

Imperial College London  
Department of Chemistry

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# Liquid-Liquid Interfaces For Sensing Applications

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## Declaration

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## Abstract

A series of unfunctionalised and hydroxyl functionalised ionic liquids were synthesised with the aim of developing an ionic liquid based sensing platform. The electrochemical, and interfacial properties, were investigated and characterised to understand their use in a liquid-liquid, ITIES, platform.

Electrochemical cells were designed and tested against model systems before the potential windows for the ionic liquid, ITIES, systems were measured. The potential windows were substantially wider than those previously reported. Initial agitation experiments with cytochrome-c showed promising results for the extraction and stabilisation, in the ionic liquids. However, protein ion transfer, under an applied potential, across the interface was not possible with any of the ionic liquids synthesised here. Capacitance results indicated, along with the cytochrome-c agglomeration, a charge build up or diffusion impedance at the interface.

To investigate the reasons for this in greater depth pulse gradient stimulated echo NMR was undertaken and combined with fluorescence correlation spectroscopy. In the first reported monitoring, of the effect of an applied electric field on a probe in an ionic liquid by FCS, the results showed a marked 80 - 90 % decrease in diffusivity and an extremely slow relaxation time after the field was removed. After 600 seconds the diffusivity at the electrode surface was found to be unchanged, while the bulk diffusivity reduction had only reduced by 7 %. These results support the application of hole theory to ion diffusion within ionic liquids.

Initial theoretical modelling to understand the ion dynamics at the interface provides intriguing evidence to support the development of theoretical tools to investigate interfacial ion dynamics, with what is believed to be the first reported use of a temporal split-step model based approach. This approach is approximately 10 - 20 times faster than previously reported methods.

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# Nomenclature

AOT bis(2-ethylhexyl) sulfo-succinate

APD Avalanche photodiode detector

B or B88 Generalised Gradient Approximation based exchange functional developed by Becke in 1988

B3LYP Becke, Three-Parameter, Lee-Yang-Paar functional

BREs Biological Recognition Elements

Cyt-c Cytochrome-c

DFT Density Functional Theory

DMSO-d6 Deuterated DMSO

DOSY Diffusion-ordered spectroscopy

FCS Fluorescence correlation spectroscopy

FIT Facilitated Ion Transfer

GGA Generalised Gradient Approximations

H-bonding Hydrogen bonding

HEWL Hen-Egg-White Lysozyme

HF Hartree-Fock approximation

IFT Interfacial tension

|        |                                                        |
|--------|--------------------------------------------------------|
| IL     | Ionic liquid                                           |
| ITIES  | Interface between Two Immiscible Electrolyte Solutions |
| ITO    | Indium-tin oxide                                       |
| LDA    | Local Density Approximation                            |
| LSDA   | Local Spin Density Approximation                       |
| MD     | Molecular dynamics                                     |
| MW     | Molecular weight                                       |
| NIST   | National Institute of Standards and Technology         |
| PDMS   | Polydimethylsiloxane                                   |
| PGSE   | Pulsed gradient spin echo                              |
| PGSTE  | Pulsed gradient stimulated echo                        |
| ppm    | parts per million                                      |
| PTFE   | Polytetrafluoroethylene                                |
| Rh123  | Rhodamine 123                                          |
| SCE    | Saturated Calomel Electrode                            |
| SHE    | Saturated Hydrogen Electrode                           |
| SIT    | Simple Ion Transfer                                    |
| SMF    | Single molecule fluorescence                           |
| STE    | Stimulated echo                                        |
| UV-Vis | Ultraviolet-visible                                    |
| VFT    | Vogel-Fulcher-Tamman                                   |

# Chapter 1

## Introduction

The “holy-grail” for the detection and classification (or identification) of chemicals, and biological, materials is a sensor platform which utilises a method that is simple, fast, sensitive, specific and can be exploited across a wide variety of applications.

One of the methods that could meet all of these varied characteristics, for the detection of a broad range of materials, is based on the extraction of compounds from one liquid to another, known as liquid-liquid extraction. To most chemists liquid-liquid extraction is only used during synthesis laboratory courses and involves a separating funnel. The extraction is usually performed to remove the desired product of a reaction from impurities i.e. unwanted by-products or unreacted starting materials, or vice versa. This is a time consuming, and usually dreaded process (due to the reliance on passive diffusion), typically having significant losses of the sample and involves the use of large volumes of toxic solvents.

Electrochemical techniques have been applied to liquid-liquid extraction in an attempt to improve the extraction methodology. This has led to the development of a method that can selectively partition ions from a mixture through the application of an interfacial potential difference (i.e. the application of a charge across the interface of the two liquids). This development has opened up a whole new area of research not just for selective extraction but for the highly sensitive detection of species within complex media.

If the liquid-liquid methodology is successful for selective extraction of specific analytes it will provide a platform capable of performing specific and sensitive

detection of materials (e.g. chemical or biological hazards) within a liquid medium, removing the need to immobilise Biological Recognition Elements (BREs) on surfaces for use in sensing platforms. This platform could also provide a full system concept for the processing, extraction and measurements of analytes in a single system.

## 1.1 Outline of Work

The aim of this work was to investigate the possible use of ionic liquids in combination with electrochemical based liquid-liquid extraction and sensing:

Chapter 2 details the experimental methods and synthetic methodology, including analytical results, used within this project.

Chapter 3 undertakes to characterise a number of unfunctionalised and hydroxyl functionalised imidazolium based ionic liquids with varying alkyl chains in regard of their applicability to biological macromolecule extraction, stabilisation and their use electrochemically in a liquid-liquid, ITIES, sensing platform.

Chapter 4 documents the use of the synthesised ionic liquids for initial agitation based extraction experiments with biological macromolecules. The design of electrochemical cells to facilitate the application of an electric field to the system is then described before testing with cytochrome-c.

Chapter 5 is an investigation into the diffusion of ions within an ionic liquid, studied via pulse gradient stimulated echo NMR and fluorescence correlation spectroscopy. Initial results show support for the application of hole theory to diffusion in ionic liquids, in disagreement with the ion-cage interpretation, and extremely long discharge times.

Chapter 6 develops initial theoretical modelling looking specifically at ion diffusion across an interface, and within the bulk of the immiscible phases, using the application of a split-step approach for the first time.

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

# Chapter 2

## Methodologies and synthesis

### 2.1 Viscosity measurements

The viscosity measurements were performed on a TA Instruments AR2000EX rheometer. The temperature was controlled through the use of a Peltier plate, and a 40 mm, 2° steel cone geometry was used for all of the measurements. Measurements were recorded over a range of temperatures with angular velocities between 0.1 and 10 rad per second. During the measurements, due to the length of time per measurement, the samples were kept under a blanket of nitrogen to ensure no ingress of water which could have distorted the results. TA Instruments states a 5 % error, however the reproducibility of the results was found to be better than this.

### 2.2 Density measurements

The density measurements recorded were performed using an Anton Paar ‘DMA38’ vibrating U-tube density meter. All readings were performed at 25 °C and repeated three times to give an averaged result. The error associated with the measurement has been given as  $\pm 0.001 \text{ g cm}^{-3}$  by the manufacturer.

## 2.3 Water content

Water content of the ionic liquids were measured via Karl-Fischer titration on a Mettler Toledo C30 Compact Karl Fischer Coulometer. Samples were repeated three times and an averaged result reported.

## 2.4 UV-Vis spectroscopy

UV-Visible spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer, calibrated to  $\pm 0.2$  nm using a holmium oxide standard, with an accuracy of 0.5 nm and using 0.1 cm zirconium cells. All readings were taken at a constant temperature of 25 °C via a thermostatic circulator controlling the sample holder temperature. The cuvettes were cleaned before each use with nitric acid:water (1:1), followed by water (x 2), ethanol (x 4) and DCM (x 6) before drying under a stream of dry nitrogen. The spectra were recorded over a range of 200 - 800 nm and were only used if the absorbance of the maximum wavelength was between 0.8 - 1.2 nm.

## 2.5 Interfacial tension (IFT) measurements

The interfacial surface tension measurements were performed using a specifically designed cell (Produced by Dr Kevin Lovelock, JRF, Imperial College London) at 20 °C.

The interfacial measurements were performed in a pendant drop manner, injecting the denser phase into the light phase. In these experiments that was the ionic liquid into a deionised water phase. The images were acquired using a Krüss EasyDrop, and the associated Drop Shape Analysis software was used for the determination of the interfacial tension of the ionic liquid:water interface (see Figure 2.5.1 - Left, for an acquired image).

Method: The setup used a one millilitre syringe on a computer controlled syringe driver. A wide bore stainless steel needle with a diameter of 1.830 mm was used to minimise the likelihood of the ionic liquid climbing the outside of the needle. External light sources were minimised and the droplet illuminated

directly from behind. The ionic liquid was injected until it was the largest stable pendant drop possible. It was injected as atmospherically wet, and the droplet was equilibrated for 5 minutes before the image was ‘frame-grabbed’ from the video using the built in frame grabber software.

Once the image is grabbed it is possible to determine the interfacial tension.

1. The image is scaled. This is performed using the lower edge of the needle as the diameter is already known accurately. Figure 2.5.1 - Left, shows the grabbed frame for  $[\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ . The two blue lines represent the area used for the scaling/magnification. The edge of the needle between these two lines is determined and then the diameter between those two extrapolated lines calculated. The size of a pixel is then determined from the known value.
2. The edge of the droplet is determined. The purple line is used to determine where the needle ends so that it is not included in the edge detection of the droplet. The edge detection is performed where the pixel value is the last black pixel. i.e. where the colour changes from black to white. The contour of the edge is then determined. This is then applied to the image, this is a red line, currently under the green line shown.
3. The Young-Laplace equation is fitted to the contour and the calculated fit is plotted on the image, represented by the bright green line.
4. The fit allows the determination of the various parameters required to determine the interfacial tension values (see Figure 2.5.1 - Right).

## 2.6 Computational modelling

### 2.6.1 Volume calculations

The ionic volumes of the ionic liquids were calculated using the Gaussian 09 software package.<sup>[5]</sup> A Becke’s three-parameter functional, with the Lee-Yang-Paar (LYP) GGA correlation functional, and 6-311+G(d,p) basis set was used.<sup>[6]</sup> The integration grid was set to ‘ultrafine’ and an electron density convergence criterion of  $10^{-9}$  used.

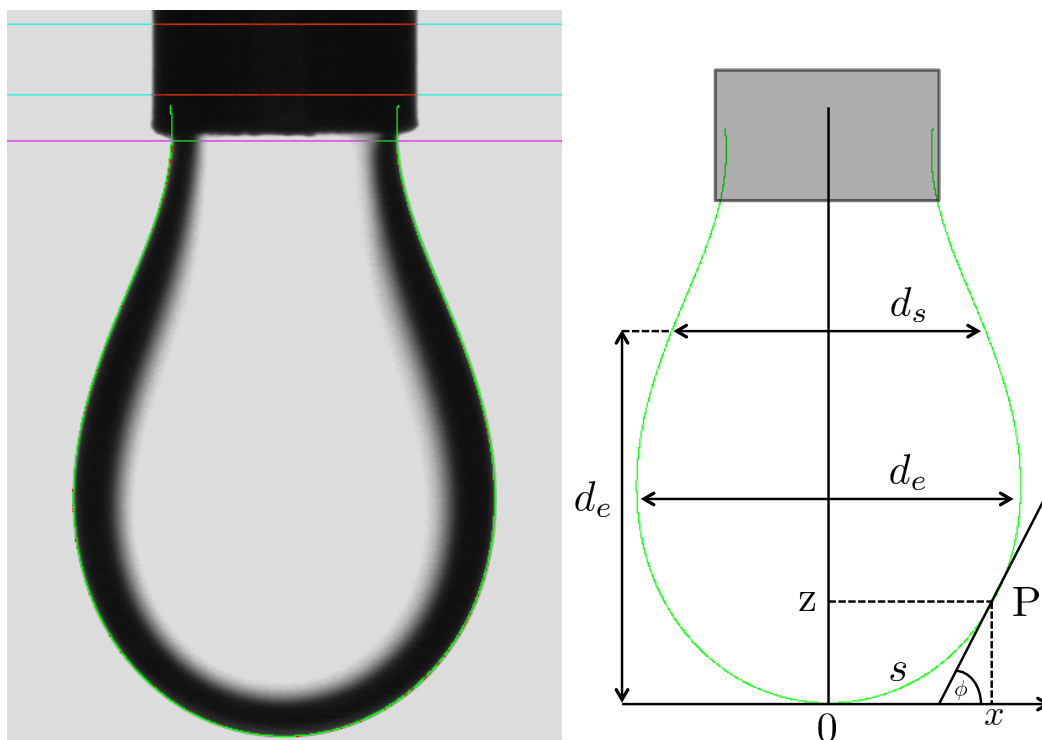


**Figure 2.5.1** – Pendant drop of  $[C_8C_{1im}][NTf_2]$  in distilled water (left). Labelled pendant drop, having extracted the Young-Laplace fit from the image (right).  $s$  is the length of the arc along the drop profile,  $\phi$  is the angle between the tangents at point  $P(x,z)$  and the x-axis.  $d_e$  is the diameter at the equator and  $d_s$  is the diameter at the selected plane at a height  $d_e$  from the x-axis.

Two methods were used for the determination of the optimised structures before calculating the volumes:

1. Structures were fully optimised (via ‘opt’) without constraints and confirmed by frequency analysis.
2. Optimised structures were determined through sequential minimisation of the energy of the dihedral angles along the long alkyl chain (using ‘scan’). This was performed in two steps, an initial coarse scan of 36 steps of 10 degrees each, followed by a fine scan of 25 step of 1 degree each in the clockwise and counterclockwise direction.

The ionic volumes were then calculated. The volume stated in Tables 3.10.1 & 3.10.2 are each the mean of 10 calculations.

### 2.6.2 Split-step model

The code for the split-step model is given in Appendix C and was run in MATLAB<sup>®</sup> (R2014b, 8.4.0.150421).

## 2.7 Agitation experiments

The agitation experiments were performed using a Lab Scale (SSL2), reciprocating shaker. The vials being agitated were placed in Falcon tubes as secondary containment and then agitated for 1 hour, 250 strokes per minute, at room temperature (20 °C).

## 2.8 Electrochemical experiments

### 2.8.1 Conductivity measurements

Conductivity measurements were performed using a custom made two-prong platinum based probe. All of the measurements were performed at 25 °C using a stabilised oil bath. The samples were allowed to equilibrate overnight before being measured. The measurements were performed under a blanket of

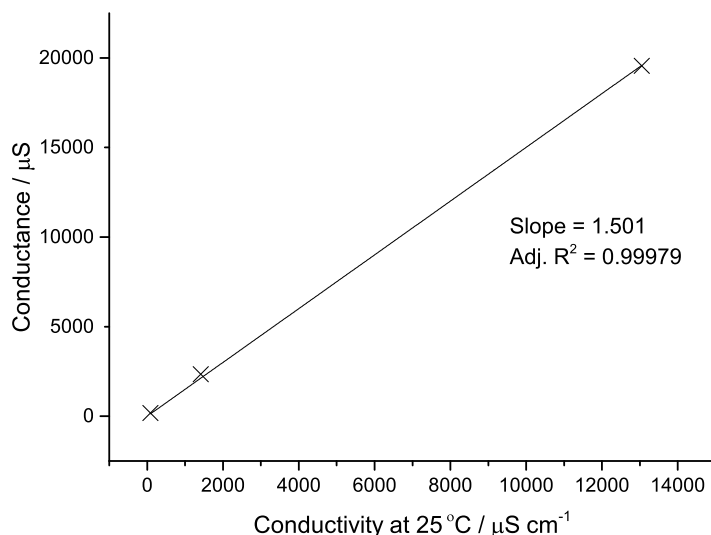


**Figure 2.8.1** – Conductivity standards tested with a custom made conductivity probe. Slope equals the cell constant of the probe.

argon, with no stirring (to avoid any field effects), on a CH Instruments, CHI760 potentiostat. To calculate the cell constant for the probe, the conductivity of three NIST traceable standards by Reagecon (purchased from Fisher Scientific), with known conductivity values, were measured before each run:  $84 \mu\text{S cm}^{-1}$ ,  $1413 \mu\text{S cm}^{-1}$  and  $12280 \mu\text{S cm}^{-1}$ . The cell constant calculated was found to be  $1.501 \text{ cm}$  (slope of Figure 2.8.1). Measurements were performed with an amplitude of  $5 \times 10^{-3} \text{ V}$  and frequency range of  $1 \text{ Hz}$  to  $1 \times 10^5 \text{ Hz}$ .

## 2.8.2 Liquid-liquid, Interface between Two Immiscible Electrolyte Solutions (ITIES)

All liquid-liquid, ITIES, experiments were performed using an Autolab, PGSTAT101 or PGSTAT302N. Data was recorded in Nova and then exported for analysis in OriginPro 9.1.

The platinum electrodes were cleaned in a hydrogen flame before use. The silver, silver chloride reference electrodes were made via chloridising with a  $1 \text{ M}$  KCl solution at a current density of  $0.4 \text{ mA cm}^{-2}$  for 30 minutes, washed with  $18$

M $\Omega$  water and aged for two days in 18 M $\Omega$  water. Previous coatings were first removed by soaking in concentrated ammonium hydroxide solution. Before use the reference electrodes were tested with a ferrocene/ferrocenium redox couple.

The electrochemical cells were cleaned using concentrated sulphuric acid overnight. In the case of the fritted cell the acid was pulled through the frit to ensure full cleaning occurred. Once soaked the cells were washed with distilled water and soaked for a further 24 hours before washing. At this stage the cells were dried and then used immediately after washing the surfaces of the cell with the aqueous solution of the type being used in the experiment.

## 2.9 NMR methods

### 2.9.1 Standard NMR experiments

NMR spectra were recorded on a 400 MHz Bruker BioSpin GmbH spectrometer, with all chemical shift values given as ppm (relative to tetramethylsilane) and J-coupling constants given in Hz.

### 2.9.2 Pulse Gradient Stimulated Echo experiments

DOSY experiments were measured at a temperature of 298 K on a Bruker 500 MHz AVANCE III HD spectrometer running TopSpin 3.2 and equipped with a z-gradient bbo/5 mm tuneable SmartProbe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5 G cm<sup>-1</sup> (5.35 G cm<sup>-1</sup>A<sup>-1</sup>).

The <sup>1</sup>H DOSY spectra were collected using the Bruker pulse program, led-bpgp2, at a frequency of 500.13 MHz with a spectral width of 5500 Hz (centred on 4.5 ppm) and 32768 data points. A relaxation delay of 12 s was employed along with a diffusion time (large delta) of 150 ms and a longitudinal eddy current delay (LED) of 5 ms. Bipolar gradients pulses ( $\delta/2$ ) of 5 ms and homospoil gradient pulses of 1.1 ms were used. The gradient strengths of the 2 homospoil pulses were -17.13 % and -13.17 %. 24 experiments were collected with the bipolar gradient strength, initially at 2 % (1<sup>st</sup> experiment), linearly increased to 95 % (24<sup>th</sup> experiment). All gradient pulses were smoothed-square shaped (SMSQ10.100) and after

each application a recovery delay of 200  $\mu$ s used. The data was processed using 16384 data points in the direct dimension applying an exponential function with a line broadening of 1 Hz and 128 data points in the indirect dimension. Further processing was achieved using the Bruker Dynamics Center software (version 2.1.7) – error estimation by Monte Carlo simulation with a confidence level of 95 %.

The  $^{19}\text{F}$  DOSY spectra used the same pulse program as above and were collected at a frequency of 470.59 MHz with a spectral width of 18800 Hz (centred on -80.4 ppm) and 65536 data points. DOSY parameters were the same as above except the diffusion time was 200 ms and bipolar gradient pulses 3 ms. The data was processed using 65536 data points in the direct dimension applying an exponential function with a line broadening of 1 Hz and 128 data points in the indirect dimension. Further processing was achieved using the Bruker Dynamics Center software (version 2.1.7) – error estimation by Monte Carlo simulation with a confidence level of 95 %.

## 2.10 Single molecule fluorescence (SMF)

All fluorescence correlation spectroscopy (FCS) experiments were carried out using a custom-built confocal spectroscopic setup (see Chapter 5, Figure 5.2.1) of the Edel Research Group, Imperial College London. It consists of a 488 nm diode laser (Coherent UK Ltd., UK). The laser beam is aligned into an IX71 microscope (Olympus) using beam steering mirrors. The laser beam width is enlarged using a beam expander (Thorlabs, UK) to entirely backfill the aperture of a  $60\times$  water immersion microscope objective ( $60\times/1.20$  NA, water immersion, Olympus, UK). A dichroic mirror (z488rdc, Chroma Technology Corp., USA) is used to reflect the 488 nm laser beam into the objective lens. The incident laser beam is focused by the objective lens. Fluorescence emission is collected by the same objective and then transmitted through the dichroic mirror. Any residual excitation light is removed by an emission filter (z488lp; Chroma Technology Corp., USA). The fluorescence is then focused onto a 75  $\mu$ m precision pinhole (Melles Griot, UK) positioned in the focal plane of the microscope objective. Subsequently, the fluorescence is filtered by an emission filter (hq540/80 m, Chroma Technology Corp., USA) and focused by a planoconvex lens ( $f = 30.0$ , i.d. 25.4 mm, Thorlabs,

UK) onto an avalanche photodiode detector (AQR-141, EG&G, Perkin Elmer). The detector is coupled to a multifunction DAQ card for data logging (PCI 6602, National Instruments) which has submicrosecond time resolution per channel. A LabView program is used to control data acquisition of the FCS measurements. Fitting of the autocorrelation curves was performed using code provided by the Edel Research Group, and modified for these experiments (see Appendix B).

The Rhodamine 123 used in these experiments was purchased from Sigma-Aldrich and was used, without any purification, at a probe concentration of 100 pM.

### 2.10.1 Polydimethylsiloxane (PDMS) cell

The PDMS cell used in the SMF experiments was made using the Sylgard<sup>®</sup> 184 Silicone Elastomer Kit from Dow Corning in the following manner:

1. PDMS curing reagent and base, in a ratio of 1:10, were mixed in a plastic beaker for 5 minutes.
2. The resulting mixture was placed in a vacuum desiccator and evacuated to remove air bubbles from the elastomer. The mixture was left for approximately 30 minutes and returned to atmosphere and re-evacuated periodically as this helped to burst any remaining air bubbles.
3. The de-gassed elastomer was then poured over a silicone wafer (Sigma-Aldrich wafer - single side polished, <100>, N-type containing no dopant) placed in a plastic petri dish, in an aluminium foil tray.
4. To achieve central void, for the ionic liquid sample in the SMF experiments, a glass vial was held in place against the wafer while pouring the elastomer to result in a cylindrical void once cured.
5. The aluminium tray, with the setting cell, was placed in an oven at 110 °C for 1 hour to fully cure.
6. The tray was removed and the resulting PDMS cell cut down to size for use in the experiments.

## 2.11 Synthetic Methodology and Analytical Results

All reagents, unless specifically stated, were purchased from Sigma-Aldrich and purified using published techniques.<sup>[7]</sup>

Mass spectrometry were recorded on a Micromass AutoSpec Premier (LSIMS) instrument. The solvent used for LSIMS sample preparation was acetonitrile, for the ionic liquid chloride salts, and dichloromethane for the final products (i.e. the imidazolium bis(trifluoromethylsulfonyl)imide ionic liquid).

Elemental analysis was carried out by Stephen Boyer at the London Metropolitan University.

### 2.11.1 Synthesis of 1-ethyl-3-methylimidazolium bromide [C<sub>2</sub>C<sub>1</sub>im][Br]

1-bromoethane (100 ml, 1340 mmol, 1.2 eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (89 ml, 1117 mmol, 1 eq) in dry ethyl acetate (150 ml). During the addition the product started to form and this was evident by the clouding of the solution. Once the addition was completed the resulting solution was left stirring overnight. By the following day stirring has ceased due to the formation of solid product throughout the majority of the solvent. The solvent was removed via cannula before the resulting crystals were washed with dry ethyl acetate (3 x 50 ml). The crystals were dried under vacuum for 6 hours before recrystallising from acetonitrile. The solution was allowed to cool to room temperature, during which time crystals started to form. The solution was then placed into the freezer (-21 °C) for 48 hours before removing the remaining solvent and drying under high vacuum overnight to yield white crystals (186.4 g, 87 % yield).

$\delta_{\text{ }^1\text{H}}$  (ppm) (400 MHz; DMSO-*d*<sub>6</sub>): 9.18 (1H, s, C(2)**H**), 7.81 (1H, s, C(4)**H**), 7.72 (1H, s, C(5)**H**), 4.2 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>3</sub>), 3.85 (3H, s, -NCH<sub>3</sub>), 1.41 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.24 (C(2)H), 123.55 (C(4)H), 121.97 (C(5)H), 118.35 (-CF<sub>3</sub>), 44.1 (-NCH<sub>2</sub>CH<sub>3</sub>), 35.70 (-NCH<sub>3</sub>), 15.12 (-NCH<sub>2</sub>CH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 111 ([C<sub>2</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 79 ([<sup>79</sup>Br]<sup>-</sup>, 100 %), 81 ([<sup>81</sup>Br]<sup>-</sup>, 97 %).

Elemental Analysis (expected): C, 37.64 (37.72); H, 5.87 (5.80); N, 14.61 (14.66).

### 2.11.2 Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>2</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (98 g, 341 mmol, 1.3 eq) was added slowly to a stirring solution of 1-ethyl-3-methylimidazolium bromide (50 g, 262 mmol, 1 eq) in dichloromethane (225 ml). The resulting solution was stirred for 48 hours. Water was then added and once the lithium bromide had dissolved the phases were separated and the dichloromethane phase washed with distilled water until the washing were negative by the silver nitrate test (17 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (100.1 g, 98 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.10 (1H, s, C(2)H), 7.77 (1H, s, C(4)H), 7.69 (1H, s, C(5)H), 4.18 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>3</sub>), 3.84 (3H, s, -NCH<sub>3</sub>), 1.41 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.45 (C(2)H), 123.79 (C(4)H), 122.18 (C(5)H), 118.36 (-CF<sub>3</sub>), 44.34 (-NCH<sub>2</sub>CH<sub>3</sub>), 35.89 (-NCH<sub>3</sub>), 15.28 (-NCH<sub>2</sub>CH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 111 ([C<sub>2</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 24.65 (24.55); H, 2.66 (2.83); N, 10.64 (10.74).

### 2.11.3 Synthesis of 1-propyl-3-methylimidazolium chloride $[\text{C}_3\text{C}_1\text{im}][\text{Cl}]$

1-chloropropane (50 ml, 568 mmol, 1.1 eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (41.2 ml, 516 mmol, 1 eq) in dry ethyl acetate (100 ml). Once the addition was completed the resulting solution was heated to 45 °C for 9 days under nitrogen. The solution was then allowed to cool to room temperature before being cooled to -21 °C for 2 days. Crystallisation of the product occurred upon cooling. The resulting crystals were washed with dry ethyl acetate (9 x 50 ml) and recrystallised from acetonitrile. Ethyl acetate was slowly added to ensure full crystallisation and the crystals were dried under a low heat (35 °C) overnight to yield white crystals (72.8 g, 88 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.27 (1H, s, C(2)**H**), 7.80 (1H, s, C(4)**H**), 7.74 (1H, s, C(5)**H**), 4.14 (2H, t, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.86 (3H, s, -NCH<sub>3</sub>), 1.80 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.85 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -N(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.59 (C(2)H), 123.61 (C(4)H), 122.27 (C(5)H), 50.22 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 35.73 (-NCH<sub>3</sub>), 22.83 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 10.41 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 125 ( $[\text{C}_3\text{C}_1\text{im}]^+$ , 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ( $[\text{Cl}]^-$ , 100 %), 37 ( $[\text{Cl}]^-$ , 30 %).

Elemental Analysis (expected): C, 52.15 (52.34); H, 8.29 (8.16); N, 17.27 (17.44).

### 2.11.4 Synthesis of 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_3\text{C}_1\text{im}][\text{N}(\text{Tf})_2]$

Lithium bis(trifluoromethylsulfonyl)imide (72.9 g, 254 mmol, 1 eq) was added slowly to a stirring solution of 1-propyl-3-methylimidazolium chloride (40.82 g, 254 mmol, 1 eq) in dichloromethane (150 ml) and water (50 ml). The resulting solution was stirred for 48 hours before separating organic phase. The DCM layer

was washed with distilled water until the washings were negative by the silver nitrate test (7 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (93.2 g, 90 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.10 (1H, s, C(2)**H**), 7.76 (1H, s, C(4)**H**), 7.70 (1H, s, C(5)**H**), 4.12 (2H, t, -N**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.85 (3H, s, -N**CH**<sub>3</sub>), 1.80 (2H, sextet,  $^3J_{\text{HH}} = 7.3$  Hz, -N**CH**<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 0.86 (3H, t,  $^3J_{\text{HH}} = 7.4$  Hz, -N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>3</sub>).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.51 (**C**(2)H), 123.64(**C**(4)H), 122.26 (**C**(5)H), 118.35 (-**CF**<sub>3</sub>), 50.27 (-N**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 35.73 (-N**CH**<sub>3</sub>), 22.83 (-N**CH**<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 10.38 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 125 ([C<sub>3</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 26.83 (26.67); H, 3.27 (3.23); N, 10.45 (10.37).

### 2.11.5 Synthesis of 1-butyl-3-methylimidazolium chloride [C<sub>4</sub>C<sub>1</sub>im][Cl]

1-chlorobutane (144 ml, 1380 mmol, 1.1 eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (100 ml, 1255 mmol, 1 eq) in dry ethyl acetate (100 ml). Once the addition was completed the resulting solution was heated to 55 °C for 14 days under nitrogen. The solution was then allowed to cool to room temperature before being cooled to -21 °C for 2 days. Further crystallisation of the product occurred upon cooling. The resulting crystals were washed with dry ethyl acetate (3 x 100 ml) and recrystallised from acetonitrile. Ethyl acetate was slowly added to ensure full crystallisation and the crystals were dried under a low heat (35 °C) overnight to yield white crystals (206 g, 94 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.22 (1H, s, C(2)**H**), 7.80 (1H, s, C(4)**H**), 7.73 (1H, s, C(5)**H**), 4.17 (2H, t, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.86 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet, -NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.26 (2H, sextet, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -NCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 0.90 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.57 (**C**(2)H), 123.61 (**C**(4)H) and 122.27 (**C**(5)H), 48.45 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 35.34 (-N**CH**<sub>3</sub>), 18.76 (-NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.26 (-NCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 35.89 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 139 ([C<sub>4</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 28 %).

Elemental Analysis (expected): C, 54.94 (55.01); H, 8.67 (8.66); N, 15.91 (16.04).

### 2.11.6 Synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (82 g, 286 mmol, 1 eq) was added slowly to a stirring solution of 1-butyl-3-methylimidazolium chloride (50 g, 286 mmol, 1 eq) in dichloromethane (250 ml). The resulting solution was stirred for 48 hours. Water was then added and once the lithium chloride has dissolved the phases were separated and the dichloromethane phase washed with distilled water until the washings were negative by the silver nitrate test (10 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu$ m PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (110.7 g, 92 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.11 (1H, s, C(2)**H**), 7.77 (1H, s, C(4)**H**), 7.70 (1H, s, C(5)**H**), 4.16 (2H, t, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.85 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet, -NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.27 (2H, sextet, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -NCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 0.91 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.98 (C(2)H), 124.10(C(4)H), 122.74 (C(5)H), 118.36 (-CF<sub>3</sub>), 48.97 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 36.21 (-NCH<sub>3</sub>), 31.81 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.23 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.72 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

$m/z$  (LSISM<sup>+</sup>): 139 ([C<sub>4</sub>C<sub>1</sub>im]<sup>+</sup>, 100%).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100%).

Elemental Analysis (expected): C, 28.75 (28.64); H, 3.51 (3.61); N, 10.19 (10.02).

### 2.11.7 Synthesis of 1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>5</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

*1-pentyl-3-methylimidazolium chloride* was kindly provided by Dr J. Griffith, Welton Research Group.

Lithium bis(trifluoromethylsulfonyl)imide (25.1 g, 87 mmol, 1.1 eq) was added slowly to a stirring solution of 1-pentyl-3-methylimidazolium chloride (15 g, 79 mmol, 1 eq) in dichloromethane (25 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (4 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (31.9 g, 93% yield).

$\delta_{^1\text{H}}$  (ppm)(400 MHz, DMSO- $d_6$ ): 9.10 (1H, s, C(2)H), 7.77 (1H, s, C(4)H), 7.70 (1H, s, C(5)H), 4.15 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.85 (3H, s, NCH<sub>3</sub>), 1.79 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.45-1.09 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 0.88 (3H, t, -N(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.96 (C(2)H), 124.09 (C(4)H), 122.78 (C(5)H), 118.36 (-CF<sub>3</sub>), 49.23 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 36.20 (-NCH<sub>3</sub>), 29.54 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 28.08 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.95 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>) 14.16 (-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 153 ([C<sub>5</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 30.54 (30.48); H, 3.75 (3.95); N, 9.78 (9.70).

### 2.11.8 Synthesis of 1-hexyl-3-methylimidazolium chloride [C<sub>6</sub>C<sub>1</sub>im][Cl]

1-chlorohexane (35 ml, 255 mmol, 1eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (18.48 ml, 232 mmol, 1 eq) in dry acetonitrile (50 ml). Once the addition was completed the solution was heated to 45 °C for 14 days under nitrogen. Two layers formed and the lower ionic liquid layer was washed with dry ethyl acetate and acetonitrile (5:1) (3 x 50 ml) before drying under vacuum. This resulted in a slightly pale yellow, viscous liquid (36.4 g, 77 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 9.38 (1H, s, C(2)**H**), 7.83 (1H, s, C(4)**H**), 7.76 (1H, s, C(5)**H**), 4.17 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 3.86 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.25 (6H, m, -N(CH<sub>2</sub>)<sub>2</sub>(**CH**<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.85 (3H, t, -N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 136.64 (**C**(2)H), 123.57 (**C**(4)H), 122.24 (**C**(5)H), 48.68 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 35.70 (N**CH**<sub>3</sub>), 30.53 (-NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 29.34 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 25.13 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.86 (-N(CH<sub>2</sub>)<sub>4</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 13.82 (-N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 167 ([C<sub>6</sub>C<sub>1</sub>im])<sup>+</sup>, 100%).

$m/z$  (LSIMS<sup>-</sup>): ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 28 %).

Elemental Analysis (expected): C, 59.36 (59.25); H, 9.59 (9.45); N, 13.72 (13.82).

### 2.11.9 Synthesis of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>6</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (35.4 g, 123 mmol, 1 eq) was added slowly to a stirring solution of 1-hexyl-3-methylimidazolium chloride (25 g, 123 mmol, 1 eq) in dichloromethane (200 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (10 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu$ m PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (43.4 g, 79 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 9.09 (1H, s, C(2)**H**), 7.76 (1H, s, C(4)**H**), 7.69 (1H, s, C(5)**H**), 4.15 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 3.84 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.26 (6H, m, -N(CH<sub>2</sub>)<sub>2</sub>(**CH**<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 0.86 (3H, t, -N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 136.49 (**C**(2)H), 123.63 (**C**(4)H), 122.27 (**C**(5)H), 118.35 (-CF<sub>3</sub>), 48.77 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 35.74 (N**CH**<sub>3</sub>), 118.35 (-CF<sub>3</sub>), 30.54 (-NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 29.33 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 25.14 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.87 (-N(CH<sub>2</sub>)<sub>4</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 13.83 (-N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>3</sub>).

*m/z* (LSIMS<sup>+</sup>): 167 ([C<sub>6</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

*m/z* (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 32.25 (32.21); H, 4.37 (4.28); N, 9.51 (9.39).

### 2.11.10 Synthesis of 1-heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>7</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

*1-heptyl-3-methylimidazolium chloride was kindly provided by Dr J. Griffith, Welton Research Group.*

Lithium bis(trifluoromethylsulfonyl)imide (21.9 g, 76 mmol, 1.1 eq) was added slowly to a stirring solution of 1-heptyl-3-methylimidazolium chloride (15 g, 69 mmol, 1 eq) in dichloromethane (25 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (11 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu$ m PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (25.3 g, 79 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 9.10 (1H, s, C(2)H), 7.77 (1H, s, C(4)H), 7.70 (1H, s, C(5)H), 4.15 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 3.85 (3H, s, NCH<sub>3</sub>), 1.78 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.28 (8H, b, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 0.87 (3H, t, -N(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 136.95 (C(2)H), 124.08 (C(4)H), 122.78 (C(5)H), 118.36 (-CF<sub>3</sub>), 49.25 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 36.20 (-NCH<sub>3</sub>), 31.48 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 29.84 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 28.84 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 25.91 (-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.43 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>3</sub>), 14.34 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>3</sub>).

*m/z* (LSIMS<sup>+</sup>): 181 ([C<sub>7</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

*m/z* (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 34.01 (33.84); H, 4.59 (4.42); N, 9.24 (9.11).

### 2.11.11 Synthesis of 1-octyl-3-methylimidazolium chloride [C<sub>8</sub>C<sub>1</sub>im][Cl]

1-chlorooctane (50 ml, 294 mmol, 1.1 eq.) was added, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (21.3 ml, 268 mmol, 1 eq.) in dry acetonitrile (100 ml). Once the addition was completed the solution was heated to reflux for 14 days under nitrogen. Two layers formed and the lower ionic liquid layer was washed with dry ethyl acetate and acetonitrile (5:1) (5 x 50 ml) before drying under vacuum overnight to yield a clear, colourless, viscous liquid (51.2 g, 83 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 9.46 (1H, s, C(2)H), 7.85 (1H, s, C(4)H), 7.78 (1H, s, C(5)H), 4.17 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 3.87 (3H, s, NCH<sub>3</sub>), 1.77 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.23 (10H, m, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 0.84 (3H, t, -N(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 137.17 (C(2)H), 124.04 (C(4)H), 122.73 (C(5)H), 49.16 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 36.18 (NCH<sub>3</sub>), 31.64 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 29.90 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 28.96 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 28.82 (-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 25.97 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.52 (-N(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>3</sub>), 14.40 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

*m/z* (LSIMS<sup>+</sup>): 195 ([C<sub>8</sub>C<sub>1</sub>im])<sup>+</sup>, 100 %).

*m/z* (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 32 %).

Elemental Analysis (expected): C, 62.30 (62.45); H, 10.16 (10.05); N, 12.01 (12.14).

### 2.11.12 Synthesis of 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>8</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (31.1 g, 108 mmol, 1 eq) was added slowly to a stirring solution of 1-octyl-3-methylimidazolium chloride (25 g, 108 mmol, 1 eq) in dichloromethane (225 ml). The resulting solution was stirred for 48

hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (9 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (42.17 g, 89 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.09 (1H, s, C(2)**H**), 7.76 (1H, s, C(4)**H**), 7.69 (1H, s, C(5)**H**), 4.14 (2H, t,  $^3J_{\text{HH}} = 7.2$  Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 3.84 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet,  $^3J_{\text{HH}} = 7.2$  Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.25 (10H, b, -N(CH<sub>2</sub>)<sub>2</sub>(**CH**<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 0.86 (3H, t, -N(CH<sub>2</sub>)<sub>7</sub>**CH**<sub>3</sub>).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.48 (**C**(2)H), 123.61 (**C**(4)H), 122.26 (**C**(5)H), 118.35 (-CF<sub>3</sub>), 48.78 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 35.74 (N**CH**<sub>3</sub>), 31.16 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 29.38 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 28.48 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 28.33 (-N(CH<sub>2</sub>)<sub>4</sub>**CH**<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>CH<sub>3</sub>), 25.49 (-N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 22.06 (-N(CH<sub>2</sub>)<sub>6</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 13.93 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 195 ([C<sub>8</sub>C<sub>1</sub>im])<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>])<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 35.49 (35.36); H, 4.80 (4.88); N, 8.96 (8.84).

### 2.11.13 Synthesis of 1-hydroxyethyl-3-methylimidazolium chloride [(HO)<sup>2</sup>C<sub>2</sub>C<sub>1</sub>im][Cl]

2-chloroethan-1-ol (46.3 ml, 690 mmol, 1.1 eq) was added dropwise, over the course of an hour, to a cooled and stirring flask containing 1-methylimidazole (50 ml, 627 mmol, 1 eq) in toluene (50 ml). Once the addition was completed, the reaction mixture was heated to 65 °C for days. After being allowed to cool, the upper layer was decanted off using a cannula and the lower phase was allowed to crystallise. To

ensure full crystallisation and no loss of product, the round bottom flask was then cooled to -21 °C overnight. The product was washed with dry ethyl acetate (3 x 50 ml) and dried under vacuum (35 °C), before recrystallising from dry acetonitrile. The product was dried under vacuum at 35 °C overnight yielding white, colourless crystals (73.2 g, 72 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.18 (1H, s, C(2)**H**), 7.75 (1H, s, C(4)**H**), 7.71 (1H, s, C(5)**H**), 5.34 (1H, bs, -N(CH<sub>2</sub>)<sub>2</sub>OH), 4.22 (2H, t, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, -NCH<sub>2</sub>CH<sub>2</sub>OH), 3.87 (3H, s, -NCH<sub>3</sub>), 3.71 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz, -NCH<sub>2</sub>CH<sub>2</sub>OH).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.85 (C(2)H), 123.29 (C(4)H), 122.65 (C(5)H), 59.27 (-NCH<sub>2</sub>CH<sub>2</sub>OH), 51.56 (-NCH<sub>2</sub>CH<sub>2</sub>OH), 35.65 (-NCH<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 127 ([ $(\text{HO})^2\text{C}_2\text{C}_1\text{im}$ ]<sup>+</sup>, 50 %), 83 ([C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 30 %).

Elemental Analysis (expected): C, 44.47 (44.32); H, 6.96 (6.82); N, 17.12 (17.23).

#### 2.11.14 Synthesis of 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [(HO)<sup>2</sup>C<sub>2</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (88 g, 307 mmol, 1 eq) was added slowly to a stirring solution of 1-hydroxyethyl-3-methylimidazolium chloride (50 g, 307 mmol, 1 eq) in dichloromethane (35 ml) and water (30 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (9 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2 μm PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (65.8 g, 53 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.07 (1H, s, C(2)**H**), 7.72 (1H, s, C(4)**H**), 7.69 (1H, s, C(5)**H**), 5.16 (1H, bs, -N(CH<sub>2</sub>)<sub>2</sub>**OH**), 4.20 (2H, t, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, -N**CH**<sub>2</sub>CH<sub>2</sub>**OH**), 3.86 (3H, s, -N**CH**<sub>3</sub>), 3.72 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>**OH**).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.82 (**C**(2)H), 123.35 (**C**(4)H), 122.66 (**C**(5)H), 118.35 (-**CF**<sub>3</sub>), 59.32 (-NCH<sub>2</sub>**CH**<sub>2</sub>**OH**), 51.63 (-NCH<sub>2</sub>CH<sub>2</sub>**OH**), 35.66 (-N**CH**<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 127 (100, [(HO)<sup>2</sup>C<sub>2</sub>C<sub>1</sub>im]<sup>+</sup>).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 23.54 (23.59); H, 2.60 (2.72); N, 10.45 (10.32).

### 2.11.15 Synthesis of 1-hydroxypropyl-3-methylimidazolium chloride [(HO)<sup>3</sup>C<sub>3</sub>C<sub>1</sub>im][Cl]

3-chloropropan-1-ol (57.7 ml, 690 mmol, 1.1 eq) was added dropwise, over the course of an hour, to cooled and stirring 1-methylimidazole (50 ml, 627 mmol, 1 eq) in toluene (100 ml). Once the addition was completed, the reaction mixture was heated to 60 °C for 4 days. After being allowed to cool, the upper layer was decanted off using a cannula and the lower phase was allowed to crystallise. To ensure full crystallisation and no loss of product, the round bottom flask was then cooled to -21 °C overnight. The product was washed with dry ethyl acetate (3 x 100 ml) and dried under vacuum (35 °C), before recrystallising from dry acetonitrile. The product was dried under vacuum at 35 °C overnight yielding white, colourless crystals (101.5 g, 92 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.28 (1H, s, C(2)**H**), 7.81 (1H, s, C(4)**H**), 7.73 (1H, s, C(5)**H**), 4.90 (1H, b, -N(CH<sub>2</sub>)<sub>3</sub>**OH**), 4.24 (2H, t, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>**OH**), 3.85 (3H, s -N**CH**<sub>3</sub>), 3.40 (2H, q, -N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>**OH**), 1.924 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, -N(CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>**OH**).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.80 (C(2)H), 123.51 (C(4)H), 122.39 (C(5)H), 56.86 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH), 46.15 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH), 35.70 (-NCH<sub>3</sub>), 32.37 (-N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH).

$m/z$  (LSIMS<sup>+</sup>): 141 ([ (HO)<sup>3</sup>C<sub>3</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 32 %).

Elemental Analysis (expected): C, 47.45 (47.60); H, 7.46 (7.42); N, 15.76 (15.86).

### 2.11.16 Synthesis of 1-hydroxypropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [(HO)<sup>3</sup>C<sub>3</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (81 g, 283 mmol, 1 eq) was added slowly to a stirring solution of 1-hydroxypropyl-3-methylimidazolium chloride (50 g, 283 mmol, 1 eq) in dichloromethane (30 ml) and water (25 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test (7 x 50 ml). The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (55.98 g, 47 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.09 (1H, s, C(2)H), 7.75 (1H, s, C(4)H), 7.69 (1H, s, C(5)H), 4.72 (1H, b, -N(CH<sub>2</sub>)<sub>3</sub>OH), 4.22 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH), 3.84 (3H, s -NCH<sub>3</sub>), 3.41 (2H, q, -N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH), 1.93 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.67 (C(2)H), 123.58 (C(4)H), 122.41 (C(5)H), 118.35 (-CF<sub>3</sub>), 57.07 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH), 46.26 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH), 35.72 (-NCH<sub>3</sub>), 32.31 (-N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH).

$m/z$  (LSIMS<sup>+</sup>): 141 ([ $(\text{HO})^3\text{C}_3\text{C}_1\text{im}$ ]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 26.62 (25.66); H, 2.65 (3.11); N, 10.20 (10.41).

### 2.11.17 Synthesis of 1-hydroxyhexyl-3-methylimidazolium chloride [ $(\text{HO})^6\text{C}_6\text{C}_1\text{im}$ ][Cl]

6-chlorohexan-1-ol (50 ml, 375 mmol, 1.2 eq) was added dropwise, over the course of an hour, to cooled and stirring 1-methylimidazole (25 ml, 312 mmol, 1 eq) in toluene (50 ml). Once the addition was completed, the reaction mixture was heated to 60 °C for 4 days. After being allowed to cool, two layers were noticeable, therefore, the upper layer was decanted off using a cannula and the lower phase cooled to -21 °C to attempt crystallisation. However, no crystallisation occurred and the viscous liquid was washed with dry ethyl acetate and acetonitrile (5:1) (5 x 50 ml). The liquid was then dried under vacuum at 35 °C overnight yielding a clear, colourless, viscous liquid (59.2 g, 87 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.33 (1H, s, C(2)**H**), 7.82 (1H, s, C(4)**H**), 7.75 (1H, s, C(5)**H**), 4.47 (1H, bs, -N(CH<sub>2</sub>)<sub>6</sub>**OH**), 4.17 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>**OH**), 3.86 (3H, s, -N**CH**<sub>3</sub>), 3.37 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>2</sub>**OH**), 1.78 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>**OH**), 1.46-1.17 (6H, m, -N(CH<sub>2</sub>)<sub>2</sub>(**CH**<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>**OH**).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.62 (**C**(2)H), 123.58 (**C**(4)H), 122.25 (**C**(5)H), 60.41 (-N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>2</sub>**OH**), 48.69 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>**OH**), 35.71 (-N**CH**<sub>3</sub>), 32.18 (-NCH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>**OH**), 29.42 (-N(CH<sub>2</sub>)<sub>4</sub>**CH**<sub>2</sub>**CH**<sub>2</sub>**OH**), 25.36 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>**OH**), 24.86 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>**OH**).

$m/z$  (LSIMS<sup>+</sup>): 183 ([ $(\text{HO})^6\text{C}_6\text{C}_1\text{im}$ ]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 31%).

Elemental Analysis (expected): C, 54.98 (54.91); H, 8.85 (8.76); N, 12.68 (12.81).

### 2.11.18 Synthesis of 1-hydroxyhexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [(HO)<sup>6</sup>C<sub>6</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

1-hydroxyhexyl-3-methylimidazolium chloride (30 g, 137 mmol, 1 eq.) was dissolved in dichloromethane (225 ml) and to this stirring solution lithium bis(trifluoromethylsulfonyl)imide (39.4 g, 137 mmol, 1 eq) was added portionwise. After stirring for 48 hrs under nitrogen, water (50 ml) was added to the solution and it was left to stir until the lithium chloride precipitate had dissolved. The resulting two phases were separated, and lower phase washed with distilled water (11 x 50 ml) until the washings were negative when tested with silver nitrate. The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu$ m PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (55.4 g, 87 % yield).

$\delta$   $^1\text{H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.19 (1H, s, C(2)H), 7.76 (1H, s, C(4)H), 7.69 (1H, s, C(5)H), 4.36 (1H, bs, -N(CH<sub>2</sub>)<sub>6</sub>OH), 4.14 (2H, t,  $^3J_{\text{HH}} = 7.2$  Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>OH), 3.84 (3H, s, -NCH<sub>3</sub>), 3.37 (2H, t, -N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OH), 1.77 (2H, quintet,  $^3J_{\text{HH}} = 7.2$  Hz, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>OH), 1.46-1.18 (6H, m, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>OH).

$\delta$   $^{13}\text{C}\{^1\text{H}\}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.50 (C(2)H), 123.62 (C(4)H), 122.27 (C(5)H), 118.35 (-CF<sub>3</sub>), 60.50 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OH), 118.35 (-CF<sub>3</sub>), 48.77 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>OH), 35.75 (-NCH<sub>3</sub>), 32.22 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>OH), 29.44 (-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 25.39 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OH), 24.89 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH).

$m/z$  (LSIMS<sup>+</sup>): 183 ([ (HO)<sup>6</sup>C<sub>6</sub>C<sub>1</sub>im ]<sup>+</sup>, 100%).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 31.22 (31.10); H, 4.05 (4.13); N, 8.95 (9.07).

### 2.11.19 Synthesis of 1-hydroxyoctyl-3-methylimidazolium chloride [(HO)<sup>8</sup>C<sub>8</sub>C<sub>1</sub>im][Cl]

8-chlorooctan-1-ol (50 ml, 296 mmol, 1.1 eq) was added dropwise, over the course of an hour, to cooled and stirring 1-methylimidazole (21.5 ml, 269 mmol, 1 eq) in toluene (50 ml). Once the addition was completed, the reaction mixture was heated to 60 °C for 7 days. After being allowed to cool, two layers were visible, and the upper layer was decanted off using a cannula and the lower phase cooled to -21 °C to attempt crystallisation. However, no crystallisation occurred and the viscous liquid was washed with dry ethyl acetate and acetonitrile (5:1) (5 x 50 ml). The liquid was then dried under vacuum at 35 °C overnight yielding a clear, colourless, viscous liquid (43.3 g, 65 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 9.13 (1H, s, C(2)**H**), 7.77 (1H, s, C(4)**H**), 7.70 (1H, s, C(5)**H**), 4.34 (1H, bs, -N(CH<sub>2</sub>)<sub>8</sub>**OH**), 4.15 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>**OH**), 3.84 (3H, s, -N**CH**<sub>3</sub>), 3.37 (2H, q, -N(CH<sub>2</sub>)<sub>7</sub>**CH**<sub>2</sub>**OH**), 1.77 (2H, quintet, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, -N**CH**<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>**OH**), 1.44-1.16 (10H, m, -N(CH<sub>2</sub>)<sub>2</sub>(**CH**<sub>2</sub>)<sub>5</sub>**CH**<sub>3</sub>**OH**).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 136.50 (**C**(2)**H**), 123.61 (**C**(4)**H**), 122.27 (**C**(5)**H**), 60.64 (-N(CH<sub>2</sub>)<sub>7</sub>**CH**<sub>2</sub>**OH**), 48.25 (-N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>**OH**), 35.74 (-N**CH**<sub>3</sub>), 32.45 (-N**CH**<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>**OH**), 29.35 (-N(CH<sub>2</sub>)<sub>6</sub>**CH**<sub>2</sub>**CH**<sub>2</sub>**OH**), 28.70 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>**OH**), 28.39 (-N(CH<sub>2</sub>)<sub>5</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>**OH**), 25.44 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>**OH**), 25.39 (-N(CH<sub>2</sub>)<sub>4</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>**OH**).

