have synthesised various imidazolium and phosphonium ionic liquids for use in the generation of FLP/IL systems. Our findings have agreed with previous experimental results, and this confirms that the new hydrogen bubbling setup is suitable. We have discovered that the FLP made from trioctylphosphine can successfully split hydrogen in both imidazolium ionic liquids tested.

Table 3 - Table of results showing which combinations of frustrated Lewis pairs and ionic liquids were able to form an FLP and split hydrogen.

Ionic Liquids (ILs)	**Lewis Acid**			**Lewis Base**
	$P(^tBu)_3$	P_{888}	$P(C_6F_5)Ph_2$	
$[C_2mim][NTf_2]$	🟩	🟩	🟦	BCF
$[C_6mim][NTf_2]$	🟨	🟨	🟨	
$[C_{10}mim][NTf_2]$	🟩	🟩	🟦	
$[OMPy][NTf_2]$	🟨	🟨	🟨	
$[P_{66614}][NTf_2]$	🟨	🟨	🟨	
d$_6$-benzene (control)	🟩	🟨	🟦	

🟩 Forms FLP and splits H_2

🟦 Doesn't form FLP

🟨 Unknown

Future Work:

FLP/IL Systems:

Future work will involve testing the remaining FLP systems for their ability to split hydrogen in $[C_6mim][NTf_2]$, $[P_{666,14}][NTf_2]$ and $[OMPy][NTf_2]$. Ideally, we would like to find a system that can reversibly split hydrogen without the decomposition of the FLP components.

FLP-IL Systems:

The five FLP-IL systems shown in Table 4 will be tested for their ability to split hydrogen. The hydrogen bubbling set up shown Figure 1 ii) will be used. Pure hydrogen will be bubbled through the FLP/IL directly in the NMR tube for 3 hours. ^1H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMRs will be recorded with a *d*$_6$-DMSO capillary.

Table 4 - FLP-IL systems that will be tested for their ability to split hydrogen.

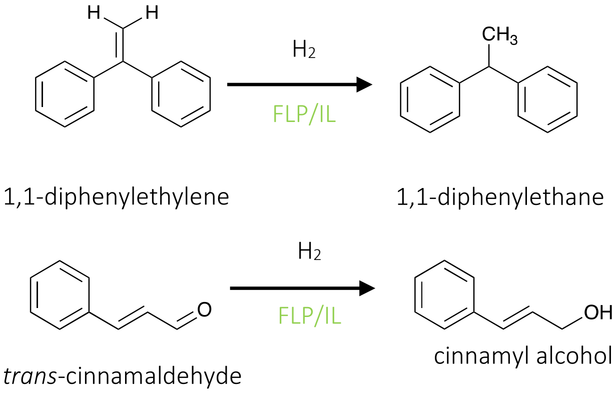
Ionic Liquids (ILs)	**Lewis Base (BCF)**
$[C_2mim][TCM]$	🟨
$[C_4mim][TCM]$	🟨
$[C_6mim][TCM]$	🟨
$[C_8mim][TCM]$	🟨
$[BMPy][TCM]$	🟨

🟨 Unknown

Hydrogenation of Organic Substrates:

Another main area of research will involve the FLP-promoted hydrogenation of organic substrates in ionic liquids. 1,1-diphenylethylene has been chosen as the first substrate to be investigated as it has been previously observed in literature to be effectively reduced by FLP systems. The reduction of 1,1-diphenylethylene to 1,1-diphenylethane and the reduction of *trans*-cinnamaldehyde to cinnamyl alcohol is illustrated in Scheme 3. There is also the possibly of conducting a kinetic study of FLP catalysis and exploring continuous flow reactions using a supported ionic liquids layer (SILP) strategy.

Scheme 3 - FLP-promoted hydrogenation of organic substrates in ionic liquids i) Reduction of 1,1-diphenylethylene to 1,1-diphenylethane and ii) Reduction of *trans*-cinnamaldehyde to cinnamyl alcohol.