*m/z* (LSIMS<sup>+</sup>): 211 ([<sup>8</sup>(HO)C<sub>8</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

*m/z* (LSIMS<sup>-</sup>): 35 [<sup>35</sup>Cl]<sup>-</sup>, 100 %, 37 [<sup>37</sup>Cl]<sup>-</sup>, 28 %.

Elemental Analysis (expected): C, 58.55 (58.41); H, 9.52 (9.39); N, 11.45 (11.35).

### 2.11.20 Synthesis of 1-hydroxyoctyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [(HO)<sup>8</sup>C<sub>8</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

1-hydroxyoctyl-3-methylimidazolium chloride (25.74 g, 104 mmol, 1 eq.) was dissolved in dichloromethane (150 ml) and water (50 ml). To this stirring

solution lithium bis(trifluoromethylsulfonyl)imide (30.43 g, 106 mmol, 1 eq) was added portionwise. After stirring for 48 hrs under nitrogen, the two phases were separated, and lower phase washed with distilled water (9 x 50 ml) until the washings were negative when tested with silver nitrate. The dichloromethane was removed under low heat on the rotary evaporator and the resulting liquid treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu\text{m}$  PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (42.1 g, 82 % yield).

$\delta_{^1\text{H}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.09 (C(2)H), 7.76 (1H, s, C(4)H), 7.69 (1H, s, C(5)H), 4.34 (1H, t, -N(CH<sub>2</sub>)<sub>8</sub>OH), 4.14 (2H, t,  $^3J_{\text{HH}} = 7.2$  Hz, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>OH), 3.84 (3H, s, -NCH<sub>3</sub>), 3.37 (2H, q, -N(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>OH), 1.77 (2H, quintet,  $^3J_{\text{HH}} = 7.2$  Hz, -NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>OH), 1.46-1.17 (10H, m, -N(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>OH).

$\delta_{^{13}\text{C}\{\text{H}\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.49 (C(2)H), 123.62 (C(4)H), 122.27 (C(5)H), 118.35 (-CF<sub>3</sub>), 60.67 (-N(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>OH), 48.78 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>OH), 35.75 (-NCH<sub>3</sub>), 32.48 (-NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>OH), 29.37 (-N(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>OH), 28.72 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>OH), 28.42 (-N(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH), 25.46 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>OH), 25.41 (-N(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OH).

$m/z$  (LSIMS<sup>+</sup>): 211 ([ (HO)<sup>8</sup>C<sub>8</sub>C<sub>1</sub>im]<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 280 ( [NTf<sub>2</sub>]<sup>-</sup>, 100 %).

Elemental Analysis (expected): C, 34.34 (34.21); H, 4.81 (4.72); N, 8.66 (8.55).

## 2.12 Ultrapure synthesis of ionic liquids

To synthesise two ultrapure ionic liquids the following additional steps were taken:

1. All new glassware was purchased.

2. All glassware was washed with piranha solution (1:3, 30% hydrogen peroxide:concentrated sulphuric acid), washed with distilled water, before soaking overnight in distilled water and washed again before storing in distilled water until required.
3. No grease was used anywhere in the setup, grease being replaced by hard PTFE sleeves when a good vacuum or seal was required.
4. The products of each step were kept stored under nitrogen and wrapped in aluminium foil.
5. Filtration through the 0.2  $\mu\text{m}$  PTFE filters was performed under only a slight pressure to avoid carry through.

### 2.12.1 Synthesis of ultrapure 1-butyl-3-methylimidazolium chloride $[\text{C}_4\text{C}_1\text{im}][\text{Cl}]$

For this ultrapure synthesis the 1-methylimidazole was stirred overnight with freshly cut sodium before distillation.<sup>[7]</sup> Additionally, the 1-chlorobutane was washed with concentrated sulphuric acid until the acid was colourless. It was then washed with water, neutralised with sodium hydrogen carbonate, before washing with water again. It was then dried with magnesium sulfate, before stirring overnight with diphosphorus pentoxide and distilling from it the following day.<sup>[7, 8]</sup>

1-chlorobutane (144 ml, 1380 mmol, 1.1 eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of 1-methylimidazole (100 ml, 1255 mmol, 1 eq) in dry ethyl acetate (100 ml). Once the addition was completed the resulting solution was heated to 45 °C for 30 days under nitrogen. The solution was then allowed to cool to room temperature before being cooled to -21 °C for 2 days. Further crystallisation of the product occurred upon cooling. The resulting crystals were washed with dry ethyl acetate (3 x 100 ml) and recrystallised from acetonitrile until the mother liquor was colourless (4 times). The crystals were dried under a low heat (35 °C) overnight to yield white crystals (164 g, 75 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.32 (1H, s, C(2)**H**), 7.82 (1H, s, C(4)**H**), 7.75 (1H, s, C(5)**H**), 4.18 (2H, t,  $^3J_{HH} = 7.1$  Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.87 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet,  $^3J_{HH} = 7.4$  Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.26 (2H, sextet,  $^3J_{HH} = 7.4$  Hz, -NCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 0.90 (3H, t, -N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$\delta_{^{13}C\{^1H\}}$  (ppm) (400 MHz, DMSO- $d_6$ ): 137.11 (C(2)**H**), 124.08 (C(4)**H**), 122.75 (C(5)**H**), 48.92 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 36.20 (-N**CH**<sub>3</sub>), 33.84 (-NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.24 (-N(CH<sub>2</sub>)<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 13.75 (-N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$m/z$  (LSIMS<sup>+</sup>): 139 ([C<sub>4</sub>C<sub>1</sub>im])<sup>+</sup>, 100 %).

$m/z$  (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 31 %).

Elemental Analysis (expected): C, 51.84 (55.01); H, 8.79 (8.66); N, 14.91 (16.04).

### 2.12.2 Synthesis of ultrapure 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>C<sub>1</sub>im][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (82 g, 286 mmol, 1 eq) was added slowly to a stirring solution of 1-butyl-3-methylimidazolium chloride (50 g, 286 mmol, 1 eq) in dichloromethane (225 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test. The dichloromethane was removed under low heat on the rotary evaporator. The liquid was washed with hexane twice (2 x 25 ml) before removing any remaining solvent at low temperature on the rotary evaporator. It was then treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2  $\mu$ m PTFE filter to ensure completed removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (95.6 g, 80 % yield).

$\delta_{^1H}$  (ppm) (400 MHz, DMSO- $d_6$ ): 9.11 (1H, s, C(2)**H**), 7.76 (1H, s, C(4)**H**), 7.70 (1H, s, C(5)**H**), 4.16 (2H, t,  $^3J_{HH} = 7.2$  Hz, -N**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 3.85 (3H, s, N**CH**<sub>3</sub>), 1.77 (2H, quintet,  $^3J_{HH} = 7.3$  Hz, -NCH<sub>2</sub>**CH**<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.27 (2H, sextet,  $^3J_{HH} = 7.4$  Hz, -NCH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>CH<sub>3</sub>), 0.91 (3H, t, -N(CH<sub>2</sub>)<sub>3</sub>**CH**<sub>3</sub>).

$\delta \text{ } ^{13}\text{C}\{\text{ } ^1\text{H}\}$  (ppm) (400 MHz, DMSO- $d_6$ ): 136.97 (C(2)H), 124.08(C(4)H), 122.72 (C(5)H), 118.36 (-CF<sub>3</sub>), 48.98 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 36.18 (-NCH<sub>3</sub>), 31.81 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.22 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.66 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

$m/z$  (LSISM<sup>+</sup>): 139 ([C<sub>4</sub>C<sub>1</sub>im]<sup>+</sup>, 100%).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100%).

Elemental Analysis (expected): C, 28.58 (28.64); H, 3.55 (3.61); N, 10.12 (10.02).

### 2.12.3 Synthesis of ultrapure

#### N-butyl-N-methylpyrrolidinium chloride

#### [C<sub>4</sub>C<sub>1</sub>pyrr][Cl]

For this ultrapure synthesis the N-methylpyrrolidine was stirred overnight with potassium hydroxide before distillation.<sup>[9]</sup> Additionally, the 1-chlorobutane was washed with concentrated sulphuric acid until the acid was colourless. It was then washed with water, neutralised with sodium hydrogen carbonate, before washing with water again. It was then dried with magnesium sulfate, before stirring overnight with diphosphorus pentoxide and distilling from it the following day.<sup>[7, 8]</sup>

1-chlorobutane (100 ml, 961 mmol, 1.1 eq) was added dropwise, over the course of an hour, to a cooled and stirring solution of N-methylpyrrolidine (93 ml, 874 mmol, 1eq) in dry ethyl acetate (100 ml). Once the addition was completed the resulting solution was heated to 45 °C for 30 days under nitrogen. The solution (and precipitated product) was then allowed to cool to room temperature before being cooled to -21 °C for 2 days to maximise crystallisation of the product. Two crops of crystals were recovered from the mother liquor and were combined. The resulting crystals were washed with dry ethyl acetate (3 x 100 ml) and recrystallised from acetonitrile until the mother liquor was colourless (3 times). The crystals were then dried under a low heat (35 °C) overnight to yield white crystals (73.5 g, 47.3 %).

$\delta \text{ } ^1\text{H}$  (ppm)(400 MHz, DMSO- $d_6$ ): 3.61-3.36 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>[pyrr]), 3.33-3.27 (2H, m, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.99 (3H, s, -NCH<sub>3</sub>), 2.08 (4H, b, -NCH<sub>2</sub>CH<sub>2</sub>[pyrr]),

1.77-1.59 (2H, m, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.32 (2H, sextet, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.00 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (400 MHz, DMSO-*d*<sub>6</sub>): 63.86 (-NCH<sub>2</sub>CH<sub>2</sub> [pyrr]), 63.29 (-NCH<sub>2</sub>CH<sub>2</sub> [pyrr]), 47.94 (-NCH<sub>3</sub>), 25.41 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 21.55 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.80 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.99 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

*m/z* (LSIMS<sup>+</sup>): 142 ([C<sub>4</sub>C<sub>1</sub>pyrr]<sup>+</sup>, 100 %).

*m/z* (LSIMS<sup>-</sup>): 35 ([<sup>35</sup>Cl]<sup>-</sup>, 100 %), 37 ([<sup>37</sup>Cl]<sup>-</sup>, 28 %).

Elemental Analysis (expected): C, 60.96 (60.83); H, 11.26 (11.34); N, 7.98 (7.88).

## 2.12.4 Synthesis of ultrapure

### N-butyl-N-methylpyrrolidinium

### bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>C<sub>1</sub>pyrr][N(Tf)<sub>2</sub>]

Lithium bis(trifluoromethylsulfonyl)imide (81 g, 281 mmol, 1 eq) was added slowly to a stirring solution of N-butyl-N-methylpyrrolidinium chloride (50 g, 281 mmol, 1 eq) in dichloromethane (225 ml). The resulting solution was stirred for 48 hours before filtering to remove the bulk of the precipitated lithium chloride. The dichloromethane phase was then washed with distilled water until the washings were negative by the silver nitrate test. The dichloromethane was removed under low heat on the rotary evaporator. The resulting liquid was washed with hexane twice (2 x 25 ml) before removing any remaining solvent at low temperature on the rotary evaporator. The liquid was then treated with activated charcoal at room temperature overnight. The bulk of the charcoal was removed with standard filtration through filter paper and then through two 0.2 μm PTFE filter to ensure complete removal of particulates. The liquid was then dried overnight at 55 °C to yield a clear, colourless liquid (33.6 g, 85 % yield).

$\delta_{^1\text{H}}$  (ppm)(400 MHz, DMSO-*d*<sub>6</sub>): 3.52-3.36 (4H, m, -NCH<sub>2</sub>CH<sub>2</sub>[pyrr]), 3.32-3.24 (2H, m, -NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 2.98 (3H, s, -NCH<sub>3</sub>), 2.08 (4H, b, -NCH<sub>2</sub>CH<sub>2</sub>[pyrr]), 1.76-1.61 (2H, m, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.32 (2H, sextet, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.94 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, -N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

$\delta_{^{13}\text{C}\{^1\text{H}\}}$  (ppm) (DMSO- $d_6$ ): 118.35 (-CF<sub>3</sub>), 63.89 (-NCH<sub>2</sub>CH<sub>2</sub> [pyrr]), 63.39 (-NCH<sub>2</sub>CH<sub>2</sub> [pyrr]), 47.97 (-NCH<sub>3</sub>), 25.89 (-NCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 21.55 (-NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.78 (-N(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 13.92 (-N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

$m/z$  (LSISM<sup>+</sup>): 142 ([C<sub>4</sub>C<sub>1</sub>pyrr]<sup>+</sup>, 100%).

$m/z$  (LSIMS<sup>-</sup>): 280 ([NTf<sub>2</sub>]<sup>-</sup>, 100%).

Elemental Analysis (expected): C, 28.75 (28.64); H, 3.51 (3.61); N, 10.19 (10.02).

## Chapter 3

# Characterisation of unfunctionalised and functionalised ionic liquids

### 3.1 Introduction

The definition of an ionic liquid which will be used within this thesis is as follows:

An ionic liquid (IL) is a low melting point salt.

The liquid state of these ionic liquids stems from their coulombic interactions. Most ionic salts have strong coulombic interactions between the highly positively charged cations and the highly negatively charged anions leading to an ordered ionic lattice structure. In the case of ionic liquids the ions tend to have a dissociated charge, be large, and asymmetrical. The asymmetrical nature of the ions disrupts the lattice structure and hence the coulombic interactions are reduced, and in turn the melting point of the ionic liquid. The Coulombic interaction is given by:<sup>[10]</sup>

$$E_c = \frac{MZ^+Z^-}{4\pi\epsilon_0 r} \quad (3.1.1)$$

where,  $M$  is the Madelung constant,  $Z^+$  and  $Z^-$  are the ion charges,  $\epsilon_0$  is the electric permittivity and  $r$  is the inter-ion separation between the ions.

It is the ability to tailor, or design, the ionic liquid to exhibit required properties which has caused the exponential growth in this field since the discovery of air and water stable room temperature ionic liquids at the start of the 1990s.<sup>[11]</sup> This ‘designability’ of the ionic liquids can be achieved by varying the cation

structure, functionalisation and/or the anion. It has been reported that the number of simple ionic liquids that can be created by possible cation/anion combinations are in the order of  $10^6$ .<sup>[12]</sup> A range of the most common cations and anions used for the synthesis of ionic liquids is illustrated in Figure 3.1.1. The naming and abbreviations are given below the respective ion, see Section 3.2 for full details on naming of ionic liquids. Ionic liquid anions are either organic or inorganic with the negative charge spread over a number of atoms (apart from in the case of the halides).

Ionic liquids are now being applied across a wide, diverse, selection of applications ranging from use as lubricants to separation processes.

## 3.2 Naming of ionic liquids

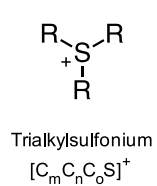
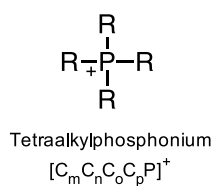
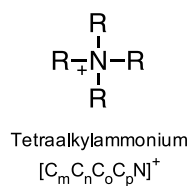
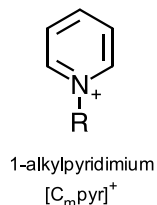
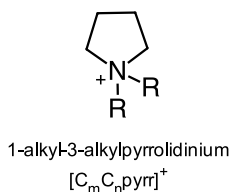
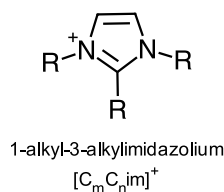
Over the last decade there has been a dramatic increase in the number of research groups working on ionic liquids. As more functionalised, and different types of, ionic liquids are developed the classical naming method for ionic liquids starts to become problematic. This classical system involved naming the ionic liquid after the long, full chemical name i.e. 1-ethyl-3-methylimidazolium chloride is represented by [emim][Cl] or [EMIM][Cl]. However, when faced with a functionalised ethyl side chain this naming method is no longer appropriate and therefore, the Welton Research Group has implemented an alphanumeric naming system for ionic liquids. This approach has been used within this thesis and is described as follows:<sup>[13]</sup>

1. The central charged cation is abbreviated e.g. an imidazolium cation is abbreviated to im, while a pyrrolidinium cation is abbreviated to pyrr (see Figure 3.1.1 for abbreviations).
2. The alkyl chains are then abbreviated, with a subscripted number to describe the chain length e.g. C<sub>2</sub> would represent an ethyl chain and C<sub>4</sub> would represent a butyl chain.

Therefore, 1-ethyl-3-methylimidazolium, using the above system becomes [C<sub>2</sub>C<sub>1</sub>im]<sup>+</sup>.

1. If the alkyl chain is not linear this can be noted using superscripted abbreviations e.g. 1-*iso*-propyl-3-methylimidazolium becomes [<sup>i</sup>C<sub>3</sub>C<sub>1</sub>im]<sup>+</sup>.

Cations:



Anions:

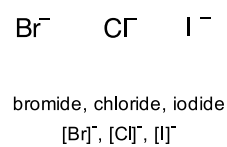
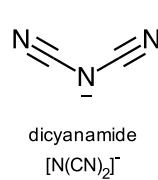
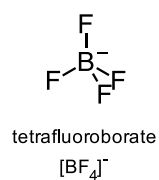
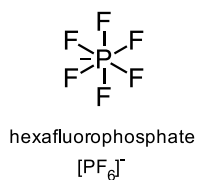
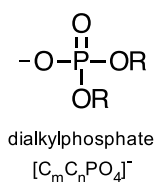
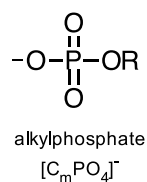
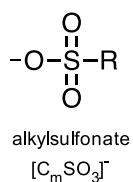
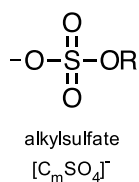
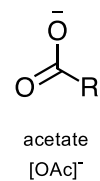
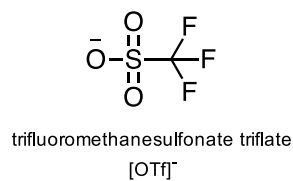
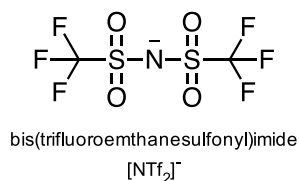


Figure 3.1.1 – Commonly used ionic liquids cations and anions.

2. Functionalisation of the side chain is noted using the usual functional group abbreviation, e.g. hydroxyl is represented by OH, and is placed in brackets with the position noted with a superscripted number. e.g. 1-hydroxyethyl-3-methylimidazolium becomes  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}]^+$ . This indicates the hydroxy group is located on the terminal carbon of the ethyl chain.
3. In-chain functionality can be illustrated, e.g.  $[(\text{C}_1(\text{O})\text{C}_3)\text{C}_1\text{im}]^+$  represents an ether present between the the third and terminal carbon on one of the alkyl chains present on the nitrogen of the imidazolium ring.

The anions of the ionic liquid are abbreviated as shown in Figure 3.1.1.

Therefore, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide would be represented as  $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ , and 1-hydroxyethyl-3-methylimidazolium trifluoromethanesulfonate triflate would be represented as  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{OTf}]$ .

### 3.3 Synthesis of ionic liquids using halide intermediates

The traditional route for synthesising ionic liquids (both hydrophobic and hydrophilic) has been via the use of halide intermediates. This synthetic pathway involves five discrete steps:<sup>[13]</sup>

1. Purification of starting materials,
2. Quaternisation of the amine/phosphine/sulfone,
3. Purification of the ionic liquid halide salt,
4. Ion metathesis or double displacement exchange, and
5. Purification of the final ionic liquid product.

#### 3.3.1 Purification of starting materials

To ensure spectroscopically pure ionic liquids, the purification process commences with the starting materials. All starting materials must be dried and colourless before use. This is achieved by stirring with an appropriate drying agent

(e.g. potassium hydroxide in the case of 1-methylimidazole) overnight before distillation over the drying agent. From this point all materials must be handled under an inert atmosphere, nitrogen or argon (Schlenk techniques should be applied). Depending of the level of purity required, and the application of the ionic liquid, pre-washing of the starting materials may be required (see Chapter 5). This is usually performed by washing the halo-alkane with concentrated sulphuric acid until it is colourless, then washing with sodium hydrogen carbonate and water before drying with magnesium sulfate (if appropriate) and then drying and distillation as documented above.<sup>[7, 8]</sup>

### 3.3.2 Quaternisation of the amine/phosphine/sulfone

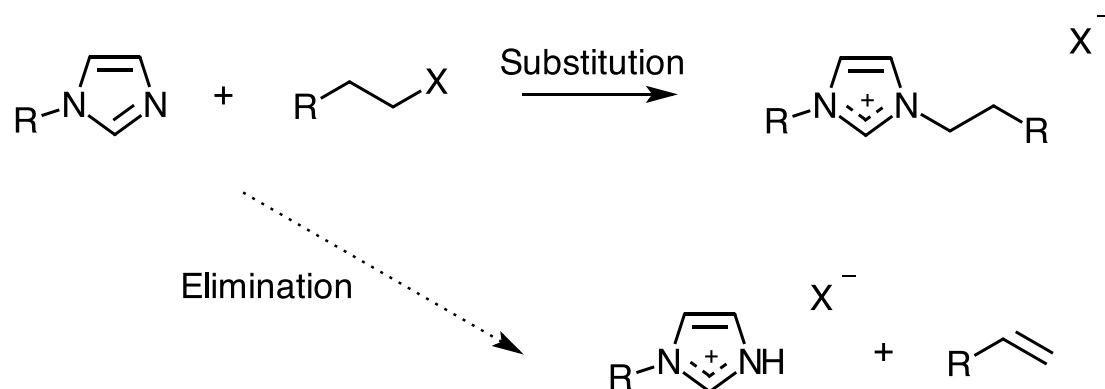


**Figure 3.3.1** – Initial alkylation step, for the ionic liquid halide salt, illustrating the elimination pathway that can occur with overheating.

The first step for the synthesis of most ionic liquids is the alkylation step usually using chloro-, bromo- or iodo-alkanes. Control of this initial reaction step is key because instead of the substitution pathway it is possible to also have an elimination pathway (see Figure 3.3.1).<sup>[14]</sup> To avoid the elimination product overheating, ‘hot-spots’, must be avoided during the addition of the halo-alkane. This can be achieved by slow dropwise addition of the haloalkane, high dilution with an appropriate solvent (which dissipates the heat of the exothermic reaction) e.g. ethyl acetate or toluene, and by cooling with ice. Normally halide intermediates are solids up to around 70 °C and therefore the solvent allows stirring to continue without solidification of the intermediate.

Once addition is completed the reaction can be heated, however most research groups have tended to heat the reaction at a low temperature and accept the associated increased reaction time.

Chloro-alkanes are preferred for this quaternisation as they are more hydrophilic than bromo-alkanes which means that they are more easily removed during the purifications stages of the ionic liquid. Additionally, bromide salts tend to form very quickly which can lead to impurities within the crystal/solid structure and hence difficulty purifying the ionic liquid halide intermediate.

The formed ionic liquid halide salts are extremely hygroscopic and turn into a ionic salt-water mixture within minutes of exposure to air, therefore Schlenk techniques must be applied from this stage forwards.

### 3.3.3 Purification of the ionic liquid halide salt

Depending on the chain length and functionalisation of the alkyl chain the halide salt of the ionic liquid cation can be a solid, a viscous liquid or a liquid. In all cases the salt is first washed with a solvent to remove unreacted starting materials (usually three or four times), usually ethyl acetate is used. If ethyl acetate is not effective enough toluene may be used. As the washing step proceeds the ethyl acetate can cause the halide salt to precipitate. Once washed solid halide salts are recrystallised, to ensure high purity, usually from acetonitrile (to which ethyl acetate may be slowly added if recrystallisation does not occur at reduced temperature) before being dried in vacuo to remove residual solvent and any remaining volatile impurities. Recrystallisation will remove any coloration of the intermediate, however only low heat should be applied to minimise degradation of the ionic liquid intermediate upon drying.<sup>[15]</sup>

### 3.3.4 Ion metathesis or double displacement exchange

To form the desired ionic liquid the halide ion is exchanged with a metal salt (usually lithium or sodium) of the desired anion e.g. lithium bis(trifluoromethylsulfonyl)imide. The usual organic solvent used for this exchange in our group is dichloromethane due to the high solubility of ionic liquid halides and the low solubility of the resulting inorganic salts, lithium (or sodium) chloride

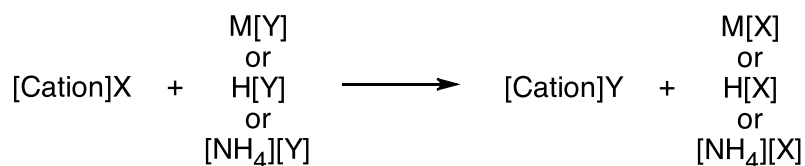


**Figure 3.3.2** – Ionic liquid metathesis route with a metal, conjugate acid of the desired anion, or with an ammonium salt.

for example. In the case of hydrophilic ionic liquids the exchange is performed directly in DCM. However, if the resulting ionic liquid is hydrophobic the reaction can be performed in an aqueous solution in which the product would separate out, or in a biphasic system, DCM/water, where the product is soluble in the DCM. Typically, a small excess of the ionic liquid precursor is dissolved up in DCM and to this solution is added the lithium or sodium salt of the desired anion. The solution is stirred for a minimum of 24 hours, more usually 48 hours to ensure complete exchange has occurred. At this stage the final ionic liquid has been formed but is not yet pure.

### 3.3.5 Purification of final ionic liquid product

The crude reaction mixture contains a number of impurities which must be removed before the ionic liquid is deemed to be pure. These tend to be precursors, lithium/sodium salts from the metathesis, and reaction solvent. To remove the bulk of the lithium/sodium halide salts the solution is first filtered before being washed with water. This aqueous washing step not only removes any remaining halide salts but also the remaining excess of ionic liquid halide salt precursors. N.B. If the formed ionic liquid is hydrophilic, the volume of water used during each washing phase must be minimised to reduce any losses of the ionic liquid. To determine when the washing has been completed the water phase is tested by the silver nitrate test (see Figure 3.3.3) and is deemed completed when the test is negative i.e. no formation of a silver halide precipitate (see Table 3.3.1 for solubility in water). To ensure total removal of any halide salts an additional wash is performed before purification is continued.

Coloration of ionic liquids tend to occur due to aggressive heating of the liquid

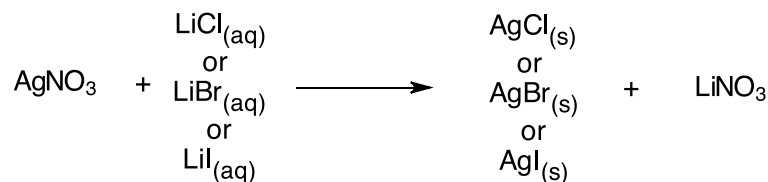


**Figure 3.3.3** – Reaction of silver nitrate with lithium halide salts to form silver halide (precipitate) and lithium nitrate.

| Solubility in water / mol L <sup>-1</sup> |                        |
|-------------------------------------------|------------------------|
| AgCl                                      | 1.3 x 10 <sup>-5</sup> |
| AgBr                                      | 7.1 x 10 <sup>-7</sup> |
| AgI                                       | 1.3 x 10 <sup>-8</sup> |

**Table 3.3.1** – Water solubilities of silver halide salts at 25 °C.<sup>[4]</sup>

during the halide salt formation or improper purification of the starting materials. If coloration has occurred the solvent is first removed using a rotary evaporator and then a high vacuum Schlenk line. Once dry and free of solvent activated charcoal is added to the liquid and allowed to stir for 24 hours. It is sometimes recommended to heat a sample while treating with activated charcoal<sup>[7]</sup> but this should be avoided to eliminate the possibility of additional coloration in the ionic liquid. Once stirred, the charcoal is removed by filtration and the ionic liquid passed over a short alumina plug - the choice of acidic, neutral or basic depends upon the ionic liquid itself.<sup>[16]</sup> It has been reported that sorbent material may be left in the ionic liquid after filtering, however the use of celite or a 0.2  $\mu\text{m}$  filter minimises any remaining material.<sup>[17]</sup> The resulting ionic liquid is then deemed to be pure and is dried further overnight *in vacuo* at 45 °C to remove any remaining water.

The use of charcoal is not recommended for strong hydrogen bonding anions or triflate based ionic liquid due to the strong interactions which would occur with the carbon.<sup>[16]</sup>

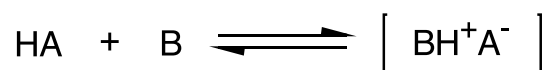


**Figure 3.4.1** – Synthesis of the ionic liquid  $[\text{BH}^+][\text{A}^-]$  via acid (HA) base (B) combination.

### 3.4 Synthesis of ionic liquids via acid base combination

Another approach to the synthesis of ionic liquids is via a simple Brønsted acid base combination - ionic liquids synthesised via this route are called protic ionic liquids (PILs). In this method stoichiometric amounts of acid (HA) and base (B) are mixed together and the proton exchange from the acid to the base forms the desired ionic liquid ( $\text{BH}^+\text{A}^-$ ). This is an equilibrium in which the position depends upon the nature of the acid and base used. Therefore, these ionic liquids tend to be mixtures of the acid, the base and the final desired ionic liquid. No ionic liquids were synthesised in this manner during this project and hence the method will not be further expanded upon here.

### 3.5 Synthesis of ionic liquids via direct alkylation

Direct alkylation of the amine, phosphone or sulfone is possible and this allows the halide intermediate salt to be avoided. Typically this synthetic route is used to form dialkylphosphate or alkyl sulfate salts. An advantage of using this route to synthesise ionic liquids is that the resulting ionic liquids are halide free and cheaper to synthesise. As with the halide intermediate route, purification of starting materials is extremely important. Alkylating agents themselves are moisture sensitive, hydrolysing to form acidic impurities. Additionally, most alkylating agents are very reactive (e.g. dimethyl sulfate) and therefore, to minimise coloration of the ionic liquid during the exothermic reaction, cooling during the addition of the alkylating agent is recommended.

### 3.6 Synthesis of ionic liquids via ion exchange chromatography

Ion exchange chromatography is another possible route for the synthesis of ionic liquids. The exchange resin itself is a quaternary ammonium based resin which associates with ions which can be used to exchange with the ionic liquid anion.

1. The exchange column is first conditioned with the desired anion. This is usually performed by flushing the column with a concentrated solution of the salt of the desired anion e.g. sodium acetate if an acetate anion ( $[\text{OAc}]^-$ ) is desired (see Figure 3.6.1 - Left).
2. A solution of the ionic liquid halide intermediate is then passed over the column. As the intermediate travels down the column the halide anion exchanges with the anion currently bound to the head groups of the ion exchange resin. In this case, if 1-ethyl-3-methylimidazolium chloride was being used, the chloride anion would exchange with the acetate to give 1-ethyl-3-methylimidazolium acetate ( $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ ) (see Figure 3.6.1 - Right).

This is normally a high yielding synthetic route resulting in pure and colourless ionic liquids. However, the product volume per batch run through the resin is limited and large quantities of resin are used, along with solvent. This synthetic methodology has been used to synthesise 20 ionic liquids with amino acid anions.<sup>[18]</sup> Here Ohno *et al.* exchanged the chloride intermediate with a hydroxide anion via the use of a hydroxide conditioned exchange column. The resulting  $[\text{C}_2\text{C}_1\text{im}][\text{OH}]$  solution was then neutralised with an aqueous solution of the desired amino acids.

Ion exchange is also possible with silver salts. Silver salts of the desired anion can be synthesised from the sodium/lithium salt of the anion and silver nitrate ( $\text{AgNO}_3$ ), exchange of the formed salt with the ionic liquid halide intermediate produces the silver(I) halide salt. The use of silver salts means that this route can be expensive and it has been documented that silver ions can remain in the ionic liquid.<sup>[19]</sup>

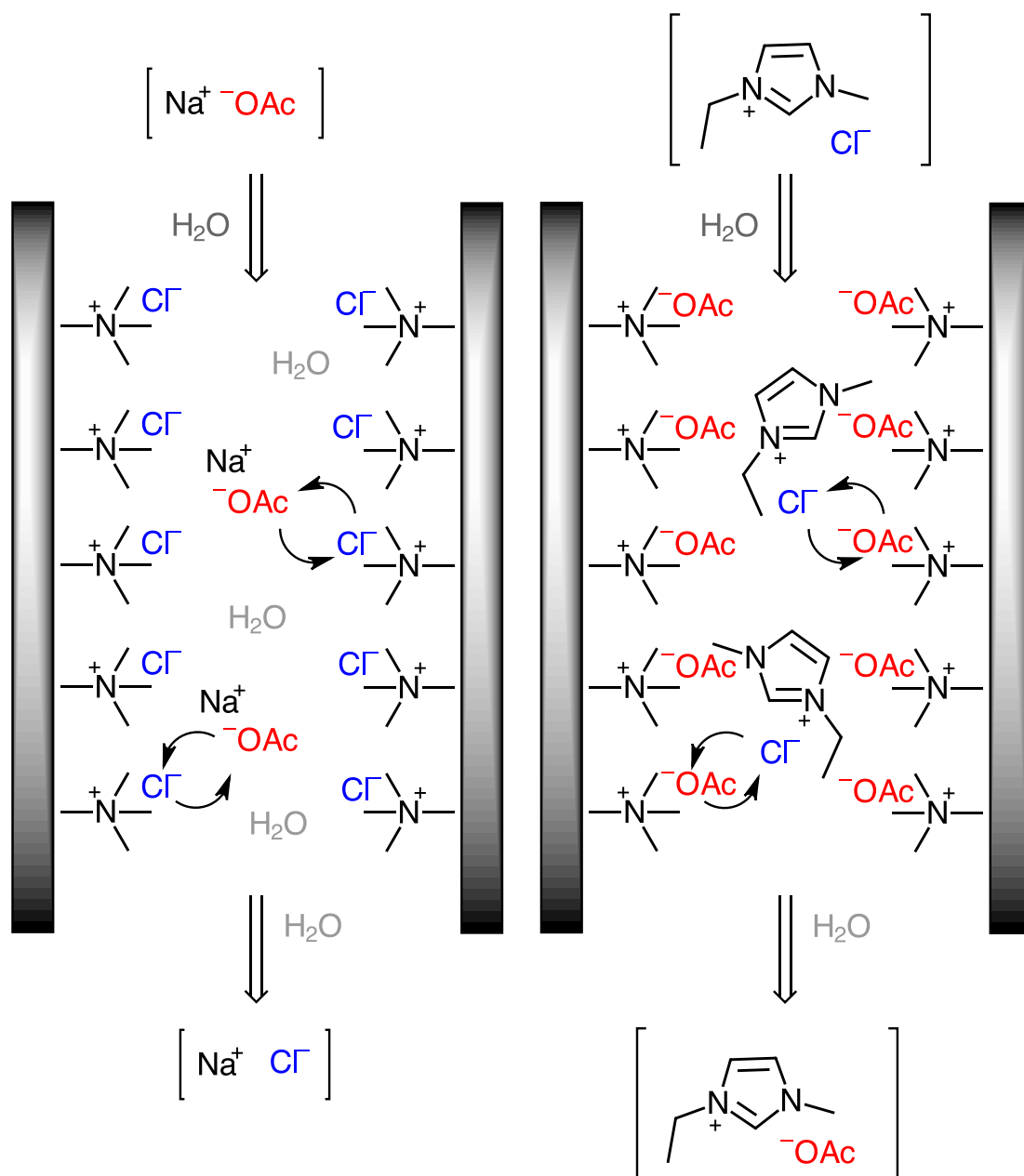


**Figure 3.6.1** – Use of an ion exchange column for the synthesis of 1-ethyl-3-methylimidazolium acetate,  $[\text{C}_2\text{C}_1\text{im}][\text{OAc}]$ .

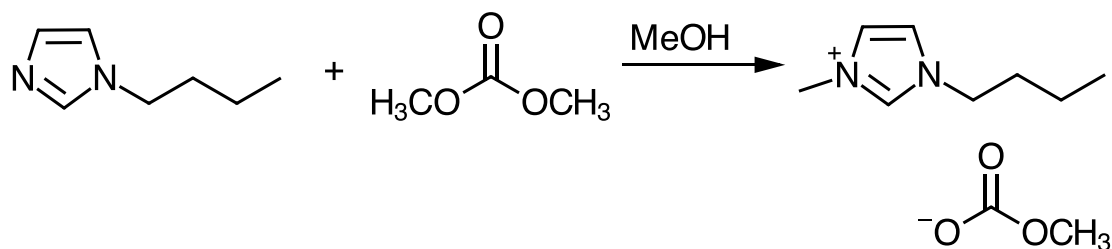


**Figure 3.7.1** – Synthesis of 1-butyl-3-methylimidazolium methyl carbonate,  $[\text{C}_4\text{C}_1\text{im}][\text{OCO}_2\text{Me}]$ , in methanol.

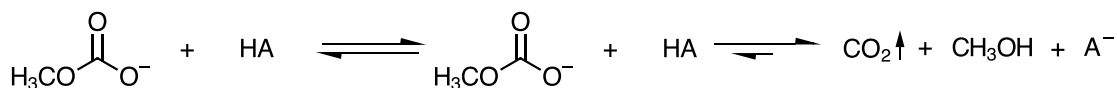


**Figure 3.7.2** – Methyl carbonate anion decomposition reaction with acid, HA, to form carbon dioxide, methanol and the desired anion,  $\text{A}^-$ .

### 3.7 Synthesis of ionic liquids via the dimethyl carbonate anion

The dimethyl carbonate route was first attempted by Rogers *et al.* in 2003.<sup>[20]</sup> This route involves forming the methyl carbonate of the imidazole (see Figure 3.7.1). This initial step is performed in methanol in a pressure reactor. This is because the temperature of the reaction is higher than the boiling points of the solvent (methanol) and the dimethyl carbonate.

The resulting methyl carbonate anion, in the presence of an acid with a  $\text{pK}_\text{a}$  lower than 5.6 (the  $\text{pK}_\text{a}$  of methyl carbonic acid is 5.6),<sup>[21]</sup> reacts to form methanol, carbon dioxide and leaves the corresponding base as the anion of the ionic liquid (see Figure 3.7.2).

This route can be classed as being more acceptable than the halide intermediate route because dimethyl carbonate is non-toxic, no dichloromethane is required (as is used for the metathesis via the halide intermediate route - Section 3.3.4), and the resulting methyl carbonate anion allows ion exchange with simple acids rather than alkali or silver salts.

## 3.8 Properties

To design an ionic liquid, especially one that has to interact with a complex molecule such as a biomolecule, there has to be a fundamental understanding of the cation and anion effects on the system. In the case here the ionic liquids synthesised all have a bis(trifluoromethylsulfonyl)imide anion in order to ensure that the ionic liquid would be immiscible with the aqueous phase and ultimately form a stable interface between the phases.

The properties investigated were:

1. Viscosity of the ionic liquids (Sections 3.8.1 & 3.9.1, for Introduction, and Results and Discussion respectively).
2. Density of the ionic liquids (Sections 3.8.2 & 3.9.2).
3. Conductivity of the ionic liquids (Sections 3.8.3 & 3.9.3).
4. Water solubility in the ionic liquids (Sections 3.8.4 & 3.9.4).
5. Ionic liquid solubility in the aqueous phase (Sections 3.8.5 & 3.9.5).
6. Interfacial tension between the ionic liquids and the aqueous phase (Sections 3.8.6 & 3.9.6).

### 3.8.1 Viscosity

Viscosity,  $\eta$ , of a fluid can be defined as the fluid's resistance to flow. All the molecules in the fluid are in motion and the internal frictional forces create this resistance. In the case of an ionic liquid being used electrochemically this is extremely important as the viscosity not only affects the movement of a target analyte into the ionic liquid, but the conductance of charge within the liquid itself.

The two plates model is used to define the parameters used here. In this case the upper plate with a wide contact area,  $A$ , is sheared with a force,  $F$  (see Figure 3.8.1).

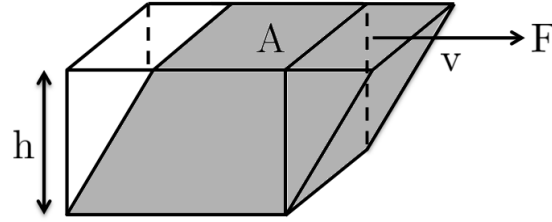


**Figure 3.8.1** – Two plate representation of applied shear force,  $F$ , and the resulting shearing effect on the sample (grey).

The shear stress is given by:

$$\tau = \frac{F}{A} \quad (3.8.1)$$

Shear stress,  $\tau$ , is defined as the ratio of the shear force,  $F$ , and the shear area,  $A$ .

With the shear rate:

$$\dot{\gamma} = \frac{v}{h} = \frac{dv}{dh}$$

Shear rate,  $\dot{\gamma}$ , with  $v$  being the velocity in meters per second and  $h$  the distance between the two plate in meters. Differential variables  $dv$  and  $dh$  can be applied in the case of planar fluid layers.

Viscosity is therefore defined as:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3.8.2)$$

i.e. the ratio of the shear stress,  $\tau$ , and the shear rate,  $\dot{\gamma}$ .

Viscosity itself is measured by placing the fluid of interest between two plates and moving those plates with a measured force and speed. The most common and reliable setup is a cone-and-plate measuring system, which allows the use of small sample volumes (Figure 3.8.2). In this setup the cone is the measuring, rotating geometry (with an angle,  $\alpha$ , of  $< 4^\circ$ ) with the plate as the static part. With this setup only a small amount of sample is required, and cleaning of the setup is very straightforward. In addition, due to the constant shear rate that is achieved in the entire conical gap, homogenous shear conditions throughout the sample are

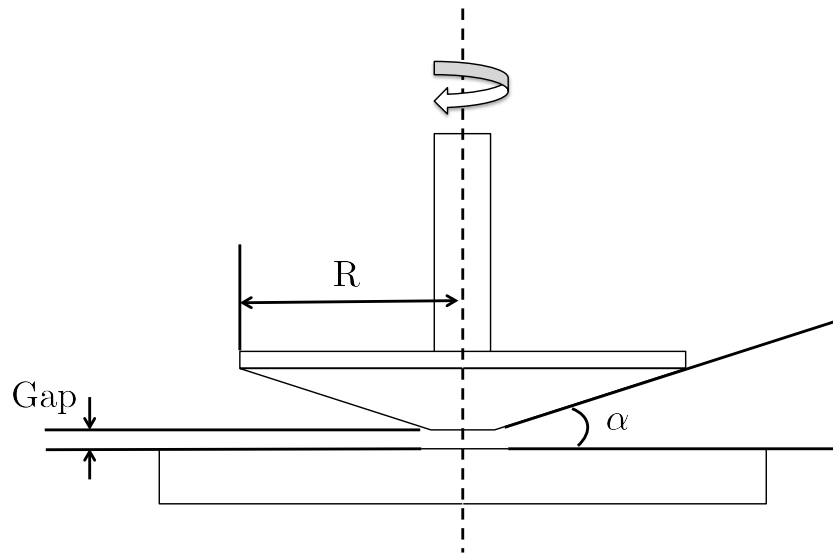


**Figure 3.8.2** – Labelled cone-and-plate rheometer setup.

achieved. This conical shape also has the advantage of aiding the removal of any air bubbles present in the system when the geometry gap is set.

The best geometry for a cone-and-plate system to use tends to be the truncated cone. The truncated cone has multiple advantages over a non-truncated cone based measuring system:

1. There is no wear and tear on the cone or the plate, as would be the case of a non-truncated cone. Hence, there are no changes of the geometry parameters.
2. There is no friction between the cone or the plate, and therefore there are no static or kinetic friction contributions from that contact, which will affect the torque and the resulting measurement.
3. In the case of large particles, the truncated cone setup can overcome the issue of additional frictional forces as it ensures that there is enough free space within the sample being tested.

The key requirement for the cone-and-plate system is the filling of the system. The shear gap must be filled completely to correctly measure the fluid. The cone should be overfilled by approximately 1 mm beyond the edge of the cone to allow for any migration effects that could occur during the measurement (see Figure 3.8.3).

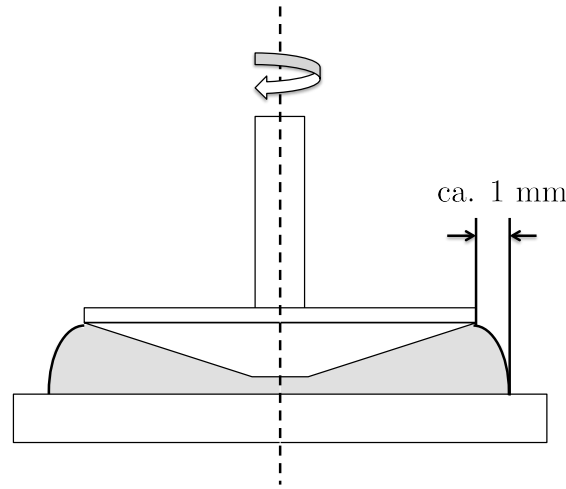


**Figure 3.8.3** – Illustration of the optimum filling of the cone-and-plate measuring system with the sample shown in grey.

The shear stress,  $\tau$ , in a cone-and-plate measuring system is shown to be:

$$\tau = \frac{3M}{2\pi R^3} \quad (3.8.3)$$

$M$  is the applied torque,  $R$  is the radius.

The shear rate,  $\dot{\gamma}$ , in this system is determined by the rotation of the cone,  $\omega$  (the angular velocity in rad/s) and the cone angle,  $\alpha$  (see Figure 3.8.2).

$$\dot{\gamma} = \frac{\omega}{\alpha} \quad (3.8.4)$$

Therefore, the viscosity of a fluid (see Equation 3.8.2) in a cone-and-plate system, if we apply Equations 3.8.3 and 3.8.4, is calculated from:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{3M\alpha}{2\pi R^3\omega} \quad (3.8.5)$$

The use of a large radius cone combined with an appropriate applied torque is a key requirement to ensure that the sample is not ejected from the cone once the shear is applied, this is of particular importance if the sample has a low viscosity. The large radius increases the resistance for the sample and therefore reduces this likelihood. This radius,  $R$ , is found to have a significant impact on the

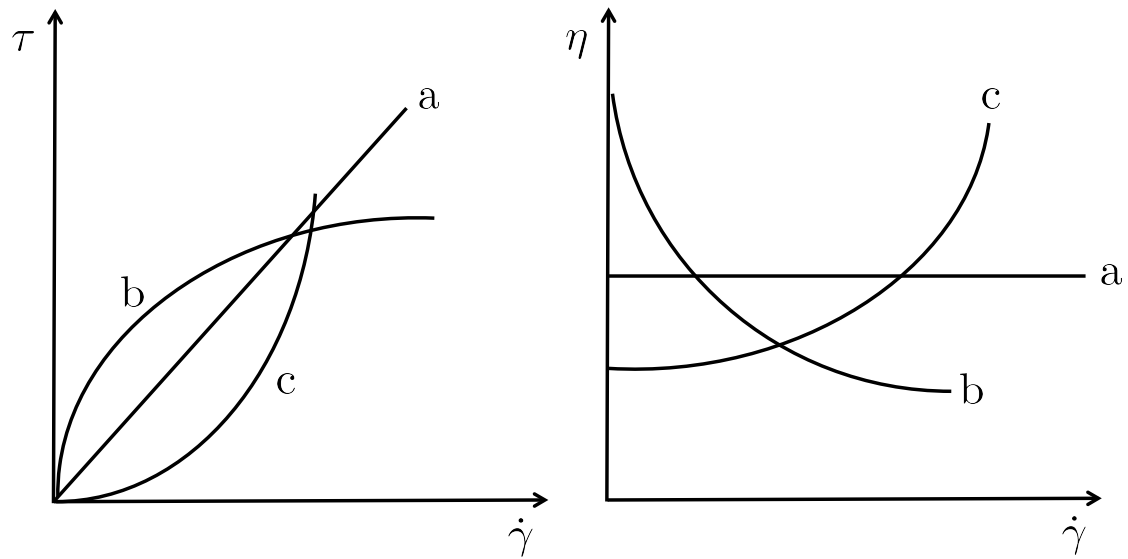


**Figure 3.8.4** – The left hand plot is a plot of the flow curve (shear stress) ( $\tau$ ) versus the shear rate ( $\dot{\gamma}$ ), with the right hand plot being viscosity ( $\eta$ ) versus shear rate ( $\dot{\gamma}$ ).

viscosity calculated from Equation 3.8.5. Therefore, the correct filling of the cone, as commented upon earlier, is very important.

The behaviour of a fluid when a shear is applied varies. Ionic liquids tend to follow Newtonian behaviour, where the shear stress and the shear rate are proportional to each other, with the viscosity being a function of temperature and pressure, constant at all shear rates.<sup>[22, 23]</sup> Some fluids' viscosity increases as the shear rate increases and this is known as 'Shear-thickening' behaviour, where the opposite behaviour (decreasing viscosity) is known as 'Shear-thinning' behaviour.<sup>[23]</sup>

These behaviours are represented in Figure 3.8.4:

- a represents ideal Newtonian behaviour.
- b represents shear-thinning behaviour.
- c represents shear-thickening behaviour.

The viscoelastic properties of a material can be determined by performing two shear stress steps - creep and creep recovery. If a constantly acting stress is applied to an ideally viscous material that material will exhibit continuous deformation,

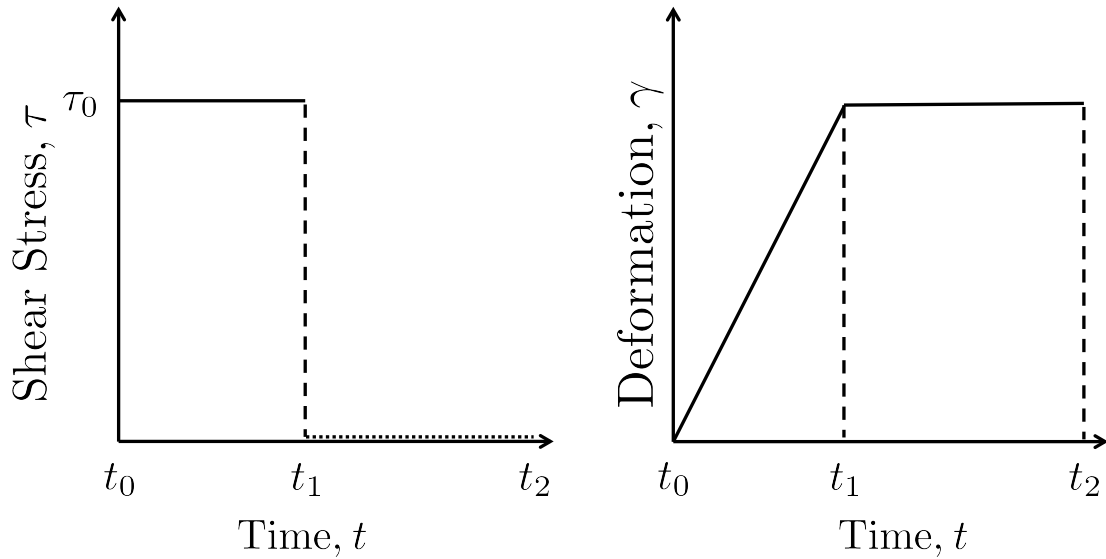


**Figure 3.8.5** – Illustrative creep, and creep recovery curves (right) upon application, and removal of, shear stress (left).

and upon removal of that load no reformation occurs because there is no elastic property associated with the material. An ideally viscous material cannot store any of the deformation energy applied to it during the load interval and hence once that load/stress is released it remains deformed to the same extent as at the end of the load/stress interval/phase.<sup>[23]</sup> To determine the visco-elastic behaviour/property of a fluid a ‘creep’ test is performed. This test comprises of two phases (Figure 3.8.5 - Left):

1. A ‘stress’ phase - a constant shear stress ( $\tau_0$ ) is applied to the fluid from time  $t_0$  to  $t_1$ .
2. A ‘rest’ phase following the ‘stress phase’ - the stress is removed and the sample left ‘at rest’ from  $t_1$  to  $t_2$ .

In the case of an ideally viscous fluid it is not able to store any of the deformation energy. Therefore, once the shear stress is removed there is no recovery, and the resulting creep and creep recovery curves look like those found in Figure 3.8.5 - Right.

### 3.8.2 Density

Density is a fundamental property of any material, be it liquid, solid or gas. In this work an ionic liquid with a density greater than water was desired and therefore ionic liquid density was measured. Furthermore, the density measurements were required for a number of calculations including:

1. Molar conductivity (See Chapter 4).
2. Interfacial tension (See Section 3.9.6).
3. Molar volume (See Section 3.10.2.2).

Density can be measured by vibrating a U-tube within a thermostatically controlled bath, and the natural frequency of the liquid measured.

$$\tau = 2\pi\sqrt{\frac{\rho v + m}{C}} \quad (3.8.6)$$

The period  $\tau$ , is given by the density of the liquid,  $\rho$ , the cell volume,  $v$ , the cell mass,  $m$ , and the spring constant  $C$ . As all but the density of the liquid are a constant it is possible to determine the density of the liquid as per:

$$\rho = \frac{\tau^2 - B}{A} \quad (3.8.7)$$

where,

$$A = \frac{4\pi^2 v}{C}, \quad B = \frac{4\pi^2 m}{C} \quad (3.8.8)$$

By calibrating the unit with two different substances (e.g. air and water) it is possible to determine the constants  $A$  and  $B$ , and therefore the density of the liquid.

### 3.8.3 Conductivity

The conductivity of an ionic liquid is a key property when being used as an electrolyte. This is especially important due to the confusing nature of ionic liquid conductivity where, in many cases, ionic liquids (even though highly charged)

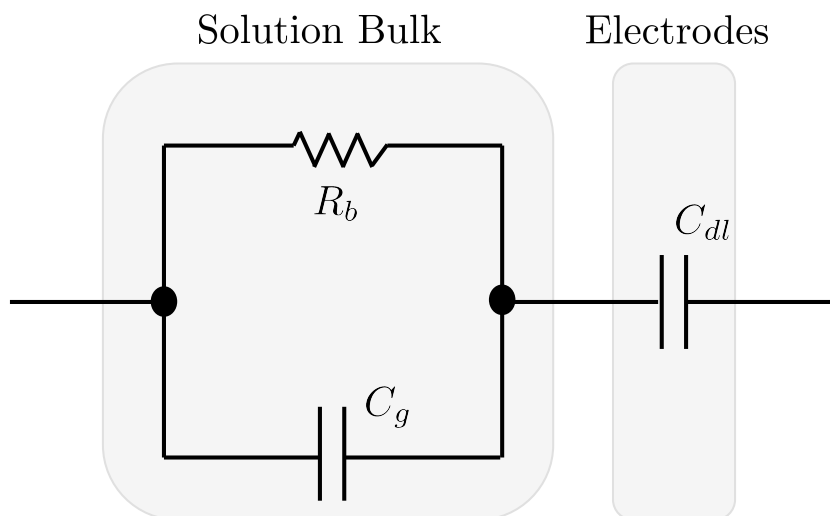


**Figure 3.8.6** – Representation of the equivalent impedance circuit of an ionic liquid between two blocking electrodes.

have been found to have conductivity values lower than those of dilute aqueous salt solutions.<sup>[24]</sup> Ionic conductivity tends to be measured using the complex-impedance method, and in this project it was performed using platinum ‘blocking’ electrodes (i.e. electrodes with which there is no charge transfer to the carrier ions in the solution).<sup>[25]</sup> Non-blocking electrodes are those which have the same element for the electrode and the carrier ion, therefore allowing charge transfer to occur.

This is termed a complex-impedance method because it consists of a real component, resistance, and an imaginary component, capacitance. Ultimately, the conductivity cell of an ionic liquids is represented by the bulk resistance ( $R_b$ ), geometric capacitance ( $C_g$ ), and double layer capacitance of the electrodes ( $C_{dl}$ ), see Figure 3.8.6.<sup>[26]</sup>

The complex-impedance,  $Z$ , is therefore given by:<sup>[27]</sup>

$$\frac{1}{Z(\omega)} = \frac{1}{R} + i\omega C \quad (3.8.9)$$

where  $Z(\omega)$  is the complex impedance at an angular frequency of  $\omega$ . This in turn can be separated into the real and imaginary terms  $Z'$  and  $Z''$  respectively:

$$Z'(\omega) = \frac{R_b}{1 + (\omega C_g R_b)^2} \quad (3.8.10)$$

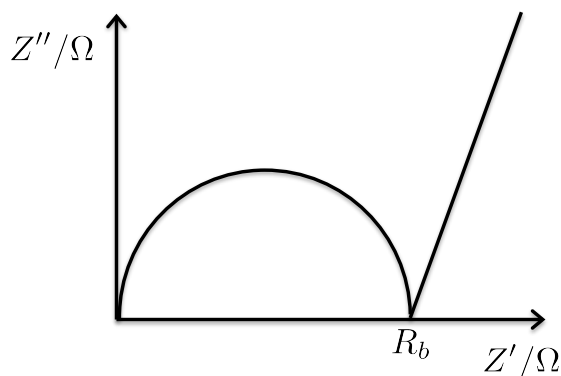


**Figure 3.8.7** – Representational Nyquist plot for equivalent impedance circuit as in Figure 3.8.6.

$$Z''(\omega) = \frac{\omega C R^2}{1 + (\omega C_g R_b)^2} \quad (3.8.11)$$

Plotting the real and imaginary impedance gives the well known Nyquist plot ( $Z''$  vs  $Z'$ ), see Figure 3.8.7, from which the conductivity value of the ionic liquid is obtained at the point of the minimum between the linear region at lower frequencies and the semi-circular region at higher frequencies.

### 3.8.4 Water solubility

Water solubility in an ionic liquid is likely to be an important property for the solubilisation/encapsulation of biological materials. The destabilisation of the tertiary structure of a biological molecule affects its conformation, and in turn can affect its activity.<sup>[28, 29, 30, 31]</sup> The presence of water within the ionic liquid could provide enough hydration for the molecule to stabilise the tertiary structure, and therefore allow not only transfer across the aqueous:non-aqueous (i.e. ionic liquid) interface, but stabilisation of the transferred molecules.

### 3.8.5 Ionic liquid solubility

The solubility of the ionic liquid cation and anion is extremely important when being used within an electrochemical liquid-liquid cell (see Chapter 4).

The imidazolium ring of the ionic liquid cation exhibits a peak at 211 nm in the

ultraviolet (UV) and it is therefore possible to use this feature to determine the ionic liquid's solubility into the aqueous phase. It should be noted however that this method only confirms the presence of the cation, not the anion, and therefore not the ion pair.

### 3.8.6 Interfacial tension

The interfacial tension is extremely important in a liquid-liquid system. The interfacial tension will affect not only the movement of the analyte of interest but the movements of the electrolyte salts when a potential difference is applied across a formed aqueous:non-aqueous interface within an electrochemical cell. Within the electrochemical cells designed here, the interfacial tension between the aqueous phase and the ionic liquid phases is affected by the solubility of water into the ionic liquid, and vice versa, the solubility of the ionic liquid cation and/or anion into the water.

Due to the density of the ionic liquids synthesised here the interfacial tension was measured by the pendant (hanging) drop method. The theoretical form of a pendant drop was first derived in 1883 by Bashforth and Adams.<sup>[32]</sup> The interfacial tension is determined from the Young-Laplace equation which describes the difference in pressure ( $\Delta p$ ) below and above a curved section of a droplet, which has principal radii of curvature  $r_1$  and  $r_2$ , and an interfacial tension  $\gamma$  (Equation 3.8.12).

$$\Delta p = \gamma \cdot \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3.8.12)$$

## 3.9 Results and discussion

### 3.9.1 Viscosity of the ionic liquids

It is possible from investigating the steady-state flow curves to determine if a liquid exhibits Newtonian behaviour i.e. it exhibits a constant viscosity across all shear rates, therefore viscosity is independent of shear rate.<sup>[23]</sup> Figure 3.9.1 shows the viscosity of  $[\text{C}_2\text{C}_{1\text{im}}][\text{NTf}_2]$  across 1 to 10  $\text{rad s}^{-1}$  at 15, 25, 35, 45, 55, 75 °C.

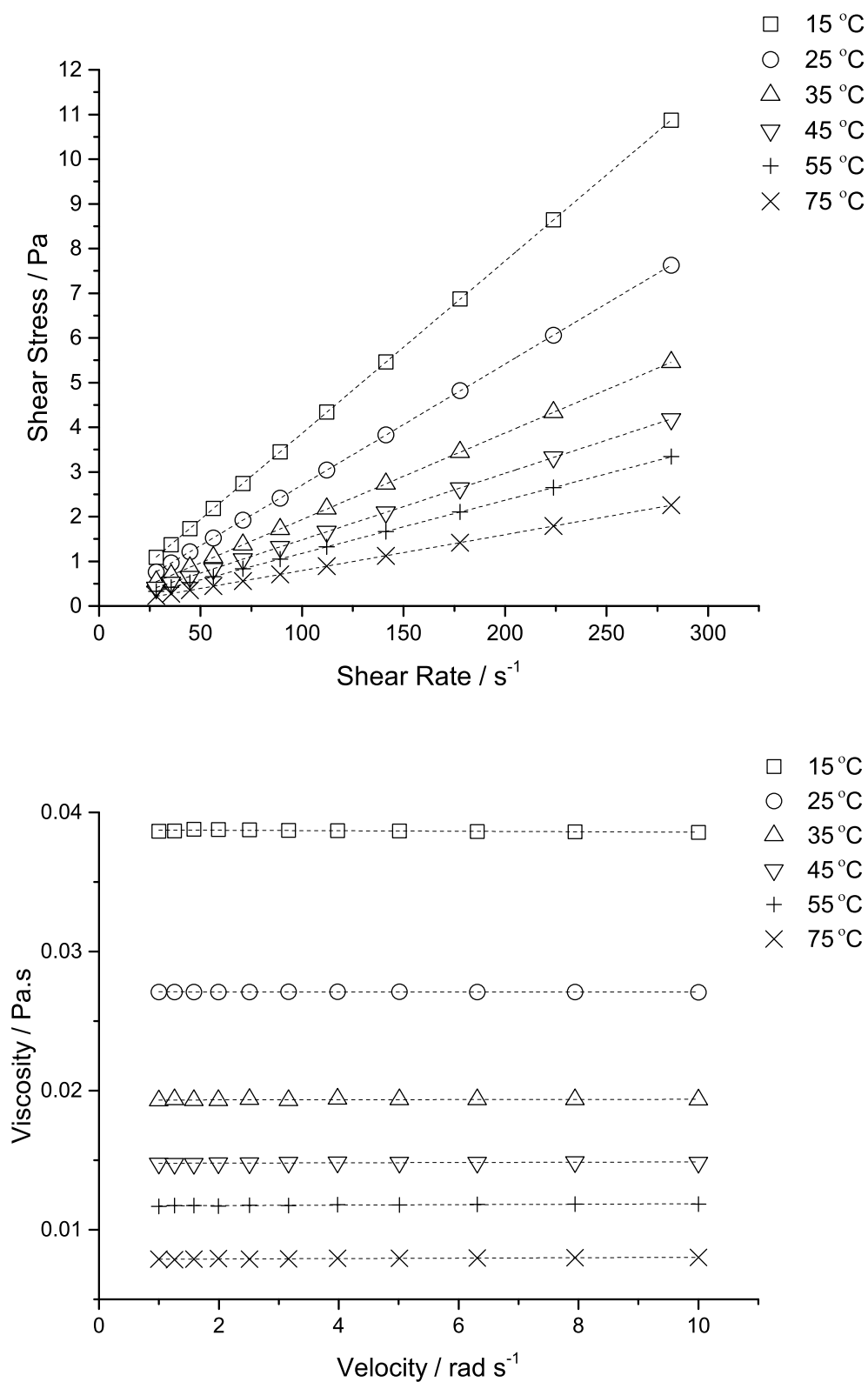


**Figure 3.9.1** – Flow and viscosity function curves for  $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ , with increasing shear rate at 15, 25, 35, 45, 55, and 75 °C.

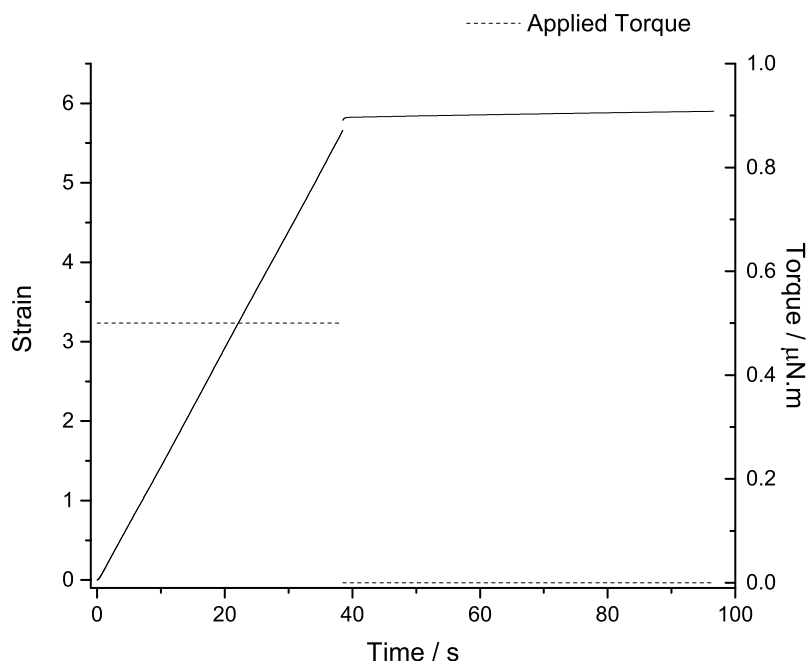


**Figure 3.9.2** – Creep and creep recovery curve (black line) upon application of torque (dashed line) for  $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ .

As can be seen, across all temperatures tested the viscosity is constant. This was found with all the ionic liquids tested here and agrees with the results of other research groups.<sup>[33, 34, 35]</sup> It has been reported that shear-thinning can occur with longer alkyl chains,  $> [\text{C}_{10}\text{C}_1\text{im}]^+$ , however ionic liquids of this length were not recorded here.<sup>[36]</sup>

This ideally viscous behaviour was confirmed for all the tested ionic liquids by investigating the creep and creep ‘recovery’ curves when a  $0.5 \mu\text{N.m}$  torque stress was applied. Figure 3.9.2 shows the creep and creep ‘recovery’ curve for  $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ . It can be seen that there is no recovery once the applied stress was removed. This is consistent with the liquid not storing any of the deformation energy during the initial stress period, and the liquid having no elastic property (Figure 3.8.5).<sup>[23]</sup>

As can be seen from the ionic liquid values (Table 3.9.1) they are significantly more viscous than standard organic solvents.

| Liquid                                                                  | Viscosity Value at 25 °C / mPa.s |
|-------------------------------------------------------------------------|----------------------------------|
| Water                                                                   | 0.890 <sup>[37]</sup>            |
| Ethanol                                                                 | 1.074 <sup>[37]</sup>            |
| Propanol                                                                | 1.945 <sup>[37]</sup>            |
| Hexanol                                                                 | 4.578 <sup>[37]</sup>            |
| Octanol                                                                 | 7.288 <sup>[37]</sup>            |
| Diethylene Glycol                                                       | 30.2 <sup>[37]</sup>             |
| Glycerol                                                                | 934 <sup>[37]</sup>              |
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 27.10 ± 0.04                     |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 43.85 ± 0.07                     |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 50.72 ± 0.35                     |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 68.05 ± 0.21                     |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 88.32 ± 0.12                     |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 77.99 ± 0.23                     |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 98.90 ± 0.18                     |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 199.87 ± 0.15                    |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 229.24 ± 0.20                    |

**Table 3.9.1** – Viscosity values for the unfunctionalised and hydroxyl functionalised ionic liquids, with organic solvent and water values, at 25 °C. (See Appendix for full data).

Looking within the classes of ionic liquid tested:

- Increasing the alkyl chain length leads to an increase in the ionic liquid's viscosity. This at first glance can seem counterintuitive, as the cation size has increased this leads to a decrease in the molar concentration and hence the electrostatic (cation-anion) associative interactions decrease.<sup>[35, 38]</sup> However, as the chain length increases the reduction in the electrostatic ion interactions are replaced by increased van der Waals interactions between the alkyl chain and the ions, and through hydrocarbon-hydrocarbon interactions.<sup>[38]</sup> The van der Waals interactions are also expected to be greater at  $\geq 4$  carbon atoms as at this distance the electron withdrawing effect of the imidazolium ring is reduced.<sup>[34]</sup> Jacquemin *et al.*,<sup>[35]</sup> suggest that micro-structuring of the ionic liquid occurs with non-polar regions forming due to the alkyl side chains, and ionic regions forming from the charged head groups and anions. The micro-structuring would indeed lead to decreased mobility within the ionic liquid and exhibit an increase in the viscosity of the liquid as the chain length is increased.
- Incorporating a single hydroxyl group on to the terminal carbon of the alkyl chain has a significant effect on the viscosity of the imidazolium ionic liquids. In comparison with the reasons given for the viscosity increase of the unfunctionalised ionic liquids:
  - The molar mass of the cation has increased by 16 mass units from the addition of an oxygen and the hydroxyl group itself allows hydrogen bonding (H-bonding) to occur between and the ionic centres of the cation, the anion and other alkyl chains.
  - As the alkyl chain length increases the H-bonding effect will become more pronounced as the electron-withdrawing effect at  $\geq 4$  will be little or none.<sup>[34]</sup>

Comparing the viscosity between that of  $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$  and  $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$  there is a 194 % increase in the viscosity exhibited compared with a 125 % increase between that of  $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$  and  $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ . This

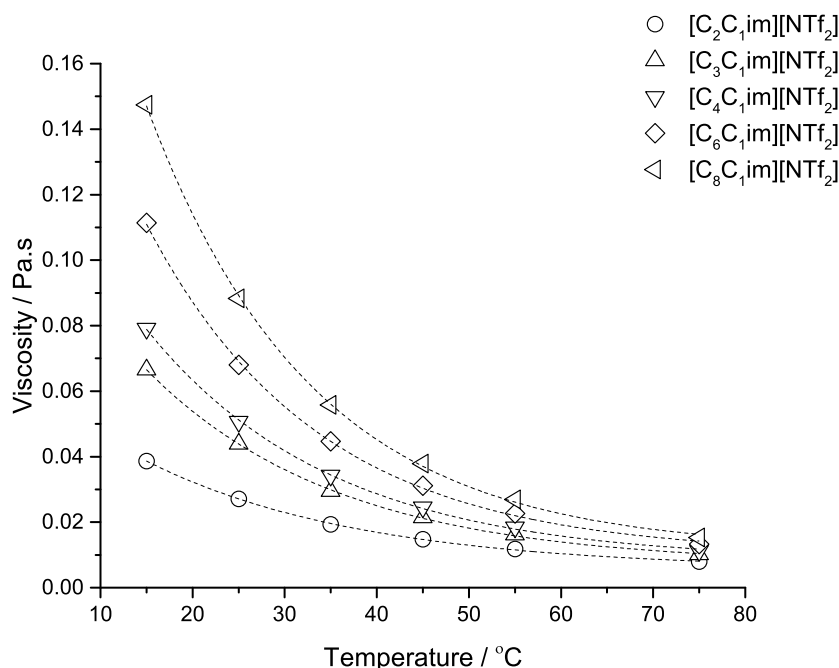


**Figure 3.9.3** – Viscosity at increasing temperatures (15, 25, 35, 45, 55, and 75 °C) for the  $[C_xC_yim][NTf_2]$ , ionic liquids.

indicates that the hydroxyl group's hydrogen bonding effect does have a greater significance when the chain length is  $\geq 4$ .

The trend for both the unfunctionalised and functionalised ionic liquids (Figures 3.9.3 & 3.9.4) as the temperature increases is that of an exponential decay which fits the Vogel-Fulcher-Tammann (VFT) model.

Using the viscosity data obtained across the temperature range (15 - 75 °C) it is possible to calculate the activation parameters for the ionic liquids. The effect of temperature on viscosity can be fitted to an Arrhenius-type of temperature relationship (Equation 3.9.1):<sup>[35, 39]</sup>

$$\eta = \eta_{\infty} e^{\left(\frac{E_a}{RT}\right)} \quad (3.9.1)$$

Where,  $\eta$  is the viscosity in Pa.s,  $E_a$  is the energy of activation for viscous flow in J mol<sup>-1</sup>,  $R$  is the gas constant (8.3144621 J mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  is the temperature in Kelvin,  $\eta_{\infty}$  is the viscosity at infinite temperature. Seddon *et al.*<sup>[34]</sup> have stated

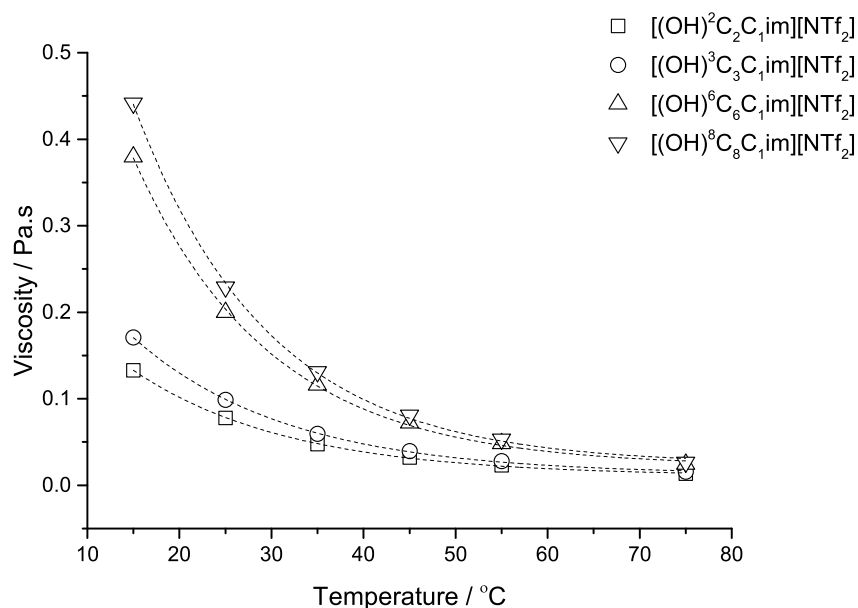


**Figure 3.9.4** – Viscosity at increasing temperatures (15, 25, 35, 45, 55, and 75 °C) for the  $[(\text{HO})^x\text{C}_x\text{C}_y\text{im}][\text{NTf}_2]$ , ionic liquids.

that Equation 3.9.1 can only be applied when there is a small temperature range and limited symmetry of the cation.

Natural log linearisation of Equation 3.9.1 gives the following:

$$\ln(\eta) = \ln(\eta_\infty) + \frac{E_a}{RT} \quad (3.9.2)$$

By plotting  $\ln(\eta)$  versus  $1/T$  it is possible to calculate the energy of activation for viscous flow from the slope of the plot which equals  $\frac{E_a}{R}$  and  $\eta_\infty$  from the intercept.

The Gibbs energy of activation,  $\Delta G^*$ , enthalpy of activation,  $\Delta H^*$ , and the entropy of activation,  $\Delta S^*$ , can be calculated from the Eyring derived equation (Table 3.9.2):<sup>[40]</sup>

$$\eta = \frac{hN_a}{V_m} e^{\left(\frac{\Delta G^*}{RT}\right)} \quad (3.9.3)$$

Where,  $h$  is Plank's constant,  $N_a$  is Avogadro's number,  $V_m$  is the molar volume,

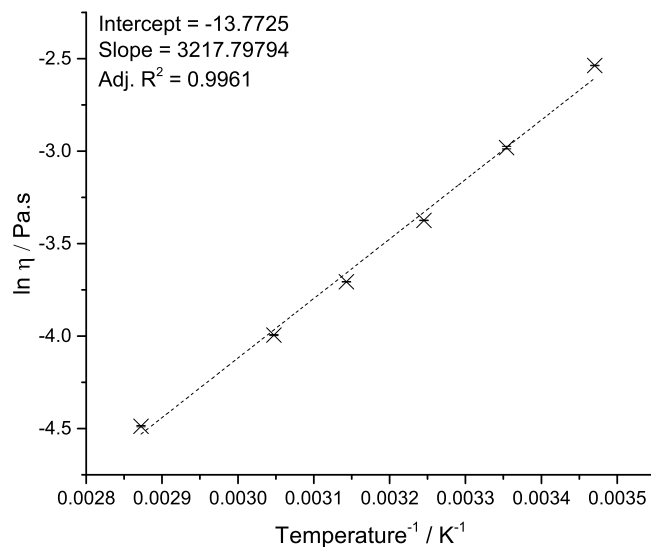


**Figure 3.9.5** – Arrhenius plot for 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>].

$R$  is the gas constant,  $\Delta G^*$  is the molar Gibbs energy and  $T$  is the temperature in Kelvin.

By taking into account that Gibbs energy is made up of enthalpy,  $H$ , and entropy,  $S$ , (equation 3.9.4) it is possible to take the natural log of Equation 3.9.3 to give Equation 3.9.5. Plotting  $\ln \left( \frac{\eta V_m}{h N_a} \right)$  versus  $1/T$  it is possible to calculate  $\Delta H^*$  from the slope,  $\frac{\Delta H^*}{R}$ , and  $\Delta S^*$  from the intercept,  $-\frac{\Delta S^*}{R}$ .

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (3.9.4)$$

$$\ln \left( \frac{\eta V_m}{h N_a} \right) = -\frac{\Delta S^*}{R} + \frac{\Delta H^*}{RT} \quad (3.9.5)$$

### 3.9.2 Density of the ionic liquids

In the case of the ionic liquids measured here the anion has been kept the same (as water immiscibility is required) and the alkyl chain length has been increased with and without a hydroxyl group functionalisation. As the alkyl chain length

| Ionic Liquid                                                            | $E_a$ / kJ mol <sup>-1</sup>                      | $\eta_\infty$ / mPa.s   | $\Delta G^*$ / kJ mol <sup>-1</sup> | $\Delta H^*$ / kJ mol <sup>-1</sup> | $\Delta S^*$ / J mol <sup>-1</sup> K <sup>-1</sup> |
|-------------------------------------------------------------------------|---------------------------------------------------|-------------------------|-------------------------------------|-------------------------------------|----------------------------------------------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 22.05 (21) <sup>[41]</sup> (22.2) <sup>[35]</sup> | 3.70 x 10 <sup>-3</sup> | 58.44                               | 22.05                               | -122.11                                            |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 26.05                                             | 1.20 x 10 <sup>-3</sup> | 59.79                               | 26.26                               | -112.52                                            |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 26.75 (26.6) <sup>[35]</sup>                      | 1.04 x 10 <sup>-3</sup> | 60.33                               | 27.09                               | -111.56                                            |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 29.00                                             | 5.66 x 10 <sup>-4</sup> | 61.35                               | 29.47                               | -106.96                                            |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 31.54                                             | 2.65 x 10 <sup>-4</sup> | 62.2                                | 31.53                               | -102.99                                            |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 31.62                                             | 2.25 x 10 <sup>-4</sup> | 61.08                               | 32.05                               | -97.41                                             |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 33.14                                             | 1.55 x 10 <sup>-4</sup> | 61.81                               | 33.31                               | -95.65                                             |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 38.74                                             | 3.42 x 10 <sup>-4</sup> | 64.01                               | 38.03                               | -87.18                                             |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 39.43                                             | 2.94 x 10 <sup>-4</sup> | 64.61                               | 38.94                               | -86.13                                             |

**Table 3.9.2** – Calculated activation parameters ( $E_a$ ,  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) for the unfunctionalised and hydroxyl functionalised ionic liquids.

| Ionic Liquid                                                            | Density / g cm <sup>-3</sup> at 25 °C |
|-------------------------------------------------------------------------|---------------------------------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.519 ± 0.00                          |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.475 ± 5.77 x 10 <sup>-5</sup>       |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.436 ± 1.16 x 10 <sup>-4</sup>       |
| [C <sub>5</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.402 ± 5.77 x 10 <sup>-5</sup>       |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.373 ± 5.20 x 10 <sup>-4</sup>       |
| [C <sub>7</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.344 ± 5.77 x 10 <sup>-5</sup>       |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.320 ± 0.0                           |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.575 ± 5.77 x 10 <sup>-5</sup>       |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.534 ± 5.77 x 10 <sup>-5</sup>       |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.430 ± 1 x 10 <sup>-4</sup>          |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.370 ± 2.52 x 10 <sup>-4</sup>       |

**Table 3.9.3** – Density values (at 25 °C) for the unfunctionalised and hydroxyl functionalised ionic liquids.

is increased the density of the ionic liquid decreases. This is to be expected as the addition -CH<sub>2</sub>- units causes an increase in the bulk of the cation and therefore an expansion of the free space within the liquid. At a given mass therefore volume increases and hence the density decreases. This is in agreement with the literature.<sup>[34, 41, 42, 43]</sup> Incorporating a hydroxyl group increases the density of the ionic liquid by approximately 0.05 - 0.059 g cm<sup>-3</sup> across the liquids, but the linear decreasing trend is also exhibited as the chain length is increased.

### 3.9.3 Conductivity of the ionic liquids

The measured unfunctionalised imidazolium based ionic liquid conductivity values are in agreement with those found in the literature (Table 3.9.4 and Figure 3.9.6).<sup>[44, 45]</sup> The amount of water within an ionic liquid can lower the viscosity of the liquid, and hence the ions in the liquid can be more mobile which in turn increases the conductivity. Widegren *et al.*<sup>[44, 46]</sup> investigated this fact by testing the conductivity of ionic liquid samples with varying weight percent of water present and found that the conductivity increased as the water weight percent increased. Therefore, deviation from those values recorded here or by other research groups can be attributed to the water content of the ionic liquid being

| Ionic Liquid                                                            | Conductivity / mS cm <sup>-1</sup> |
|-------------------------------------------------------------------------|------------------------------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 10.27 ± 0.076                      |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 5.80 ± 0.095                       |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 4.46 ± 0.040                       |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 2.55 ± 0.022                       |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.27 ± 0.012                       |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 3.38 ± 0.053                       |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 2.52 ± 0.022                       |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 0.96 ± 0.008                       |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 0.76 ± 0.009                       |

**Table 3.9.4** – Conductivity values (at 25 °C) for the unfunctionalised and hydroxyl functionalised ionic liquids.

tested.

The inclusion of the hydroxyl group was expected to increase the viscosity of the liquid and reduce the conductivity exhibited by the liquid. The viscosities of the functionalised ionic liquids were found to be greater than the unfunctionalised liquids - see Section 3.8.1. With the increased viscosity the conductivity of the ionic liquid is reduced (Figure 3.9.7). The conductivity of hydroxyethyl, hydroxypropyl and hydroxyhexyl is reduced by 60 % and for hydroxyoctyl it is reduced by 40 % by incorporating the terminal hydroxyl functional group.

### 3.9.4 Water solubility in the ionic liquids

The water content of the ionic liquid is important as a certain percentage of water is required to stabilise any biological materials that are extracted into the ionic liquid ('organic') phase. To test this the ionic liquids were dried at 50 °C overnight before the water content was measured via Karl-Fisher measurements. These are the stated 'Dried water content' values given in Table 3.9.5. The 'Wet' water content values were obtained from shaking one millilitre of ionic liquid with ten millilitres of distilled water for two hours and then leaving to settle overnight.

As the alkyl chain length increases the hydrophobicity of the ionic liquid increases due to the addition of extra -CH<sub>2</sub>- units. These values are in agreement

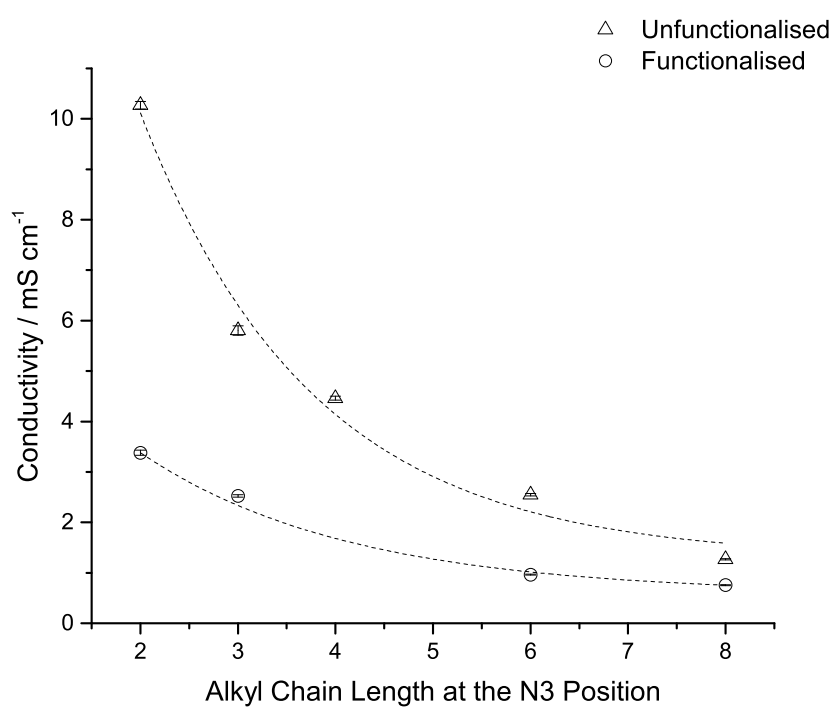


**Figure 3.9.6** – Conductivity versus increasing alkyl chain length at the N3 position for unfunctionalised and hydroxyl functionalised ionic liquids.

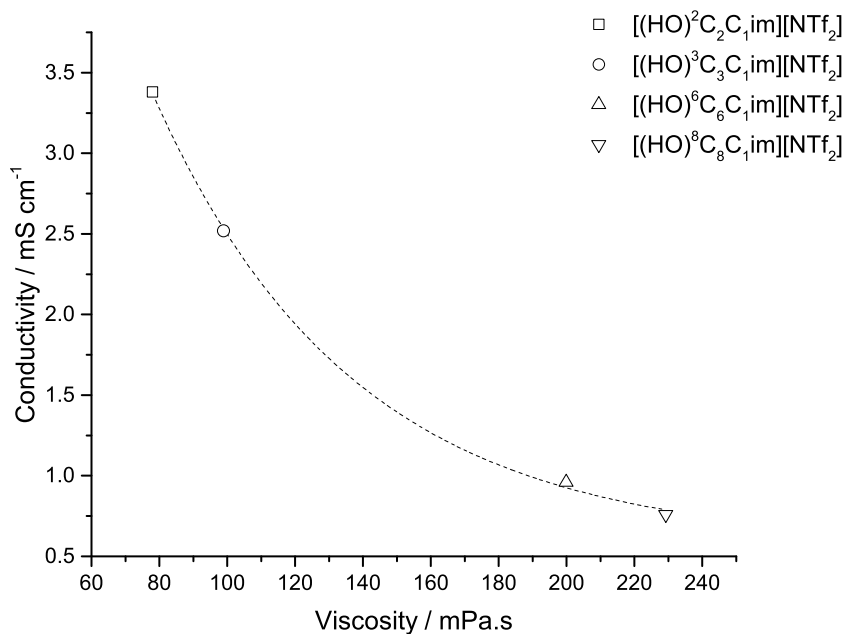
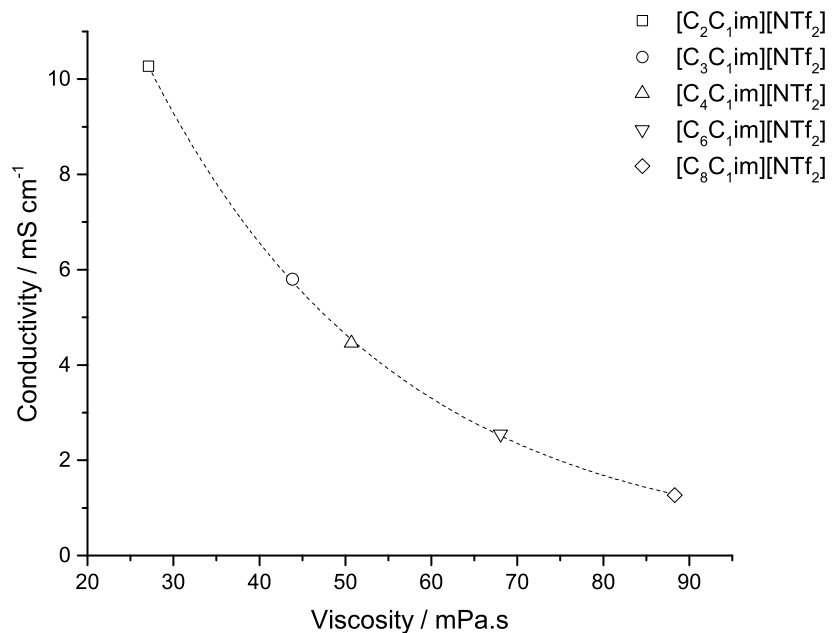


**Figure 3.9.7** – Conductivity versus viscosity for the unfunctionalised (top) and hydroxyl functionalised (bottom) ionic liquids at 25 °C.

| Ionic Liquid                | Dried water Content / ppm | 'Wet' water content / ppm |
|-----------------------------|---------------------------|---------------------------|
| $[C_2C_{1im}][NTf_2]$       | $24.3 \pm 2.3$            | $20636 \pm 342$           |
| $[C_3C_{1im}][NTf_2]$       | $22.0 \pm 3.4$            | $16539 \pm 222$           |
| $[C_4C_{1im}][NTf_2]$       | $21.8 \pm 2.0$            | $13269 \pm 601$           |
| $[C_6C_{1im}][NTf_2]$       | $24.3 \pm 3.5$            | $10867 \pm 661$           |
| $[C_8C_{1im}][NTf_2]$       | $30.8 \pm 5.7$            | $9538 \pm 25$             |
| $[(HO)^2C_2C_{1im}][NTf_2]$ | $67.7 \pm 3.0$            | $88483 \pm 1017$          |
| $[(HO)^3C_3C_{1im}][NTf_2]$ | $64.4 \pm 2.9$            | $87374 \pm 2407$          |
| $[(HO)^6C_6C_{1im}][NTf_2]$ | $65.1 \pm 1.6$            | $58461 \pm 1071$          |
| $[(HO)^8C_8C_{1im}][NTf_2]$ | $49.7 \pm 7.7$            | $41188 \pm 1966$          |

**Table 3.9.5** – Water content of dried and water saturated unfunctionalised  $[C_xC_{yim}][NTf_2]$  and hydroxyl functionalised  $[(HO)^xC_xC_{yim}][NTf_2]$  ionic liquids.

| Ionic Liquid                                                            | IL in water content / ppm |
|-------------------------------------------------------------------------|---------------------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 2324 ± 38                 |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1766 ± 15                 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1130 ± 05                 |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 441 ± 25                  |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 304 ± 03                  |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 11925 ± 120               |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 10256 ± 096               |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 4162 ± 059                |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1572 ± 011                |

**Table 3.9.6** – Unfunctionalised [C<sub>x</sub>C<sub>y</sub>im][NTf<sub>2</sub>] and hydroxyl functionalised [(OH)<sup>x</sup>C<sub>x</sub>C<sub>y</sub>im][NTf<sub>2</sub>] ionic liquid concentration present in water after agitation.

with those found by Luo *et al.*<sup>[47]</sup> The addition of the terminal alkyl hydroxyl group has a substantial effect on the water uptake of all the ionic liquids. This is to be expected as the hydrogen bonding ability of the liquid has been increased due to the presence of the hydroxyl group. In the case of the hydroxyethyl and hydroxypropyl imidazoliums the hydrogen bonding and the electrostatic forces dominate within the liquid meaning that the small hydrophobic increase of the additional -CH<sub>2</sub>-unit is negligible hence the similar water content value. It should also be noted that the dried water contents of the ionic liquids were approximately equal within the unfunctionalised and hydroxyl functionalised sets.

### 3.9.5 Ionic liquid solubility in the aqueous phase

It has been shown that not only the anion affects the ionic solubility but the cation as well.<sup>[33, 48]</sup> Coutinho *et al.* showed that as the hydrophobic nature of the cation increased, by the increasing alkyl chain length of one of the side chains of the ionic liquid, solubility in the water phase decreased.<sup>[48, 49, 50, 51]</sup> This was found to be the case with both the unfunctionalised imidazolium and the hydroxyl functionalised ionic liquids measured here (Table 3.9.6).

Incorporating the single terminal hydroxyl group has the expected effect of making the ionic liquid more water soluble. There is an assumption with the

| Ionic Liquid                                                            | Interfacial Tension / mN m <sup>-1</sup> |
|-------------------------------------------------------------------------|------------------------------------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 8.44 ± 0.023                             |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 10.56 ± 0.016                            |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 13.02 ± 0.029                            |
| [C <sub>5</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 13.89 ± 0.051                            |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 15.48 ± 0.017                            |
| [C <sub>7</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 17.35 ± 0.035                            |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 21.17 ± 0.245                            |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.85 ± 0.018                             |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 1.98 ± 0.088                             |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 4.55 ± 0.088                             |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 7.74 ± 0.038                             |

**Table 3.9.7** – Interfacial tensions between ionic liquid and water measured via the pendant drop method.

measurements carried out here that the cation and anion move as an ion pair across into the water phase, as the UV-Vis measurement only technically observes the the 211 nm UV peak from the imidazolium ring structure.

### 3.9.6 Interfacial tension between the ionic liquids and the aqueous phase

It has been hypothesised that the interfacial tension between ionic liquids and aqueous solutions will decrease as the alkyl chain length increases.<sup>[52]</sup> This is because of the increased number of imidazolium cations present at the interface, with their alkyl chains extending into the non-aqueous (ionic liquid) phase. This is contrary to the results obtained here (Table 3.9.7). The results of the interfacial tension measurements obtained here show that as the chain length increases the interfacial tension increased in a linear relationship for the unfunctionalised ionic liquids. This is in agreement with other research groups<sup>[53, 54]</sup> with variations being attributed to drop equilibration time variation.<sup>[55]</sup>

The addition of the single hydroxyl group onto the end of the long alkyl chain reduces the interfacial tension exhibited between water and the bis-imide based ionic liquids: 63 % reduction for C<sub>8</sub> and 71 % for C<sub>6</sub>.

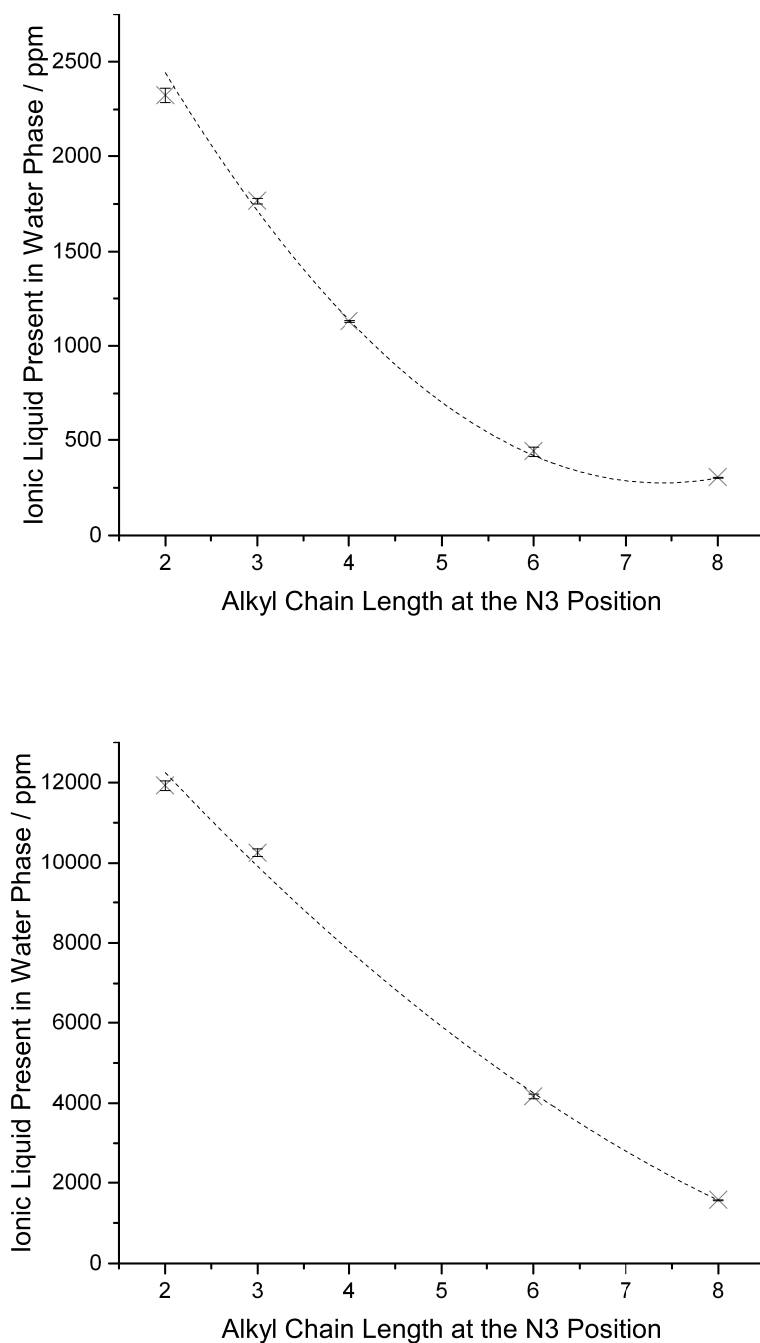


**Figure 3.9.8** – Unfunctionalised (upper) and hydroxyl functionalised (lower) ionic liquid concentration present in water after agitation versus alkyl chain length at the N3 position.

In the case of the hydroxyethyl and hydroxypropyl imidazolium ionic liquids the interfacial tension is extremely low and there were difficulties forming a stable pendant drop on the end of the wide bore needle. The increase by one  $\text{-CH}_2\text{-}$  unit does not have a large effect on the interfacial tension. This is likely to be due to the hydroxyl group H-bonding effect outweighing the additional hydrophobic properties of the additional  $\text{-CH}_2\text{-}$  unit. As the chain length increases though this effect will become more pronounced.

## 3.10 Theoretical calculations

Theoretical calculations were also utilised within this project to determine the molecular, ionic, volumes of the ionic liquids which were synthesised. This was to be able to estimate the ‘free’ volume present within the ionic liquid for a biological molecule. There are two methods used for the determination of molecular volumes:

1. Calculation based upon crystal structures
2. Computational calculations

### 3.10.1 Computational methods

Computational methods can be broadly separated into two major electronic structure class types:

1. Semi-empirical - These methods employ empirical parameters which in turn tend to mean that the method is inexpensive compared to *Ab initio* computational methods.
2. *Ab initio* - These methods contain no experimental/empirical parameters and are only mathematical approximations totally based upon quantum mechanics and basic physical constraints.

#### 3.10.1.1 Schrödinger equation

To allow access to the properties of a system the wave function of that system must first be solved. This is achieved by solving the Schrödinger equation, Equation

3.10.1, for the system:

$$\hat{H}\Psi(\mathbf{q}, t) = -\frac{\hbar\partial\Psi(\mathbf{q}, t)}{i\partial t} \quad (3.10.1)$$

The wave function,  $\Psi$ , depends on the spatial and spin orbital represented by  $\mathbf{q}$  and time,  $t$ . In principle this fully defines a system and a usual simplification is the time independent form:

$$\hat{H}\Psi(\mathbf{q}) = E\Psi(\mathbf{q}) \quad (3.10.2)$$

The Hamiltonian operator,  $\hat{H}$ , describes the total energy, kinetic and potential, of the electrons and nuclei present within the system, in the absence of any magnetic or electrical fields. The electrons and nuclei energy terms can be separated due to the fact that they have significantly difference masses. This assumption is the *Born-Oppenheimer approximation*. This means that the nuclei, which are heavier, move at a significantly slower rate compared with the electrons that surround them. Hence, it is possible to treat the nuclei as being stationary in relation to electrons, i.e. electrons moving in a field of fixed nuclei, this is known as the *clamped-nuclei approximation*, and combined it allows the reduction of the Hamiltonian operator down to the electronic Hamiltonian,  $\hat{H}_{elec}$ :<sup>[56]</sup>

$$\hat{H}_{elec} = \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} \quad (3.10.3)$$

$$\hat{T} = -\frac{1}{2} \sum_i^N \nabla_i^2 \quad (3.10.4)$$

$$where, \nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad (3.10.5)$$

$$\hat{V}_{Ne} = \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} \quad (3.10.6)$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j>1}^M \frac{1}{r_{ij}} \quad (3.10.7)$$

The electronic Hamiltonian consists of the kinetic energy of the electrons,  $\hat{T}$ , the potential energy of the electron-nuclei interactions (often termed as the external potential in density functional theory),  $\hat{V}_{Ne}$ , and the electron-electron interaction,  $\hat{V}_{ee}$ . Where,  $N$  represents the number of electrons present in the system,  $M$  the number of nuclei and  $Z$  the charge of those nuclei.

This approximation in turn simplifies Equation 3.10.2 to:

$$\hat{H}_{elec}\Psi_{elec}(\tilde{\mathbf{q}}) = E_{elec}\Psi_{elec}(\tilde{\mathbf{q}}) \quad (3.10.8)$$

The physical interpretation of the wavefunction,  $\Psi$ , is only associated with the square of the wavefunction as this represents the probability of the electrons being found within a volume  $\partial x_1, \partial x_2, \dots, \partial x_N$ . As electrons are fermions with spin of a half-integer there is a physical requirement for the wavefunction to be anti-symmetric with respect to exchange of any spatial or spin coordinates of any indistinguishable electrons. This is the antisymmetry principle (i.e. generalisation of Pauli's exclusion principle):

$$\Psi(\vec{q}_1, \vec{q}_2 \dots \vec{q}_N) = -\Psi(\vec{q}_1, \vec{q}_2 \dots \vec{q}_N) \quad (3.10.9)$$

Integrating the square of the wavefunction, with respect to all the variables equals one, i.e. the probability of finding the electrons in space is unity, and if the wavefunction satisfies this requirement it is said to be normalised:

$$\int \dots \int |\Psi(\vec{q}_1, \vec{q}_2 \dots \vec{q}_N)|^2 d\vec{q}_1 d\vec{q}_2 \dots d\vec{q}_N = 1 \quad (3.10.10)$$

### 3.10.1.2 Variation principle

Ultimately, to calculate the energy of the system the expectation value,  $\langle \hat{O} \rangle$ , of the Hamiltonian needs to be calculated. It is first normalised as per Equation 3.10.10:

$$\langle \hat{O} \rangle = \int \dots \int \Psi_{calc}^* \hat{O} \Psi_{calc} d\tilde{\mathbf{q}} \equiv \langle \Psi_{calc} | \hat{O} | \Psi_{calc} \rangle \quad (3.10.11)$$

According to the variation principle the calculated energy value from Equation 3.10.11 will be the upper bound to the true energy of the ground state energy:

$$\langle \Psi_{calc} | \hat{H} | \Psi_{calc} \rangle = E_{calc} \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (3.10.12)$$

Minimising the functional  $E[\Psi]$  by searching through all acceptable N-electron wavefunctions allows the ground state energy, and the wavefunction, to be determined, where  $\Psi \rightarrow N$  is an allowable N-electron wave function. It is made up of three distinct terms: kinetic energy of the electrons,  $\hat{T}$ , the potential energy of the electron-nuclei interactions,  $\hat{V}_{Ne}$ , and the electron-electron interaction,  $\hat{V}_{ee}$ :

$$E_0 = \min_{\Psi \rightarrow N} E[\Psi] = \min_{\Psi \rightarrow N} \langle \Psi | \hat{T} + \hat{V}_{Ne} + \hat{V}_{ee} | \Psi \rangle \quad (3.10.13)$$

### 3.10.1.3 Hartree-Fock, HF, approximation

To solve Equation 3.10.13, a subset is first determined which is a physically appropriate approximation of the wavefunction. The subset matrix contains all the electron wavefunctions,  $\chi$ , in columns with all the spatial positions,  $\mathbf{q}$ , in rows. The antisymmetrised product of these wavefunctions is known as the *Slater determinant*,  $\Phi_{SD}$ , Equations 3.10.14 and 3.10.15:

$$\Psi_0 \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\tilde{\mathbf{q}}_1) & \chi_2(\tilde{\mathbf{q}}_1) & \cdots & \cdots & \chi_N(\tilde{\mathbf{q}}_1) \\ \chi_1(\tilde{\mathbf{q}}_2) & \chi_2(\tilde{\mathbf{q}}_2) & \cdots & \cdots & \chi_N(\tilde{\mathbf{q}}_2) \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ \chi_1(\tilde{\mathbf{q}}_N) & \chi_2(\tilde{\mathbf{q}}_N) & \cdots & \cdots & \chi_N(\tilde{\mathbf{q}}_N) \end{vmatrix} \quad (3.10.14)$$

$$\Psi_0 \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \{ \chi_1(\tilde{\mathbf{q}}_1) \cdots \chi_N(\tilde{\mathbf{q}}_N) \} \quad (3.10.15)$$

The one-electron functions, i.e. spin orbitals, are composed of a spatial orbital  $\phi(\mathbf{r})$  and a variable spin function  $\mathbf{s}$ :

$$\chi(\tilde{\mathbf{q}}) = \begin{pmatrix} \phi(\mathbf{r})\alpha(\mathbf{s}) \\ \phi(\mathbf{r})\beta(\mathbf{s}) \end{pmatrix} \quad (3.10.16)$$

These spin functions are orthonormal:

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \quad (3.10.17)$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \quad (3.10.18)$$

Using the variation principle it is possible to determine the best (i.e. closest) Slater determinant, to the ground state energy. The Hartree-Fock limit is as close to the real value as the basis subset will allow:

$$E_{HF} = \min_{\Phi_{SD} \rightarrow N} E[\Phi_{SD}] \quad (3.10.19)$$

Hartree-Fock model based methods are based upon an electron moving in a static field of nuclei (*clamped-nuclei approximation*), and therefore does not take into account any electron correlation. Due to the variation principle (Equation 3.10.12) the  $E_{HF}$  value, Equation 3.10.19, is always larger than the ground state energy,  $E_0$ .