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QUILL Quarterly Report

August 2022 – October 2022

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

Liquid Coordination Complexes for the Synthesis of Semiconductor Nanoparticles

Background

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

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

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

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

Objective of this work

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

Progress to date

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

Energy dispersive x-ray fluorescence (ED-XRF) has been used to determine the metal concentration of the aqueous phase pre-extraction, post-extraction and post-metal stripping. For accurate determination of the metal content in the aqueous phase, several multi-metal stock solutions were prepared in 6M HCl with decreasing metal concentration, allowing a calibration curve for each metal present in the zinc leachate to be created by empirical analysis (EMP) on ED-XRF.

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

Additional eutectic systems have also been tested, with the aim of either reducing Fe(III) to Fe(II) or forming a complex with iron in the eutectic phase. As of yet, no system has been found to achieve this aim without also hindering the amount of gallium recovered.

Conclusions and future work

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

Firstly, the identification of eutectic mixtures was completed in the screening study of various HBDs in combination with TOPO. This allowed for the eutectic mixtures to be scaled up and tested as extractants for gallium from a simulated zinc leachate solution. Although in the extraction study, the eutectic systems in this work showed high metal coextraction, therefore, demonstrating low selectivity towards gallium, the benefits of these systems are later highlighted in the metal stripping studies. Both TOPO:malonic acid ($\chi_{TOPO} = 0.60$), and TOPO:erythorbic acid ($\chi_{TOPO} = 0.68$) systems have been shown to successfully recover gallium from a simulated zinc leachate solution.

For future work, further studies to improve the selectivity of the process is required, such as trying different HBDs in combination with TOPO that have the ability to complex or reduce

Fe(III). This would result in higher selectivity towards gallium, when the metals are recovered from the eutectic phase post-stripping.

Future work also includes undertaking the same extraction experiments using the DES systems with real zinc mine tailings, to see if similar results are obtained. Furthermore, to fully utilise this chemistry, studies on the recyclability of the eutectic system should also be carried out to show the system could be reused in successive extractions without the extraction efficiency decreasing.

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QUILL Quarterly Report

August 2022 – October 2022

Name:	Hugh O'Connor		
Supervisor(s):	Prof Peter Nockemann, Dr Stephen Glover and Dr Josh Bailery		
Position:	PhD Student		
Start date:	October 2019	**Anticipated end date:**	Match 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 stored in the electrolyte reservoir tanks. This makes RFBs highly customisable, allowing them to be tailored to meet the demands of various power grids. 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 topologies resulting in a better performing cell.

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

During the early stages of my research, 3D-printing was identified as a powerful tool in the development of laboratory scale redox flow battery cells that can be used to develop new electrolyte technologies or materials. This 3D-pritning platform also allows for unparalleled freedom of design which has been utilised to investigate the performance of a number of previously untested cell geometries. 3D-printing has also been used to generate miniaturised cells to carry out in-situ micro X-ray CT imaging at the Diamond light source synchrotron. In the previous quarter, extensive work has been carried out to improve the reproducibility and repeatability of results from electrochemical testing of flow cells. The data generated is being used to develop a test procedure and recommendations for gaining reliable data from lab scale flow battery testing. Lastly, the development of a couple electrochemical/ fluid flow model has continued, with results showing good correlation with those from literature and experimental results.

Conclusions and future work

Work using our 3D-printing platform has continued and is being used in tandem with electrochemical/ fluid flow simulations to improve redox flow battery design. Work has also been carried out to improve the repeatability of results gained from lab scale testing. Ongoing work involves the manufacture, testing, and simulation of novel cell geometries to evaluate their performance.

Publications

O'Connor *et al.,* An open-source platform for 3D-printed redox flow battery test cells, RSC Sustainable Energy & Fuels, 10.1039/d1se01851e

QUILL Quarterly Report

August 2022 – October 2022

Name:	Liam O'Connor		
Supervisor(s):	Dr O Istrate and Prof B Chen		
Position:	PhD Student		
Start date:	01st Oct 2020	**Anticipated end date:**	30th Sept 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 mechanical properties of the TPU/PA11/GNP have been characterised. The 3D printing conditions for the TPU/PA11/GNP filaments have been calibrated. SEM images of the samples are being collected. The electromechanical properties have been characterised.