#### 3.10.1.4 Density Functional Theory

Density Functional Theory (DFT)<sup>[56]</sup> tends to be placed into the *Ab initio* class and DFT models have gained prominence in recent years due to the fact that they include electron correlation effects. That is to say that they include the fact that electrons actually react to each other within a system and actively avoid each other. DFT is based upon functionals\* of the electron density in the system. DFT approximate functionals usually partition the electronic energy into the sum of several functional terms:

$$E_{electronic} = E_{Kinetic} + E_{Coulomb} + E_{Exchange} + E_{Correlation} + E_{External} \quad (3.10.20)$$

When undertaking a DFT based method approximations are sought for the kinetic energy from the electron motion,  $E_{kinetic}$ , exchange energy,

---

\*A functional is a function which is described as a function, i.e. a function of a function

$E_{Exchange}$ , and correlation energy,  $E_{Correlation}$ . Early models included work by Thomas, Fermi and Dirac.<sup>[57, 58, 59]</sup> However, it is based upon two theorems by Hohenberg and Kohn:<sup>[60]</sup>

1. ‘the external potential  $\hat{V}_{ext}$  is (to within a constant) a unique functional of  $p(\tilde{\mathbf{r}})$ .’- Looking back at equation 3.10.3,  $\hat{V}_{Ne}$ (the potential energy of the electron-nuclei interactions) is  $\hat{V}_{ext}$ .
2. Variation principle - revisited for DFT: Taking into account electron density, the functional  $F_{HF}[p]$  will only deliver the lowest energy state of the system if the inputted electron density is the true ground state density  $p_0$ .

$$\begin{aligned} \hat{T}[p_{calc}] + \hat{V}_{ee}[p_{calc}] + \int p_{calc}(r)V_{ext}dr &= \langle \tilde{\Psi}_{calc} | \hat{H} | \tilde{\Psi}_{calc} \rangle \\ &= E_{calc}[p] \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \end{aligned} \quad (3.10.21)$$

To actually make use of electron density in a usable manner Kohn and Sham<sup>[61]</sup> introduced the concept of a non-interacting reference system (basis set) using orbitals such that as much of the exact kinetic energy of the system is computed, therefore leaving only a small part of the system’s energy to be determined by a functional. The Kohn-Sham operator allows the calculation of the exact kinetic energy of a non-interacting reference state and is described by a Slater determinant similar to Equation 3.10.14.

Kohn and Sham separated the functional into the following terms:

$$F[p] = T_s[p] + J[p] + E_{XC}[p] \quad (3.10.22)$$

Where,  $T_s[p]$  represents the exact kinetic energy of the system (with non-interacting electrons) with an electron density of  $p$ ,  $J[p]$  represents the classical coulomb repulsion (Hartree) and  $E_{XC}[p]$  represents the exchange-correlation energy. The exchange-correlation energy terms contains the remaining kinetic energy not accounted for from the exact kinetic energy term  $T_s[p]$ . In principle, the solution is exact, within the limitations of the basis set being used, however the exact values for the exchange-correlation potential are rarely known and hence the DFT approach is to use different approximations to determine  $E_{XC}$ .

### 3.10.1.5 Local (spin) Density Approximations

These functions are only in terms of the spatial variable  $\vec{r}$  and are independent of the effective local potential at any other position. Hence, the usual method for determining the exchange-correlation potential is via a ‘local density approximation’, LDA. By including the spin of the system it is possible to improve the approximation. This is known as ‘local spin density approximation’, LSDA. Nearly all DFT exchange-correlation functions are based upon this. Examples of this are the Slater Exchange functional:[62]

$$E_X^{LSDA}[\rho_\alpha, \rho_\beta] = -2^{\frac{1}{3}} C_X \int \rho_\alpha(\vec{r})^{\frac{4}{3}} + \rho_\beta(\vec{r})^{\frac{4}{3}} d\vec{r}$$

$$C_X = \frac{3}{4} \left( \frac{3}{\pi} \right)^{\frac{1}{3}} \quad (3.10.23)$$

and the Vosko, Wilk and Nusair functional,  $E_C^{VWN}$ . [63]

LDA/LSDA was for many years only used for solid-state related calculations until the gradient of the charge density at a particular point ( $\vec{r}$ ) was taken into account (this allows the assumption that the charge density is not uniform within a system but varying slowly) and hole constraints applied. These functionals are known as Generalised Gradient Approximations, GGA.

Becke88, usually abbreviated as B or B88, is an example of a GGA based exchange functional:[64]

$$E_X^{B88} = E_X^{LSDA/LDA} - \beta \sum_{\sigma=\alpha,\beta} \int p_\sigma^{\frac{4}{3}} \frac{x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} d\vec{r}$$

$$x_\sigma = \frac{|\nabla p_\sigma|}{p_\sigma^{\frac{4}{3}}}$$

$$\beta = 0.0042 \quad (3.10.24)$$

### 3.10.1.6 Hybrid functionals

Hybrid functionals allow the mixing of different methods, usually in this case it is the mixing of the Hartree-Fock exchange correlation potential with the DFT exchange correlations potential to give the best result. One of the most popular hybrid functionals used in DFT computational modeling is Becke's three-parameter functional, B3LYP, Equation 3.10.25. This functional takes into account the local Slater exchange, the exact Hartree-Fock exchange, the Beck88 GGA correction (to the Hartree-Fock), the Vosko, Wilks and Nusair (VWN) local correlation functional and the Lee-Yang-Paar (LYP) GGA correlation functional.<sup>[6]</sup> Becke's functional includes coefficients that allow the weighting over the various components of the functional. Coefficient  $a$  controls the exact exchange functional, with  $b$  and  $c$  controlling the exchange and correlation gradient correction, via local density approximation, respectively. These optimum constants, (Equation 3.10.25), were determined by Becke from a linear least-squares fit of a number of atomisation energies, ionisation potentials, proton affinities and total atomic energies.<sup>[65]</sup>

$$\begin{aligned}
 E_{XC}^{B3LYP}[\rho_\alpha, \rho_\beta] = & (1 - a) \cdot E_X^S[\rho_\alpha, \rho_\beta] + a \cdot E_X^{HF} + b \cdot \Delta E_X^{B88}[\rho_\alpha, \rho_\beta] \\
 & + (1 - c) \cdot E_C^{VWN}[\rho_\alpha, \rho_\beta] + c \cdot E_C^{LYP}[\rho_\alpha, \rho_\beta]
 \end{aligned}$$

$$\begin{aligned}
 a &= 0.20 \\
 b &= 0.72 \\
 c &= 0.81
 \end{aligned}
 \tag{3.10.25}$$

This is the hybrid functional used within this thesis. The methodology involves performing optimisation calculations on a molecule, followed by frequency calculations on the optimised structure and finally the calculation of the desired property of the molecule. With this functional a 6-311+G(d,p) basis set was used:<sup>[66]</sup>

- The basic basis set here is the 6-311G basis set. This describes the core orbitals using basis functions with a fixed contraction of six primitive functions (6-311G).
- Per valence orbital there are three basis functions provided/applied, 6-311G,

with one being the contraction of three primitives (6-311G), and the remaining two being a contraction of one primitive each (6-311G).

- Additions to this basic set are polarisation basis sets. Before this is applied the valence basis set is allowed to change size but not shape. Polarised basis sets removes this limitation and hence can add p functions to hydrogen atoms, d/f functions to heavy atoms. Diffuse functions are important if the system has electrons based relatively far from the nucleus e.g. lone pairs, anions etc. 6-311+G. ++ adds diffuse function to all atoms. while + adds diffuse function to all atoms but the hydrogens.

Therefore, the basis set used here is a diffuse, polarised basis set. For these calculations the integration grid was set to ‘ultrafine’ and an electron density convergence criterion of  $10^{-9}$ , (SCF=conver=9) used.

## 3.10.2 Results and discussion

### 3.10.2.1 Ionic volumes

The ionic volumes for the cations and anions were calculated via DFT using the B3LYP functional and are reported in Table 3.10.1.

Between the two methods applied, standard optimisation of the structure using ‘opt’, and optimisation of the structure by scanning round each dihedral angle (‘scan’), it can be seen that there are slight variations but nothing significant for these ions. As is expected, the ionic volume of the cations increase as the chain length increases and this trend is exhibited with both the unfunctionalised and hydroxyl functionalised cations. The values calculated are in agreement with those reported in the literature by Krossing *et al.*<sup>[67]</sup>, and however, disagree with those reported by Maroncelli *et al.*<sup>[68]</sup> whom also performed DFT calculations.

### 3.10.2.2 Free volumes

The ‘free’ volume within a solution of the ionic liquid (or in fact any molecules) can be calculated by subtracting the calculated/theoretical volume (determined by crystal structures or computational calculations) from the real volume. The real

| Ionic Liquid Ion                                                  | Effective Ionic Volume / cm <sup>3</sup> mol <sup>-1</sup> |        |
|-------------------------------------------------------------------|------------------------------------------------------------|--------|
|                                                                   | ‘Opt’                                                      | ‘Scan’ |
| [C <sub>2</sub> C <sub>1</sub> im] <sup>+</sup>                   | 95.29                                                      | 96.30  |
| [C <sub>3</sub> C <sub>1</sub> im] <sup>+</sup>                   | 108.79                                                     | 107.58 |
| [C <sub>4</sub> C <sub>1</sub> im] <sup>+</sup>                   | 121.75                                                     | 119.38 |
| [C <sub>5</sub> C <sub>1</sub> im] <sup>+</sup>                   | 138.03                                                     | 136.50 |
| [C <sub>6</sub> C <sub>1</sub> im] <sup>+</sup>                   | 149.77                                                     | 152.17 |
| [C <sub>7</sub> C <sub>1</sub> im] <sup>+</sup>                   | 163.42                                                     | 166.46 |
| [C <sub>8</sub> C <sub>1</sub> im] <sup>+</sup>                   | 176.14                                                     | 178.16 |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im] <sup>+</sup> | 102.14                                                     | 100.93 |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im] <sup>+</sup> | 116.36                                                     | 110.98 |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im] <sup>+</sup> | 158.06                                                     | 158.40 |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im] <sup>+</sup> | 181.27                                                     | 185.62 |
| [NTf <sub>2</sub> ] <sup>-</sup>                                  | 124.16                                                     | -      |

**Table 3.10.1** – DFT calculated effective ionic volumes for the unfunctionalised and hydroxyl functionalised ionic liquid cations and anion.

volumes can be determined from molecular weight of the molecule and its density,  $\rho$  (Equation 3.10.26):

$$V_{Mol} = \frac{\text{Molecular Weight}}{\rho} \quad (3.10.26)$$

In terms of an ionic liquid, the ionic volumes of the cation and anion are determined and then combined to give the overall calculated volume of the ionic liquid itself:<sup>[67, 69]</sup>

$$V_{Calc} = V_{Cation}^* + V_{Anion}^* \quad (3.10.27)$$

The free volume ( $Vol_{Free}$ ) of the ionic liquids synthesised here were calculated from the determined real volumes ( $Vol_{Mol}$ ) and computational calculations ( $Vol_{Calc}$ ) (Table 3.10.2).

As the volume of the ionic liquid increases the free volume within the liquid also increases. It is hypothesised that the larger the free volume within the ionic

| Ionic Liquid                                                            | Molar Volume / $\text{cm}^3 \text{ mol}^{-1}$ |                           |                            |                                 |                                  |
|-------------------------------------------------------------------------|-----------------------------------------------|---------------------------|----------------------------|---------------------------------|----------------------------------|
|                                                                         | Vol <sub>Mol</sub>                            | Vol <sub>Calc</sub> (Opt) | Vol <sub>Calc</sub> (Scan) | Vol <sub>Free</sub> ('Opt') (%) | Vol <sub>Free</sub> ('Scan') (%) |
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 257.66                                        | 219.45                    | 220.46                     | 38.21 (6.7)                     | 37.20 (6.9)                      |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 274.79                                        | 232.95                    | 231.74                     | 41.85 (6.6)                     | 43.06 (6.4)                      |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 291.97                                        | 245.91                    | 243.54                     | 46.06 (6.3)                     | 48.44 (6.0)                      |
| [C <sub>5</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 309.06                                        | 262.19                    | 260.66                     | 46.87 (6.6)                     | 48.40 (6.4)                      |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 325.89                                        | 273.95                    | 276.33                     | 51.96 (6.3)                     | 49.56 (6.6)                      |
| [C <sub>7</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 343.40                                        | 287.57                    | 290.61                     | 55.83 (6.2)                     | 52.79 (6.5)                      |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 360.15                                        | 300.30                    | 302.32                     | 59.85 (6.0)                     | 57.83 (6.2)                      |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 258.54                                        | 226.30                    | 225.09                     | 32.24 (8.0)                     | 33.45 (7.7)                      |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 274.59                                        | 240.51                    | 235.14                     | 34.08 (8.1)                     | 39.45 (7.0)                      |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 324.12                                        | 282.22                    | 282.56                     | 41.89 (7.7)                     | 41.56 (7.8)                      |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 358.72                                        | 305.43                    | 309.78                     | 53.29 (6.7)                     | 48.94 (7.3)                      |

**Table 3.10.2** – Calculated real molar volumes for the ionic liquids and the determined 'free' volume.

liquid the greater the space and hence probability of a molecule ‘fitting’ into the ionic liquid, and hence a greater likelihood of transference across an aqueous:non-aqueous interface (as long as all other conditions are met). Due to the significant size differences between a biological molecule and standard chemical molecules, it is unlikely that a biological molecule will be fully encapsulated by a single chemical molecule’s free volume. However, depending upon the chemical composition of the molecule, multiple chemical molecules could encapsulate specific regions allowing solubilisation, or at least stabilisation of the tertiary structure thereby keeping the molecule conformationally stable.

### 3.11 Conclusion

Within a liquid-liquid system balancing the properties of the two phases and their interaction is paramount. For the system being designed here the criteria for the required liquid are that:

1. It is immiscible with water and salt solution of water.
2. It forms a stable interface, with a low interfacial tension, with around 10 % water content.
3. It is conductive.
4. It is denser than water.
5. It will not lose ions easily into a water phase.
6. It has a sufficiently low viscosity to allow ion movement in and out of the non-aqueous ionic liquid phase.

It was known from the literature that bis(trifluoromethylsulfonyl)imide based ionic liquids would give water immiscible ionic liquids (depending on the functionalisation of the cation), and the imidazolium cation ring structure allowed relatively ‘easy’ functionalisation and so they were chosen as the liquids of choice for investigation.

All of the ionic liquids characterised here met the criteria listed above. Before a down-selection is performed, their electrochemical potential windows and extractive ability will be investigated. It is anticipated from these results that the 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide will perform the best, based on its characteristics:

- It is denser and immiscible with water.
- It has the lowest interfacial tension measured for the synthesised ionic liquids.
- Its water content is found to be approximately nine percent when ‘wet’ and it is a good conductor.



# Chapter 4

## Interfacial electrochemistry

### 4.1 Introduction

Electrochemistry can be described in multiple ways depending upon the application in mind. Historically, electrochemistry has been used for the isolation of various elements (most of the alkali metal series) and in the present day it is the basis of all batteries, both rechargeable and single use. These are now widely used in our electronic devices and starting to be used for solid state electronics.<sup>[70]</sup> The applications of electrochemistry are varied, and wide ranging, and therefore the best definition for the liquid-liquid extraction/detection electrochemistry methodology being described here is: ‘[Being] concerned with the behaviour of ions in solution and the properties shown by these solutions’<sup>[71]</sup>.

The aim of this investigation was to determine whether the behaviour of ions could be exploited, with or without the use of complexing agents for the sensing of target analytes, in liquids, at an Interface between Two Immiscible Electrolyte Solutions (**ITIES**).<sup>[72, 73, 74]</sup>

### 4.2 ITIES

When two immiscible solutions (typically these are aqueous and organic solutions) are placed into contact with each other a liquid-liquid interface is formed at the point of contact, and when these phases contain electrolytes this is known as an

ITIES. Through the use of an external power source a potential difference can be applied across these two phases, charging the phases and polarising the interface. This polarisation causes the ions within the system to redistribute themselves. If an imbalance of charge forms across the interface, equilibrium is achieved by ion transfer across the interface either from the aqueous phase to the non-aqueous phase, or in the opposite direction. This ion movement across the interface generates a current and when plotted as a function of the potential being applied gives a voltammogram. The Gibbs energy of (interfacial) transfer depends upon the ion itself, and this imparts an inherent level of selectivity into an ITIES sensing platform.<sup>[75]</sup>

The behaviour of target analytes under electric potential at, or across, an interface is used in the field of detection for specific analytes for several key reasons:<sup>[76, 77, 78, 79, 80]</sup>

1. Ions which do not readily undergo reduction or oxidation, or where the products of such redox reactions are problematic, can be electroactive at an ITIES and hence detected.
2. Tagging/labelling of the target analytes is not required – the only requirement is that the analytes can be moved under an applied field, i.e. contain a positively or negatively charged molecular group. This provides a potential means of label-free detection of a variety of analytes.
3. Because no solid surface exists at the sensing interface within a liquid-liquid sensing platform this means that the substantial challenges associated with functionalisation of surfaces with Biological Recognition Elements (BREs), and non-specific binding of background materials to solid surfaces, may therefore be avoided and/or overcome.<sup>[81, 82, 83, 84, 85]</sup>
4. Existing classical electrochemical techniques can be used and miniaturisation of instrumentation is possible allowing the development of small, low burden sensing platforms.
5. The same electrochemical techniques allowing the detection and quantification of a target analyte in a liquid-liquid, ITIES, system could potentially

also be exploited to extract those analytes from complex matrices. This could allow the development of an integrated sample extraction/purification, concentration and quantification sensor platform.<sup>[86]</sup>

These characteristics provide the opportunity for a novel class of specific and sensitive sensing platforms for the detection of a wide range of materials within a liquid medium.

### 4.3 Components of a liquid-liquid, ITIES, electrochemical cell

A standard liquid-liquid, ITIES, electrochemical cell consists of three main components:

1. An electrode system - this can be a four, three or even two electrode system.
2. An aqueous phase electrolyte.
3. An non-aqueous phase electrolyte.

#### 4.3.1 Electrode system

The typical liquid-liquid, ITIES, electrochemical setup is a four-electrode system composed of one counter electrode and one reference electrode in the aqueous phase; and the same within the non-aqueous phase.<sup>[87, 88]</sup> When compared with a standard electrochemistry system, where electron transfer occurs from the electrolyte to a solid electrode, in an ITIES based electrochemical system two charge transfer processes can take place:<sup>[89, 90]</sup>

1. Transfer, across the interface, of an ion from the aqueous phase to the non-aqueous phase, or in the reverse direction.
2. Electron transfer between a redox couple in one phase and a redox couple in another phase.



**Figure 4.3.1** – Overall redox reactions for a silver, silver chloride based reference electrode.

Platinum is usually used as the counter electrode in electrochemistry as it is an inert and highly conductive metal.<sup>[91]</sup> Within a liquid-liquid, ITIES, electrochemical cell the interface between the phases acts as the working electrode, the role of the counter electrodes is to maintain the voltage at the working electrode, and therefore the counter electrodes must have a surface area larger than that of the working electrode in order to avoid any inhibition of an electrochemical response from the cell.<sup>[92]</sup>

The reference electrode is the electrode which delivers a constant potential via a reduction-oxidation (redox) reaction. Common reference electrodes include:

- the standard hydrogen electrode (SHE),
- the saturated calomel electrode (SCE), and
- the silver-silver chloride electrode (Ag|AgCl).

Due to the toxicity of mercury, mercury based electrodes (calomel, SCE) are being phased out of laboratories and therefore, the recommended reference electrode for use in a liquid-liquid, ITIES, electrochemical cell is the silver-silver chloride electrode (see Figure 4.3.1 for the overall redox reaction). An advantage of the silver-silver chloride electrode is that it is convenient to make using a chloride based aqueous solution and a freshly cleaned silver wire.<sup>[91]</sup>

Nearly all reference electrode systems are based on their being used in an aqueous system and hence their use in a non-aqueous (i.e. the lower (or indeed upper - depending upon density) phase of an ITIES system) is formally incorrect. To ensure that the Nernst-Donnan equation<sup>[90]</sup> (see Equation 4.3.1) is fulfilled a pseudo silver, silver chloride electrode must be used within the non-aqueous phase. This comprises a silver, silver chloride electrode enclosed within a saturated electrolyte mixture containing the chloride salt of the base electrolyte present

in the non-aqueous phase e.g. if the non-aqueous phase electrolyte is tetraalkylammonium tetrphenylborate, the aqueous solution would be of the tetraalkylammonium chloride salt.<sup>[93]</sup> Technically this can be termed an ion-selective electrode as the reference electrode is selective to the chloride ion.

$$\Delta_{\beta}^{\alpha}\phi = \Delta_{\beta}^{\alpha}\phi^o + \frac{RT}{zF} \ln \left( \frac{a_{\beta}}{a_{\alpha}} \right) \quad (4.3.1)$$

where  $\Delta_{\beta}^{\alpha}\phi^o$  is the standard ion transfer potential,  $R$  is the gas constant,  $T$  is the temperature in Kelvin,  $z$  is the number of the charge of the potential determining ion,  $F$  is Faraday's constant, and  $a_{\alpha}$  and  $a_{\beta}$  are the activities of the potential determining ion in the non-aqueous phase ( $\beta$ ) and aqueous phase ( $\alpha$ ) respectively.

Platinum may also be used as a psuedo-reference electrode. In this case the potential within the electrochemical system is steady however it is not predictable due to it being unpoised, this however can be overcome by using an internal standard (such as a redox couple) or by comparing with a conventional reference electrode such as silver, silver chloride. The main advantages of using a platinum pseudo-reference electrode are that it is a low-impedance reference (standard reference electrodes have a higher resistance), and can be polarised.<sup>[91]</sup> It has been reported that platinum wire:

1. can be used within high-resistance media,<sup>[94]</sup>
2. in mesh form is found to give reproducible results and,<sup>[95]</sup>
3. that it can be used reliably under a wide range of conditions for aqueous, non-aqueous, gel or frozen electrolytes.<sup>[96]</sup>

### 4.3.2 Liquid components

As is stated in the abbreviation ITIES, the liquid components of a liquid-liquid, ITIES, electrochemical cell are immiscible with each other. The system requires a stable interface to be formed between the upper and lower phases. In a standard setup this is an interface between an aqueous phase and non-aqueous (usually organic) phase.

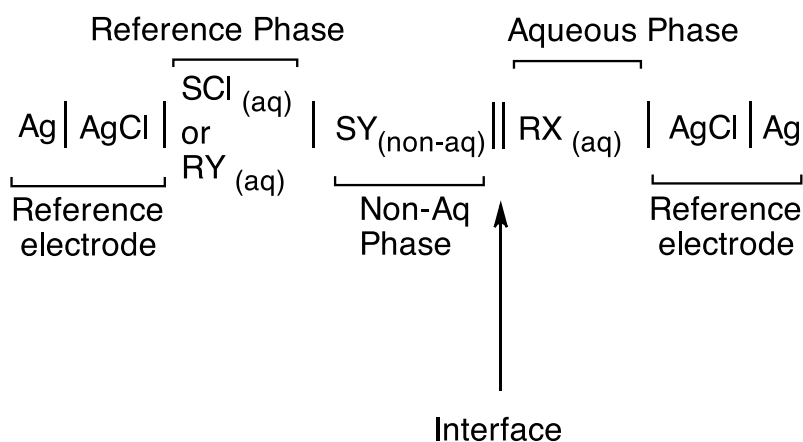


**Figure 4.3.2** – Representational electrochemical scheme for a liquid-liquid, ITIES, electrochemical cell.

Ultimately, the potential window of the liquid-liquid, ITIES, electrochemical cell (see Figure 4.3.2) depends upon the nature of the ‘base’ or background electrolytes within the aqueous/non-aqueous phases and is defined as the region between the transfer potentials of the base/background electrolytes:

- The ion transfer occurring at a positive potential difference (potential applied to the right hand reference electrode with respect to the left is denoted as positive) is due to the transfer across the interface of:
  - $\text{R}^+$  from the aqueous phase to the non-aqueous phase, or,
  - $\text{Y}^-$  from the non-aqueous phase to the aqueous phase
- The ion transfer occurring at a negative potential difference is due to the transfer across the interface of:
  - $\text{S}^+$  from the non-aqueous phase to the aqueous phase, or,
  - $\text{X}^-$  from the aqueous phase to the non-aqueous phase

It is the transfer of these charged and highly mobile electrolytes forwards and backwards across the interface that polarises the interface between the two phases. If the Gibbs energy of transfer of the electrolytes is similar to that of the target

analyte they could (especially as they are in excess in the system) swamp the electrochemical response of the ion transfer of the target. Therefore, to minimise this risk, electrolytes with a high Gibbs energy of transfer are chosen.

In the case of the aqueous phase, most ITIES systems are based on group I and II alkali metals and their chloride or sulphate salts. Schiffrin *et al.* investigated the salting out effect of the non-aqueous phase base electrolytes by controlling the aqueous phase electrolytes, therefore affecting their Gibbs energy of transfer and hence the potential window of the system.<sup>[97]</sup> The non-aqueous, organic, phase for most ITIES systems has been based upon salts dissolved in nitrobenzene, 1,2-dichloroethane, or 1,6-dichlorohexane.<sup>[98]</sup> The majority of the salts used within those solvents have been ammonium salts due to their high Gibbs energy of transfer. A fully ‘organic’ ITIES electrochemical cell has been recently reported where the ITIES was formed between an oil and an ionic liquid.<sup>[99]</sup> This setup would not be suited for biomolecule extraction and detection, as the pre-ITIES sampling is likely to be carried out with water. Additionally, the potential window of the system was extremely limited.

## 4.4 Ion transfer in a liquid-liquid, ITIES, electrochemical cell

Cation or anion transfer within the electrochemical cell can be classed as simple or facilitated.<sup>[100]</sup>

- **Simple Ion Transfer (SIT):** This is direct transfer of the ion of interest (which can be a cation or anion) across the aqueous/non-aqueous interface once a potential difference is applied to the electrochemical cell. This type of transfer is only possible if the Gibbs energy of transfer of the ion is within the available potential window for the cell being used.
- **Facilitated Ion Transfer (FIT):** Facilitated ion transfer is where an ion of interest first binds to an ionophore. IUPAC defines an ionophore as ‘A compound which can carry specific ions through membranes of cells or organelles’<sup>[101]</sup>. The complexation of the ion to the ionophore affects the

transfer characteristics and lowers the Gibbs energy of transfer. This could be lowered within the available potential window of the system, or in fact be lowered into the available potential window allowing a transfer not previously possible.<sup>[102, 103]</sup> Most ionophores are however not specific e.g. crown ethers, and therefore any molecule that can complex with the ionophore could have its Gibbs energy of transfer lowered and be transferred across the interface.

There is also facilitated ion transfer of the organic phase anion. In this situation macromolecules are adsorbed at the interface (not transferred across it). By being adsorbed at the interface these macromolecules facilitate the transfer of the smaller, more mobile, non-aqueous phase electrolyte ions into their hydrophobic pockets allowing their detection.<sup>[1, 104]</sup>

Careful choice of ionophore and aqueous/non-aqueous base electrolytes is therefore paramount to overcome, or at least minimise, this possible interference. Arrigan *et al.* reported that the effect of varying the aqueous phase base electrolyte from lithium chloride to magnesium chloride, in the presence of a crown ether ionophore, improved the limit of detection from 10  $\mu\text{M}$  to 2  $\mu\text{M}$ .<sup>[105]</sup> In this situation the fact that magnesium is a di-cation meant that it was less likely to complex with the crown ether compared with lithium, and hence the crown ether was free to complex the target analyte. Therefore, careful selection of the electrochemical cell components can enhance the sensitivity of the sensor, e.g. SIT gave a detection limit of 0.3 - 0.5  $\mu\text{M}$ , compared with a detection limit of 0.05  $\mu\text{M}$  via FIT for dopamine.<sup>[106, 107]</sup>

## 4.5 Literature review - progress to date of liquid-liquid extraction and detection of biological molecules

Separating the literature by the molecular weight of the molecule/s being investigated, i.e. chemicals, amino acids, peptides and proteins, as suggested in Arrigan and Herzog's review of 'Electrochemical strategies for the label-free detection of amino acids, peptides and proteins'<sup>[79]</sup> allows identification of the existing method-

ologies that have been developed to overcome the difficulties associated with the transfer of a molecule across an interface. Therefore, the following sections have been divided into:

1. Small molecule detection/extraction using liquid-liquid, ITIES, electrochemistry – drugs, amino acids, and peptides (see Section 4.5.1).
2. Macromolecule detection/extraction using liquid-liquid, ITIES, electrochemistry – polypeptides, and proteins (see Section 4.5.2).

#### **4.5.1 Small molecule detection/extraction using liquid-liquid, ITIES, electrochemistry – drugs, amino acids, and peptides**

Exploitation of liquid-liquid, ITIES, electrochemical methods have developed substantially since the 1970s and as a results of the inclusion of flow-injection methods, quantitative analysis has been made possible.<sup>[86]</sup> There are two reported methods for small molecule detection/extraction via liquid-liquid, ITIES, electrochemistry:

1. Simple Ion Transfer – of the molecules across the interface.
2. Facilitated Ion Transfer – via the use of ionophores.

##### **4.5.1.1 Dopamine**

Dopamine (MW = 153) is a key neurotransmitter which has two centres that are of interest electrochemically (see Figure 4.5.1).<sup>[80, 106]</sup> Standard electrochemical techniques are aimed at redox electrochemistry. However, ascorbate is always present in physiological samples of dopamine (see Figure 4.5.1 - right). As both molecules contain the same catechol group this means that when oxidation of dopamine occurs so too does the oxidation of the ascorbate's (present in the sample) redox centre.<sup>[108, 109, 110, 111]</sup> Due to the excess of ascorbate within physiological samples, compared with dopamine, the dopamine signal is swamped.<sup>[105, 107]</sup>

Through the use of a liquid-liquid, ITIES, electrochemistry it has been demonstrated that it is possible to selectively transfer dopamine (1 mM) while in the presence of an excess of ascorbate (20 mM).<sup>[106]</sup> This simple ion transfer is possible due

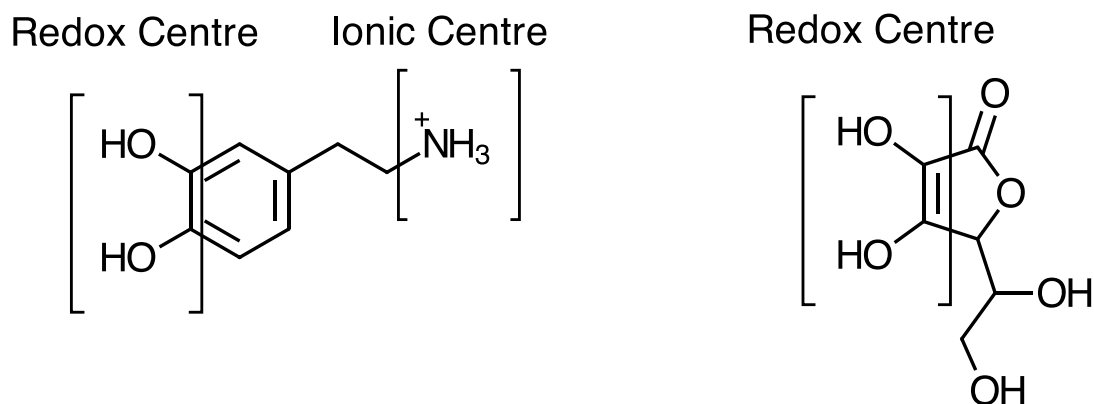


**Figure 4.5.1** – Molecular structure of dopamine (with the redox and ionic centres highlighted) and ascorbate (with the redox centre highlighted).

to the protonated amine group (ionic centre) allowing the interaction of dopamine with an applied potential being applied across the ITIES, while ascorbate, which does not contain an ionic centre is left unaffected. This ionic centre also offers the possibility of making use of an ionophore and to undertake facilitated ion transfer of the dopamine (see Section 4.4). This has been reported by Arrigan *et al.* who were able to selectively detect and transfer dopamine in the presence of ascorbate up to ratios of  $10^4:1$  (ascorbate:dopamine).<sup>[105]</sup> As part of their study the group also investigated the choice of the aqueous phase base/background electrolyte, with magnesium chloride giving the widest potential window and allowing a detection of ca. 2  $\mu\text{M}$  of dopamine.

A different approach has been through the cell design, and it has been reported that the lowest detected concentration of dopamine was ca. 0.3 – 0.5  $\mu\text{M}$  via simple ion transfer and 0.05  $\mu\text{M}$  via facilitated ion transfer through the use of micro-interfaces.<sup>[106, 107]</sup> Micro-interfaces have not been used in this work and therefore, no further discussion will be included in this thesis.

#### 4.5.1.2 Amino acids

The FIT (using dibenzo-18-crown-6 as the ionophore) of 10 out of 20 amino acids has been demonstrated by Chen *et al.*<sup>[112]</sup> As was to be expected, the success of this transfer was attributed to the lowering of the Gibbs energy of transfer

through the crown ether interaction with the amino acid's amine group. It was hypothesised that the remaining ten amino acids did not transfer due to steric hinderance affecting the amino acid : crown interaction. Amino acid transfer with an ionophore had been investigated previously and was found to be only partially sucessful.<sup>[113]</sup> This was most probably due to the ionophore : amino acid interaction not lowering the Gibbs energy of transfer into the available potential window of the electrochemical cell used by Sawada *et al.*.

The investigation (Chen *et al.*) did not report the detection limits for the amino acids which were successfully transferred; however, it does highlight that the larger a molecule is the greater the likelihood of steric hindrance for FIT. Additionally, they chose to use magnesium chloride as the aqueous phase base/-background electrolyte to avoid competitive binding with the ionophore. This supports the requirement for highly specific/selective (or possibly controllable i.e biological recognition element related) ionophores.

#### 4.5.1.3 Peptides

Building on the dopamine work, Osakai *et al.*<sup>[114]</sup> investigated the hydrophobicity of a range of peptides via simple ion transfer and facilitated ion transfer. The interaction of the ionophore (dibenzo-18-crown-6) with the peptide backbone was thought to alter the hydrophobicity of the peptide, and therefore allow FIT to occur. Arrigan *et al.*<sup>[115]</sup> undertook an investigation into oligopeptide detection via microinterfaces which supported this hypothesis. Limits of detection (LOD), for di-lysine, in a mixture with diphenylalanine of 1.0  $\mu\text{M}$  were achieved through the use of stripping voltammetry.<sup>[116, 117, 118, 119]</sup> In comparison, the LOD for the diphenylalanine was 9.7  $\mu\text{M}$ . This difference was attributed to the di-lysine signal dominating in the mixture (the LOD in absence of di-lysine was 1.3  $\mu\text{M}$ ). The overall conclusions of both groups was that the ionophore interaction, and resulting hydrophobicity of the complex, was key for interfacial transfer and detection of the peptides.

#### 4.5.1.4 Ionised drugs

In a practical application of liquid-liquid, ITIES, electrochemistry the aim is to be able to selectively detect and/or extract a target analyte from complex media. The Arrigan group have demonstrated selective extraction of ionised drugs (namely propranolol and timolol) from artificial urine across the interface into the organic phase.<sup>[86]</sup> The aim of the study was selective extraction rather than detection, however calibration curves were performed over a range of 25 - 195  $\mu\text{M}$  and 25 - 52  $\mu\text{M}$  for propranolol and timolol respectively. Their study highlights the utility of a liquid-liquid, ITIES platform which combines both sample extraction and specific analyte detection of targets within complex sample matrix.

#### 4.5.2 Macromolecule detection/extraction using liquid-liquid, ITIES, electrochemistry – polypeptides, and proteins

In the field of biological detection, it is the detection and/or extraction of larger macro molecules such as polypeptides and proteins that is of most interest. It is however the sheer size, and complexity, of these macro molecules that means they are inherently difficult to transfer across a liquid-liquid interface, be it electrochemically or via agitation.<sup>[120, 121]</sup> In the 1980's attempted transfers of protein in a liquid-liquid, ITIES, cell showed that the protein was adsorbed at the interfaces and precipitated out of solution. Such precipitation has been associated with contact denaturing of the protein. It is hoped through the tailoring of the properties of the non-aqueous phase that these issues can be overcome allowing liquid-liquid, ITIES, electrochemistry to offer a mechanism for label-free, selective and specific detection of macromolecules.

There are four reported methods for protein detection/extraction via liquid-liquid, ITIES, electrochemistry:

1. Simple Ion Transfer – transfer of the protein across the interface.
2. Facilitated Ion Transfer – transfer via the use of surfactant ionophores.

3. Facilitated Ion Transfer – transfer of an non-aqueous phase ion via macromolecule-interface interactions.
4. Impedance measurement of adsorbed macromolecules at the interface.<sup>[122]</sup>

#### 4.5.2.1 Protamine

Amemiya *et al.* developed methods for simple and facilitated transfer of protamine (MW  $\approx$  4100)<sup>[123]</sup> across an liquid-liquid, ITIES, interface.<sup>[124, 125]</sup> In the case of the FIT, dinonylnaphthalenesulfonate (DNNS) was used to allow facilitated transfer of protamine.<sup>[125]</sup> It was proposed that a reverse micelle was formed via the complexation of 20 DNNS molecules to the 20 charged groups available within the protamine structure. The formation of this reverse micelle has been investigated by various groups and Shinshi *et al.* made use of the properties of the surfactant bis(2-ethylhexyl) sulfo-succinate (AOT) to facilitate protamine transfer.<sup>[126, 127]</sup>

#### 4.5.2.2 Insulin

With insulin (MW  $\approx$  5800), it was found that with the large insulin molecule, and no ionophore present, facilitated ion transfer was occurring. This was via adsorption of the target analyte (insulin) at the interface and then transfer of the non-aqueous phase electrolyte anion into the aqueous phase.<sup>[104]</sup> This adsorption at the interface can be measured through impedance measurements, and Østergaard *et al.* were able to detect insulin concentrations as low as 0.1  $\mu$ M.<sup>[128]</sup>

#### 4.5.2.3 Cytochrome-c

With cytochrome-c (Cyt-c, MW  $\approx$  12400) in the absence of AOT, facilitated transfer of the non-aqueous phase anion also occurred, whereas in the presence of AOT, facilitated transfer of the Cyt-c occurred.<sup>[126]</sup> Dryfe *et al.* has also demonstrated electron transfer at a liquid-liquid, ITIES between cytochrome-c and an organic phase electron donor – 1,1'-dimethylferrocene.<sup>[129]</sup> No SIT has been reported for Cyt-c in a liquid-liquid, ITIES, electrochemical cell.

#### 4.5.2.4 Hen-Egg-White Lysozyme

A comparison of hen-egg-white lysozyme (HEWL, MW  $\approx 14300$ )<sup>[130]</sup> and insulin has shown the importance of the charges on the protein for transfer of the organic phase anion. HEWL is three times the molecular weight of insulin and has a greater positive charge. Even though it is larger the greater positive charge means that HEWL has a greater ability to transfer organic anions across the interface.<sup>[131]</sup> This study also demonstrated that multiple charged molecules do not require the use of stripping/pulse voltammetric methods to achieve sub micromolar detection in comparison to smaller, single charged molecules such as dopamine.

#### 4.5.2.5 Haemoglobin

Arrigan *et al.*<sup>[1]</sup> have demonstrated that the large molecular weight protein haemoglobin (MW  $\approx 68000$ ) is adsorbed at the interface (in the absence of an ionophore) as would be expected from work with other proteins. When the pH of the aqueous phase is less than the isoelectric point of the protein, the protein is positively charged. This positively charged protein can then interact with the negatively charged anion of the organic phase electrolyte.<sup>[1, 132]</sup> Unsurprisingly, a negatively charged protein does not interact with the negative anion. The anion itself had a marked affect on the voltammograms of haemoglobin, whereas the cation has little or no influence.<sup>[1, 104, 133]</sup> Their studies have shown that the nature of the aqueous phase plays an important role in the behaviour, and therefore, detection of proteins at a liquid-liquid ITIES. Investigations into the counter-ion binding of protamine with a range of differently sized anions, by Samec *et al.* agreed with the Amemiya group's work concluding reduced ion-pair stability as the anion size increased.<sup>[134]</sup> The structure of the protein also has an impact on the performance of electrochemical methods. Denaturation of haemoglobin has been shown to cause a decrease in the detection signal.<sup>[135]</sup> This is due to conformational changes in the protein, which cause the destruction of the hydrophobic pockets present in the protein thereby reducing the interaction with the organic phase anion.

#### 4.5.2.6 DNA detection

Little work has been done on DNA detection via liquid-liquid, ITIES. The most recent, carried out by Vagin *et al.*<sup>[136]</sup> has shown the use of a liquid-liquid ITIES as an electrochemical probe for DNA hybridisation and a limit of detection, via impedance spectroscopy, for the target oligonucleotide was found to be 0.01  $\mu\text{M}$ . Hardt and Hahn have recently designed a device based upon mass transfer resistance at a liquid-liquid interface allowing the concentration and separation of DNA samples.<sup>[137]</sup> This is reported as a novel method for the direct separation and pre-concentration of DNA samples by the authors.

### 4.5.3 Summary of requirements for an ITIES electrochemical cell

For small molecules:

- Ionophores can increase the sensitivity of the system, they are however not required to transfer molecules across the interfaces. The ionophore may preferentially transfer other ‘interferent ions’ e.g. alkali metal ions from the base/background electrolytes in the aqueous phase.
- Sub micromolar detection is possible with the combination of FIT and choosing the electrochemical methodology e.g. stripping/pulse voltammetry methods

For large molecules:

- FIT is likely to be required as the size increases. Interference from the base/background electrolytes is possible. Therefore, judicial choice of the electrolytes, the ionophore itself and the targeted molecular groups on the analyte is key.
- Impedance based electrochemical methods can be applied to the system if transfer does not occur, or detection via transfer of a non-aqueous phase ion (and its detection) is possible i.e. indirect measurement of the presence of the target adsorbed at the interface.

- Cyclic voltammetry may achieve sub micromolar detection without the use of more complex stripping/pulse voltammetry methods, if the target analyte contains multiple charges.

## 4.6 Uses of ionic liquids in liquid-liquid, ITIES, systems

Ionic liquids combine the advantages of molten salts with those of aqueous media. However, it was only with the advent of non-haloaluminate ionic liquids that investigations began into the range of possible uses in electrochemical systems. Due to the ability to functionalise ionic liquids in nearly anyway you desire (as long as it can be synthesised) the field of electrochemistry with ionic liquids is still expanding. The first reported use of an ionic liquid in a liquid-liquid, ITIES, system was by Quinn *et al.* in 2002.<sup>[138]</sup> Kakiuchi's research group has been the most active investigating the possible applications of ionic liquids in liquid-liquid, ITIES, systems. Since 2002 they have been highlighting the advantageous uses of ionic liquids.<sup>[139, 140, 141, 142]</sup>

Electrode modification with ionic liquids is outside the scope of this project and for further information the excellent review by Opallo and Lesniewski is recommended.<sup>[143]</sup>

## 4.7 Agitation experiments

Agitation experiments were conducted with the synthesised ionic liquids (see Chapter 2 & 3) to determine if extraction/transfer of a biological molecule across the interface into the non-aqueous ionic liquid phase would even occur. Work by Goto *et al.* had shown that cytochrome-c extraction, using the crown ether dicyclohexano-18-crown-6 (see Figure 4.7.1), was possible into hydroxyl and ether functionalised imidazolium based ionic liquids.<sup>[144, 145]</sup> Therefore, the chosen biomolecule of interest for these, and subsequent experiments, was cytochrome-c (Cyt-c) because of its reasonable molecule size (molecular weight of 12,384 g mol<sup>-1</sup>) and also because its pink/red colour allowed easy detection of its location when used

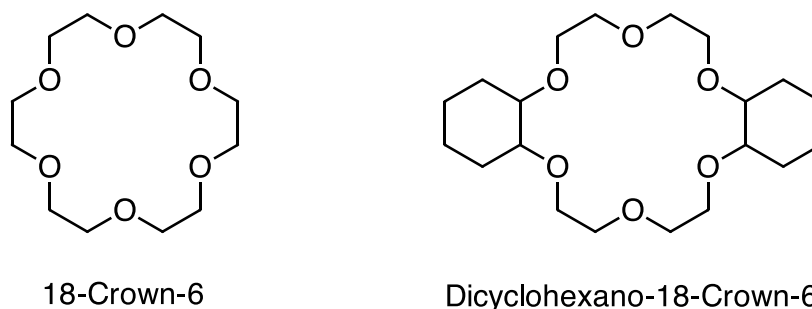


**Figure 4.7.1** – Molecular structures of the crown ethers 18-crown-6 and dicyclohexano-18-crown-6.

via agitation or electrochemically. This crown ether was chosen due to its increased lipophilicity, because of the cyclohexyl side chains, compared with 18-crown-6.<sup>[146]</sup> The increased lipophilicity means that the crown ether should prefer to be solubilised within the ionic liquid, and hence aid the biomolecule transfer into the ionic liquid. Cytochrome-c is a lysine rich protein and the  $\text{NH}_3^+$  groups fit into the DCH-18-crown-6 cavity.

### 4.7.1 Results and discussion

From Figures 4.7.3 and 4.7.4 it is easy to see the amount of Cyt-c transfer across the aqueous:ionic liquid interface after agitation. The concentrations of the extracted Cyt-c present in the ionic liquid was determined from the Soret band and are reported in Table 4.7.1.

The distribution coefficient for Cyt-c with these ionic liquids was calculated (see Table 4.7.2) from Equation 4.7.1:<sup>[47]</sup>

$$D_{\text{Cyt-c}} = \left\{ \frac{C_i - C_f}{C_f} \right\} \frac{Vol_{\text{aq}}}{Vol_{\text{IL}}} \quad (4.7.1)$$

Where,  $C_i$  is the initial concentration of Cyt-c, and  $C_f$  is the final concentration of Cyt-c in the aqueous phase. The volume ratio ( $\frac{Vol_{\text{aq}}}{Vol_{\text{IL}}}$ ) allows the distribution coefficient to take into account differences between the volume of the aqueous (aq) and ionic liquid (IL) phases. In this case, the volumes of the phases were identical and the ratio becomes one. Overall, a distribution coefficient  $\geq 1$  represents a preference for the Cyt-c to be in the ionic liquid rather than the aqueous phase.

| Ionic Liquid                                                 | Cytochrome-c in IL phase / $\mu\text{M}$ | Percentage cytochrome-c extracted / % |
|--------------------------------------------------------------|------------------------------------------|---------------------------------------|
| $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$              | $2.61 \pm 1.23$                          | 5.22                                  |
| $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$              | $16.34 \pm 0.84$                         | 32.68                                 |
| $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$              | $26.73 \pm 0.62$                         | 53.46                                 |
| $[\text{C}_5\text{C}_1\text{im}][\text{NTf}_2]$              | $31.64 \pm 0.55$                         | 63.28                                 |
| $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$              | $32.64 \pm 0.60$                         | 73.28                                 |
| $[\text{C}_7\text{C}_1\text{im}][\text{NTf}_2]$              | $42.28 \pm 0.87$                         | 84.56                                 |
| $[\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$              | $44.04 \pm 0.41$                         | 87.32                                 |
| $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ | $49.33 \pm 0.09$                         | 98.66                                 |
| $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ | $49.44 \pm 0.19$                         | 98.88                                 |
| $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ | $0.27 \pm 1.26$                          | 0.54                                  |
| $[(\text{HO})^8\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ | $39.54 \pm 0.26$                         | 79.08                                 |

**Table 4.7.1** – Concentration of Cyt-c extracted into the ionic liquid phase, and the calculated percentage of total extraction.

| Ionic Liquid                                                 | Distribution coefficient ( $D_{\text{Cyt-c}}$ ) | Preferred phase |
|--------------------------------------------------------------|-------------------------------------------------|-----------------|
| $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$              | 0.06                                            | Aqueous         |
| $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$              | 0.49                                            | Aqueous         |
| $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$              | 1.15                                            | Ionic Liquid    |
| $[\text{C}_5\text{C}_1\text{im}][\text{NTf}_2]$              | 1.72                                            | Ionic Liquid    |
| $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$              | 1.88                                            | Ionic Liquid    |
| $[\text{C}_7\text{C}_1\text{im}][\text{NTf}_2]$              | 5.47                                            | Ionic Liquid    |
| $[\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$              | 7.39                                            | Ionic Liquid    |
| $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ | 74.06                                           | Ionic Liquid    |
| $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ | 88.50                                           | Ionic Liquid    |
| $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ | 0.01                                            | Aqueous         |
| $[(\text{HO})^8\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ | 3.78                                            | Ionic Liquid    |

**Table 4.7.2** – Calculated distribution coefficients for the extraction ability of the tested ionic liquids, and the preferred phase for the Cyt-c.

Therefore, only in the case of  $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ ,  $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$  and  $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$  is the aqueous phase preferred to the ionic liquid phase.

Looking at the unfunctionalised ionic liquids (Figure 4.7.3), the progressively increasing extractive ability of the ionic liquid phase can clearly be seen. Of the unfunctionalised alkyl chain lengths tested the best was 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide which extracted 87.32 % of the Cyt-c. Plotting concentration of Cyt-c versus alkyl chain length gives a logarithmic fit (Figure 4.7.2), which implies that a plateau would be reached at the longer alkyl chain lengths ( $> \text{C}_8$ ).

It can be seen that as the alkyl chain at the N3 position increases, for the unfunctionalised imidazolium ionic liquids, the Cyt-c is starting to become more resolved to the interface. This trend, visually, seems to be linear with increasing alkyl chain length and can be attributed to the increasing hydrophobicity of the ionic liquid (see Chapter 3, Section 3.9.4) causing the protein to be extracted (with the DCH-18-crown-6) into water rich ionic liquid interfacial regions. Testing of ionic liquids with longer alkyl chains would confirm this.