Conclusions and future work

The TPU/PA11/GNP blend is ductile, like the TPU/GNP composite. It has an electrical percolation threshold like the PA11/GNP composite. SEM images show that the GNPs are attracted to the interface between the TPU/PA11. Electromechanical results show that the only sample with an electrical response to mechanical strain is PA11 /10GNP. The next stage is to 3D print the filament in different directions and see what effect that has on the mechanical and electrical properties.

QUILL Quarterly Report

August 2022 – October 2022

Name:	Lauren O’Neill		
Supervisor(s):	Prof Gosia Swadzba-Kwasny and Prof John Holbrey		
Position:	PhD Student		
Start date:	1/09/22	**Anticipated end date:**	30/09/25
Funding body:	DfE CAST/ Diamond Light Source and ISIS Neutron and Muon Source		

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

Background

Lewis acidic borenium cations are of interest as possible metal-free catalysts. An example of the applications of these FLP-ILs is hydroboration or small-molecule activation. Many of the borenium ILs in question contain catechol and a weakly-coordinating anion, bis(trifluoromethanesulfonyl)imide or $[NTf_2]^-$. The components of these systems are selected to impart low-melting points while also maintaining high catalytic activity.

Objective of this work

To generate and test new borenium-based FLP-ILs for application in catalysis. This includes incorporating them on solid-support and analysing their capabilities through various methods, including soft x-ray spectroscopy and neutron scattering.

Progress to date

At the beginning of September, I travelled to Diamond to run experiments on the soft-xray beamline using FLP-ILs that had been made my myself and other students in QUILL. The collected data has yet to be analysed.

Since starting, I have been gaining experience in the synthesis of FLP-ILs, while also assisting with extra experimental work for a paper in review. This involved the synthesis and testing of many FLP-ILs for hydrogen activation and use as catalysis. For the successful tests, an olefin was then added into the mix to test if the FLP-ILs were capable of not only activating hydrogen, but also transferring it to a substrate. A full range of NMR spectra were also required for multiple nuclei and all of the reported ILs.

Conclusions and future work

A range of FLP-ILs were tested for hydrogen activation. Going forward, these can be incorporated on solid-support and more data can be collected using the facilities at ISIS and Diamond.

For the previously collected and future data from ISIS/Diamond, I will need to learn how to plot and extrapolate information from what I’ve gotten. This will include learning how to use DISSOLVE and simulate data based on structural information.

QUILL Quarterly Report

August 2022 – October 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 my previous report, I discussed the difficulties I had been facing with reproducibility of electroanalytical experiments due to the very small-scale nature of the work. I also detailed the steps that were then underway to tackle these difficulties, with the use of stock solutions and careful preparation of experimental setups. Since then, Gas Chromatography (GC) and electrochemical results show significantly improved experimentally reproducibility, allowing us to move forward with the study.

We have focused on a combination of chronoamperometric (CA) and chronopotentiometric (CP) studies for understanding catalyst performance more fully. Current status quo in electrocatalysis is to compare catalyst performances using a combination of rate constants and required overpotentials to activate the catalysts in the form of catalytic molecular Tafel plots. We are proposing that catalysts should be presented alongside CA data as this can provide further information on catalyst-system stability; we have demonstrated that comparisons of Tafel plots can be misleading, where some catalysts may have their performance significantly overstated. This is currently being explored further and formal experiments are being designed to stress-test a series of catalysts and determine their real-world performance.

CP studies are proving interesting but will require further work. We are able to monitor a system and observe currents and potentials at which different specific components begin to break down. This is early preliminary work, but we will be exploring this further going forward.

Additionally, our work on the TEMPO-derivative polymer, PIPO, is still underway. We are currently designing experiments to use an immobilised form of PIPO to turnover an alcohol substrate into an aldehyde under benign conditions in aqueous buffer solution.

Conclusions and future work

The main take-away from our work is that the status quo of catalytic Tafel plots are not sufficient for a complete picture of catalyst performance. We propose that Tafel plots be presented alongside amperometric data, and maybe potentiometric data, to provide the reader / user with the information required.

Going forward, we will be performing amperometric studies with a formalised method. We will be pairing this with cyclic voltammetry studies to narrow down causes of instability. We will be moving onto a preparative scale electrosynthesis using a selection of our TEMPO-derivative catalysts. We will then move onto developing a study on potentiometry, exploring the potential uses of chronopotentiometry as an analytical technique.

QUILL Quarterly Report

August 2022 – October 2022

Name:	Junzhe Quan		
Supervisor(s):	Prof John Holbrey and Dr Leila Moura		
Position:	PhD Student		
Start date:	01/10/2019	**Anticipated end date:**	01/10/2023
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 system to test and evaluate draw fluid characteristics and parameters of selected systems
4. Optimize ionic liquid to use as draw fluid, developing a proof-of-concept ionic liquid-based FO desalination demonstrator for benchmarking
5. Examine the applicability of these draw fluids to water-processing of a range of feeds and product streams (desalination, waste concentration, biomass dewatering)
6. Measure the energy consumption and compare with typical method of water treatment

Progress to date

A large quantity of thermos-sensitive ionic liquid $[P_{4444}][TsO]$ has been prepared and fully characterized by NMR, FT-IR and TGA. $[P_{4444}][TsO]/H_2O$ solutions from 0.5M-2.0M are tested by SVM to make sure their smoothness in FO test system tubes. The lab-scale forward osmosis performance test system has been finished built up and start to output series data by combining with TOC, ICP and NMR.

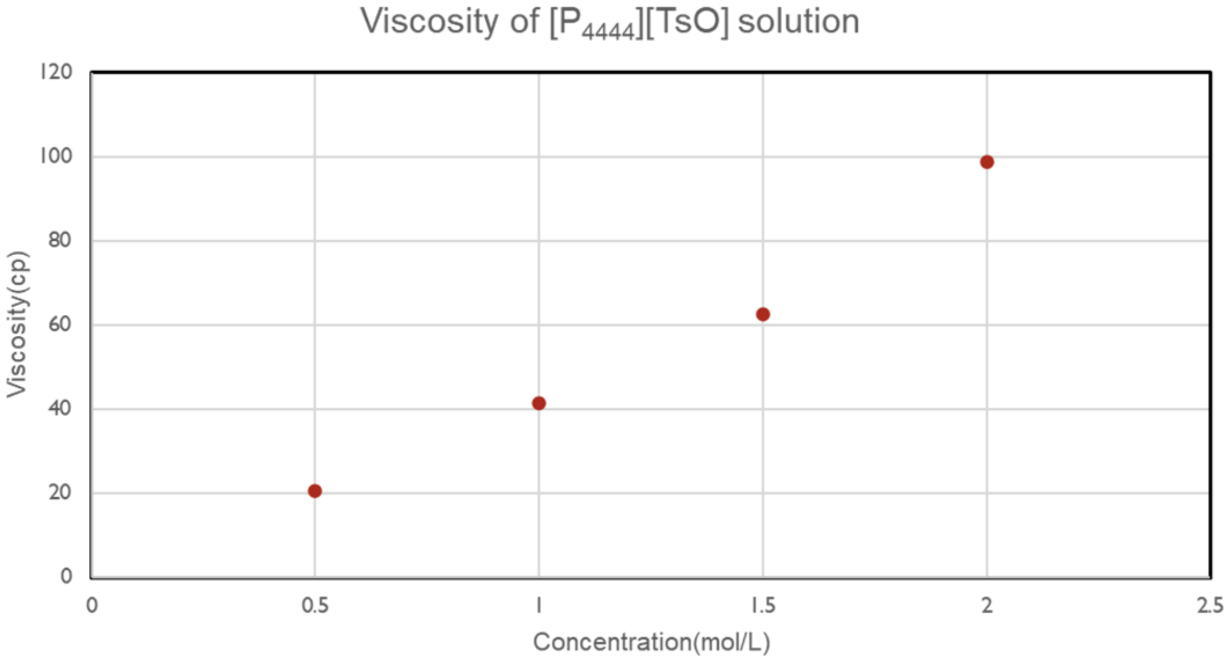

Figure 1 – Viscosity of $[P_{4444}][TsO]$ solution

Conclusions and future work

After the preliminary experiments, we determined that we need about 300 mL draw solute for every test. The reason for needing these large quantities is that there will be about 250 mL fluids recycled in cell and tubes. We also can determined that we now have the capacity to explore a range of LCST type IL draw solute particularly extracting relative performance indicators from this system.