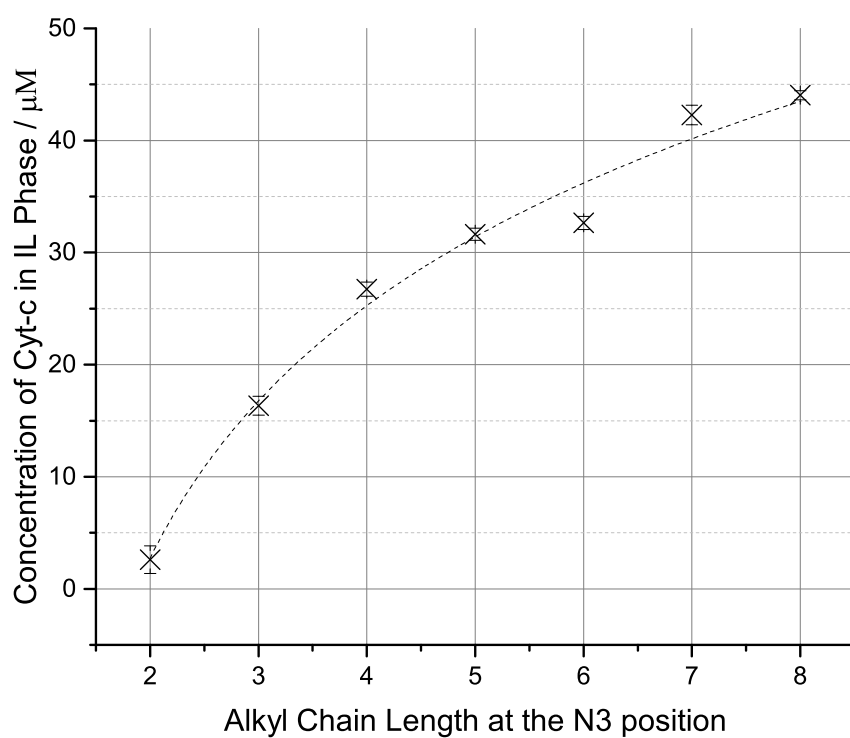


**Figure 4.7.2** – Extracted Cyt-c concentration versus increase alkyl chain length for the unfunctionalised ionic liquids.

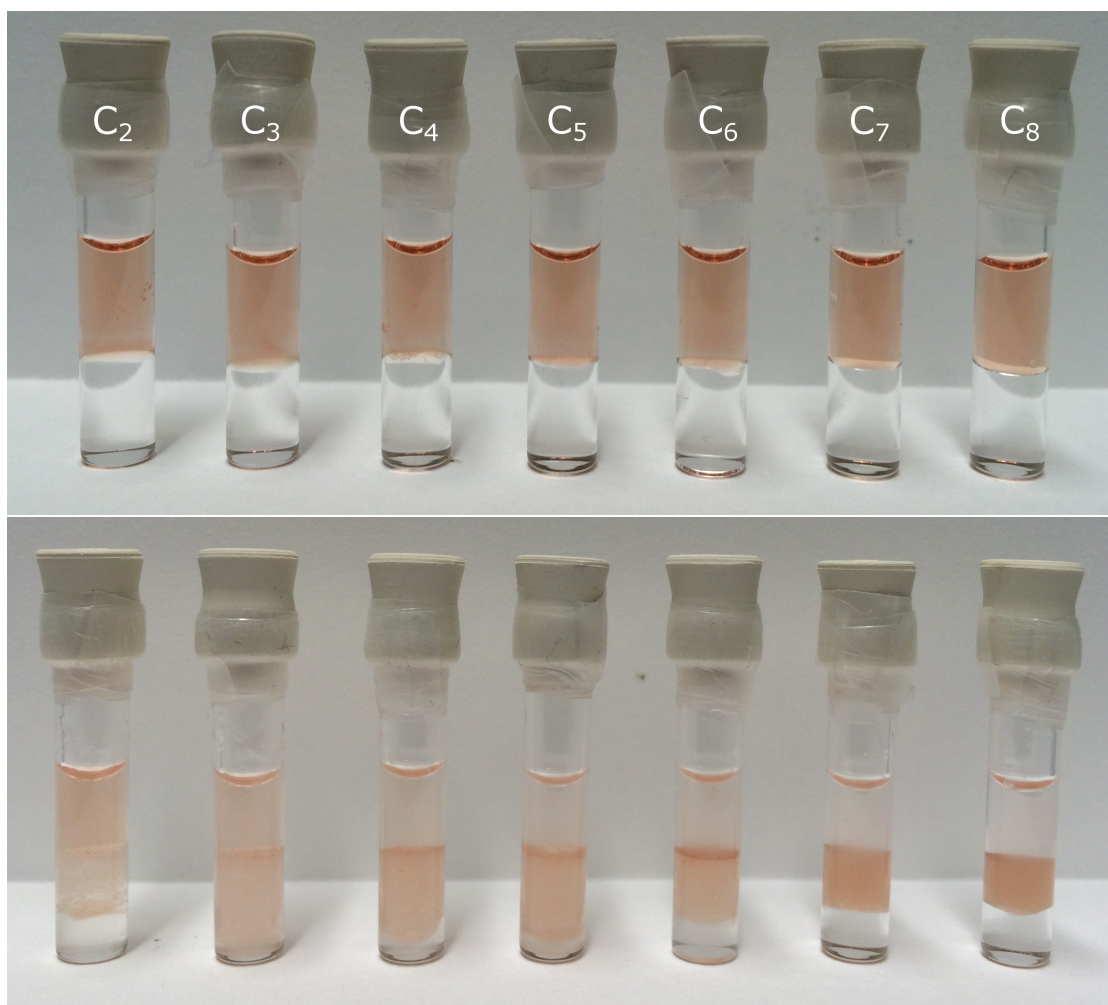


**Figure 4.7.3** – Photos of the Cyt-c before (top) and after (bottom) agitation with unfunctionalised imidazolium bis(trifluoromethylsulfonyl)imide based ionic liquids containing DCH18C6 (Increasing chain length from left to right starting with [C<sub>2</sub>C<sub>1</sub>im][NTf<sub>2</sub>] labelled C<sub>2</sub>).

The effect of adding a hydroxyl group is varied. For the ethyl and propyl side chains there is a substantial increase on the Cyt-c transfer:

1. For the  $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$  adding a hydroxyl group onto the terminal carbon (forming  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ ) increases the distribution coefficient by approximately 123,000 %.
2. For the  $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$  adding a hydroxyl group onto the terminal carbon (forming  $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ ) increases the distribution coefficient by approximately 18,000 %.

The results for the hydroxyethyl and hydroxypropyl based ionic liquids agree with those in the literature.<sup>[145]</sup> However, for the  $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$  only 0.54 % of the cytochrome-c was extracted compared with approximately 55 % by Goto *et al.*<sup>[145]</sup> This result was unexpected and therefore the experiment was repeated six times with fresh crown ether and fresh ionic liquid samples, and the result was the same each time. It is clear from the vial itself (see Figure 4.7.4) that only a slight reddening of the ionic liquid phase has occurred after agitation and in comparison to before agitation, visually, the majority of the Cyt-c is still present in the aqueous phase. There could be an aspect of alkyl chain folding here with the hydroxyl group being positioned over the imidazolium ring. If this was the case the hydroxyl group's effect may become negligible and the extractive capability could be the equivalent of a much shorter, unfunctionalised ionic liquid. This requires further investigation to determine the exact reason for this result.

It should be noted that the inclusion of a hydroxyl group onto the terminal carbon of the 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide slightly reduces the extractive ability of the ionic liquid. This implies that the alkyl chain property dominates at this chain length. From viewing the actual extraction (see Figure 4.7.4) it can be seen that the Cyt-c is not as cleanly extracted. An aspect of impacting and agglomeration of the protein at the interface looks to be occurring. Goto *et al.* reported approximately 30 % extraction with a 20 % error at this chain length but did not comment upon any agglomeration.

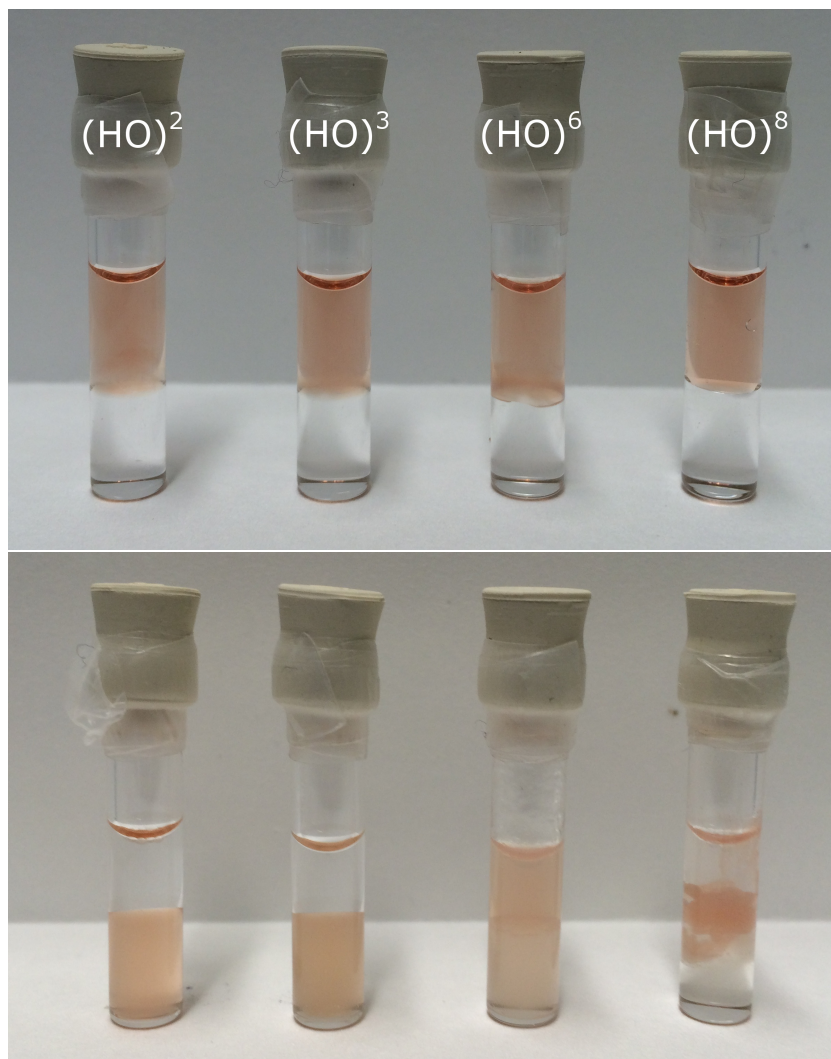


**Figure 4.7.4** – Photos of the Cyt-c before (top) and after (bottom) agitation with functionalised imidazolium bis(trifluoromethylsulfonyl)imide based ionic liquids containing DCH18C6 (Increasing chain length from left to right starting with  $[(HO)^2C_2C_{1im}][NTf_2]$  labelled  $(HO)^2$ ).

### 4.7.2 Conclusion

From these results it can be concluded that extraction of Cyt-c into all the unfunctionalised, and the shorter alkyl chained hydroxyl functionalised imidazolium based bis(trifluoromethylsulfonyl)imide ionic liquids is possible with the aid of DCH-18-crown-6. 1-hydroxyhexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide has been unsuccessful at extracting Cyt-c. Because of this lack of success and the agglomeration at the interface (and like reduction in activity) of the Cyt-c, this ionic liquid should be discounted for use in the liquid-liquid, ITIES, system.

The ionic liquids offering the best extractive power amongst those tested were:

1. 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ ,
2. 1-hydroxypropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,  $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ , and
3. 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide,  $[\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ .

### 4.7.3 Biotin and streptavidin extraction

Due to the success of the Cyt-c extraction into the ionic liquid using the ionophore DCH-18-crown-6 a test extraction was performed using 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to determine if biotin, streptavidin and their complex could be extracted into the ionic liquid phase from water (Figure 4.7.5). Fluorescent versions were chosen and purchased from Sigma-Aldrich Ltd.

Looking at each extraction in turn it can be visually determined that:

- There has been partial extraction of streptavidin into the ionic liquid phase, however the majority of this is centred around the interface - vial  $\text{S}_2$ .
- There has been biotin extraction into the whole of the ionic liquid phase - vials  $\text{B}_1$  &  $\text{B}_2$ .

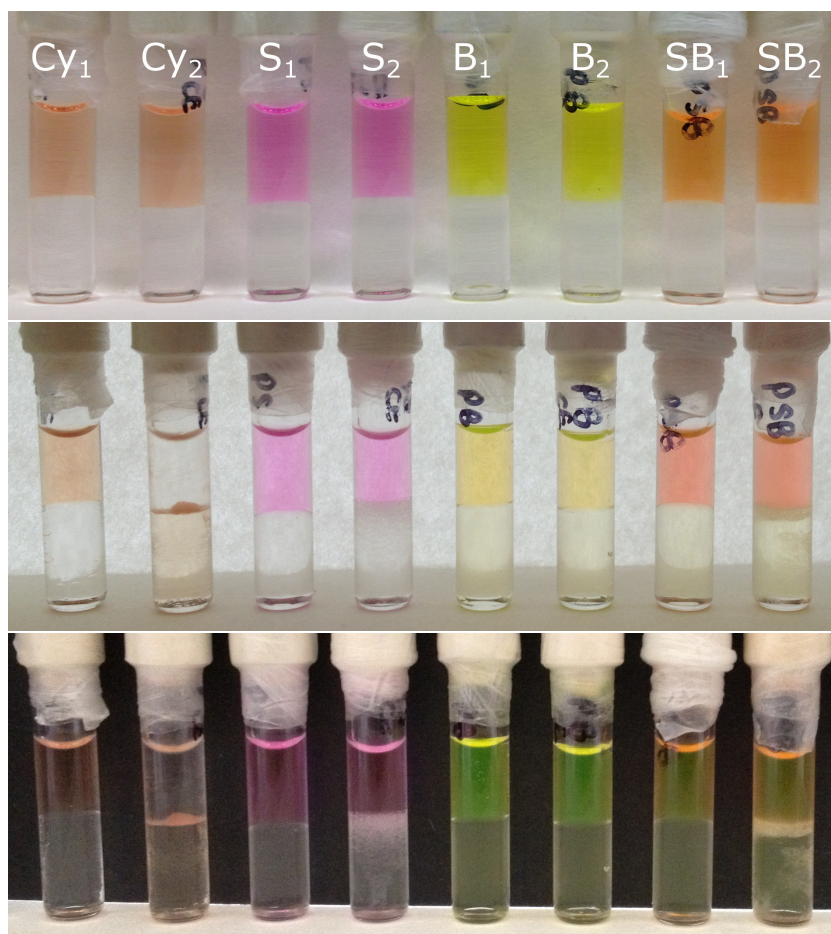


**Figure 4.7.5** – Photos of the extraction of Cyt-c (Cy<sub>1</sub> [no DCH18C6] & Cy<sub>2</sub> [with DCH18C6]), streptavidin (S<sub>1</sub> [no DCH18C6] & S<sub>2</sub> [with DCH18C6]), biotin (B<sub>1</sub> [no DCH18C6] & B<sub>2</sub> [with DCH18C6]) and streptavidin:biotin complex (SB<sub>1</sub> [no DCH18C6] & SB<sub>2</sub> [with DCH18C6]) before (top) and after (middle & bottom) agitation with  $[(\text{HO})^2\text{C}_2\text{C}_{1\text{im}}][\text{NTf}_2]$ .

- There has been extraction of biotin from the streptavidin:biotin complex, including some extraction of the complex itself, centred around the interface (as with the streptavidin extraction) - vial SB<sub>2</sub>.

The results imply that biotin is reasonably extracted into the ionic liquid phase. This could be due to a complexation with the crown ether, or standard solubilisation. What is very surprising is the result of the complex extraction. The streptavidin:biotin complex has a dissociation constant of  $10^{-15}$  M, and is one of the strongest non covalent interactions known in nature.<sup>[147]</sup> From this preliminary result here the (streptavidin:biotin) - ionophore - ionic liquid interaction appears to be stabilising the biotin sufficiently to cause disruption of the complex. This would need to be investigated further to confirm this.

It would be possible, due to the designability of the ionic liquid cations (and anions) to build the biotin functionality into the ionic liquid. This has indeed been undertaken as an ionic liquid self assembled monolayer for surface plasmon resonance.<sup>[148]</sup> This approach could offer a BRE based ionic liquid for the selective extraction of streptavidin and would show the utility of BREs (or even any selectivity moiety) incorporated into ionic liquids.

## 4.8 Electrochemical cell design

As discussed earlier the components of the electrochemical cell are key to any liquid-liquid, ITIES, based electrochemical sensor. This includes the actual physical electrochemical cell itself. Many different cell designs have been suggested and used over the years, however, Arrigan *et al.*<sup>[1]</sup> was the only paper where a photograph of the liquid-liquid electrochemical cell being used was shown (see Figure 4.8.1). From this and after reading various review articles<sup>[90, 98, 149, 150]</sup> a new cell was designed as shown in Figure 4.8.2).

The requirements for the cell included:

- An ability to remove the platinum counter electrodes for cleaning (both the electrodes and the cell - hence the use of ground glass joints to allow the electrodes to be removed but also form a liquid tight seal).

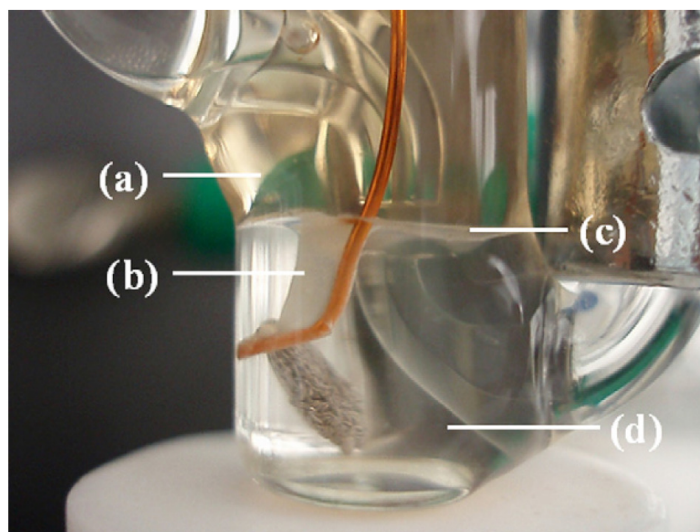


**Figure 4.8.1** – Electrochemical liquid-liquid, ITIES, cell used by Arrigan *et al.*<sup>[1]</sup> Where, (a) indicated the aqueous phase, (b) a haemoglobin film being held down into the organic phase with a copper wire, (c) the interface and (d) the organic phase.

- An ability to adjust the liquid-liquid interface present between the two Luggin capillaries - achieved by the side arms being level, therefore allowing the balancing of the volumes of the reference electrode phases.
- Correct placement of the Luggin capillaries directly opposite each other and at the correct distance from the interface:
  - The placement of the Luggin capillaries is a key feature of the electrochemical cell, as it is these capillaries which measure the current when ions transfer across the interface. Therefore, they need to be placed close to the interface. Luggin capillary distance from the interface was determined as  $2d$  where  $d$  is the outer diameter of the Luggin capillary.<sup>[151]</sup> The distance from each other was therefore twice the outer diameter of the capillary as the outer diameters of the capillaries were equal.
  - The best Luggin capillaries are designed to have a narrow tip which then widens rapidly to ensure no resistance build up within the cell.<sup>[92, 152]</sup>

This prototype cell was produced *in-house* by Stephen Ramsey (Imperial College London, Chemistry Research Technicians) see Figure 4.8.2 and additional units

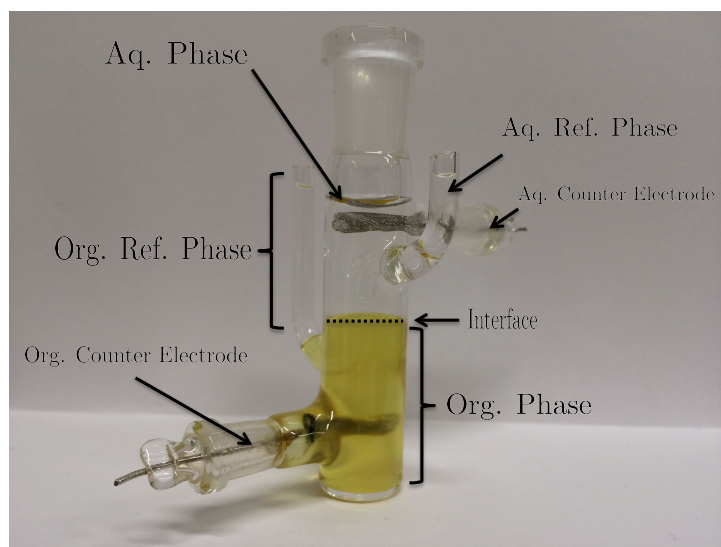


**Figure 4.8.2** – Designed and produced in-house liquid-liquid, ITIES, electrochemical cell.

were produced by GPE Scientific Limited based on this design.



**Figure 4.8.3** – Electrochemical liquid-liquid, ITIES, scheme by Koryta *et al.* used for testing of the electrochemical cell design.<sup>[2]</sup>

To test the cell one of the original liquid-liquid, ITIES, experiments was chosen as a test ion transfer (see Figure 4.8.3 for the electrochemical scheme).<sup>[2]</sup> Here Koryta *et al.* used a four electrode based system with Luggin capillaries for sensing the current, and two counter electrodes (one in the aqueous phase, and one in the organic phase) to provide the potential. The counter electrodes were separated from the bulk electrolyte by sintered frits.<sup>[2]</sup> The target analyte in this system was tetramethylammonium ( $\text{TMA}^+$ ) which gave peaks at approximately +0.33 V on the forward sweep and +0.22 V on the reverse sweep within the potential window of the tetrabutylammonium tetraphenylborate (TBATPB) and the lithium chloride (LiCl) base/background electrolytes. The potential window for this system is from the inflection point of the peak on the left (labelled A, Figure 4.8.4) to the inflection point of the dip on the right (labelled B). These are the points at which the base

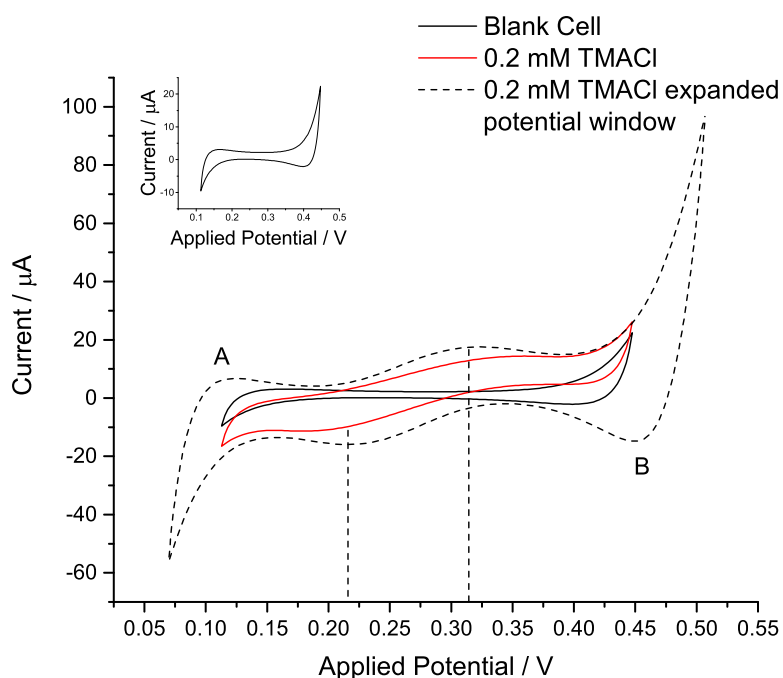


**Figure 4.8.4** – Cyclic voltammograms of the  $\text{TMA}^+$  ion transfer, from the water to the nitrobenzene (and back), in the designed electrochemical liquid-liquid, ITIES, cell. Inset plot is the blank cell cyclic voltammogram for ease of comparison.

electrolytes start to move under the potential being applied to the system.

The resulting cyclic voltammograms for the test ion transfer in the designed electrochemical cell are shown in Figure 4.8.4. These results matched the literature values nearly identically. To test the cell further and to check the organic reference phase was functioning as per the Nernst-Donnan equation (see Section 4.3.1) a new electrochemical cell was setup using sodium chloride as the aqueous phase base/background electrolyte, and TBACl as the reference (i.e. ion selective to the TBA), and then with NaTPB as the reference (i.e. ion selective to the TPB) phase for the reference electrode in the organic phase (see Figure 4.8.5).

In theory, as scan rate increases, the peak current exhibited on the forward and reverse sweeps should increase in a linear manner. This was found to be the case with both the TBACl based organic phase reference system and the NaTPB based organic phase reference system, across the range of  $5 \text{ mV s}^{-1}$  -  $200 \text{ mV s}^{-1}$  (see Figure 4.8.5).

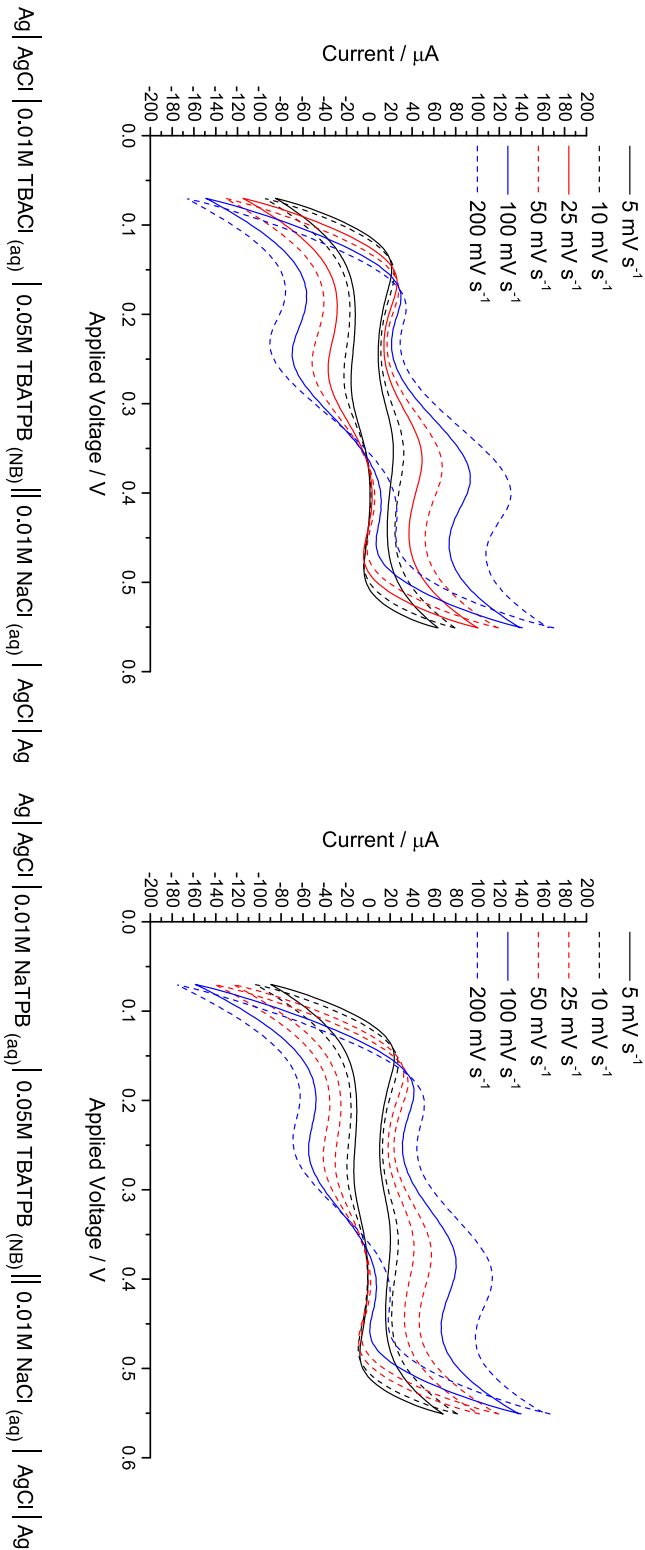


**Figure 4.8.5** – Cyclic voltammograms of the electrochemical cell with a TBACl based non-aqueous phase reference (left) and a NaTPB based non-aqueous phase reference (right) with their corresponding electrochemical schemes beneath.

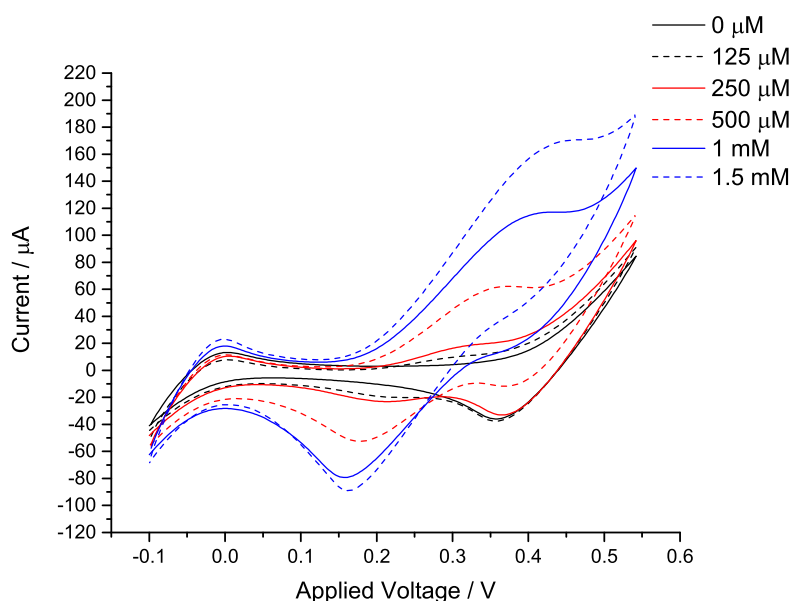


**Figure 4.8.6** – Cyclic voltammograms of dopamine in the electrochemical liquid-liquid, ITIES cell shown in Figure 4.8.2. Recorded at a scan rate of  $5 \text{ mV s}^{-1}$ .

Having tested and confirmed successful use of the designed cell, dopamine was chosen as a suitable target analyte to transfer across the interface. The 2005 study performed by Arrigan *et al.* was duplicated over the concentration range of 0 - 1.5 mM of dopamine (see Figures 4.8.6 - 4.8.7).<sup>[105]</sup>

## 4.9 Electrochemical experiments

Having successful confirmation that the uniquely designed and produced cell worked with a range of target analytes the next step was to combine the electrochemical cell with an ionic liquid and attempt to electrochemically transfer Cyt-c into the ionic liquid.

The chosen electrochemical cell is detailed in Figure 4.9.1, 10 mM lithium chloride was used as the reference phases for both the aqueous and ionic liquid phases, with silver, silver chloride reference electrodes. The ionic liquid, 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, was used neat as the organic phase for the cell with 50 mM of DCH-18-crown-6.

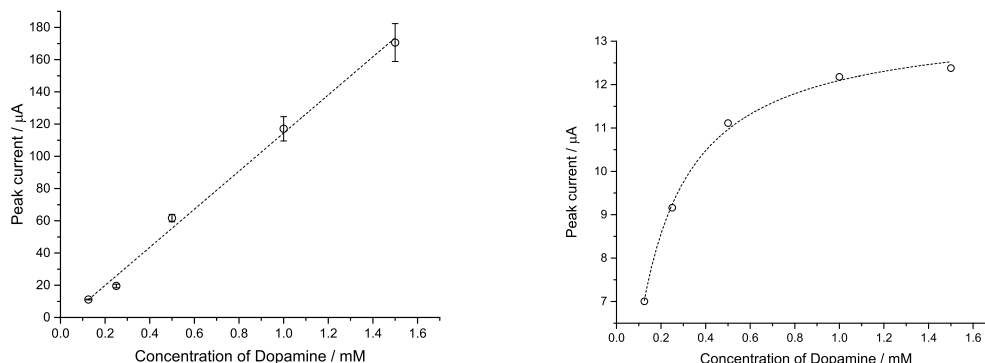


**Figure 4.8.7** – Peak current against concentration via cyclic voltammetry (left) and differential pulse voltammetry (right) for the dopamine test of the electrochemical cell (Figure 4.8.6).

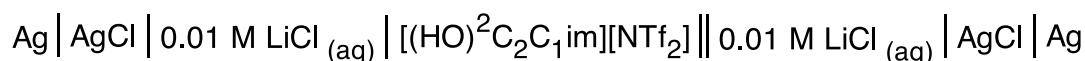


**Figure 4.9.1** – Electrochemical scheme for the ionic liquid based liquid-liquid, ITIES, cell based on  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ .

Performing a cyclic voltammogram on the electrochemical cell gave a slanted voltammogram (see Figure 4.9.2). This indicated added resistance in the cell, normally this is associated with problems with the reference electrodes e.g. bubbles within the Luggin capillaries or the reference electrolyte solution.<sup>[91]</sup> However, upon checking and refilling the cell a worse CV was obtained (Figure 4.9.2 - Right), having lost the slight definition that was there on the first scan (Figure 4.9.2 - Left). This is representative of the CVs obtained on all later attempts.

There are multiple explanations why there might be ohmic distortion within an electrochemical cell:<sup>[91]</sup>

1. The concentration of the base/background electrolytes within the system could be too low and therefore the conductivity across the whole system is too low - an ionic liquid is effectively 100 % ions, and therefore is unlikely to affect the charge carrying within the cell, and the concentration of lithium chloride had been shown to be sufficient in the tests of the electrochemical cell.

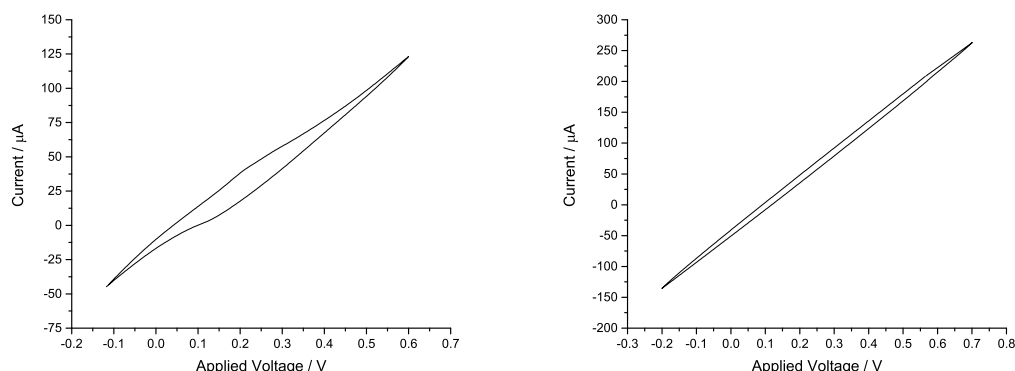


**Figure 4.9.2** – Resulting resistive cyclic voltammograms from the electrochemical scheme shown in Figure 4.9.1.

2. The Luggin capillaries may be incorrectly placed - this however is not the case as shown by the test results in Section 4.8.
3. The ability of the base/background electrolytes to move within the applied electric field is limited - this usually occurs with viscous liquids, in the case of the ionic liquid used here it has a viscosity substantially higher than that of water and therefore the ion mobility within the ionic liquid could have been causing the resistance.

#### 4.9.1 Frit based electrochemical cell

It was considered possible that reducing the volume of the ionic liquid would reduce the resistivity associated with the system and it was found in the literature that Kakiuchi *et al.*<sup>[153]</sup> had demonstrated the use of a fritted electrochemical cell for some initial experiments using room temperature ionic liquids. Therefore, a range of fritted cells were designed and procured from H. Baumbach and Co. Ltd. The quartz frits were of a 10 mm diameter with 5 cm of quartz tube above and below the frit (as per Figure 4.9.3) with five different porosities for initial testing (see Table 4.9.1).

For those frits with porosity grade of 0 and 1, the pore sizes were too large and did not give enough surface (and hence interfacial) tension to the ionic liquid placed upon it. This was even more marked when the potential difference was

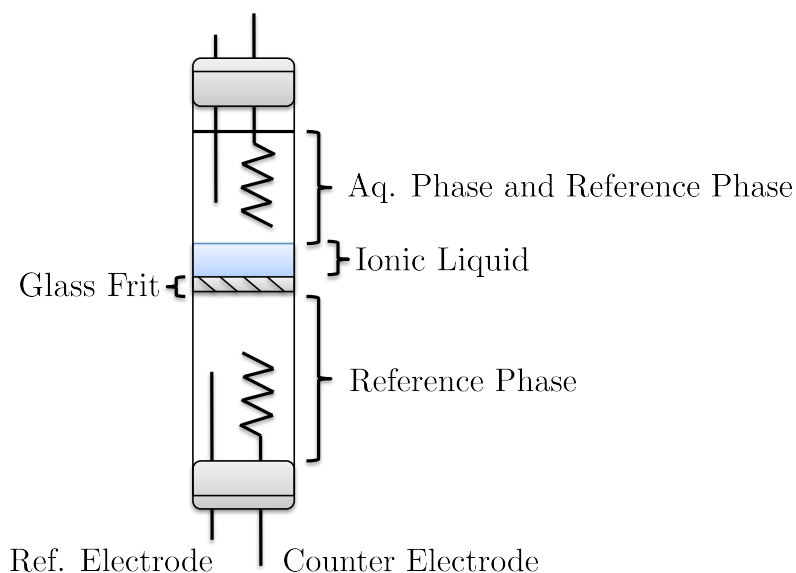


**Figure 4.9.3** – Frit based electrochemical cell for use with room temperature ionic liquids.

| Porosity Grade | Average Pore Size / $\mu\text{m}$ |
|----------------|-----------------------------------|
| 0              | 160 - 250                         |
| 1              | 100 - 160                         |
| 2              | 40 - 100                          |
| 3              | 16 - 40                           |
| 4              | 10 - 16                           |

**Table 4.9.1** – Porosity grade, and their corresponding average pore sizes, for the frit within the electrochemical cell (Figure 4.9.3).

applied. Under the applied potential, movement of the ions within the two phases affects the surface tension the liquid.<sup>[52]</sup> Vice versa, frits with a porosity grade of 3 and 4 were found to be resistive, giving CVs similar to that found in Figure 4.9.2. This is due to the small pore sizes impacting on the ion diffusion, of the reference phase, when under an applied potential difference. A frit with porosity of grade 2 was found to be the best. It gave a high enough surface tension for the ionic liquid to sit on the surface and avoid excessive disturbance when the potential difference was applied. Additionally, the resulting CVs showed low resistance (i.e. mainly flat rather than slanted), and the resistance shown was attributed to the movement of the non-aqueous phase ions themselves.

The fritted cell was tested (as per Section 4.8) with the electrochemical scheme of Koryta *et al.* (Figure 4.8.3).<sup>[2]</sup> The resulting cyclic voltammograms agreed with the previous results and showed that the fritted cell design was suitable for use as a liquid-liquid, ITIES, electrochemical cell (Figure 4.9.4). Furthermore, the cell was tested with dopamine as a target analyte (see Figure 4.9.5). The resulting CVs showed stable voltammograms, and a greater sensitivity for dopamine compared with the previous cell (c.f. Figures 4.8.6 & 4.9.5), with the upper limit of detection for the fritted cell being approximately 500  $\mu\text{M}$  (c.f. with  $> 1.5 \text{ mM}$  previously).

In addition, the use of difference electrode systems was tested. This included:

1. Standard four electrode system ([One reference electrode (S), one platinum counter electrode (WE)] - aqueous phase, and [one reference electrode (RE), one platinum counter electrode (CE)] - non-aqueous phase).
2. Three electrode system ([One reference electrode (S), one platinum counter electrode (WE)] - aqueous phase, and one platinum counter/reference electrode (CE/RE) - non-aqueous phase).
3. Two electrode system (One platinum counter/reference electrode (WE/S) - aqueous phase and one platinum counter/reference electrode (CE/RE) - non-aqueous phase).

It was found that the optimum electrode system was the standard four electrode system. However, a three electrode system (because of the concentrated nature of the ionic liquid phase), with a fully platinum based electrode in the non-aqueous

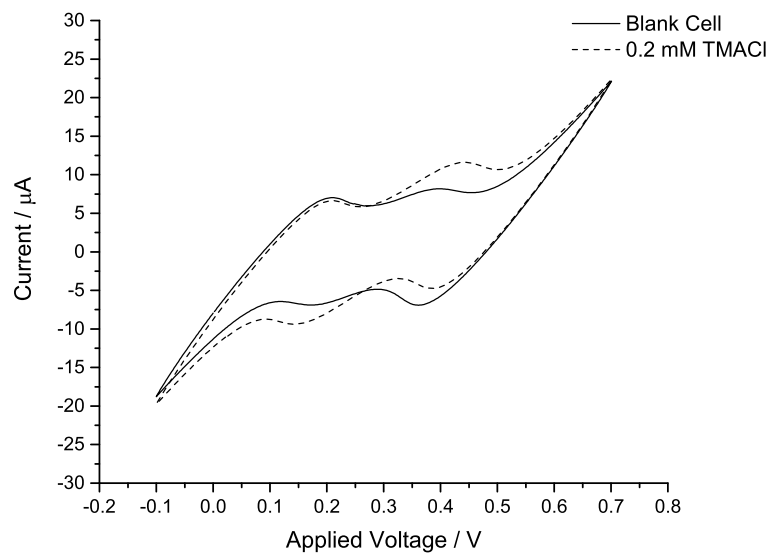


**Figure 4.9.4** – Cyclic voltammogram of the electrochemical scheme (Figure 4.8.3) tested in the fritted cell.

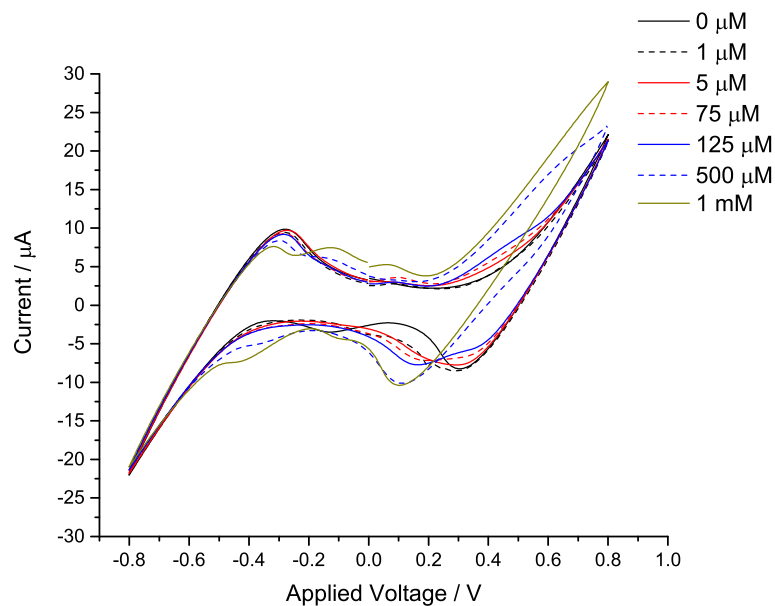


**Figure 4.9.5** – Cyclic voltammograms of dopamine in the fritted electrochemical cell shown in Figure 4.9.3. Recorded at a scan rate of  $5 \text{ mV s}^{-1}$ .

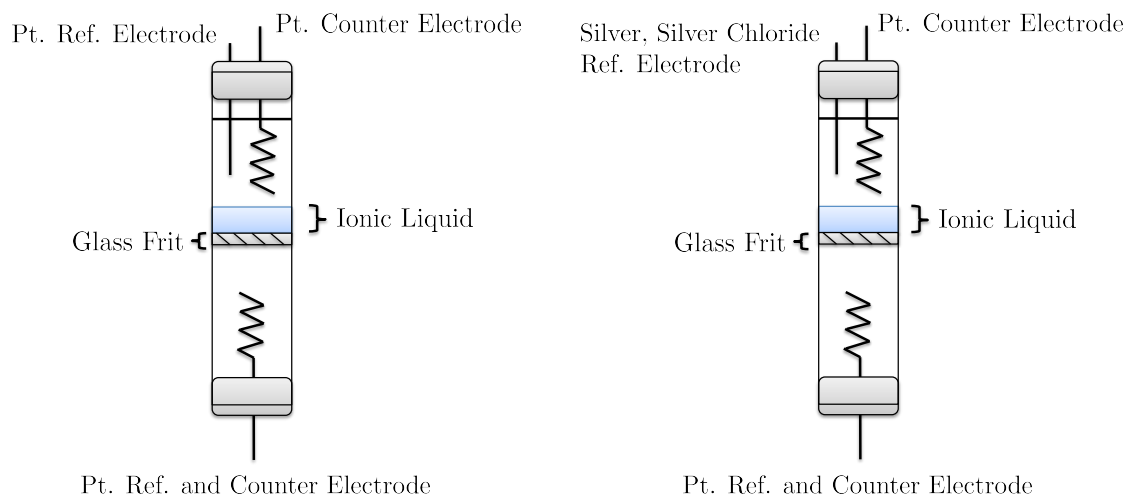


**Figure 4.9.6** – Three-electrode setups used with the fritted electrochemical cell. Left - Fully platinum based system with a platinum reference system in the aqueous phase. Right - Silver, silver chloride reference system in the aqueous phase.

(ionic liquid) reference phase (see Figure 4.9.6), was found to be the most stable and reproducible. It has been reported that the use of platinum foil within a molten salt was neither stable or polarised and therefore could not be used as a pseudo-reference electrode.<sup>[154]</sup> Therefore, in this electrochemical design, the non-aqueous phase platinum electrode is separated from the ionic liquid to ensure that the platinum reference remains stable and reproducible. The use of a silver, silver chloride reference electrode in the aqueous phase of this system allowed the potentials to be formally defined (by the silver chloride redox couple - Section 4.3.1); however, as shown from the potentials windows (see Sections 4.9.2.1 and 4.9.2.2) the cyclic voltammograms recorded had the exact same shape in both setups.

## 4.9.2 Results and discussion

With an electrochemical cell designed, produced, and tested with the reference electrochemical scheme, all the synthesised ionic liquids were tested to ensure that a stable electrochemical potential window could be obtained before testing with a biological molecule. Figure 4.9.7 is the resulting cyclic voltammogram of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The upper plot is a plot

of all of the CV scans (20 scans), whereas the lower plot is the final full CV scan. At this stage the electrochemical cell has become stabilised, the CV scans are identical, and it is ready for use. From the inflection point at either end of the CV scan the ionic liquid is found to have a potential window of around 900 mV. From the literature it is recommended that a potential window should be at least 200 mV wide to be able to detect the transfer of an ion across an interface.

Two cyclic voltammograms are reported for each ionic liquid, one using a silver, silver chloride reference electrode in the aqueous phase, and the other using a platinum reference electrode in the aqueous phase. This was because the redox potential of the silver, silver chloride reference is known compared to the platinum pseudo reference (see Section 4.3.1). As can be noted there is a negative shift of approximately 400 mV compared with using a fully platinum based electrochemical cell.

#### **4.9.2.1 Unfunctionalised imidazolium ionic liquid liquid-liquid potential windows**

The cyclic voltammograms (and hence electrochemical potential windows), with a three electrode setup (Figure 4.9.6), in the fritted electrochemical cell for the synthesised unfunctionalised ionic liquids are given in Figures 4.9.8 - 4.9.14. The CVs recorded, along with the potential windows, are found to substantially exceed those reported by Conboy *et al.* for their undiluted ionic liquid system.<sup>[52, 155]</sup> It should be noted that the electrochemical cells (and their electrochemical composition) used by Conboy was different to that used here, which highlights the importance of the cell design as well as the choice of electrodes and base/background electrolytes.

#### **4.9.2.2 Hydroxyl functionalised imidazolium ionic liquid liquid-liquid potential windows**

The cyclic voltammograms (and hence electrochemical potential windows), with a three electrode setup (Figure 4.9.6), in the fritted electrochemical cell for the synthesised hydroxyl functionalised ionic liquids are given in Figures 4.9.15 - 4.9.18.

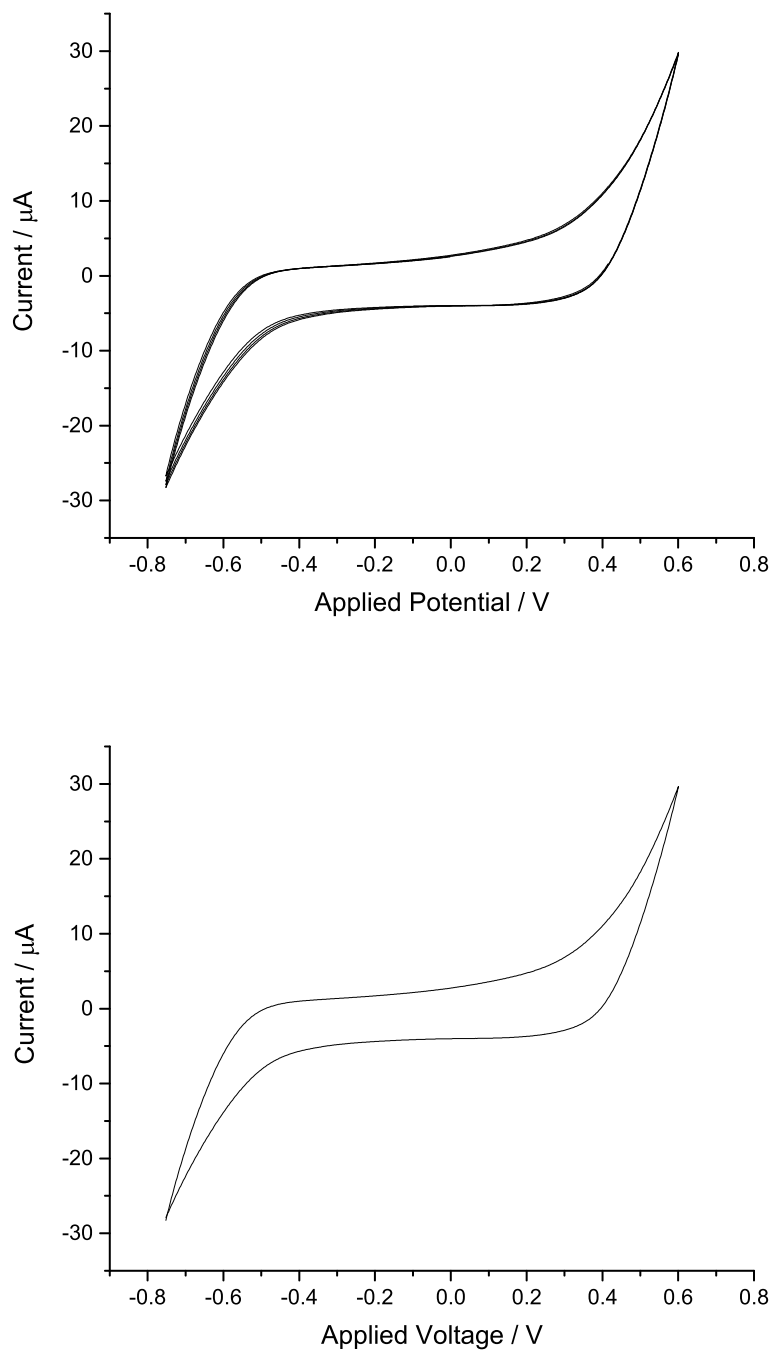


**Figure 4.9.7** – Cyclic voltammograms for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in the fritted electrochemical cell, with a three platinum electrode setup. Top - 20 full CV scans. Bottom - CV of the final stabilised scan.

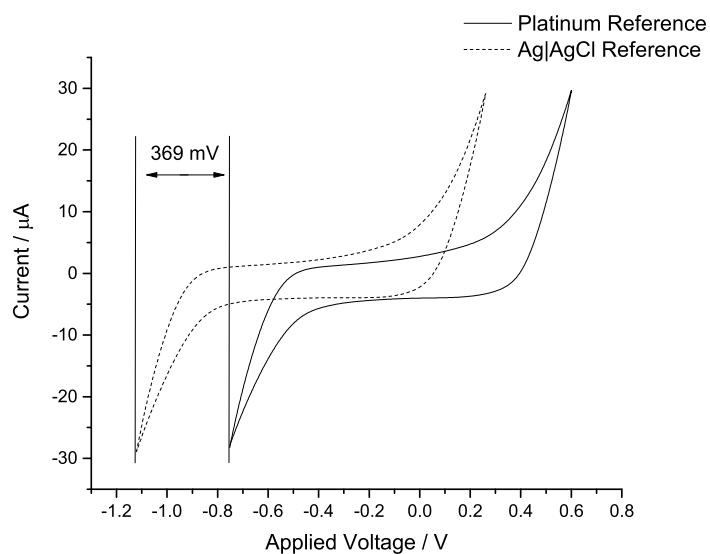


**Figure 4.9.8** – Cyclic voltammograms illustrating the available potential window of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference). Indicated shift is associated with the different reference systems tested.