About the future work, we plan to test two materials([P4444][TsO] and [P4444][Ph-tet]) in this system and compare their FO performance. Then, we will focus on test more LCST type IL materials to select and optimize the best one for different industry application. After testing these thermo-sensitive ILs, we can also test some other kinds of draw solutes just like switchable CO_2-stimuli materials. Then compare them to explore the difference between them to show IL draw solute's advantages.

QUILL Quarterly Report

Aug 2022 – Oct 2022

Name:	Richard Woodfield		
Supervisor(s):	Dr Stephen Glover and Prof Peter Nockemann		
Position:	PhD Student		
Start date:	03/06/2019	**Anticipated end date:**	03/05/2023
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

To date work has been published on the use of vanadium redox flow batteries in ferry applications 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

Modelling work has begun investigating the use of vanadium redox flow batteries in hybrid bus applications, where initial models show promise.

QUILL Quarterly Report

August 2022 – October 2022

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

Gas Separation Technologies

Background

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

Currently biogas upgrading is multistep, with scrubbing used for carbon dioxide removal from the biogas stream to concentrate methane. This involves the use of liquid amines such as MEA (monoethanolamine) where carbon dioxide is captured through a chemisorption process. Regeneration of the amines requires high energy inputs in the form of steam at 100-150^{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.

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.

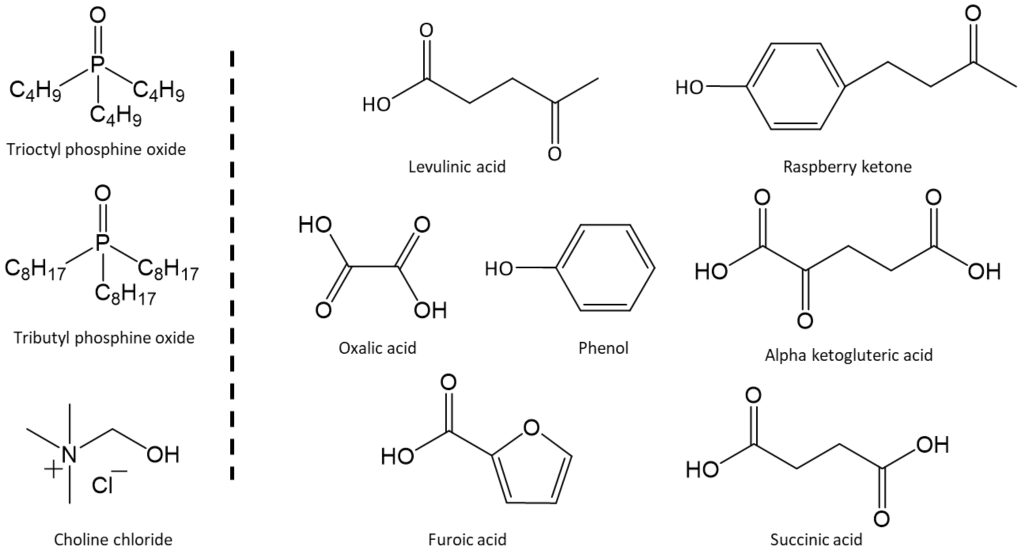

Figure 1 - Structures of hydrogen bond acceptor (left) and hydrogen bond donor (right) components of TOPO-based HLMMs used in this work

Gas uptake measurements have shown that these materials have exceptionally high CO_2 uptake when compared with other DES physisorbents 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.

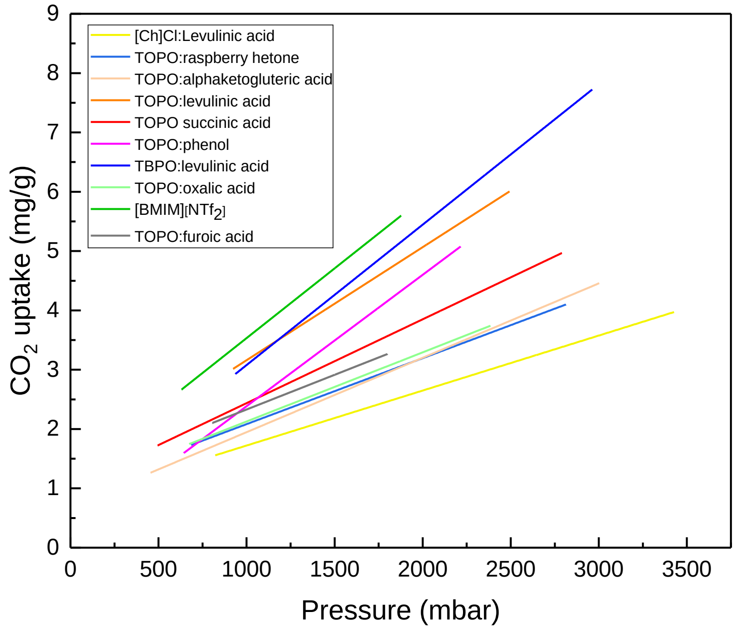

Figure 2 - Plot of CO_2 uptake in mg/g as a function of pressure in various TOPO based deep eutectic solvents using [BMIM][NTf_2] as a comparative standard ionic liquid

VOC uptake in TOPO-based hydrophobic low melting mixtures

These same materials were tested for their VOC uptake capacity using a static headspace GC methodology. It weas found that these materials have partition coefficients which are lower than some traditional solvents such as PEG 200. These LMMs were tested with several different classes of VOC (siloxane, terpene and toluene) which are commonly found in biogas streams. These measurements add a possibility of these LMMs being able to remove multiple contaminants form a biogas stream simultaneously. This would be highly desirable in small scale applications where the space occupied by the upgrading technology could be limited.

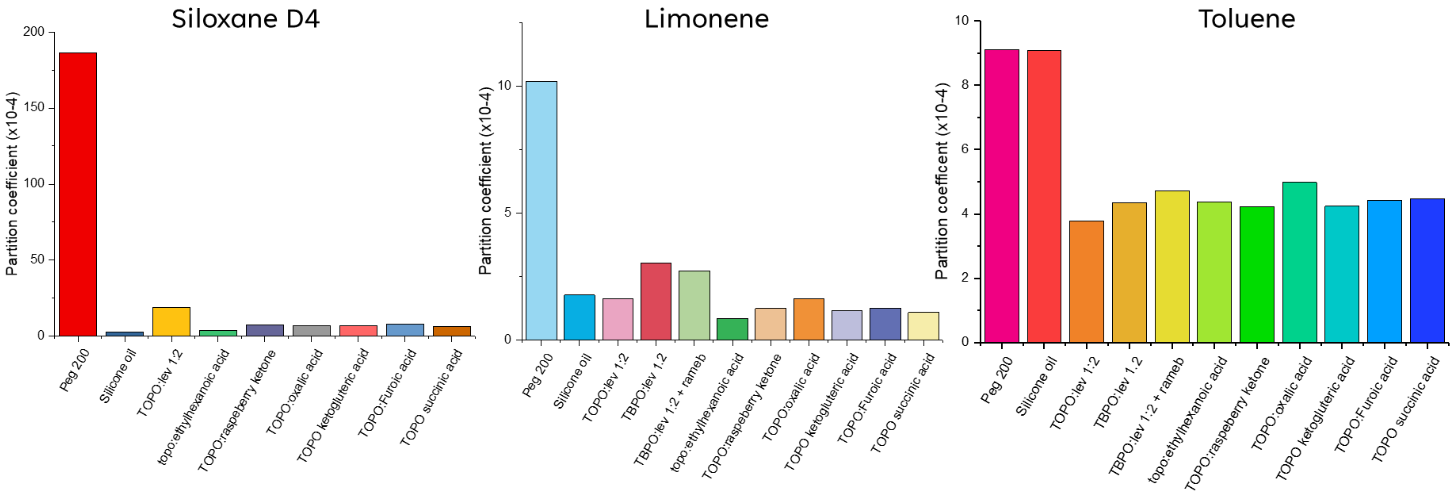

Figure 3 - Plots of partition coefficients of standard materials and LMMs with various classes od VOC

Future work

Gas uptake measurements will be completed using the gas system for our most promising absorbents, including measurements at elevated temperatures which are commonly carried out industrially. This will serve to confirm the results and also confirm the accuracy of the GC methodology. Once these studies have been completed along with validation of the GC methodology, the results will be published in two separate papers.

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