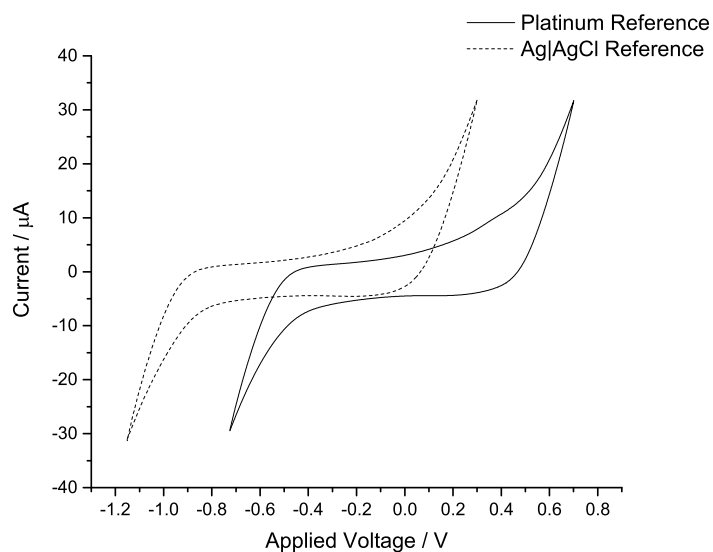


**Figure 4.9.9** – Cyclic voltammograms illustrating the available potential window of 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

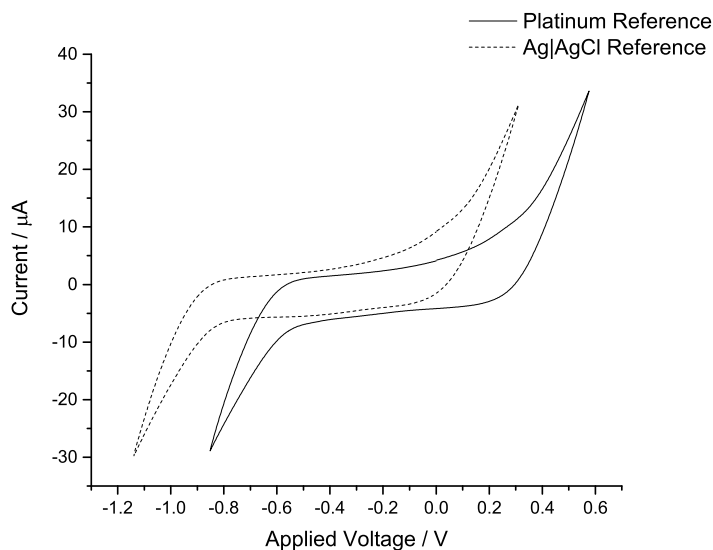


**Figure 4.9.10** – Cyclic voltammograms illustrating the available potential window of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

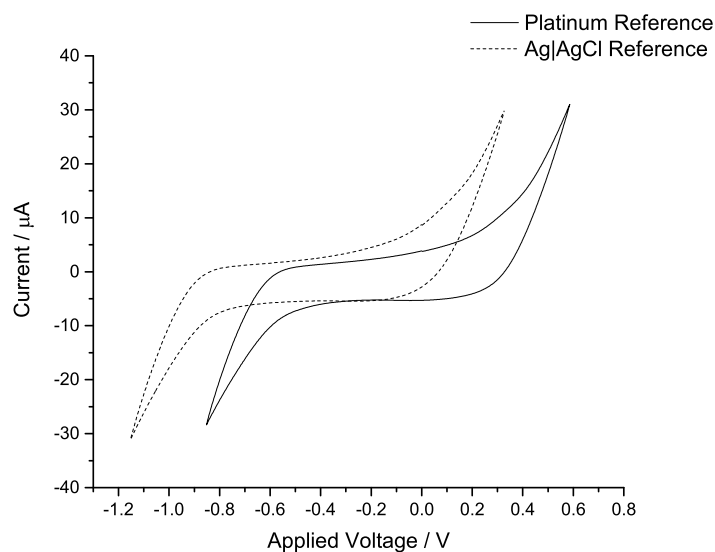


**Figure 4.9.11** – Cyclic voltammograms illustrating the available potential window of 1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

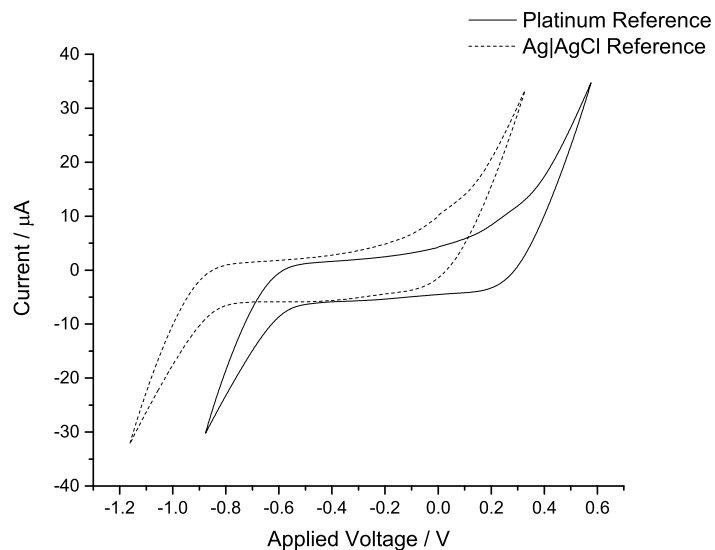


**Figure 4.9.12** – Cyclic voltammograms illustrating the available potential window of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

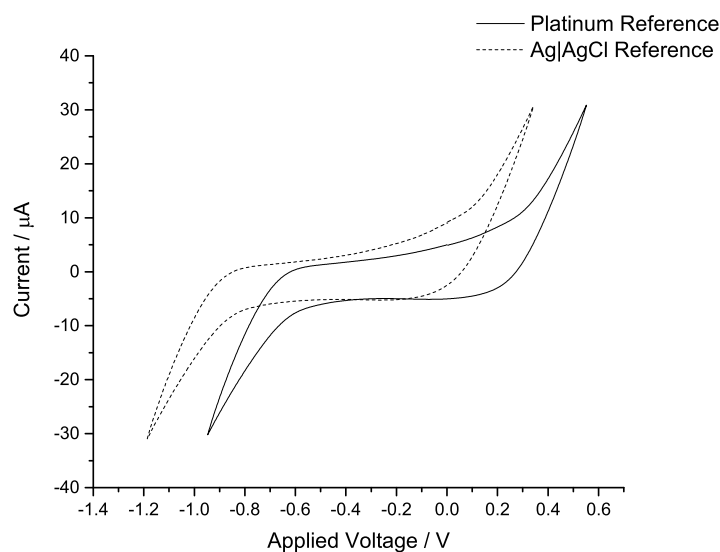


**Figure 4.9.13** – Cyclic voltammograms illustrating the available potential window of 1-heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

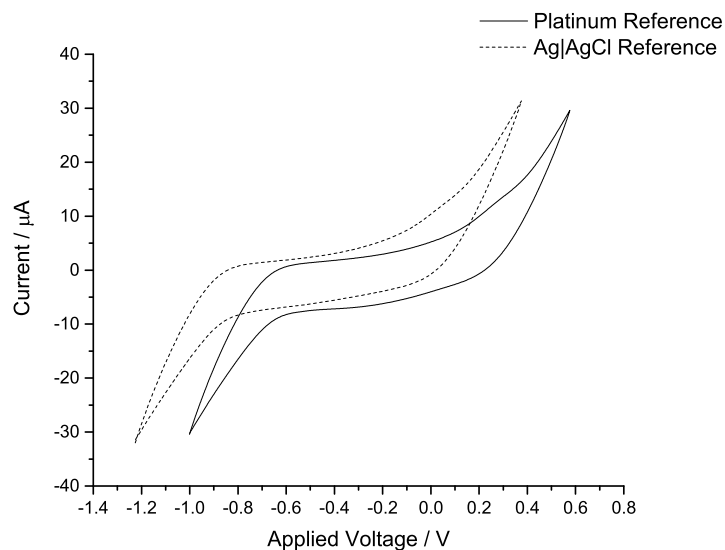


**Figure 4.9.14** – Cyclic voltammograms illustrating the available potential window of 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

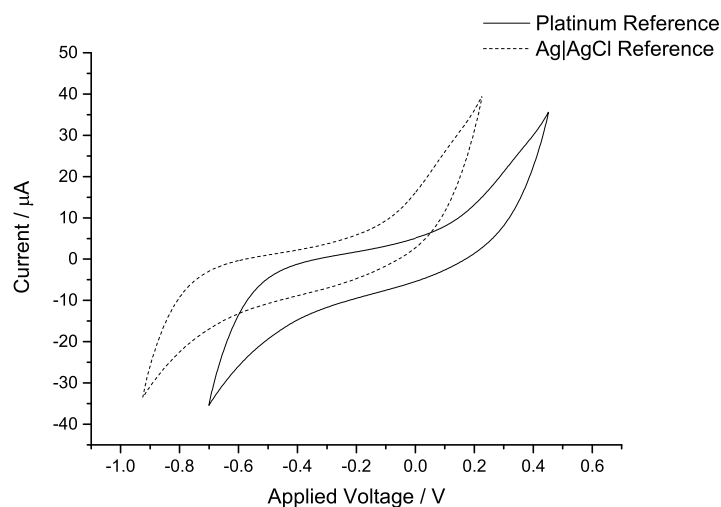


**Figure 4.9.15** – Cyclic voltammograms illustrating the available potential window of 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

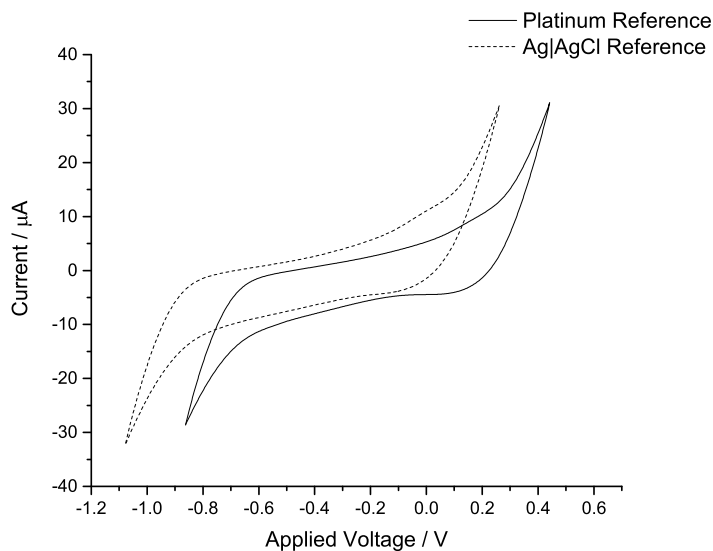


**Figure 4.9.16** – Cyclic voltammograms illustrating the available potential window of 1-hydroxypropyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

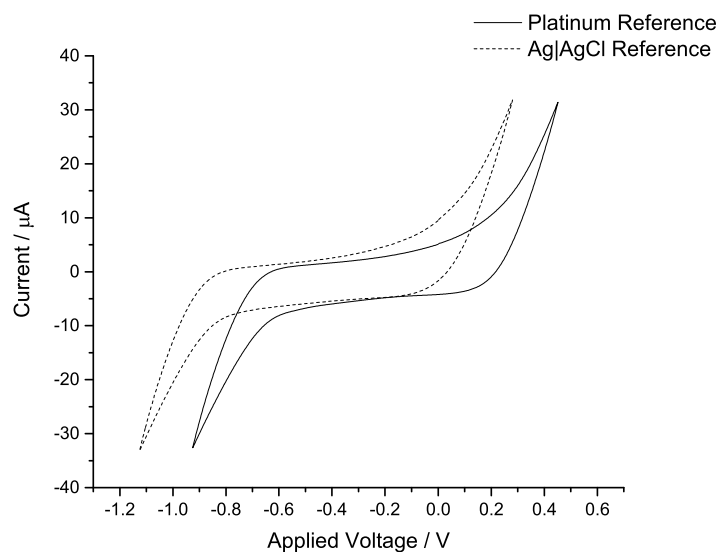


**Figure 4.9.17** – Cyclic voltammograms illustrating the available potential window of 1-hydroxyhexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

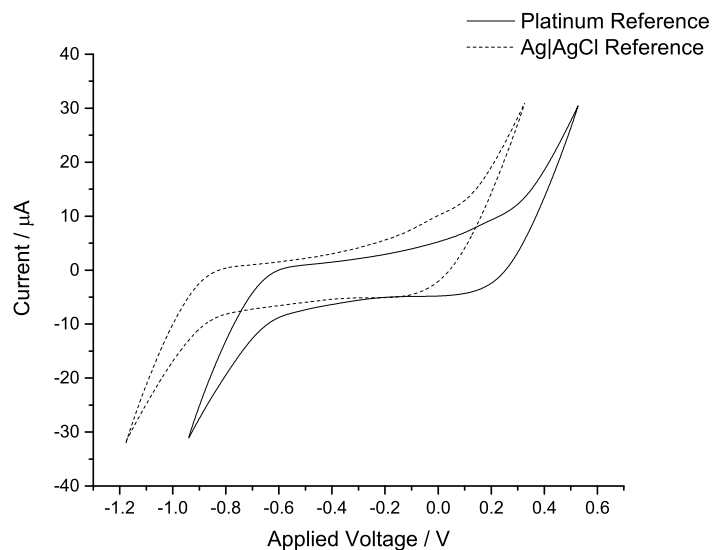


**Figure 4.9.18** – Cyclic voltammograms illustrating the available potential window of 1-hydroxyoctyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide performed in the fritted electrochemical cell (solid line - platinum reference, dashed line - silver, silver chloride reference).

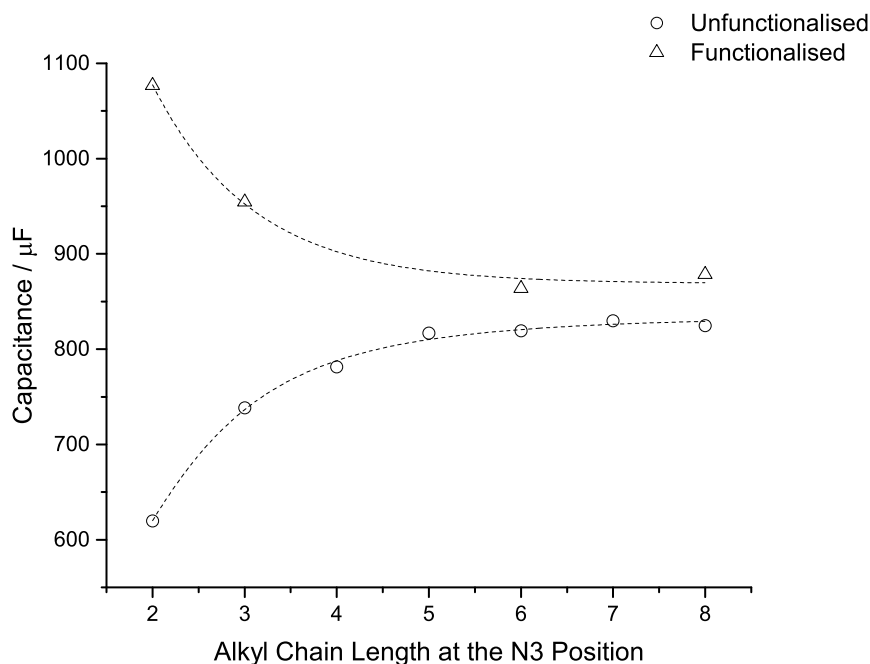


**Figure 4.9.19** – Capacitance of the liquid-liquid interface, for the unfunctionalised and functionalised ionic liquids, calculated from the CVs measured in Figures 4.9.8 - 4.9.18.

### 4.9.2.3 Capacitance of the liquid-liquid interface

From the cyclic voltammograms recorded in Sections 4.9.2.1 and 4.9.2.2, it was possible to calculate the capacitance of the aqueous:non-aqueous interface that was formed between the chosen ionic liquid and the aqueous phase using equation 4.9.1:<sup>[156]</sup>

$$C_{L-L} = \frac{\int_{t_2}^{t_1} i(t) \cdot dt}{2(\psi_{max} - \psi_{min})} \quad (4.9.1)$$

where  $C_{L-L}$  is the capacitance of the liquid-liquid, ITIES, interface,  $\psi_{max}$  and  $\psi_{min}$  are the potential cutoffs for the potential window of the recorded cyclic voltammogram,  $i(t)$  is the current recorded, and  $\int_{t_2}^{t_1} i(t) \cdot dt$  is the charge calculated by integrating the current with respect to time for the positive (forward) and negative (reverse) sweeps of the CV between  $\psi_{max}$  and  $\psi_{min}$ .

| Ionic Liquid                                                 | Percentage increase / % |
|--------------------------------------------------------------|-------------------------|
| $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ | 74                      |
| $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ | 29                      |
| $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ | 5                       |
| $[(\text{HO})^8\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ | 7                       |

**Table 4.9.2** – Percentage change in capacitance with the addition of a terminal hydroxyl group.

The capacitance for the ionic liquids tested here are plotted in Figure 4.9.19. For the unfunctionalised ionic liquids, as the chain length at the N3 position is increased, the capacitance increases to a plateau around  $829 \mu\text{F}$  (from the logistic fitting model). In the case of the hydroxyl functionalised ionic liquids, the increasing chain length reduced the capacitance value to a plateau (within the range of those liquids tested here) around  $870 \mu\text{F}$  (from the exponential decay fitting model). This highlights what has been seen previously (Chapter 3) that the incorporation of a hydroxyl functional group on the terminal carbon of the alkyl chain has a great influence on the ionic liquids properties at shorter chain lengths. Whereas, as the chain length increases the effect of the functional group diminishes (Table 4.9.2).

### 4.9.3 Cytochrome-c extraction

With a defined, and working, electrochemical cell the extraction and detection of Cyt-c (into  $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$  with DCH-18-crown-6) was tested again. Upon addition to the cell the Cyt-c was immediately drawn to the interface between the aqueous phase and the ionic liquid. Although the Cyt-c was clearly present at the interface, there was no detectable change in the cyclic voltammogram when scanning over the full potential window range of the ionic liquid. The cell was left running for 20 scans to give the protein time to complex with the crown ether present in the ionic liquid and be drawn across the interface. However, no transfer was detected even after these scans (Figure 4.9.20 - Left). This agreed with the visual inspection of the cell (Figure 4.9.20 - Right) where it can clearly be seen that the Cyt-c is present at the interface but no protein is visible in the ionic

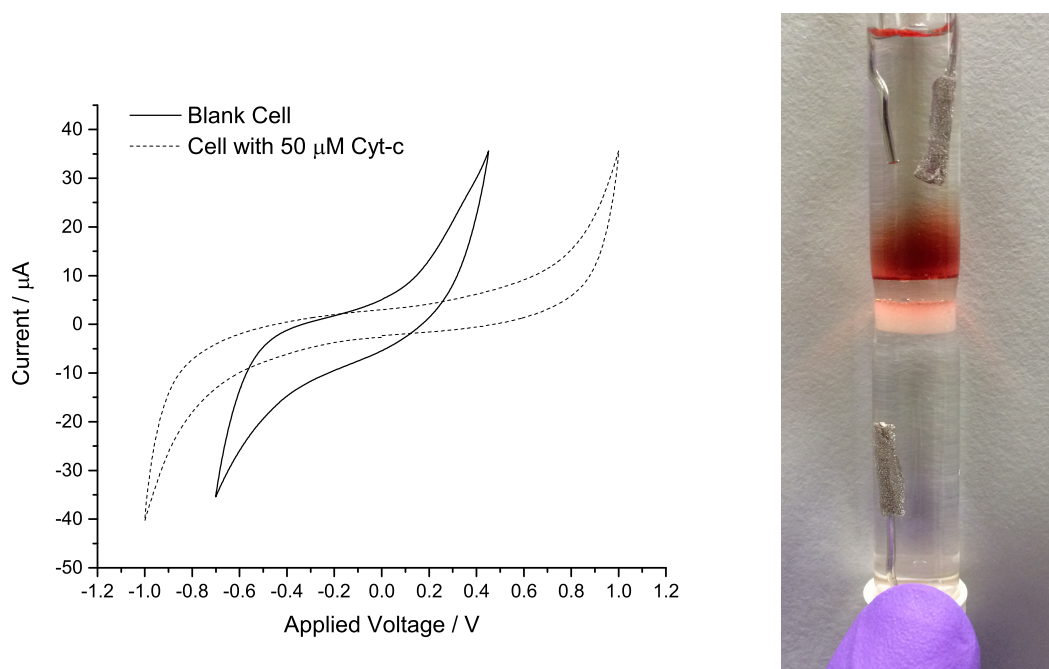


**Figure 4.9.20** – Cyclic voltammogram before (black) and after (dotted - with attempted increased potential window) addition of Cyt-c to the fritted cell, with the resulting agglomerated Cyt-c shown on the right.

liquid itself. Upon removal of the water phase it was found that the protein had formed a gel-like seal against the ionic liquid. This could have been made up of a semi-hydrated crown complexed protein. This result was a typical representation for all the ionic liquids when Cyt-c extraction was attempted.

## 4.10 Conclusion

Electrochemical cells have been designed, produced and shown to function, using model electrochemical systems, with reproducible results. However, the use of ionic liquid for the transfer of biomolecules has proved to be problematic. It highlights the careful decision making that is required for the transfer of molecules across an interface, through the selection and off-setting of different ionic liquid properties.

Ion transfer of protonated Cyt-c was unsuccessful in the designed cell forming an agglomeration at the interface of the water and ionic liquid, with no protein visible in the ionic liquid. The capacitance values show that the ionic liquids

based electrochemical cells have a high capacitance at the shorter alkyl chain lengths when functionalised (c.f. lower capacitance when unfunctionalised) which then are reasonably equal at longer chain lengths ( $\geq 5$ ). Capacitance is due to surface charge on an electrode surface.<sup>[52]</sup> In the case of a liquid-liquid, ITIES, electrochemical cell, the “surface” is the interface. Therefore, when the system is under an applied field the charge builds up at the interface, resulting in a high capacitance through out the system (namely the ionic liquid phase). This charge build up, due to the ion diffusion under the applied field, then seems to act as a barrier to ion transfer across the interface. This is especially evident when targeting a large biomolecule. To understand the restrictions of an ionic liquid based liquid-liquid, ITIES, system the diffusion of the ions within the system must be investigated.



## Chapter 5

# Ion diffusion in ionic liquids

As shown in chapter 4, transfer across from an aqueous solution into an ionic liquid has proven to be substantially more difficult than first envisaged. From the agitation experiments undertaken (Section 4.7) it has been shown that extraction of cytochrome-c (chosen target protein) is possible into all of the ionic liquids synthesised with varying degrees of success. However, the electrochemical extraction approach was found to be problematic. One of the problems encountered was the ‘impact’ of the protein onto the interface. This occurred as a result of the concentration of the protein between the two liquids following successful electrophoresis. However, an apparent barrier existed between the two liquids that could not be breached by the protein.

On the basis of the evidence gathered so far it was hypothesised that the application of a potential to the pure ionic liquid could have unusual effects, which may impede the protein (biomolecule) transfer process. Therefore, it was decided to investigate the actual diffusive nature of a charged analyte within the ionic liquid itself and to determine the effect, on diffusion, that an applied electrical field had. Two methods were chosen to investigate the diffusivity:

1. Nuclear Magnetic Resonance (NMR) - specifically Pulsed Gradient Stimulated Echo (PGSTE)
2. Single Molecule Fluorescence (SMF) Spectroscopy - specifically Fluorescence Correlation Spectroscopy (FCS)

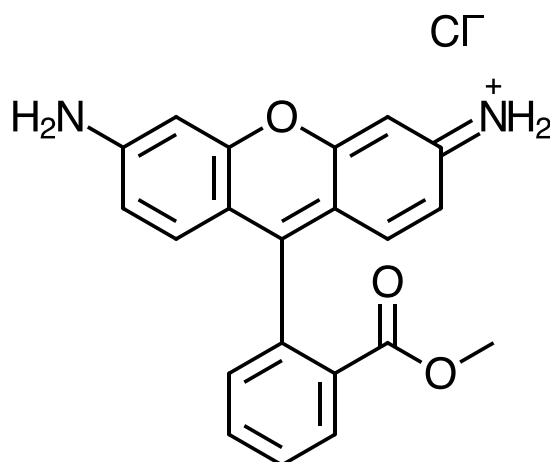


**Figure 5.0.1** – Chosen fluorescence probe - Rhodamine 123.

In both cases a positively charged analyte was needed. To be as representative as possible to the ionic liquid environment a probe was desired that had a single positive charge. Additionally, it was desirable to use the same probe for both techniques as this would allow a comparison of the methods, and to give a robustness to the results of either method. Therefore, Rhodamine 123 (Rh123, see Figure 5.0.1) was chosen as it:

1. Contains a single positive charge - i.e. will act like a cation in the ionic liquid.
2. Is relatively small, and therefore, as close to the size of an ionic liquid cation or anion as possible.
3. Has a quantum yield of 0.9 (in comparison ATTO 488 has a quantum yield of 0.8) and hence will have a strong fluorescence response.<sup>[157]</sup>
4. Contains multiple aromatic protons which are found downfield of the majority of the ionic liquid's NMR signal, therefore making the Rh123 easily identifiable.

## 5.1 Diffusivity measurements - Pulse Gradient Stimulated Echo

Fick's first law of diffusion states that the flux of molecules (or matter),  $J$ , moving through a plane in space is given by the concentration gradient across that plane:<sup>[158]</sup>

$$J = -D \frac{\partial C(x, t)}{\partial x} \quad (5.1.1)$$

where,  $D$  is the diffusion coefficient for the molecule/ion diffusing within the material of interest. e.g. solvent, air, etc, and  $\frac{\partial C(x, t)}{\partial x}$  is the concentration gradient within that medium.

Hahn's observations that fluctuations in the local magnetic field (and therefore molecular translational diffusion) influenced spin-echo intensity is the basis of time domain NMR.<sup>[159, 160]</sup>

Ultimately, if the magnetic field gradient's amplitude and duration being applied is known, it is possible to calculate, from the echo (spin or stimulated) attenuation, the diffusion coefficient. Originally, continuous magnetic field gradients were used for these measurements however, the working by Stejskal and Tanner demonstrated the utility of pulsed gradients, which were used here to measure diffusion of the Rh123.<sup>[161]</sup> Simply put, the diffusion coefficient,  $D$ , (the mobility of molecules or ions within a system)<sup>[158, 162]</sup> is determined through the application of magnetic field gradients during the dephasing and rephasing periods (see Figure 5.1.1 - Top) i.e.:<sup>[3]</sup>

1. Following the standard 90° pulse a magnetic field gradient (with length  $\delta$  and a field strength  $g$ ) is applied after a short delay. The 90° pulse rotates all the vectors into a magnetisation ribbon in the plane of rotating reference frame. The magnetic field variations, due to local inhomogeneities of the magnetic field, means that different protons within the sample experience a different local magnetic field and precess with varying Larmor frequencies therefore losing coherency (and magnetisation).
2. The loss of coherency is reversed by following the 90° pulse, at time  $\tau$ , by

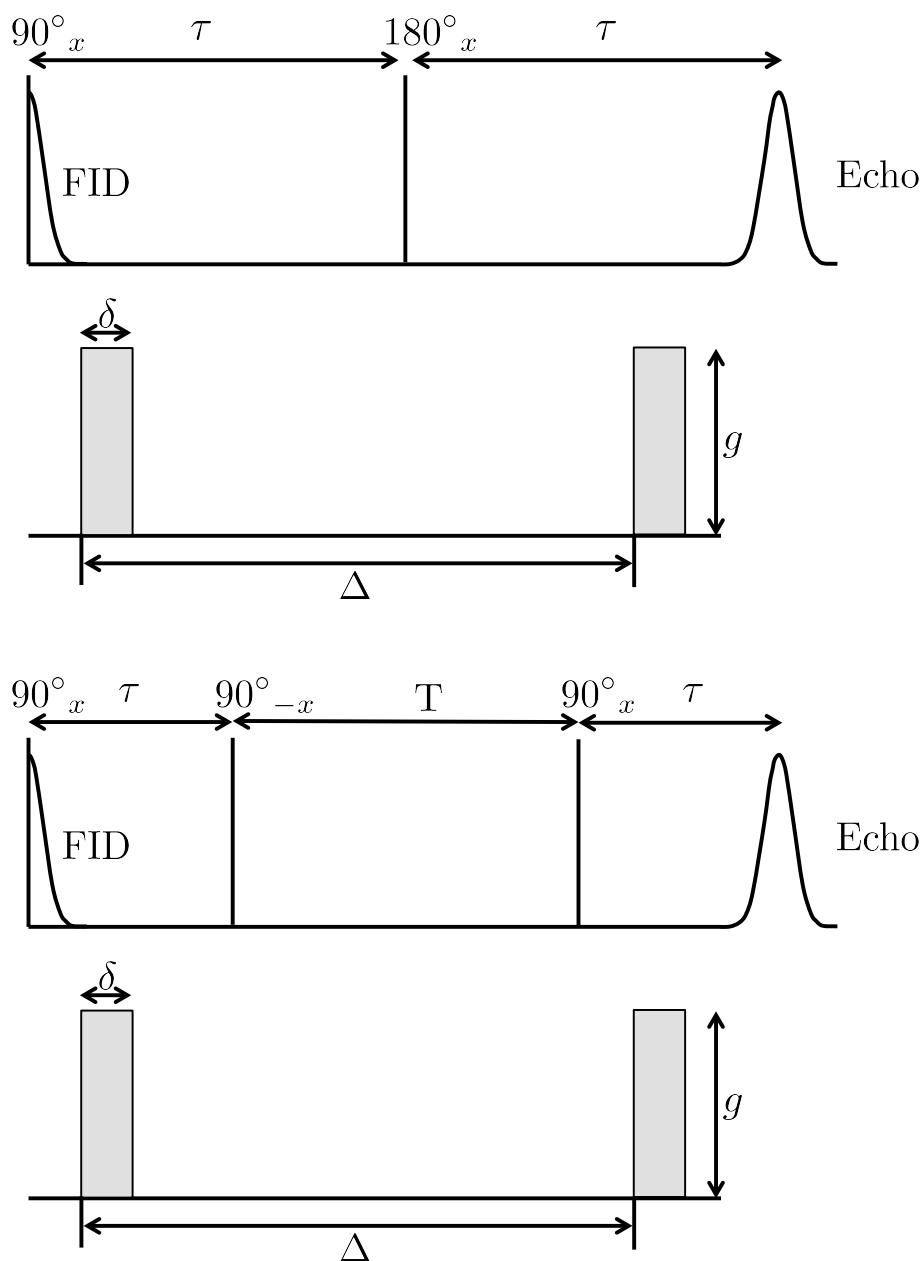


**Figure 5.1.1** – Representation of the application of magnetic field gradients during the de- and re-phasing periods of the PGSE (top) and PGSTE (bottom) experiments.<sup>[3]</sup>

a  $180^\circ$  pulse which allows the system to reach full coherency resulting in a measurable NMR signal - the spin-echo (SE).

3. Following the  $180^\circ$  pulse the effect of the first applied magnetic field gradient is reversed with the application of an identical magnetic field gradient. If the nuclei being targeted has not moved within the time scale between the two gradient pulses ( $\Delta$ ) there is no effect on the spin-echo intensity. However, if the spatial position of the nuclei has changed (it has moved), the application of the second magnetic field gradient does not fully reverse the first and therefore the spin-echo is affected. The more mobile the molecule containing the nuclei being targeted is, the greater the reduction in the intensity of the spin-echo.

The spin echo's intensity is calculated from:<sup>[161]</sup>

$$\ln \frac{I_{2\tau}}{I_0} = -\gamma^2 \delta^2 g^2 \left( \Delta - \frac{\delta}{3} \right) D \quad (5.1.2)$$

where,  $I$  is the echo's intensity,  $\gamma$  is the gyromagnetic ratio,  $\delta$  is the length of the applied magnetic field gradient,  $g$  is the applied field strength,  $D$  is the diffusion coefficient. The diffusion coefficient is then calculated from the slope of  $\ln \frac{I_{2\tau}}{I_0}$  versus a series of applied magnetic field strengths,  $g^2$  (see Figure 5.1.2 - Right, for an example).

Hahn also investigated two and three  $90^\circ$  pulse sequences and found that three pulse sequences could generate up to five spin-echos.<sup>[160]</sup> This has led to the more complicated pulsed gradient stimulated echo (PGSTE) pulse sequence for diffusion measurements via NMR (see Figure 5.1.1 - Bottom) - the first pulse after the third pulse is known as the stimulated echo (STE). The choice of the pulse sequence used for the measurement of ionic liquid diffusion coefficients is extremely important. Forsyth *et al.*<sup>[163]</sup> reported errors of up to 20 % when using a PGSE pulse sequence compared to a PGSTE pulse sequence. Therefore, to measure the diffusion coefficient of Rh123 in ionic liquid, a PGSTE pulse sequence was used.

### 5.1.1 Results and discussion

The diffusivity of the ionic liquid's cation and anion, along with that of the probe molecule, were measured via the Bruker diffusion analysis software (Figure 5.1.2) and are reported in Table 5.1.1.

From Figures 5.1.3 and 5.1.4, it can be seen that the  $[\text{NTf}_2]^-$  anion diffusion coefficient is reasonably similar across the measured ionic liquids. The slight decrease in the diffusion coefficient can be attributed to the increasing viscosity within the ionic liquid as the alkyl chain length is increased (see Chapter 3, Section 3.9.1). As would be expected, the increasing alkyl chain length affects the cation (see Figure 5.1.5) substantially, and the exponential decay is a trend exhibited across most of the fundamental properties measured for these ionic liquids (see Chapter 3). The hydroxyl group, as seen previously, has a decreasing effect on the diffusion coefficient as the chain length increased. Understandably, the hydroxyl functional group led to smaller diffusion coefficients due to the increased hydrogen bonding that occurs within the ionic liquid, increasing viscosity and thereby impeding movement. In the case of the Rh123 (see Figure 5.1.6), even though the probe itself is not changing, the surrounding ionic liquid environment it is experiencing is, and therefore the same trend is exhibited.

#### 5.1.1.1 'Ionicity'

From the measured NMR diffusivity data, and the ionic liquid conductivity data from Chapter 3 (Section 3.9.3) it is possible to calculate the 'ionicity' (Haven ratio,  $R_H$ ) of the ionic liquid (Equation 5.1.3):<sup>[26, 38, 45, 164]</sup>

$$R_H = \frac{\Lambda_{m,imp}}{\Lambda_{m,NMR}} \quad (5.1.3)$$

The calculation of  $\frac{\Lambda_{m,imp}}{\Lambda_{m,NMR}}$  determines the degree of ionic association (neutral ion pair or cluster formation) that is occurring in the ionic liquid, and hence, the proportion of the ionic liquid's diffusing ions which are involved in conductivity.<sup>[164]</sup> The molar conductivity is calculated from the NMR diffusion data using the

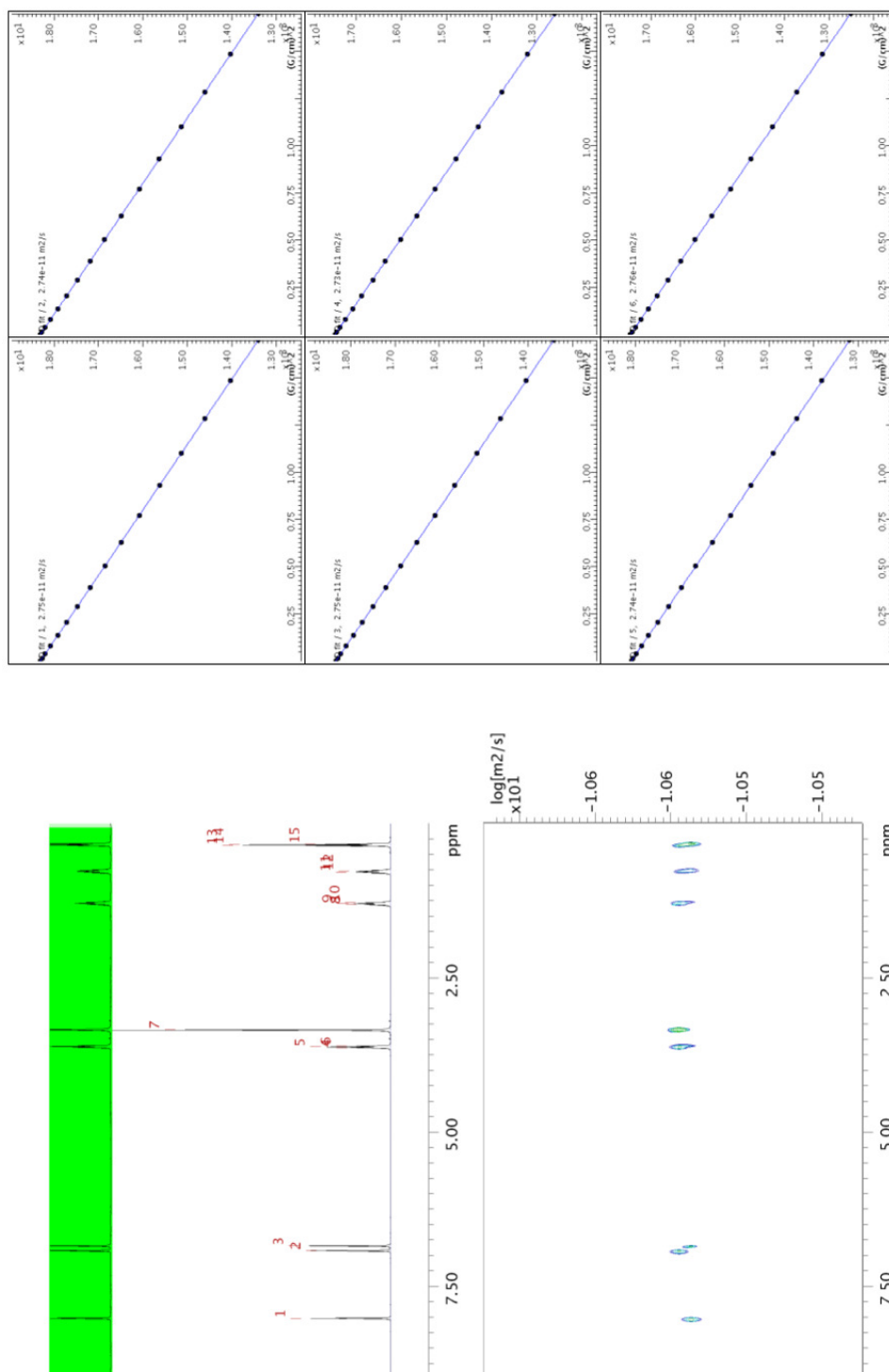


**Figure 5.1.2** – Part of the report produced by the Bruker Diffusion Analysis Software showing the picked NMR signals (left) and the corresponding plots of  $\ln I_{zz}/I_0$  versus a series of applied magnetic field strengths,  $g^2$  for peaks 1-6 (right).

| Ionic Liquid                                                 | Cation Diffusivity / $\text{m}^2 \text{s}^{-1}$ | Anion Diffusivity / $\text{m}^2 \text{s}^{-1}$  | Probe Diffusivity / $\text{m}^2 \text{s}^{-1}$  |
|--------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| $[\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$              | $5.41 \times 10^{-11} \pm 2.32 \times 10^{-13}$ | $1.60 \times 10^{-11} \pm 2.00 \times 10^{-13}$ | $1.59 \times 10^{-11} \pm 1.07 \times 10^{-12}$ |
| $[\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$              | $3.74 \times 10^{-11} \pm 1.34 \times 10^{-13}$ | $7.00 \times 10^{-12} \pm 4.20 \times 10^{-13}$ | $1.16 \times 10^{-11} \pm 5.68 \times 10^{-13}$ |
| $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$              | $2.75 \times 10^{-11} \pm 2.83 \times 10^{-13}$ | $8.71 \times 10^{-12} \pm 1.05 \times 10^{-13}$ | $1.12 \times 10^{-11} \pm 6.95 \times 10^{-13}$ |
| $[\text{C}_5\text{C}_1\text{im}][\text{NTf}_2]$              | $2.12 \times 10^{-11} \pm 9.49 \times 10^{-14}$ | $1.78 \times 10^{-11}$                          | $9.02 \times 10^{-12} \pm 6.38 \times 10^{-13}$ |
| $[\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$              | $1.93 \times 10^{-11} \pm 4.55 \times 10^{-13}$ | $1.14 \times 10^{-11} \pm 4.71 \times 10^{-12}$ | $7.47 \times 10^{-12} \pm 7.40 \times 10^{-13}$ |
| $[\text{C}_7\text{C}_1\text{im}][\text{NTf}_2]$              | $1.42 \times 10^{-11} \pm 2.75 \times 10^{-13}$ | $7.33 \times 10^{-12}$                          | $6.25 \times 10^{-12} \pm 6.08 \times 10^{-13}$ |
| $[\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$              | $1.20 \times 10^{-11} \pm 1.19 \times 10^{-13}$ | $8.36 \times 10^{-12} \pm 2.25 \times 10^{-12}$ | $5.64 \times 10^{-12} \pm 5.10 \times 10^{-13}$ |
| $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ | $1.83 \times 10^{-11} \pm 5.10 \times 10^{-13}$ | $6.86 \times 10^{-12} \pm 6.95 \times 10^{-13}$ | $6.73 \times 10^{-12} \pm 2.44 \times 10^{-13}$ |
| $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ | $1.37 \times 10^{-11} \pm 5.08 \times 10^{-13}$ | $6.24 \times 10^{-12} \pm 2.25 \times 10^{-12}$ | $6.17 \times 10^{-12} \pm 2.02 \times 10^{-13}$ |
| $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ | $6.00 \times 10^{-12} \pm 1.58 \times 10^{-13}$ | $4.36 \times 10^{-12} \pm 5.90 \times 10^{-13}$ | $3.85 \times 10^{-12} \pm 5.53 \times 10^{-13}$ |
| $[(\text{HO})^8\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ | $4.82 \times 10^{-12} \pm 3.76 \times 10^{-13}$ | $3.63 \times 10^{-12} \pm 1.60 \times 10^{-13}$ | $3.93 \times 10^{-12}$                          |

**Table 5.1.1** – The diffusivity values determined from the PGSTE experiment for the ionic liquid's cations and anion, and that of the probe, Rh123.

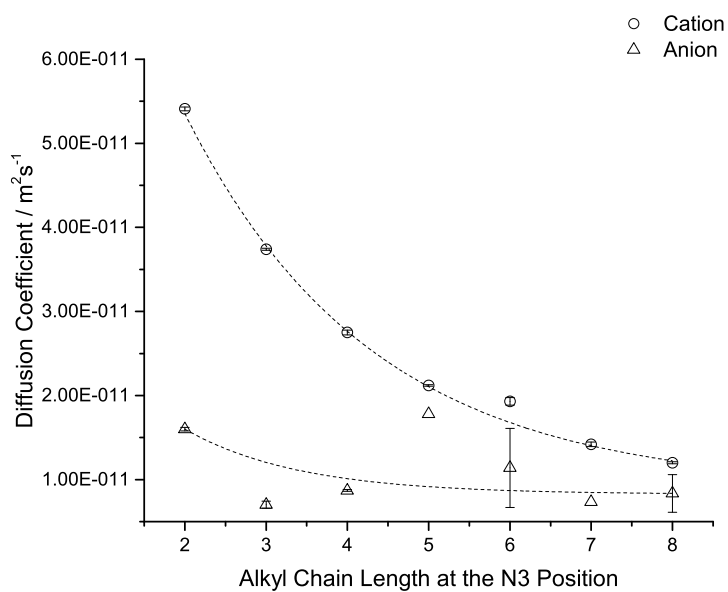


**Figure 5.1.3** – Cation and anion diffusion coefficients for the unfunctionalised ionic liquids with increased alkyl chain length.

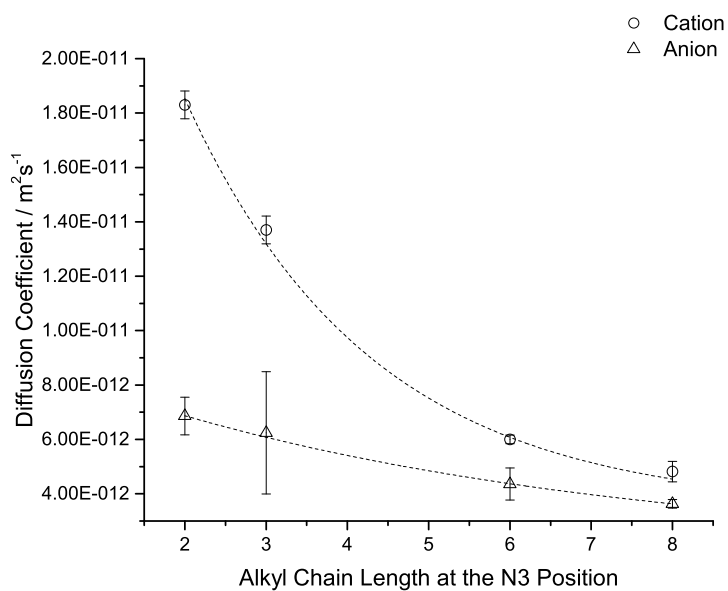


**Figure 5.1.4** – Cation and anion diffusion coefficients for the hydroxyl functionalised ionic liquids with increased alkyl chain length.

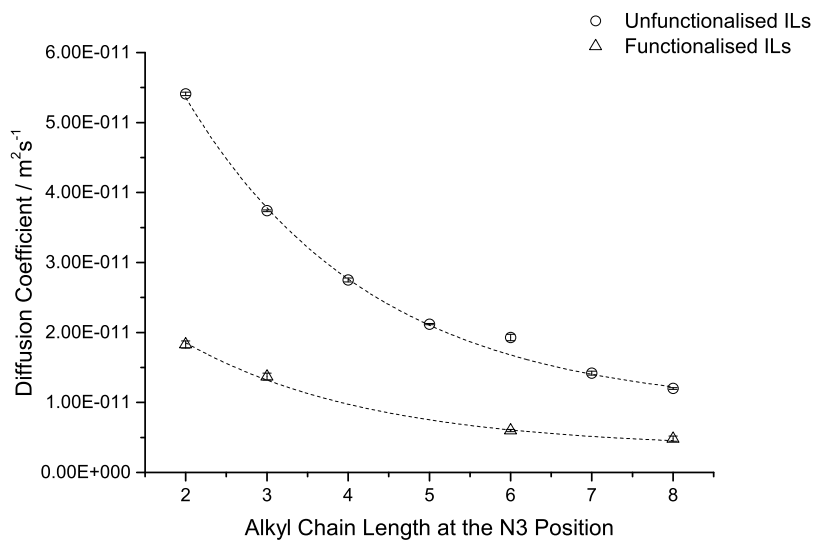


**Figure 5.1.5** – A comparison of the diffusion coefficients of the cations of the unfunctionalised and hydroxyl functionalised ionic liquids.

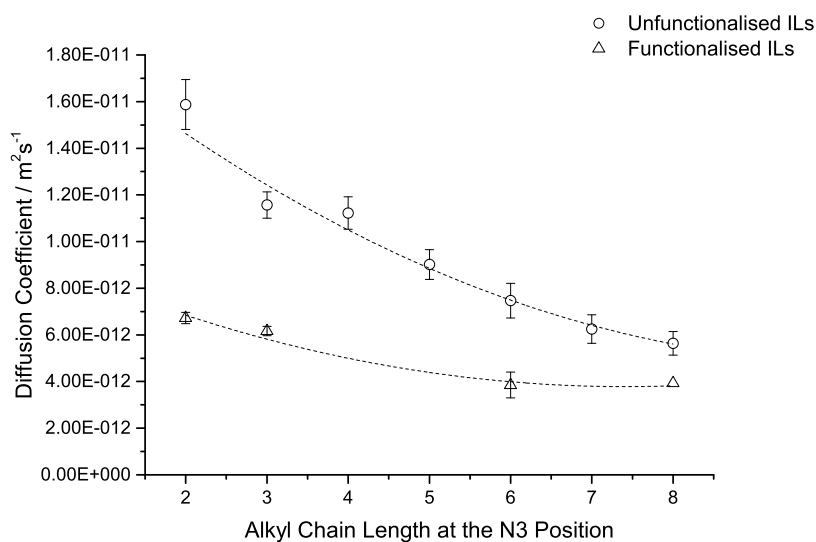


**Figure 5.1.6** – A comparison of the diffusion coefficient of the Rh123 in the unfunctionalised and hydroxyl functionalised ionic liquids.

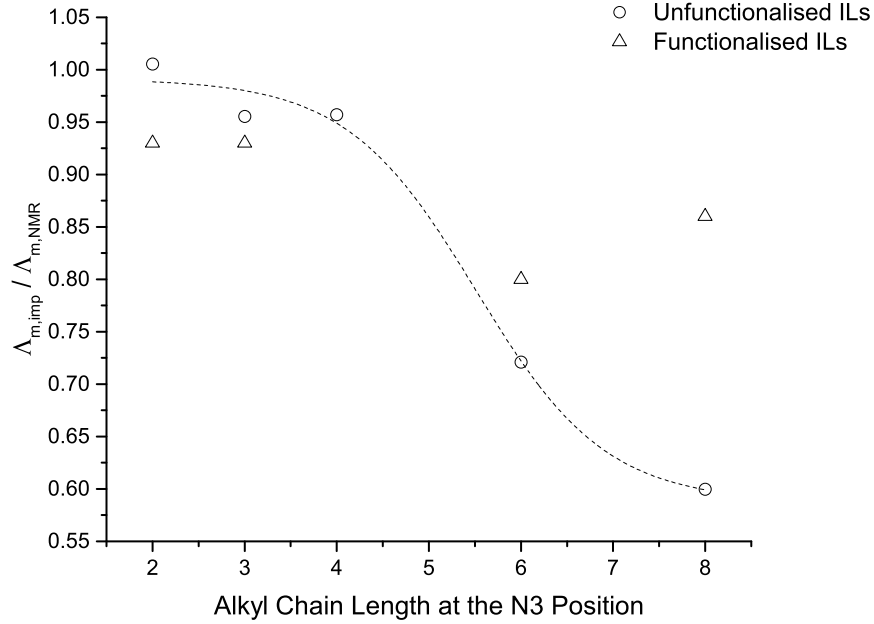


**Figure 5.1.7** – Haven ratio for the unfunctionalised and hydroxyl functionalised ionic liquids with increase long alkyl chain length.

Nernst-Einstein equation:<sup>[26, 165]</sup>

$$\Lambda_{m,NMR} = \frac{N_A e^2}{k_B T} (|z_+|^2 D^+ + |z_-|^2 D^-) = \frac{F^2}{RT} (|z_+|^2 D^+ + |z_-|^2 D^-) \quad (5.1.4)$$

where,  $\Lambda_{m,NMR}$  is the molar conductivity,  $N_A$  is Avagadro's number,  $e$  is the electric charge,  $k_B$  is Boltzman's constant,  $F$  is the Faraday constant,  $R$  is the gas constant,  $T$  is the temperature, in Kelvin,  $z$  is the ion charge number ( $z_+$  for cation,  $z_-$  for anion) and  $D$  is the diffusion coefficient ( $D^+$  for cation,  $D^-$  for anion).

The Haven ratio was calculated to be less than unity for all but one of the liquids tested (see Table 5.1.2 & Figure 5.1.7) with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide giving a value of 1.01 - with the error of the measurements, and calculations, it is assumed to be one and hence indicate a fully dissociated state for this ionic liquid. For the other tested liquids, the value

| Ionic Liquid                                                            | $\Lambda_{m,imp}$ / S m <sup>2</sup> mol <sup>-1</sup> | $\Lambda_{m,NMR}$ / S m <sup>2</sup> mol <sup>-1</sup> | Haven Ratio |
|-------------------------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|-------------|
| [C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 2.65 x 10 <sup>-4</sup>                                | 2.63 x 10 <sup>-4</sup>                                | 1.01        |
| [C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.59 x 10 <sup>-4</sup>                                | 1.67 x 10 <sup>-4</sup>                                | 0.96        |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 1.30 x 10 <sup>-4</sup>                                | 1.36 x 10 <sup>-4</sup>                                | 0.96        |
| [C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 8.31 x 10 <sup>-5</sup>                                | 1.15 x 10 <sup>-4</sup>                                | 0.72        |
| [C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]                   | 4.57 x 10 <sup>-5</sup>                                | 7.63 x 10 <sup>-5</sup>                                | 0.60        |
| <hr/>                                                                   |                                                        |                                                        |             |
| [(HO) <sup>2</sup> C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 8.74 x 10 <sup>-5</sup>                                | 9.44 x 10 <sup>-5</sup>                                | 0.93        |
| [(HO) <sup>3</sup> C <sub>3</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 6.92 x 10 <sup>-5</sup>                                | 7.48 x 10 <sup>-5</sup>                                | 0.93        |
| [(HO) <sup>6</sup> C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 3.11 x 10 <sup>-5</sup>                                | 3.89 x 10 <sup>-5</sup>                                | 0.80        |
| [(HO) <sup>8</sup> C <sub>8</sub> C <sub>1</sub> im][NTf <sub>2</sub> ] | 2.73 x 10 <sup>-5</sup>                                | 3.17 x 10 <sup>-5</sup>                                | 0.86        |

**Table 5.1.2** – Calculated molar conductivity values for the listed unfunctionalised and hydroxyl functionalised ionic liquids, and their determined Haven Ratio.

less than unity implies that not all of the ionic liquid's ions are involved in the conduction process in these liquids when an electric field is applied. This agrees with the work by Tokuda *et al.*<sup>[38, 45, 164]</sup> From Figure 5.1.7 it can be implied that the ionicity at longer alkyl chain lengths is greater for the hydroxyl functionalised ionic liquids compared with the unfunctionalised.

### 5.1.2 Conclusion

The data acquired here for the range of ionic liquids was generated with a view to allow a comparison with those values obtained via the subsequent single molecule fluorescence experiments. With the unfunctionalised ionic liquids tested here it is shown that the diffusion coefficient for the ions decreases as the alkyl chain length at the N3 position increases. In the case of the hydroxyl functionalised ionic liquids, this effect is duplicated with the diffusion coefficient values themselves being lower than those of the unfunctionalised ionic liquids (see Figure 5.1.5).

## 5.2 Diffusivity measurements - SMF Spectroscopy

Simply put, the basis of single molecule fluorescence is that excitation light illuminates the sample at the objective of the microscope and the resulting fluorescence is collected and delivered to an avalanche photodiode detector (APD).

The experimental setup can be divided into 4 sections - see Figure 5.2.1:

1. Excitation source - Laser, 488 nm wavelength.
2. Excitation delivery to sample - Excitation light, 488 nm (Figure 5.2.1 - Blue).
3. Sample illumination - via objective.
4. Emission Collection - APD.

The movement of a probe (i.e. fluorescent dye molecule) through the observation volume, defined by the focused excitation beam, causes a burst of fluorescence (Figure 5.2.2) which is detected via the APD's and the intensity of the burst over time is recorded. The burst's intensity is analysed in terms of its intensity at

APD = Avalanche Photodiode Detector

BE = Beam Expander

CCD = Charge-coupled device

DM = Dichroic Mirror

FW = Filter wheel

L = Lens

Obj = Objective

RM = Removable Mirror

■ Excitation Light, 488 nm

■ Fluorescence signal

■  $\lambda = 660 - 750$  nm

■  $\lambda = 505 - 640$  nm

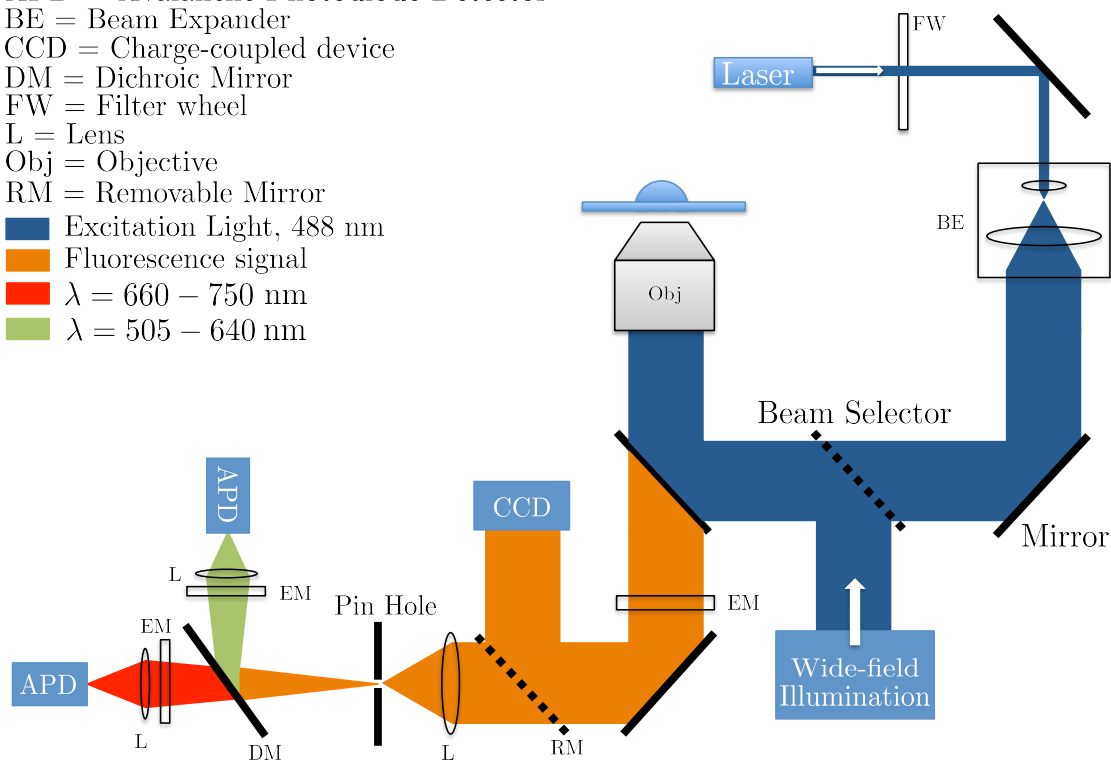


**Figure 5.2.1** – Experimental setup for FCS experiments.

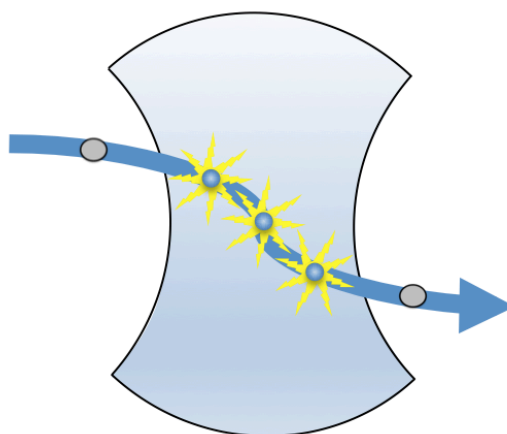


**Figure 5.2.2** – Representational observation volume with diffusing molecules fluorescing as they pass through.

time,  $t$ , and then after a time delay of  $\tau$ . This is given by its temporal autocorrelation function,  $G(\tau)$ :

$$G(\tau) = \frac{\langle \delta F(t) \delta F(t + \tau) \rangle}{\langle F(t) \rangle^2} \quad (5.2.1)$$

where,  $\delta F(t)$  and  $\delta F(t + \tau)$  are the amplitudes of the fluctuations from the mean at time  $t$  and  $t + \tau$  respectively, and  $\langle F(t) \rangle^2$  is the mean value of the signal. Once the autocorrelation function is defined (using Equation 5.2.1), a physical model is fitted to this function. This model incorporates the physical parameters of interest. The model used here, developed by Rigler *et al.* aims to fit an autocorrelation function whose fluctuations are derived from a combination of diffusion and triplet crossings (caused by intermittent fluorescence); which is based upon the model by Aragon and Pecora for diffusion in and out of a three-dimensional Gaussian observation volume.<sup>[166, 167]</sup>

$$G(\tau) = \frac{1}{N} \left(1 + \frac{\tau}{\tau_D}\right)^{-1} \left(1 + \frac{\tau}{K^2 \tau_D}\right)^{-\frac{1}{2}} \left[ F_T \exp\left(-\frac{\tau}{\tau_T}\right) + (1 - F_T) \right] + DC \quad (5.2.2)$$

where,  $N$  is the average number of probe molecules (fluorescent molecules) within the observation volume,  $\tau_D$  is the molecular diffusion time (also known as the correlation time),  $F_T$  is the “triplet fraction”, i.e. the proportion of the diffusing molecules which spend time in the triplet state,  $\tau_T$  is the associated triplet crossing diffusion time,  $DC$  is the value when  $\tau \rightarrow \infty$  (which is typically  $DC = 1$ ) i.e. baseline offset,  $K = \frac{z_0}{\omega_0}$  where  $z_0$  is the  $\frac{1}{e^2}$  radii in the direction of the optical axis and  $\omega_0$  is the  $\frac{1}{e^2}$  radius perpendicular to the optical axis. The triplet state can be used as probe for the molecular environment.<sup>[167]</sup> In this work however this aspect of the fit was not investigated further.

The translational diffusion coefficient can then be calculated from:<sup>[168]</sup>

$$\tau_D = \frac{\omega_0^2}{4D} \quad (5.2.3)$$

It must be noted that Equation 5.2.3 is only applicable for one-photon excitation.<sup>[169, 170]</sup> By using known translational diffusion coefficient values, and  $\tau_D$  from the autocorrelation fit,  $\omega_0$  can be determined (N.B. depending upon the

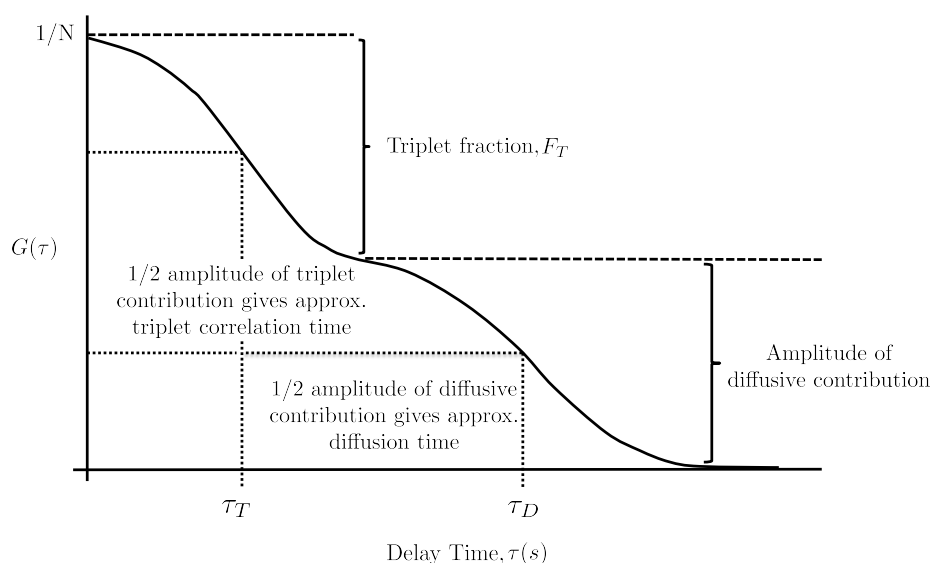


**Figure 5.2.3** – Representational autocorrelation curve with the parameters of Equation 5.2.2 indicated.

optical setup being used there is often another pre-factor to the denominator of Equation 5.2.3).<sup>[168]</sup>

When applying an electric field to the ionic liquid the advantages of using a SMF spectroscopy setup becomes evident. Indium-tin oxide (ITO) is optically transparent and electrically conductive and therefore replacing the originally used standard glass microscope slide with an ITO coated slide means that the slide itself can now act as an electrode. The setup used for the SMF spectroscopy measurements is shown in Figure 5.2.4 with the upper platinum wire electrode lowered into the ionic liquid held within a polydimethylsiloxane (PDMS) cube. Here the orientation of the electrode does not matter, in all cases when a field was applied the positive 3 V is applied from the ITO coated slide.

## 5.2.1 Results and discussion

### 5.2.1.1 Ultra pure synthesis of ionic liquids

It was found that for the single molecule fluorescence studies undertaken here the ionic liquids produced via the standard synthetic routes were insufficiently pure

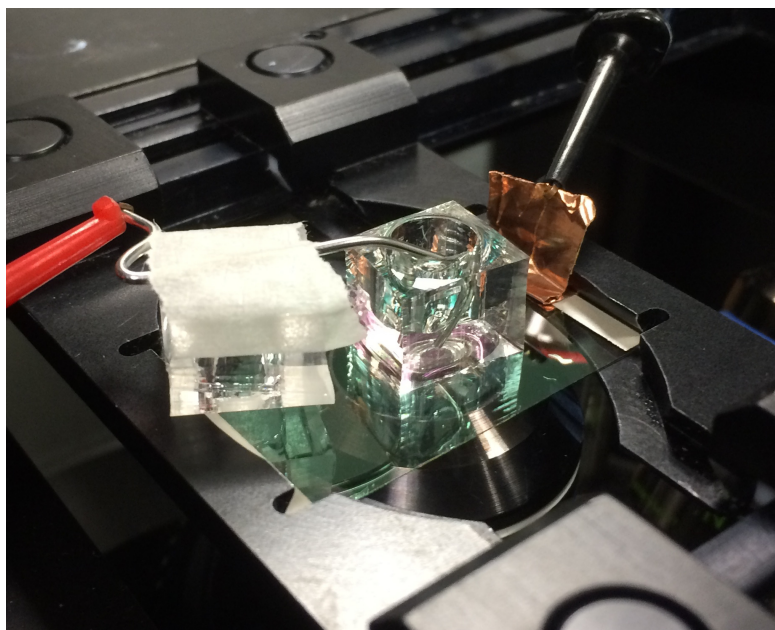


**Figure 5.2.4** – Experimental setup used for the FCS measurements. Ionic liquid is present in the PDMS cell, and the field is applied through the ITO coated slide, and the platinum wire.

enough for two reasons:

1. The background inherent fluorescence of the ionic liquids tested initially were excessively high and this meant that any probe present in the sample would have been masked by the raised baseline.
2. The baseline for the ionic liquids were also found to be noisy with multiple ‘events’ (sharp spikes) occurring without any probe being present in the ionic liquid - these peaks could be due to any number of reasons, including the presence of dust particles, any large particles, particles of charcoal from the purification process etc.

To ensure the highest purity of ionic liquid synthesised extra steps were taken during the synthesis including:

- Purification of the starting materials - all starting materials were purified before use to ensure they were as pure as possible. This is key as this is the basis of the ionic liquid.

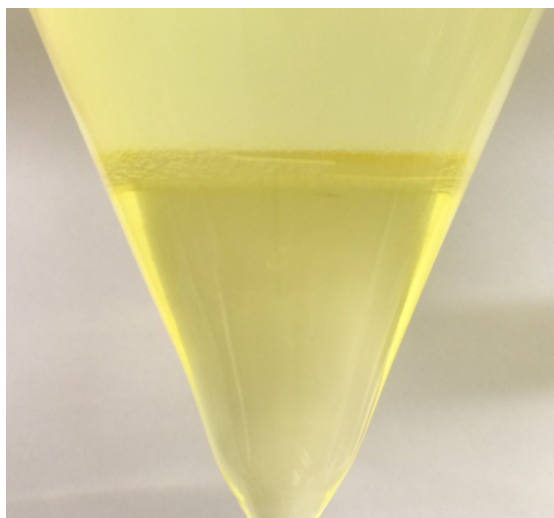


**Figure 5.2.5** – Photo of the two phases from washing 1-chlorobutane with conc. sulphuric acid.

- In the case of the haloalkane this involved an extra pre-washing step with concentrated sulphuric acid, neutralising the resulting acidic solution, ‘rough’ drying using magnesium sulphate before fractional distillation (Figure 5.2.5 shows the resulting coloration of 1-chlorobutane upon washing with concentrated sulphuric acid - washing was continued until no colour was present in the acid).
- Additionally, I have found that distillation of the 1-methylimidazole over freshly cut sodium seems to have long lasting beneficial effects on the inherent fluorescence of the ionic liquid, compared with the standard distillation from potassium hydroxide used within the Welton Research Group.
- Ultra-clean glassware - to ensure that there was minimal contamination from the glassware, initially new glassware was purchased and cleaned with Piranha solution (1:3, 30% hydrogen peroxide:concentrated sulphuric acid) before being stored under freshly distilled water prior to use. Furthermore, no grease was used during any of the purification or reaction steps and if a seal was required thick walled PTFE sleeves were used.
- Low reaction temperatures - this ensured the minimal production of

impurities from the reaction itself (see Chapter 3, Section 3.3.2). These colder reaction conditions did however mean longer reaction times.

- Purifications of intermediates - even with the long and cold reaction conditions, impurities can still form, and therefore the halide intermediate was washed and then recrystallised until the mother liquor was clear and colourless. It was found in practice that three or four recrystallisations were required.
- Purification of final product - it has been reported that the use of alumina for purification actually increased the fluorescence signal in the ionic liquid, therefore no alumina purification was performed, only ultra-pure, acid washed, steam activated, charcoal (Norit<sup>®</sup> SX ultra) was used.<sup>[171]</sup> To ensure no particles remained in the ionic liquid it was slowly filtered through two sterile, 0.2  $\mu\text{m}$  PTFE filters before use.<sup>[17]</sup>

Two ionic liquids were synthesised using this ultra-pure route for testing with the SMF spectroscopy experiments for determining the diffusivity values of the probe. These were:

1. 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide,  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  (Figure 5.2.6 - Left)
2. 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide,  $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$  (Figure 5.2.6 - Right)

### 5.2.2 Diffusivity - Autocorrelation curves

The diffusivity of the Rh123 was measured in two ultra-pure ionic liquids and water as a comparison control. The autocorrelation curves were recorded for the liquids in three situations:

1. Autocorrelation when no electric field was applied (pre field).
2. Autocorrelation when an electric field of +3 V was applied to the ionic liquid (positive at the ITO coated slide surface).

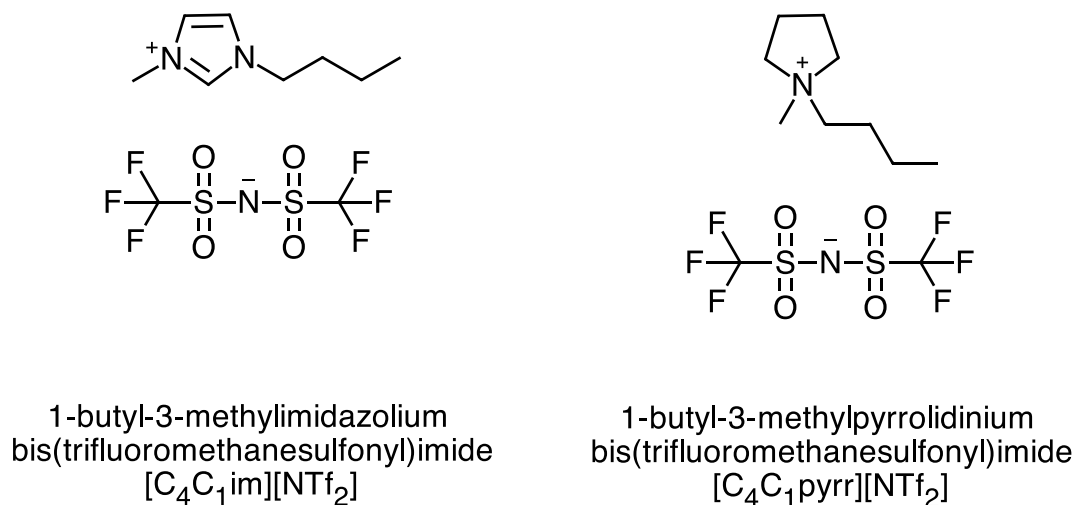


**Figure 5.2.6** – Chemical structures of both the ultrapure ionic liquids synthesised.

3. Autocorrelation after the +3 V field has been removed (post field).

The resulting FCS autocorrelation curves were fitted, using modified MATLAB<sup>®</sup> code (original code provided by the Edel Research Group, Imperial College London), with the initial parameters estimated from the data (see Figure 5.2.3), and the upper and lower bounds were adjusted so that variation of the diffusion coefficient, due to the choice of the end point of the fit, was minimised. The end point of the fit was chosen to be the region at which the autocorrelation curve plateaued at a  $G(\tau)$  of one. In a few cases noise was present at a  $\tau$  of  $5 \times 10^{-1}$ . Therefore, the end points of the fit were determined at  $1 \times 10^{-1}$ ,  $2 \times 10^{-1}$ ,  $3 \times 10^{-1}$  and  $4 \times 10^{-1}$  s respectively and averaged. The autocorrelation curve and the estimated fit for the curve, for [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>], are shown in Figures 5.2.7 - 5.2.9 along with the percentage error of the fit. The estimated fits for the water and [C<sub>4</sub>C<sub>1</sub>pyrr][NTf<sub>2</sub>], along with the fit parameters are given in Appendix B. The translational diffusion coefficients are reported in Table 5.2.1.

The diffusivity of the probe, Rh123, was measured under no applied electric field in water, [C<sub>4</sub>C<sub>1</sub>im][NTf<sub>2</sub>] and [C<sub>4</sub>C<sub>1</sub>pyrr][NTf<sub>2</sub>] and compared with the diffusivity values obtained via the NMR diffusivity measurement (Table 5.2.1 - Lines 1 and 2). This was to allow confirmation that the diffusivity being measured via the FCS method was indeed the same as that obtained via a very different technique.

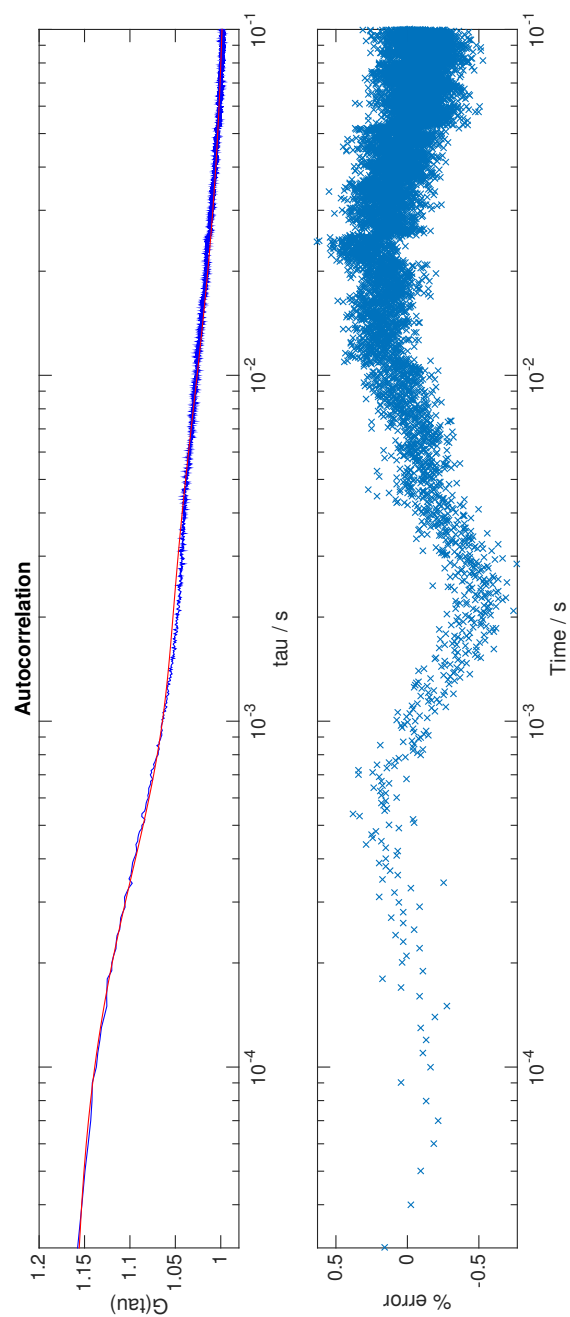


**Figure 5.2.7** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[\text{C}_4\text{C}_{1\text{im}}][\text{NTf}_2]$ , pre applied field, at the ITO slide surface.

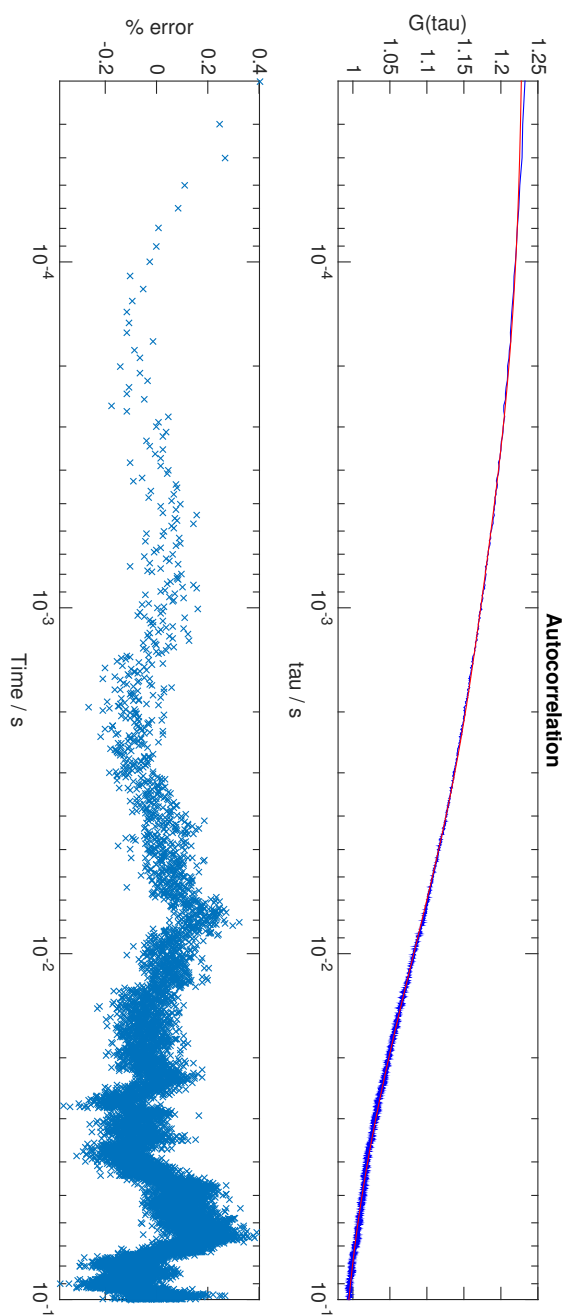


**Figure 5.2.8** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_{1im}][NTf_2]$ , with a +3 V applied field, at the ITO slide surface.

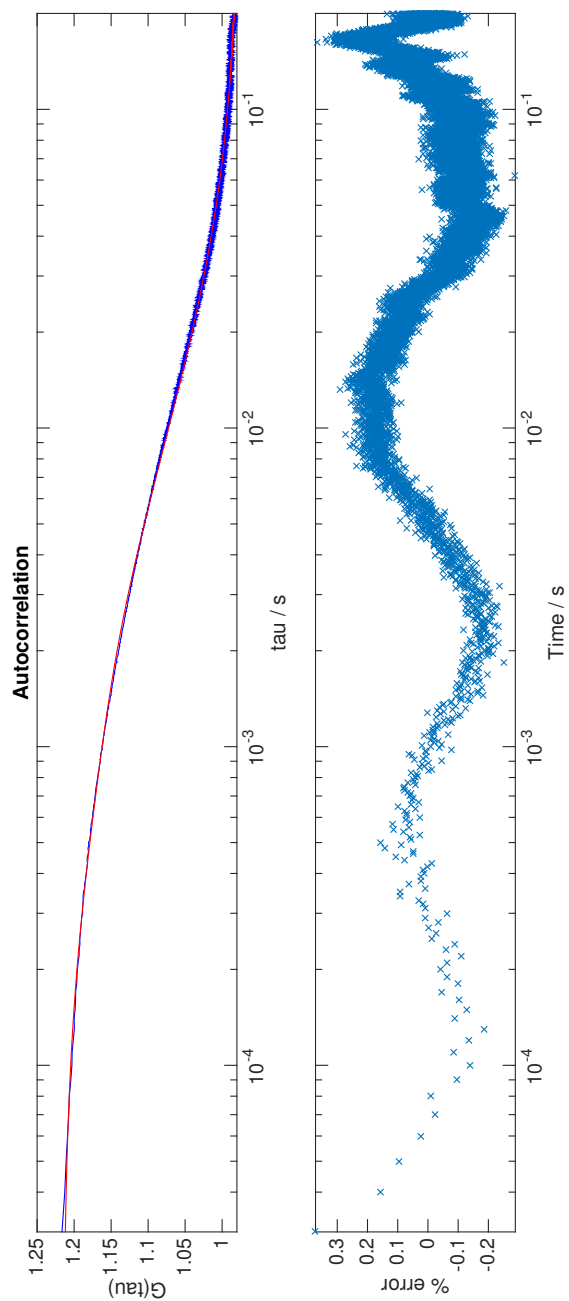


**Figure 5.2.9** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_1im][NTf_2]$ , post applied field, at the ITO slide surface.

|                       |  | Translational Diffusion Coefficient / $\text{m}^2 \text{s}^{-1}$ |                                                           |                                                        |                                                             |
|-----------------------|--|------------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------|-------------------------------------------------------------|
|                       |  | Water, Bulk                                                      | $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ , Surface | $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ , Bulk | $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$ , Surface |
| NMR                   |  | $4.80 \times 10^{-10}$                                           | $1.12 \times 10^{-11}$                                    | $1.12 \times 10^{-11}$                                 | $5.83 \times 10^{-12}$                                      |
| Pre applied field     |  | $4.08 \times 10^{-10}$                                           | $1.15 \times 10^{-11}$                                    | $1.15 \times 10^{-11}$                                 | $5.88 \times 10^{-12}$                                      |
| Applied field of +3 V |  | $4.76 \times 10^{-10}$                                           | $1.38 \times 10^{-12}$                                    | $1.68 \times 10^{-12}$                                 | $9.77 \times 10^{-13}$                                      |
| Post applied field    |  | $4.08 \times 10^{-10}$                                           | $1.54 \times 10^{-12}$                                    | $2.49 \times 10^{-12}$                                 | $9.95 \times 10^{-13}$                                      |

**Table 5.2.1** – Determined diffusion coefficients from the fitting of the recorded autocorrelation curves, pre applied field, with applied field and post applied field.

The  $\omega_0$  for the equipment has been determined to be  $5.68 \times 10^{-7}$  m, by the Edel research group, having used known diffusion values to determine this. This value agrees with those calculated (with experimental error) from the diffusion coefficients measured by NMR for the ionic liquids ( $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ ,  $\omega_0$  of  $5.59 \times 10^{-7}$  m, and for  $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$ ,  $\omega_0$  of  $5.66 \times 10^{-7}$  m). There was a slight variation for the  $\omega_0$  value from the diffusion values of Rh123 in water ( $\omega_0$  of  $6.07 \times 10^{-7}$  m), however, the trend exhibited for the water based samples is still correct.

Once the pre applied field autocorrelation curves were recorded and confirmed, an electric field was applied directly to the sample through the use of the ITO coated slide (+) and a platinum wire (-). The electric field was produced using a function generator which was set at +3 V. Upon application of the electric field the diffusivity in the ionic liquids ( $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  and  $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$ ) both decreased. In the case of the water sample, the application of the field increases the diffusivity values obtained.

The electric field was applied for 120 seconds in all experiments reported here. Once the field had been applied, the built up capacitance was allowed to discharge naturally via the connected electrodes. This was monitored on the function generator's oscilloscope to ensure that it was fully discharged. As was to be expected, the capacitance was slower to discharge in the ionic liquids compared with the water/probe sample. After the complete discharge of the capacitance had been observed, the diffusivity values for the probe were recorded for 600 seconds. This was performed to determine the return of the diffusivity values to the initial pre field diffusivity values:

- In the case of the water/probe sample the value did return to that determined before the +3 V electric field was applied.
- In the case of the ionic liquids, the diffusivity values remained closer to that measured when the +3 V field was applied. The diffusivity value was shown to be increasing at the point when measured after the field has been removed (600 seconds), thus implying that the diffusivity was returning to a pre applied field state extremely slowly.

Taking the ionic liquid values and looking at them in detail:

- For the  $[C_4C_1im][NTf_2]$  the translational diffusion coefficient of the Rh123 reduces by 88 % upon application of the +3 V electric field.
- For the  $[C_4C_1pyrr][NTf_2]$  the translation diffusion coefficient of the Rh123 reduces by 83 % upon application of the +3 V electric field.

This is to be expected, within the ionic liquid the Rh123 is moving within a charged environment which is itself now all polarised and moving. Viewing the autocorrelation curves while recording did show an increase in the diffusion coefficient during the first few seconds which then was averaged out as the experiment continued. With the writing of the appropriate MATLAB<sup>®</sup> coding it should be possible to extract this data and to determine the translational diffusion coefficient at varying time intervals. This would give an understanding on the timescales of this effect, and also a greater physical meaning. However, this effect is only present for a short time scale in this experiment, at the longer longer time scales it is not applicable to the results found here.

With the field off and the capacitance discharged, it was expected, with the 600 second timescale, for the diffusivity values to return to the pre field initial state. This however was not the case:

- For the  $[C_4C_1im][NTf_2]$ , post field (i.e. after discharge and 600 seconds) the translational diffusion coefficient of the Rh123 is 87 % smaller than the pre field value.
- For the  $[C_4C_1pyrr][NTf_2]$ , post field (i.e. after discharge and 600 seconds) the translational diffusion coefficient of the Rh123 is 83 % smaller than the pre field value. Exactly the same as when the field was being applied.

It can be seen that even after 600 seconds the post field diffusion coefficients are nearly identical to those when the field is being applied. These initial measurements were performed at  $\approx 1\mu m$  above the surface of the ITO coated slide to ensure the diffusion coefficients were those found in and around the electrode (as would be experienced in the liquid-liquid, ITIES cell). This position was determined via the detection of the slide via the response in the red channel of the

setup. The focus was then adjusted until it was just above the slide surface ( $\approx 1 \mu\text{m}$ ) and the experiment performed as documented above. However, the maximum detected layering distance reported is 7 nm from a charged surface (surface force balance<sup>[172, 173]</sup> and atomic force microscopy<sup>[174, 175, 176]</sup>).

To investigate any possible layer formation, informing the diffusion around the electrode surface of a non-ionic liquid probe compared with the bulk, the diffusivity of Rh123 was measured in  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  at a  $50 \mu\text{m}$  measurement depth. In this case:

- The pre field value matched that determined via the PGSTE NMR, and also that of the previous sample. i.e.  $1.15 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ .
- Upon application of the +3 V electric field there was a reduction in the diffusivity of the probe by 85 %. This is in agreement with the result found at the surface of the ITO when under an applied field.
- The post field value is found to be 78 % smaller than the pre field diffusivity value.

These results seem to indicate the following:

1. Upon the application of an electric field, the diffusivity through the sample (within 120 seconds) is reduced by around 80 - 90 % for these ionic liquids.
2. Once the field is removed the ionic liquid starts to return to the initial pre field state, however this seems to be a very long process.
3. Initial experiments with varying depth (with  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$ ) indicate that there is varying diffusivity dependent up the distance from the electrode. Additional experiments are required to determine the effect of distance for the  $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$  as only the diffusivity of Rh123 in the bulk of  $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$  was measured in the bulk.

Various theories exist that have looked at structural and dynamic changes of ionic liquids with applied fields. One of these is the application of cage theory<sup>[177]</sup> to ionic liquids.<sup>[178, 179]</sup> Simply described, the ion-cage theory states that a central ion is surrounded by its neighbouring counter-ions, the electrostatics of this interaction

means that the ions are trapped within the cage for a long time and hence there are very slow dynamics exhibited.<sup>[180]</sup> Wang and Shi undertook molecular dynamics (MD) simulations looking at the structural and dynamic changes of ionic liquids under an applied field.<sup>[181]</sup> They reported that only in strong applied fields ( $10^7 - 10^9 \text{ V m}^{-1}$ ) did deformation of the ion-cage occur and this in turn led to an increase in the ion mobility within the system in the direction of the applied field. The applied field in these experiments was approximately ( $10^4 \text{ V m}^{-1}$ ) and therefore it can be implied from their work this is not a strong enough field for the ion cage to be deformed. Hence, this would mean that ion mobility would remain relatively unchanged. It is evident from the results here that the application of the electric fields decreases the diffusivity within the system for Rh123. Therefore, an ion-cage based interpretation cannot be applied here. This experimental setup does offer the ability to investigate this interpretation and therefore, a range of applied field strengths should be investigated to determine their effect.

Another theory is that of hole theory; hole theory assumes that within the ionic liquid there are free volumes, or holes, and it is via migration of these holes that ion diffusion occurs.<sup>[182, 183, 184, 185]</sup> It can be hypothesised that the application of the applied field and therefore, charging of the ionic liquid provides enough energy for an ion to move into one of the existing holes, however as time passes and microstructuring starts to form (out from the electrodes), and holes migrate towards the centre of the cell. Around this central zone the availability of holes decreases rapidly, reducing the mobility in the liquid. If the observed increase in diffusion coefficient followed rapidly by a slowing down can be confirmed, this could be proof of the applicability of hole theory to ionic liquids under an applied electric field.

A very surprising result from these experiments was the post field values after the ionic layer has had a +3 V electric field applied. It was assumed that with the capacitance discharged, via the electrodes, to the function generator and hence to earth, that the diffusivities would relax back to the pre electric field values quickly (as seen with the water sample). However, even after 600 seconds, there is still a profound effect from the electric field especially in the region close to the 'interface'/electrode. More investigation of this effect is required to understand exactly what is occurring here. As demonstrated here it is possible to take

readings at varying depths, and this would allow a data cube for the translational diffusion coefficient of Rh123 to be built up. The determining factor here is the observation window itself and ultimately the accuracy of the microscope stage. When one considers the impact of this prolonged remaining charging effect the impact to a liquid-liquid, ITIES, system can be seen. With the first initial cyclic voltammogram sweep (positive or negative) the polarisation of the interface occurs and hence of the two phases. As the return to ‘pre sweep’ (i.e. pre field) values is an extremely slow process, this will mean that with each sweep the return to the previous state becomes progressively longer and longer. This builds up what could be thought of as a wall at the interface, which in the case of the macromolecule hinders the FIT across it. Indeed, it is likely that ion migration within the ionic liquid has pushed the ionophore into the bulk and therefore it would not be available to complex with the target.

According to available published literature this is the first measurement of a probe’s diffusivity in an ionic liquid under an applied field via FCS. Further investigation of these fascinating results is required and future experiments should include:

1. Investigation into the prolonged nature of the ‘charging’ of the ionic liquid
  - How does the length of applied field affect the discharge time back to the initial pre field state? Can the state be reversed through the application of an equal and opposite charge or due to the lack of available holes, and having to first reorganise the whole liquid would this be an extremely slow process?
2. Variation of the ionic liquid - The size of holes or free volume within the ionic liquid increases with alkyl chain length; therefore, does increasing the chain length reduce the time taken to return to the pre field state?
3. Variations of electric fields - Would pulsing of the field have an effect? If you offset the pulse toward the positive or negative would a prolonged charge state still form? It is possible to assume yes, however it would take a substantially longer time. Would higher field strength lead to a increase in mobility as found in the MD simulations by Wang and Shi?

### 5.3 Conclusion

The results obtained with the SMF spectroscopy measurements performed here, gives an insight into the reasons behind the failure of the electrochemical transfer across the liquid-liquid, ITIES reported in Chapter 4. Looking at each liquid separately we have recorded an increase in the diffusion of the probe in water, and a substantial decrease in mobility in an ionic liquid. The region of the cell that is of interest here is the interface, the movement once the macromolecule has transferred across the interface is of less interest in a liquid-liquid, ITIES platform. The implication of the results here is that the application of the applied electric field, via the cyclic voltammogram builds up a ‘charge wall’ that increases as the CV sweeps continue. Therefore, this ‘charge wall’ forms exactly that, a wall, to the passage of the biomolecule.

Studies of the dye molecule diffusion coefficients, in ionic liquids, using FCS have been previously been reported.<sup>[186, 187, 188]</sup> According to available literature however, this is the first time the translational diffusion coefficient of a probe molecule has been determined in an ionic liquid with an electric field, being applied, via SMF spectroscopy. Additionally, the results documented here seem to be support the application of hole theory when looking at diffusion of ions under an applied field.

Further work is clearly required to understand not only the physical reasoning and exact build up of possible layers within the ionic liquid structure but also their persistence and effect in the bulk. Determining the resulting diffusion coefficients under an applied field across the face of the electrode surface, and at varying depths is of extreme importance for the development of not only electrochemical applications of ionic liquids but their application to a liquid-liquid, ITIES, sensing platform.

## Chapter 6

# Theoretical modelling - electrolyte ion (carrier) diffusion across interfaces

*The theoretical work reported in this section was undertaken in collaboration with Dr P.K. Milsom, Sensors and Countermeasures Department, Dstl, Porton Down, Salisbury, Wiltshire, SP4 0JQ.*

This work was undertaken in an attempt to provide the basis of a theoretical model which could be used to investigate the reported results from the SMF spectroscopy measurements.

When two immiscible liquids are brought into contact, differential solvation results in charge separation, ions diffuse across the liquid-liquid ITIES at different speeds and an opposing electric field is established. The potential and charge distributions established near to the interface have been the subject of many experimental and theoretical studies since the end of the nineteenth century.<sup>[189, 190, 191, 192]</sup> It was however, only in 2011 that the first study of early stage dynamics was published.<sup>[193]</sup> Zhurov *et al.*, made the assumption of semi-infinite liquids to reduce the problem to a single spatial dimension,  $x$ , and developed a model based on the numerical integration of coupled charge diffusion equations. A finite difference technique with a variable mesh was used to describe regions of rapidly varying electric potential and Dirichlet boundary

conditions were used for  $x \rightarrow \pm\infty$ . At the interface fixed concentration ratios and fluxes were specified. Iterative application of the Newton-Raphson method gave solutions for the spatial and temporal variation in electrolyte ion (carrier) concentrations and electric potential. Zhurov *et al.*'s integration method was found to be slow, requiring hours of CPU time to find a self-consistent solution, and therefore we applied a split-step integration scheme<sup>[194]</sup> and concentrate on the case where the carriers move under the influence of the internal field only, with the applied external field set to zero.

## 6.1 Theoretical model

### 6.1.1 General considerations

The base/background electrolyte (i.e. charge carrier) motion in the solutions comprising an ITIES depends upon:

1. The applied potential difference, the electric field, driving the electrolyte ions through the liquid;
2. The internal electric fields due the positive and negative ions in the liquid;
3. The concentration differences in the electrolytes (in the aqueous and non-aqueous phases) which drive diffusion within the whole cell;
4. The interfacial boundary condition at the interface between the immiscible electrolyte solutions;

The physics of the problem involves coupling drift-diffusion equations for both the positive and negative ions, with the Poisson equation describing the internal electric field.

The ion current in a liquid is driven by both the electric fields, formed by the applied potential difference, and the concentration gradients within and between the two liquids. For species  $i$ , this can be represented by the simple, and familiar, form:

$$\underline{J}_i = -D_i \nabla n_i - \frac{\sigma_i}{e} \underline{E} \quad (6.1.1)$$

$\underline{J}_i$  is a flux representing the number of ions passing through unit area per second; it is not an electric current density. The conductivity,  $\sigma_i$ , is divided by the electric charge,  $e$ , in the second term to make the conversion and the conductivity is related to the ion mobility,  $\mu_i$ , through

$$\sigma_i = n_i z_i e \mu_i \quad (6.1.2)$$

where  $z_i$  is the charge carried by the ion, giving:

$$\underline{J}_i = -D_i \nabla n_i - n_i z_i \mu_i \underline{E} \quad (6.1.3)$$

Mobility,  $\mu_i$ , is related to the diffusivity through the Einstein relation,

$$\mu_i = \frac{e}{k_B T} D_i = \frac{F}{RT} D_i \quad (6.1.4)$$

The current density divergence is related to ion density changes through

$$\frac{\partial n_i}{\partial t} = -\nabla J_i \quad (6.1.5)$$

giving, with substitution in of Equation 6.1.4:

$$\begin{aligned} \frac{\partial n_i}{\partial t} &= -\nabla(-D_i \nabla n_i - n_i z_i \mu_i \underline{E}_i) \\ &= D_i \nabla^2 n_i + z_i \mu_i \nabla(n_i \underline{E}) \\ &= D_i \nabla^2 n_i + z_i \mu_i (n_i \nabla \underline{E} + \underline{E} \nabla n_i) \\ &= D_i (\nabla^2 n_i + \frac{z_i F}{RT} (n_i \nabla \underline{E} + \underline{E} \nabla n_i)) \end{aligned}$$

Taking  $n_i = C_i C_i^*$  where  $C_i^*$  is the bulk concentration and  $C_i$  is a relative concentration gives:

$$\frac{\partial C_i}{\partial t} = D_i (\nabla^2 C_i + \frac{z_i F}{RT} (C_i \nabla \underline{E} + \underline{E} \nabla C_i)) \quad (6.1.6)$$

In one dimension, in this case  $x$ , this reduces to:

$$\frac{\partial C_i}{\partial t} = D_i \left( \frac{\partial^2 C_i}{\partial x^2} + \frac{z_i F}{RT} \left( C_i \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial \phi}{\partial x} \cdot \frac{\partial C_i}{\partial x} \right) \right) \quad (6.1.7)$$

which is identical to the Zhurov form (see Zhurov *et al.* Equation 2.3).

The Nernst condition, at the interface between the two liquids, results in a current and charge separation occurring which produces an opposing field. Under certain conditions, when the ion ratios are equal and opposite across the interface, the ion densities tend towards a steady state which can be used to test the long-term behaviour of the dynamic model. When this symmetry is not exact, there is no true steady state, the positive and negative ion densities tend to cancel at large distances away from the interface and diffusion continues, establishing a double layer.<sup>[193]</sup> Here the problem is re-examined using a temporal split-step technique, similar to that used in nonlinear optics. The nonlinearity is first ignored, light is propagated a short distance and then the nonlinearity is included as a correction. The approach is proven and delivers accurate results to nonlinear optics problems provided the propagation distance is short. The same approach can be used to study the nonlinear diffusion equations in the ITIES problem. Here the ion densities are allowed to evolve for a short time under the influence of a constant electric field, after which the new charge distributions are used to update the electric field. This process is stable and accurate provided the process is iterated and the iteration time step is short compared with the characteristic diffusion time. Convergence can be checked and time-steps optimised by examining how the results are affected when the number of iterations is increased.

### 6.1.2 Electrolyte ion (carrier) diffusion in the ITIES system

Our initial studies concentrated on the direct solution of the ion diffusion equations. Due to the difficulties of including the Nernst boundary condition, a method based upon the finite difference approach was pursued.

In this approach the sample is divided into a series of cells (see Figure 6.1.1). The concentrations and potentials were evaluated at the positions represented by the solid lines and they were used to calculate the derivatives ( $\frac{\partial \phi_i}{\partial x}$ ) and the currents ( $J_{i,}$ ) in the middle of the cells, represented by the dashed lines. Increases

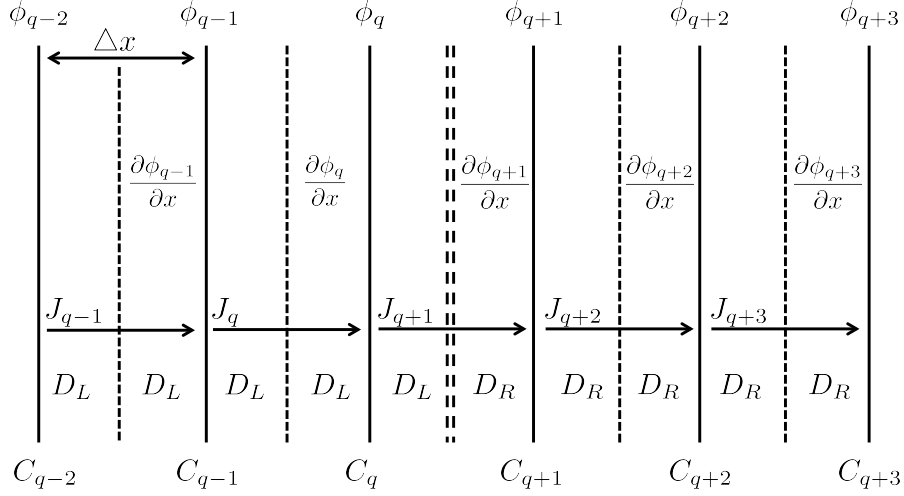


**Figure 6.1.1** – A schematic of the region near the ITIES interface (double dashed line) showing how currents and derivatives are calculated at the centre of each cell. The solid lines indicate the positions where the concentrations and potentials are known. Current,  $J_i$ , flows into element,  $i$ , and is driven by the potential gradient,  $\frac{\partial \phi_i}{\partial x}$  at the middle of each cell. The concentration at the middle of each cell is taken as the average of the neighbouring concentrations.

in the concentrations at the solid lines were evaluated by taking into account any differences between the calculated currents.

The electrolyte density was discretised in both space and time. Here the position in the sample,  $x = j\Delta x$ , and the time,  $t = n\Delta t$ , where  $j$  and  $n$  are integers, so that  $C_i(x, t) = C_{i,j}^n$ ,  $C_i(x, t + \Delta t) = C_{i,j}^{n+1}$ , and  $C_i(x + \Delta x, t) = C_{i,j+1}^n$ .

The interface is between the solid lines at  $\phi_q$  and  $\phi_{q+1}$ , represented by the double dashed line with the diffusion coefficients changing from  $D_L$  on the left hand side of the interface to  $D_R$  on the right hand side. Current within the cell is continuous, the different diffusion coefficients, and the Nernst condition, means however that the ion density is discontinuous. The Nernst condition sets the ratio of the ion densities on either side of the interface, thereby effectively producing a current source within the cells.

Current  $J_i$  flows into element  $i$  and is driven by the field at the middle of each cell. The concentration at the middle of each cell is taken as the average of the neighbouring concentrations, whilst the field is evaluated from the difference in neighbouring potential values. With these definitions it is a simple matter to note

down the current density  $J_i$ , provided  $i$  is not equal to  $q + 1$ , which corresponds to the liquid-liquid interface.

Two contributions make up the current within the cell, the electrolyte diffusion and the electrolyte drift. In the following expressions concentration is measured in moles and the pre-factor  $\beta = \frac{z_i F}{RT}$  where  $z_i = \pm 1$  depending on whether the ion is positively (+1) or negatively (-1) charged.

If  $i < q + 1$  (i.e. Left of the interface):

$$\begin{aligned} J_i &= -D_L \left( \frac{\partial C}{\partial x} + \beta C \frac{\partial \phi}{\partial x} \right) \\ &= -D_L \left( \frac{C_i - C_{i-1}}{\Delta x} + \beta \frac{C_i - C_{i-1}}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \right) \\ &= a_i C_{i-1} + b_i C_i \end{aligned} \quad (6.1.8)$$

where,

$$\begin{aligned} a_i &= +\frac{D_L}{\Delta x} - \frac{\beta D_L}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \\ \beta_i &= -\frac{D_L}{\Delta x} - \frac{\beta D_L}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \end{aligned}$$

This relates the current flowing in between the nodes to the concentration values at the nodes. Similar expressions exist for all of the cells, including the cell containing the interface. As the current  $J_i$  flowing into element  $i$  and  $J_{i+1}$  is the current flowing out, the increase in concentration in the element in time  $\Delta t$  is given by:

$$\begin{aligned} \frac{C_i^{n+1} - C_i^n}{\Delta t} &= \frac{J_i - J_{i-1}}{\Delta x} = \frac{(a_i C_{i+1}^n + b_i C_i^n) - (a_{i+1} C_i^n + b_{i+1} C_{i+1}^n)}{\Delta x} \\ &= \frac{a_i C_{i+1}^n + (b_i - a_{i+1}) C_i^n - b_{i+1} C_{i+1}^n}{\Delta x} \end{aligned} \quad (6.1.9)$$

Where the time index,  $n$ , has been included explicitly. This equation is unstable when iterated over time ( $n$ ). This instability can be removed if the right hand side

of Equation 6.1.9 is re-written in terms of an average over time step  $n$  and time step  $n + 1$ , i.e.

$$\begin{aligned} \frac{C_i^{n+1} - C_i^n}{\Delta t} &= \frac{a_i C_{i+1}^{n+1} + (b_i - a_i) C_i^{n+1} - b_{i+1} C_{i+1}^{n+1}}{2\Delta x} \\ &+ \frac{a_i C_{i+1}^n + (b_i - a_{i+1}) C_i^n - b_{i+1} C_{i+1}^n}{2\Delta x} \end{aligned} \quad (6.1.10)$$

Collecting terms and multiplying through by  $\Delta t$  gives:

$$\begin{aligned} &C_{i-1}^{n+1} \left( -\frac{a_i \Delta t}{2\Delta x} \right) + C_i^{n+1} \left( 1 - \frac{(b_i - a_{i+1}) \Delta t}{2\Delta x} \right) + C_{i+1}^{n+1} \left( \frac{b_{i+1} \Delta t}{2\Delta x} \right) \\ &= C_i^n + \frac{\Delta t (a_i C_i^n - 1 + (b_i - a_{i+1}) C_i^n - b_{i+1} C_{i+1}^n)}{2\Delta x} \end{aligned}$$

The right hand side of this expression only depends on time step  $n$  and can be evaluated using the concentration from the previous time step. There is an equation for each position, value of  $i$ , and these can be written in matrix form. The equations can then be solved quickly using standard tri-diagonal matrix routines.

On the right hand side of the liquid interface the form of the equations is the same provided  $i \neq q + 1$ , hence the only difference is the diffusion coefficient giving:

$$\begin{aligned} a_i &= +\frac{D_L}{\Delta x} - \frac{\beta D_L}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \quad (i < q) \\ &= +\frac{D_R}{\Delta x} - \frac{\beta D_R}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \quad (i > q + 1) \end{aligned} \quad (6.1.11)$$

$$\begin{aligned} b_i &= -\frac{D_L}{\Delta x} - \frac{\beta D_L}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \quad (i < q) \\ &= -\frac{D_R}{\Delta x} - \frac{\beta D_R}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \quad (i > q + 1) \end{aligned} \quad (6.1.12)$$

These simple equations can be used to treat every cell, apart from the one containing the liquid interface. The diffusion process at the interface is addressed in the next section.

### 6.1.3 Treating the liquid interface

At the ITIES there are two conditions that must be met:

1. Charge is conserved within the system and therefore the current of the positive and negative ion species through the interface must be continuous.
2. The ratio of these positive and negative ion species either side of the interface must satisfy the Nernst condition.

As illustrated in Figure 6.1.1, the interface (double dashed line) is in the middle of a defined cell and this means that care must be taken when taking into account these two conditions. Ultimately, the aim is to derive an expression for the current at the interface. From this the matrix mechanism (Section 6.1.2) can be applied.

The concentration at the interface has two values, on the left hand side  $C_L^0$  and on the right  $C_R^0$ . Although the absolute concentrations are unknown at this stage, the ratio of these concentrations is fixed. However, the current of positive and negative charges is continuous at the boundary and can be expressed in terms of the ion gradients and fields, allowing the determination of the instantaneous absolute values.

On the left hand side of the interface the concentration gradient can be written as:

$$\frac{\partial C_L^0}{\partial x} = \frac{C_L^0 - C_q}{(\frac{\Delta x}{2})}$$

Similarly for the right hand side of the interface:

$$\frac{\partial C_R^0}{\partial x} = \frac{C_{q+1} - C_R^0}{(\frac{\Delta x}{2})}$$

The gradient of the potential in the current expressions is the same on both the left and right hand sides of the interface and the currents have the form (see Equation 6.1.8):

$$J_L^0 = -D_L \left( 2 \frac{C_L^0 - C_q}{\Delta x} + \beta C_L^0 \frac{\partial \phi_{q+1}}{\partial x} \right) \quad (6.1.13)$$

$$J_R^0 = -D_R \left( 2 \frac{C_{q+1} - C_R^0}{\Delta x} + \beta C_R^0 \frac{\partial \phi_{q+1}}{\partial x} \right) \quad (6.1.14)$$

Equating the two currents and writing the Nernst condition as  $C_L^0 = k C_R^0$ , where  $k$  is a constant, gives an expression for the concentration  $C_R^0$  (and hence  $C_L^0$ ) at the interface:

$$C_R^0 = \frac{1}{\alpha} (\delta C_{q+1} + C_q)$$

where,

$$\alpha = k + \frac{\beta}{2} k \frac{\partial \phi_{q+1}}{\partial x} \Delta x + \frac{D_R}{D_L} - \frac{\beta}{2} \frac{D_R}{D_L} \frac{\partial \phi_{q+1}}{\partial x} \Delta x$$

and

$$\delta = \frac{D_R}{D_L}$$

Substituting  $C_R^0$  back into the expression for  $J_R^0$  gives:

$$J_L^0 = a_{q+1} C_q + b_{q+1} C_{q+1}$$

where,

$$a_{q+1} = \left( \frac{2D_L}{\Delta x} - \frac{2\gamma D_L}{\Delta x} - \beta\gamma D_L \frac{\partial\phi_{q+1}}{\partial x} \right)$$

$$b_{q+1} = \left( -\frac{2\delta\gamma D_L}{\Delta x} - \beta\delta\gamma D_L \frac{\partial\phi_{q+1}}{\partial x} \right)$$

and  $\gamma = \frac{k}{a}$ .

When  $k = 1$  and  $D_L = D_R$  (equal diffusion coefficients either side of the interface),  $\delta = 1$ ,  $a = 2$  and  $\gamma = \frac{1}{2}$ , the expressions for  $a_{q+1}$  and  $b_{q+1}$  reduce to:

$$a_{q+1} = \left( \frac{D_L}{\Delta x} - \frac{\beta}{2} D_L \frac{\partial\phi_{q+1}}{\partial x} \right) \quad (6.1.15)$$

$$b_{q+1} = \left( -\frac{D_L}{\Delta x} - \frac{\beta}{2} D_L \frac{\partial\phi_{q+1}}{\partial x} \right) \quad (6.1.16)$$

Equation 6.1.15 and 6.1.16 are identical to those obtained in the bulk of the liquid. This is a useful check and therefore allows the algorithm to be completed.

#### 6.1.4 Summary of the time dependent algorithm

The currents found in the bulk of the liquid and at the interface have been expressed in terms of the neighbouring electrolyte concentrations:

$$J_i = a_i C_{i-1} + b_i C_i \quad (6.1.17)$$

The only difference lies in the coefficients  $a_i$  and  $b_i$ , given by the following expressions:

$$\begin{aligned}
a_i &= +\frac{D_L}{\Delta x} - \frac{\beta D_L}{2} \frac{\phi_i - \phi_{i+1}}{\Delta x} \quad (i \leq q) \\
&= \left( \frac{2D_L}{\Delta x} - \frac{2\gamma D_L}{\Delta x} - \beta\gamma D_L \frac{\phi_i - \phi_{i-1}}{\Delta x} \right) \quad (i = q+1, \text{ the interface}) \\
&= +\frac{D_R}{\Delta x} - \frac{\beta D_R}{2} \frac{\phi_i - \phi_{i-1}}{\Delta x} \quad (i > q+1) \\
b_i &= -\frac{D_L}{\Delta x} - \frac{\beta}{2} D_L \frac{\phi_i - \phi_{i+1}}{\partial x} \quad (i \leq q) \\
&= \left( -\frac{2\delta\gamma D_L}{\Delta x} - \beta\gamma D_L \frac{\phi_i - \phi_{i-1}}{\Delta x} \right) \quad (i = q+1, \text{ the interface}) \\
&= -\frac{D_R}{\Delta x} - \frac{\beta D_R}{2} \frac{\phi_i - \phi_{i+1}}{\partial x} \quad (i > q+1)
\end{aligned}$$

The tri-diagonal matrix is formed from the generating equation:

$$\begin{aligned}
C_{i-1}^{n+1} \left( -\frac{a_i \Delta t}{2\Delta x} \right) + C_i^{n+1} \left( 1 - \frac{(b_i - a_i) \Delta t}{2\Delta x} \right) \\
+ C_{i+1}^{n+1} \left( \frac{b_{i+1} \Delta t}{2\Delta x} \right) = C_i^n + \frac{\Delta t (a_i C_{i-1}^n + (b_i - a_{i+1}) C_i^n - b_{i+1} C_{i+1}^n)}{2\Delta x}
\end{aligned} \tag{6.1.18}$$

and standard matrix methods can be used to solve for  $C_i$ .

The description presented in this section allows the ion densities to be updated in the presence of a static electric field (i.e. field ON or OFF, not cycling as in a cyclic voltammogram) and forms one half of the split-step method.

### 6.1.5 Solving Poisson's equation

In this section the electrolyte ion (carrier) densities are used to update the field before the whole process is iterated. The matrix solution of Poisson's equation is a standard problem in one-dimension and forms the second half of the split-step approach. Poisson's equation has the usual form:

$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{\rho(x)}{\varepsilon_S \varepsilon_0} \tag{6.1.19}$$

where  $\varphi$  is the electric potential and  $\rho(x)$  is the charge density.  $\epsilon_S$  and  $\epsilon_0$  are the relative permittivity of the liquid within which the ions are present, and the permittivity of free space, respectively. Using a central difference approximation Equation 6.1.19 is discretised on a regular mesh with grid spacing  $\Delta x$ , for the  $i^{th}$  cell, giving:

$$\varphi_{i+1} + \varphi_{i-1} - 2\varphi_i = -\frac{\rho_i(\Delta x)^2}{\epsilon_S \epsilon_0} \quad (6.1.20)$$

which can be written in the matrix form  $M\varphi = Q\varphi$ , where:

$$M = \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & \dots \\ 1 & -2 & 1 & 0 & 0 & 0 & \dots \\ 0 & 1 & -2 & 1 & 0 & 0 & \dots \\ 0 & 0 & 1 & -2 & 1 & 0 & \dots \\ 0 & 0 & 0 & 1 & -2 & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & 0 & 0 & 1 \end{vmatrix} \quad (6.1.21)$$

$$\varphi = \begin{vmatrix} \varphi_1 \\ \varphi_2 \\ \dots \\ \varphi_n \end{vmatrix} \quad \text{and} \quad Q = \begin{vmatrix} V_1 \\ V_2 \\ \dots \\ V_n \end{vmatrix} \quad (6.1.22)$$

whose formal solution, with the potentials of the boundary fixed by the first and last rows of the matrix  $\varphi_1 = V_1$  and  $\varphi_n = V_n$ , is :

$$\varphi = M^{-1}Q \quad (6.1.23)$$

The algorithm was implemented in MATLAB<sup>®</sup> (see Appendix C for the MATLAB<sup>®</sup> coding) and accurately solved equation 6.1.19 for a specified analytical potential function.

The charge density due to the positive and negative ions, in an ITIES system, is

normally expressed in terms of ionic molar concentrations and therefore Equation 6.1.20 (i.e. Poisson's equation) can be modified to give:

$$\varphi_{i+1} + \varphi_{i-1} - 2\varphi_i = - \frac{(\Delta x)^2 F \sum_{Species, S} z_S C_i^S}{\varepsilon_S \varepsilon_0} \quad (6.1.24)$$

where  $F$  is Faraday constant (the charge carried by one mole of electrons,  $9.64853 \times 10^4 \text{ C mol}^{-1}$ ),  $C_i^S$  is the concentration of species  $S$  in the  $i^{th}$  cell, the summation extends over all ionic species and  $z_S$  is the charge carried by each ionic species (including sign). The Equations 6.1.19 to 6.1.24 forms the second half of the split-step model.

Choosing a time step shorter than a typical diffusion time and solving for the field and the ion distributions alternately, gives accurate and stable solutions to the applied field diffusion problem.

## 6.2 The steady state

In the steady state, the current densities and the electric field are constant with drift occurring in response to the self-consistent internal field. The three equations describing the ion distribution on one side of the liquid-liquid, ITIES are simply:

$$J_+ = -D_+ \left( \frac{\partial C_+}{\partial x} + \frac{zF}{RT} C_+ E \right) \quad (6.2.1)$$

$$J_- = -D_- \left( \frac{\partial C_-}{\partial x} - \frac{zF}{RT} C_- E \right) \quad (6.2.2)$$

$$\frac{\partial E}{\partial x} + \frac{zF(C_+ - C_-)}{\varepsilon_0 \varepsilon_1} = 0 \quad (6.2.3)$$

Here  $C_+$  and  $C_-$  are the ion concentrations whilst  $J_+$  and  $J_-$  are the ionic currents. The first two equations (6.2.1 & 6.2.2) describe the flow of positive and negative ions respectively, whilst the third equation (6.2.3) describes how differences in electrolyte ion concentrations modifies the internal field. When

there is no current flowing, drift due to the internal electric field is balanced by diffusion. The equation may be solved by writing the field in terms of the potential,  $E = -\frac{\partial\phi}{\partial x}$ , and setting the current densities to zero, giving:

$$C_+ = C^* \exp\left(-\frac{zF}{RT}(\phi - \phi_0)\right) \quad (6.2.4)$$

and

$$C_- = C^* \exp\left(\frac{zF}{RT}(\phi - \phi_0)\right) \quad (6.2.5)$$

Where  $\phi_0$  is the asymptotic potential at large  $x$  values. The potential satisfies the differential equation:

$$-\frac{\partial^2\phi}{\partial x^2} = -\frac{zF}{\varepsilon_0\varepsilon_1}C \left[ \exp\left(\frac{zF}{RT}(\phi - \phi_0)\right) - \exp\left(-\frac{zF}{RT}(\phi - \phi_0)\right) \right] \quad (6.2.6)$$

Writing

$$\bar{\phi} = \frac{zF}{RT}(\phi - \phi_0) \quad (6.2.7)$$

gives:

$$-\frac{\partial^2\phi}{\partial x^2} = -\frac{zF}{\varepsilon_0\varepsilon_1} \frac{zF}{RT} C^* [\exp(\bar{\phi}) - \exp(-\bar{\phi})] \quad (6.2.8)$$

Introducing the Debye length through

$$\frac{1}{l_D^2} = \frac{zF}{\varepsilon_0\varepsilon_1} \frac{zF}{RT} C^* \quad (6.2.9)$$

and the dimensionless quantity  $\zeta = \frac{x}{l_D}$  gives:

$$\frac{\partial^2\phi}{\partial \zeta^2} = [\exp(\bar{\phi}) - \exp(-\bar{\phi})] \quad (6.2.10)$$

Multiplying through by  $\frac{\partial\bar{\phi}}{\partial\zeta}$  and integrating term by term gives:

$$\frac{\partial^2\phi}{\partial \zeta^2} \frac{\partial\bar{\phi}}{\partial \zeta} = \left[ \exp(\bar{\phi}) \frac{\partial\bar{\phi}}{\partial \zeta} - \exp(-\bar{\phi}) \frac{\partial\bar{\phi}}{\partial \zeta} \right] \quad (6.2.11)$$

$$\frac{1}{2} \left( \frac{\partial \bar{\phi}}{\partial \zeta} \right)^2 = [\exp(\bar{\phi}) + \exp(-\bar{\phi})] + K_1 \quad (6.2.12)$$

where,  $K_1$  is an integration constant. At large  $\zeta$  when there is no current flowing, the field approaches zero,  $C_+$  approaches  $C_-$  and the potential tends to zero, consequently  $K_1 = -2$  and

$$\left( \frac{\partial \bar{\phi}}{\partial \zeta} \right) = \sqrt{2 [\exp(\bar{\phi}) + \exp(-\bar{\phi})] - 4} \quad (6.2.13)$$

The solution gives the concentrations and the field in terms of the parameter  $q(\zeta)$  :

$$C_+ = C^* \exp \left( \frac{zF}{RT} (\phi - \phi_0) \right) = C^* q(\zeta) \quad (6.2.14)$$

$$C_- = C^* \exp \left( -\frac{zF}{RT} (\phi - \phi_0) \right) = \frac{C^*}{q(\zeta)} \quad (6.2.15)$$

$$E(\zeta) = - \left( \frac{\partial \bar{\phi}}{\partial \zeta} \right) = - \sqrt{2 \left[ q(\zeta) + \frac{1}{q(\zeta)} \right] - 4} \quad (6.2.16)$$

Where,  $q(\zeta)$  is defined by

$$q(\zeta) = \tanh^2 \left( -\frac{1}{\sqrt{2}} (\zeta + \zeta_r) \right) \quad (6.2.17)$$

$$\zeta_r = +\sqrt{2} \tanh^{-1}(\sqrt{q_0}) \quad (6.2.18)$$

The parameter  $q_0$  fixes the potential at the boundary and is determined uniquely by the ratio of the ion concentrations at the interface through:

$$q_0 = \sqrt{\frac{C_+(0)}{C_-(0)}} = \exp \left( \frac{zF}{RT} (\phi_i - \phi_0) \right)$$

where,  $\phi_i$  is the potential at the boundary. The potential and the steady state ion densities are then fixed by the single variable  $q(\zeta)$ ,

$$C_{-}(\zeta) = \frac{C^{*}}{q(\zeta)'} \quad (6.2.19)$$

$$C_{+}(\zeta) = C^{*} q(\zeta) \quad (6.2.20)$$

and

$$\phi(\zeta) = \frac{RT}{zF} \ln q(\zeta) + \phi_0 \quad (6.2.21)$$

Results from these steady state expressions are shown as the black points in the figures in Section 6.3.

### 6.3 Initial results from the split-step ITIES code

The algorithms in Sections 6.1.4 and 6.1.5 were combined in a MATLAB<sup>®</sup> code (see Appendix B). In this section the initial results from the code and the dynamics are presented. It is shown that the long time behaviour obtained using the numerical method is in excellent agreement with the analytical steady state results obtained in Section 6.2.

Figure 6.3.1 show some initial outputs, from the split-step approach, for a simple example where the diffusion constants for the positive and negative species are identical. The solid and dashed lines represent the long time behaviour calculated using the split-step method, whilst the points were calculated using the analytical steady state model in Section 6.2. The relative permittivity is set equal either side of the boundary. This is an unphysical problem, but provides a simple problem to begin evaluating the split-step approach. The agreement with the steady state is encouraging and gives confidence in this approach. Figure 6.3.2 show how the ion densities (Figure 6.3.2 - Top) and the potential (Figure 6.3.2 - Bottom) evolves on the way to equilibrium (i.e. steady state).

As stated earlier, a true steady state only exists when the ion ratio at the boundary is exactly anti-symmetric. At long distances, from the interface, the positive and negative ion densities are approximately equal and the field term no longer constrains the ion motion. This results in a double layer near the interface, with diffusion continuing into the bulk of the liquid. Figure 6.3.3 shows the

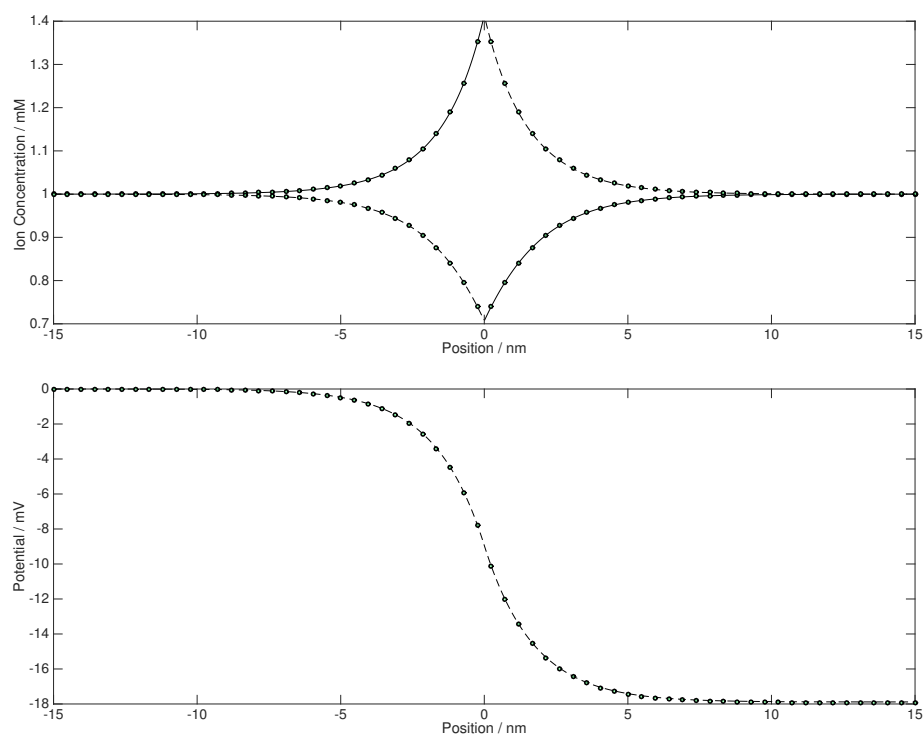


**Figure 6.3.1** – Initial outputs, long time behaviour, using the split-step approach in the case of identical diffusion coefficients for the positive and negative ions in the system. Top - ion concentrations (positive - solid line, negative - dashed line) at steady state (points). Bottom - potential curve with the black points representing the steady state.

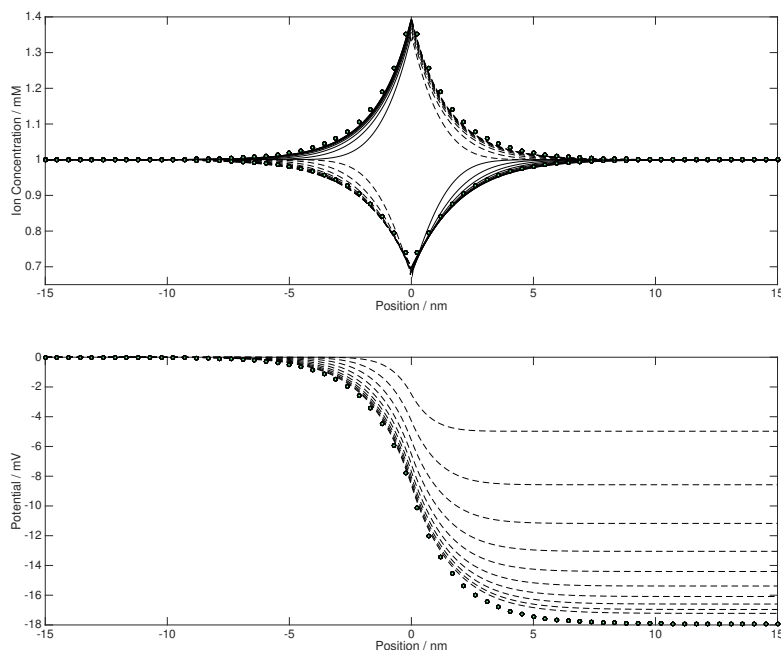


**Figure 6.3.2** – The evolving ion densities and potential on the way to steady state equilibrium., calculated every 200 ns.

effect of introducing a slight imbalance in the ion ratios and illustrates the charge cancellation effect which leads to a long diffusion tail in each liquid.

## 6.4 Conclusion

A temporal split-step integration scheme has been used to study ion transport at the interface between two immiscible liquids. It is shown that two very simple equations (Equations 6.1.17 and 6.1.18), describing current flow, can be used to treat the whole problem, both in the bulk and at the liquid interface:

- In the bulk material, the coefficients in the equations are determined from ion continuity arguments.
- At the interface the coefficients are modified slightly to take account of the Nernst boundary conditions.

The method has been found to be 10 - 20 times faster than previously reported approaches, with results that agree well with the steady state values and show

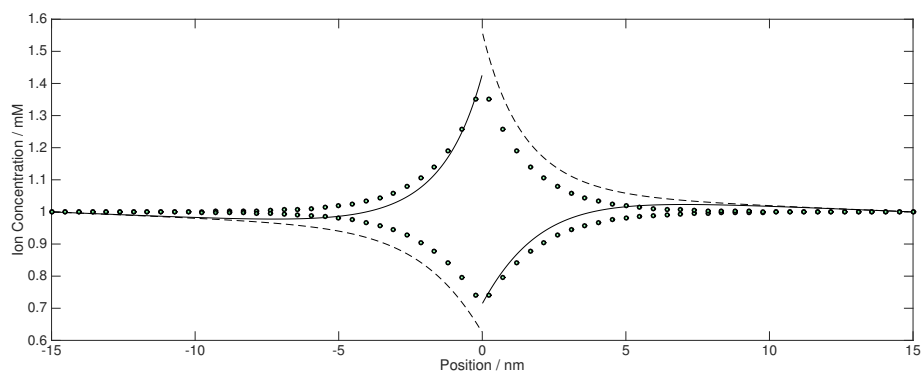


**Figure 6.3.3** – Effect of imbalances in ion ratios causing the formation of a long diffusion tail either side of the interface.

similar behaviour to that reported by Zhurov *et al.* It is anticipated that the method will shorten analysis timescales considerably.

Modification of the existing coding should allow the incorporation of a changing diffusion coefficient giving an opportunity to model the effects seen in Chapter 5, with the FCS experiments, the key requirement will be to take into account the continuity of the current and densities especially if applying a temporal and spatial change to the diffusion coefficient.



# Chapter 7

## Overall Conclusion

The ultimate aim of this project was to take the designability of ionic liquids and combine them with the novel extraction and sensing methodology offered by liquid-liquid, ITIES, electrochemistry for the selective, high sensitivity detection and identification of biomolecules while avoiding the inherent non-specific binding problems that exist with current surface based biosensors.

The ionic liquids synthesised here, when tested against the ‘model’ protein of cytochrome-c performed extremely well with extraction possible for all the ionic liquids synthesised, when using an agitation method and an ionophore. The incorporation of a terminal hydroxyl group proved to have a profound effect on the extraction efficiency especially at the short alkyl chain lengths. To test the application of ITIES extraction methods against protein biomolecules, electrochemical cells were designed from the seminal works of the founding fathers of the ITIES electrochemistry field. The reproducibility of not only their results but that of other workers in the field proved extremely promising. The melding together of these two promising areas has however proved to be fundamentally difficult. Initial experiments with the target macromolecule showed that:

- Cytochrome-c is extracted into a short chain hydroxyl functionalised imidazolium based bis(trifluoromethylsulfonyl)imide with near complete extraction.
- Cytochrome-c is drawn to the interface between the aqueous and ionic liquid phases under an applied field.

- However, once at the interface there is no transfer across into the ionic liquid and indeed there is a clear and obvious adsorption. This was counter to the results obtained with standard agitation experiments and has led to investigations into the diffusion of ions within an ionic liquid under an applied electric field.

Currently, the diffusion of ions within an ionic liquid is not fully understood. This is especially the case when extra variables such as a cycling or pulsing electric field is introduced; with the inclusion of varying ion concentrations, molecular volumes and binding events this can become even more complicated. This is an area that must be investigated further to gain a greater understanding of the nuances of ionic liquid responses under applied electric fields, and hence, the impact on ionic liquid based electrochemical methods. This work has started to explain this area through the first reported monitoring of the diffusivity of a probe molecule within an ionic liquid experiencing an applied electric field. The results to date confirm the differences in diffusivities as distance from an electrode varies. The results have also indicated a prolonged charging effect once the electric field is removed. This supports the use of hole migration theory to explain ion diffusion within those ionic liquids tested here. Additionally, initial work has shown the applicability of a temporal split-step integration scheme to study ion diffusion at the interface between two immiscible liquids, which has been found to be 10 - 20 times faster than existing approaches.

In summary:

- A range of ionic liquids have been synthesised and characterised focusing on their applicability to a liquid-liquid, ITIES, based electrochemical sensing platform.
- Liquid-liquid extraction, with these ionic liquids, via agitation has been confirmed as possible, and the incorporation of a terminal hydroxyl shown to be beneficial to the extraction capabilities of short alkyl chained imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids.
- Electrochemical cells have been produced that give reliable and reproducible results for a range of standard electrochemical methods, and

a frit based electrochemical cell has been shown to be preferable for high resistivity ionic liquid electrolytes. This frit based cell has been used to determine the potential windows of the synthesised ionic liquids and the stability of the design has meant that potential windows have been achieved that are wider than those reported in the literature.

- Liquid-liquid, ITIES, based extraction of cytochrome-c into the ionic liquids was not possible and investigations into the diffusion of ions within ionic liquids, experiencing an applied electric field, has for the first time been undertaken via FCS. This work has highlighted a possible persistence in the field effect once removed and this in combination with the main results supports the use of hole theory to describe ion migration in an ionic liquid.
- Ultrapure synthetic approaches have been developed to produce spectroscopically pure and clean ionic liquids for the use with SMF.
- A temporal split-step integration scheme has been developed which is 10 - 20 times faster than current approaches and initial calculations show its use for ion based diffusion across an interface.

Future work should be focused on the understanding of diffusion in ionic liquids. Until there is a greater understanding of the effects electric fields have on target analytes in ionic liquids (and on the ionic liquid cations and anions themselves) it is unlikely that ionic liquids can be used within a liquid-liquid, ITIES, based electrochemical sensing platform. However, the methods developed here offer a wealth of investigations to be undertaken in order to understand some of the fundamental properties of this rapidly developing group of novel functionalised solvents.



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# Appendix A

## Viscosity data

The tables provided here document the viscosity values recorded for the unfunctionalised (Table A.0.1) and the hydroxyl functionalised (Table A.0.2) ionic liquids over the temperature range of 15 - 75 °C:

| Temperature | Viscosity / Pa.s                |                                 |                                 |                                 |                                 |
|-------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|             | $[C_2C_{1im}][NTf_2]$           | $[C_3C_{1im}][NTf_2]$           | $[C_4C_{1im}][NTf_2]$           | $[C_6C_{1im}][NTf_2]$           | $[C_8C_{1im}][NTf_2]$           |
| 15 °C       | $0.039 \pm 7.21 \times 10^{-5}$ | $0.067 \pm 1.45 \times 10^{-4}$ | $0.079 \pm 1.27 \times 10^{-4}$ | $0.110 \pm 1.10 \times 10^{-4}$ | $0.147 \pm 2.04 \times 10^{-4}$ |
| 25 °C       | $0.027 \pm 4.30 \times 10^{-5}$ | $0.044 \pm 6.54 \times 10^{-5}$ | $0.051 \pm 3.46 \times 10^{-4}$ | $0.068 \pm 2.09 \times 10^{-4}$ | $0.088 \pm 1.23 \times 10^{-4}$ |
| 35 °C       | $0.019 \pm 3.98 \times 10^{-5}$ | $0.030 \pm 4.71 \times 10^{-5}$ | $0.034 \pm 5.57 \times 10^{-5}$ | $0.045 \pm 7.03 \times 10^{-5}$ | $0.056 \pm 5.70 \times 10^{-5}$ |
| 45 °C       | $0.015 \pm 4.25 \times 10^{-5}$ | $0.021 \pm 3.47 \times 10^{-5}$ | $0.025 \pm 3.53 \times 10^{-5}$ | $0.031 \pm 4.70 \times 10^{-5}$ | $0.038 \pm 6.47 \times 10^{-5}$ |
| 55 °C       | $0.012 \pm 5.24 \times 10^{-5}$ | $0.016 \pm 3.39 \times 10^{-5}$ | $0.018 \pm 5.17 \times 10^{-5}$ | $0.023 \pm 3.52 \times 10^{-5}$ | $0.027 \pm 4.79 \times 10^{-5}$ |
| 75 °C       | $0.008 \pm 4.89 \times 10^{-5}$ | $0.010 \pm 3.13 \times 10^{-5}$ | $0.011 \pm 3.29 \times 10^{-5}$ | $0.013 \pm 2.66 \times 10^{-5}$ | $0.015 \pm 2.33 \times 10^{-5}$ |

**Table A.0.1** – Viscosity values for the unfunctionalised ionic liquids, over a temperature range of 15 - 75 °C.

| Viscosity / Pa.s |                                                              |                                                              |                                                              |                                                              |  |
|------------------|--------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------|--|
| Temperature      | $[(\text{HO})^2\text{C}_2\text{C}_1\text{im}][\text{NTf}_2]$ | $[(\text{HO})^3\text{C}_3\text{C}_1\text{im}][\text{NTf}_2]$ | $[(\text{HO})^6\text{C}_6\text{C}_1\text{im}][\text{NTf}_2]$ | $[(\text{HO})^8\text{C}_8\text{C}_1\text{im}][\text{NTf}_2]$ |  |
| 15 °C            | $0.133 \pm 2.80 \times 10^{-4}$                              | $0.171 \pm 4.05 \times 10^{-4}$                              | $0.380 \pm 1.14 \times 10^{-3}$                              | $0.442 \pm 1.08 \times 10^{-3}$                              |  |
| 25 °C            | $0.078 \pm 2.31 \times 10^{-4}$                              | $0.099 \pm 1.81 \times 10^{-4}$                              | $0.200 \pm 1.45 \times 10^{-5}$                              | $0.229 \pm 1.99 \times 10^{-4}$                              |  |
| 35 °C            | $0.048 \pm 6.61 \times 10^{-5}$                              | $0.059 \pm 1.11 \times 10^{-4}$                              | $0.116 \pm 1.76 \times 10^{-5}$                              | $0.131 \pm 1.97 \times 10^{-4}$                              |  |
| 45 °C            | $0.032 \pm 6.85 \times 10^{-5}$                              | $0.040 \pm 5.80 \times 10^{-5}$                              | $0.072 \pm 7.15 \times 10^{-5}$                              | $0.081 \pm 1.20 \times 10^{-4}$                              |  |
| 55 °C            | $0.023 \pm 4.96 \times 10^{-5}$                              | $0.028 \pm 5.61 \times 10^{-5}$                              | $0.048 \pm 5.50 \times 10^{-5}$                              | $0.053 \pm 1.01 \times 10^{-4}$                              |  |
| 75 °C            | $0.013 \pm 4.64 \times 10^{-5}$                              | $0.016 \pm 4.24 \times 10^{-5}$                              | $0.025 \pm 3.26 \times 10^{-5}$                              | $0.027 \pm 4.31 \times 10^{-5}$                              |  |

**Table A.0.2** – Viscosity values for the hydroxyl functionalised ionic liquids, over a temperature range of 15 - 75 °C.



## Appendix B

### Autocorrelation Curves

Provided here are the autocorrelation curves, and their fits, for Rh123 in water (measured in the bulk), Rh123 in  $[C_4C_{1im}][NTf_2]$  (measured in the bulk) and Rh123 in  $[C_4C_{1pyrr}][NTf_2]$  (measured at the surface of the ITO coated slide). The determined fit parameters from the MATLAB® are given in Table B.0.1.

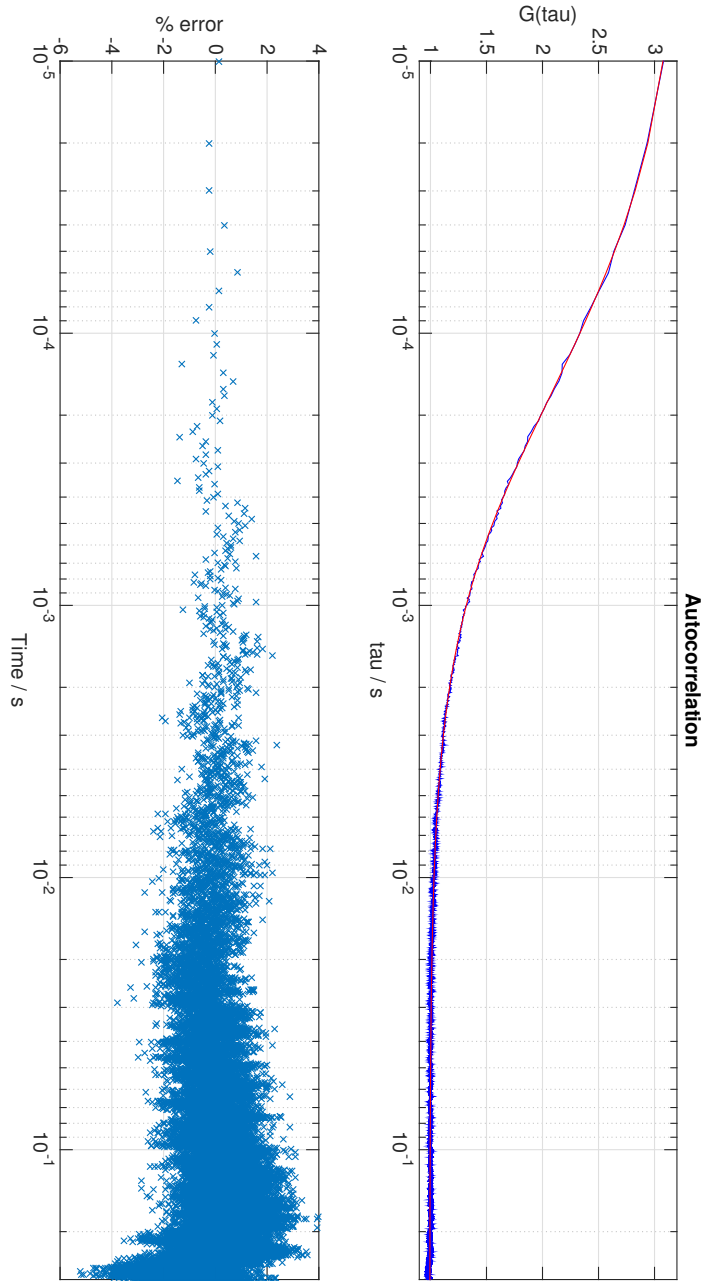


**Figure B.0.1** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for water, pre applied field, in the bulk.

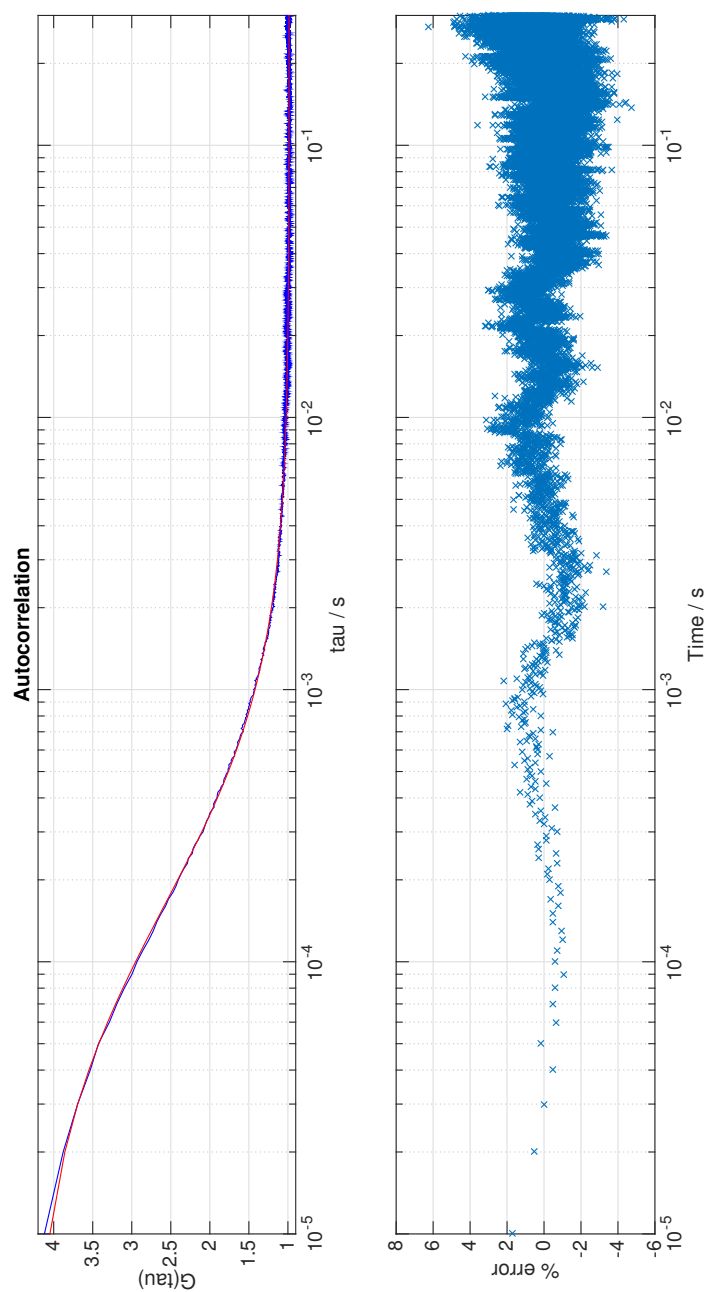


**Figure B.0.2** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for water, with a +3 V applied field, in the bulk.

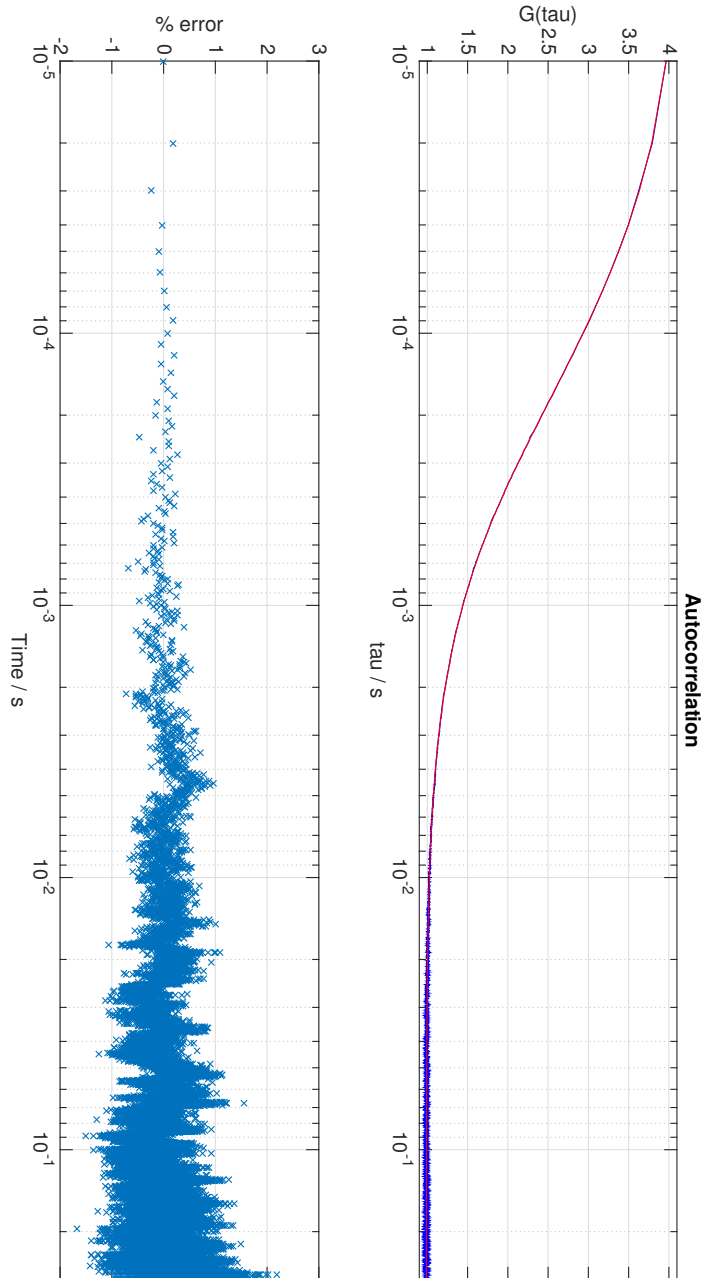


**Figure B.0.3** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for water, post applied field, in the bulk.

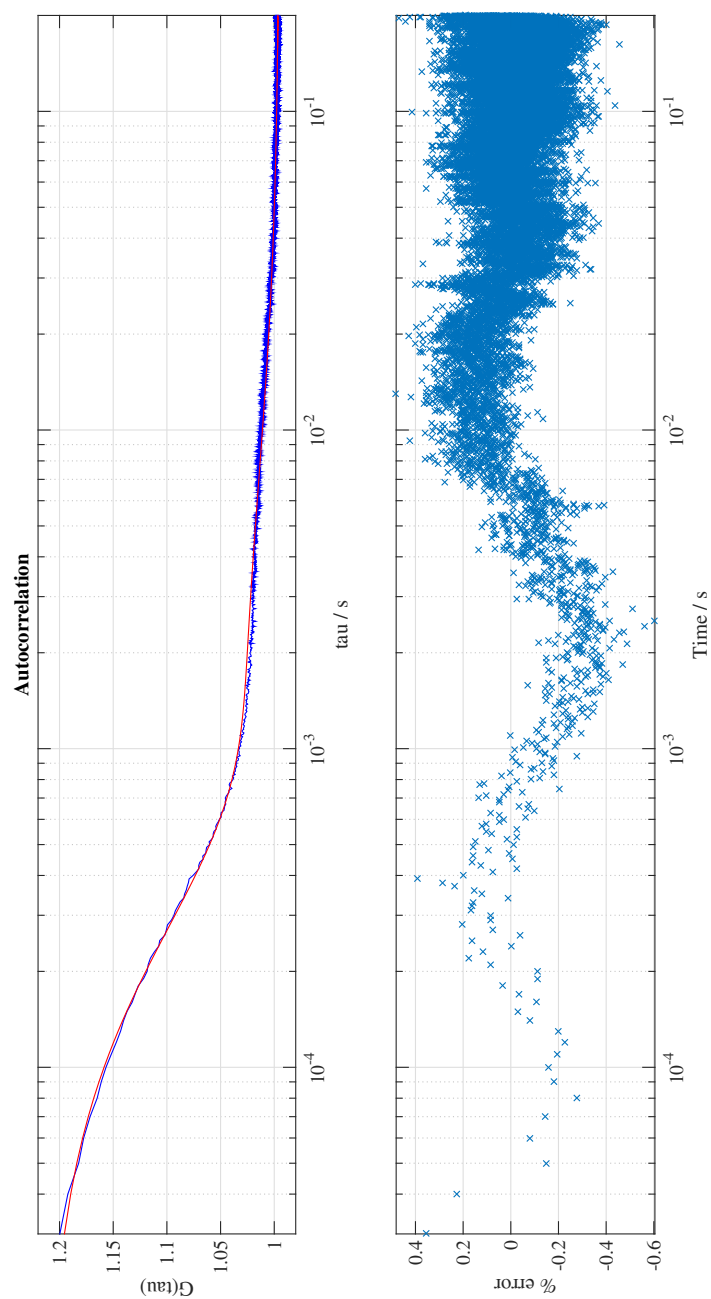


**Figure B.0.4** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_{1im}][NTf_2]$ , pre applied field, in the bulk.

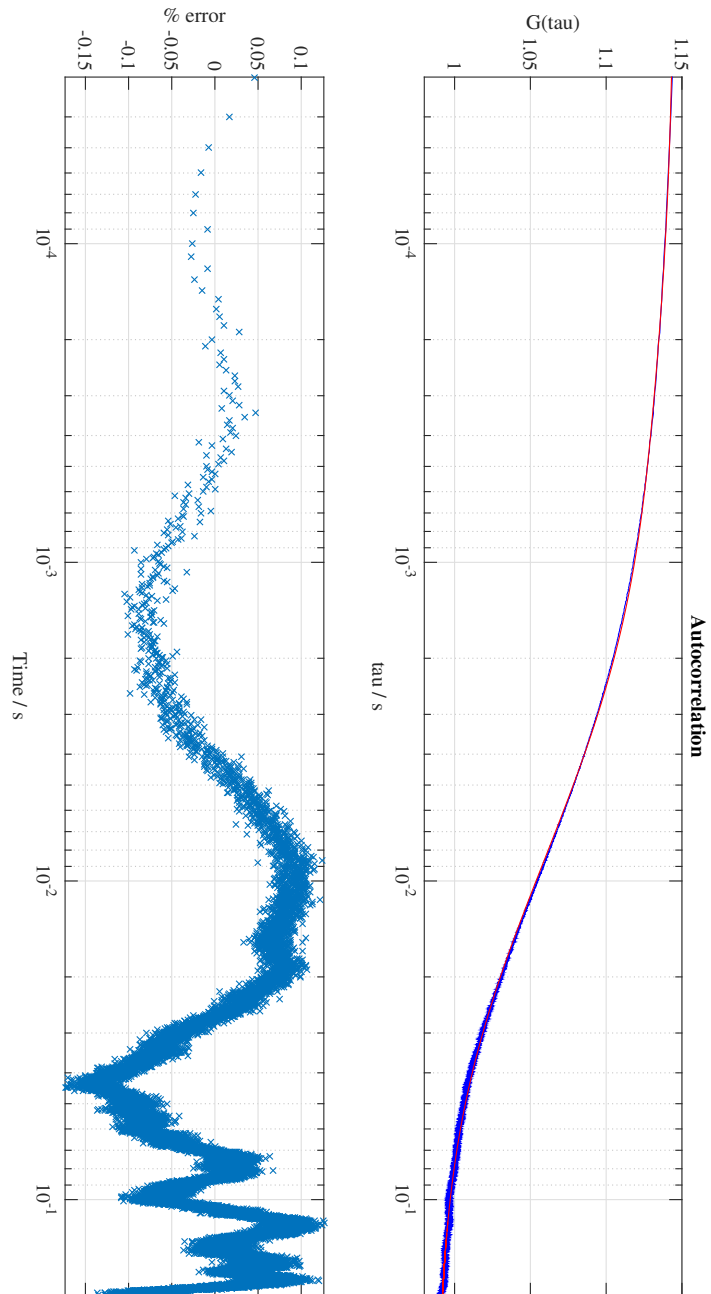


**Figure B.0.5** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4 C_1 \text{im}][\text{NTf}_2]$ , with a +3 V applied field, in the bulk.

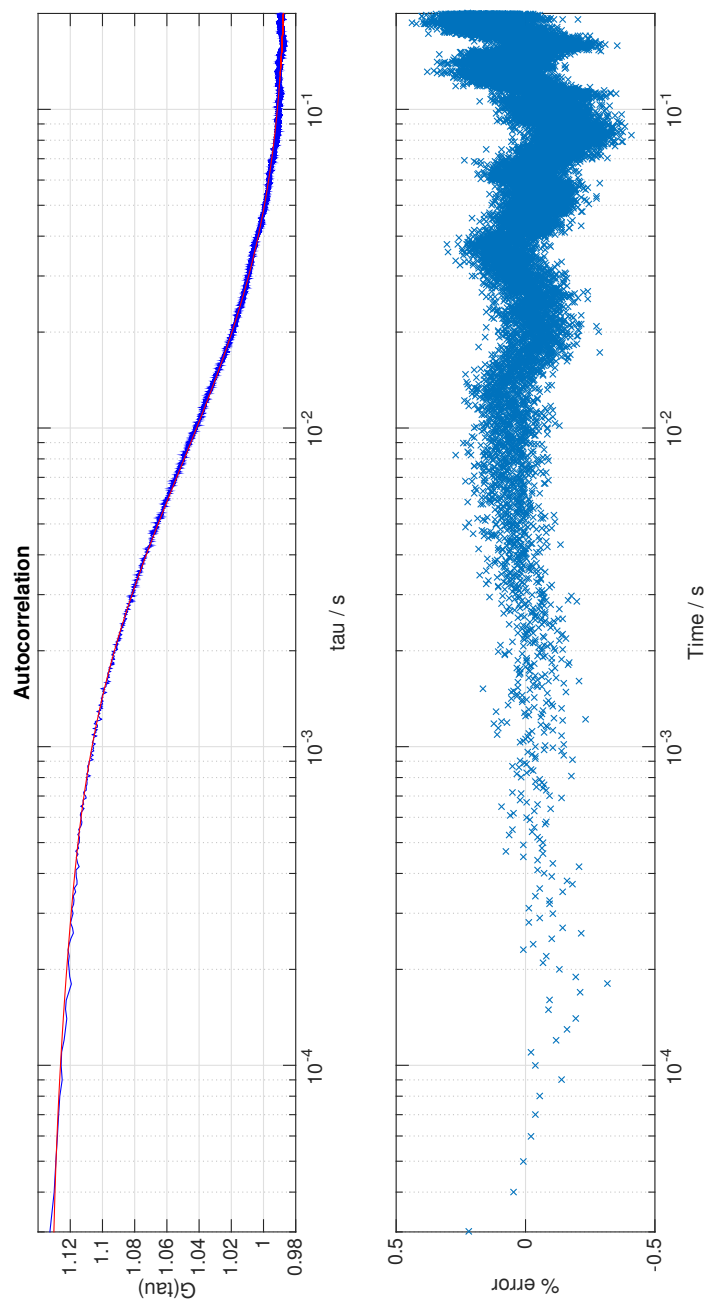


**Figure B.0.6** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_{1im}][NTf_2]$ , post applied field, in the bulk.

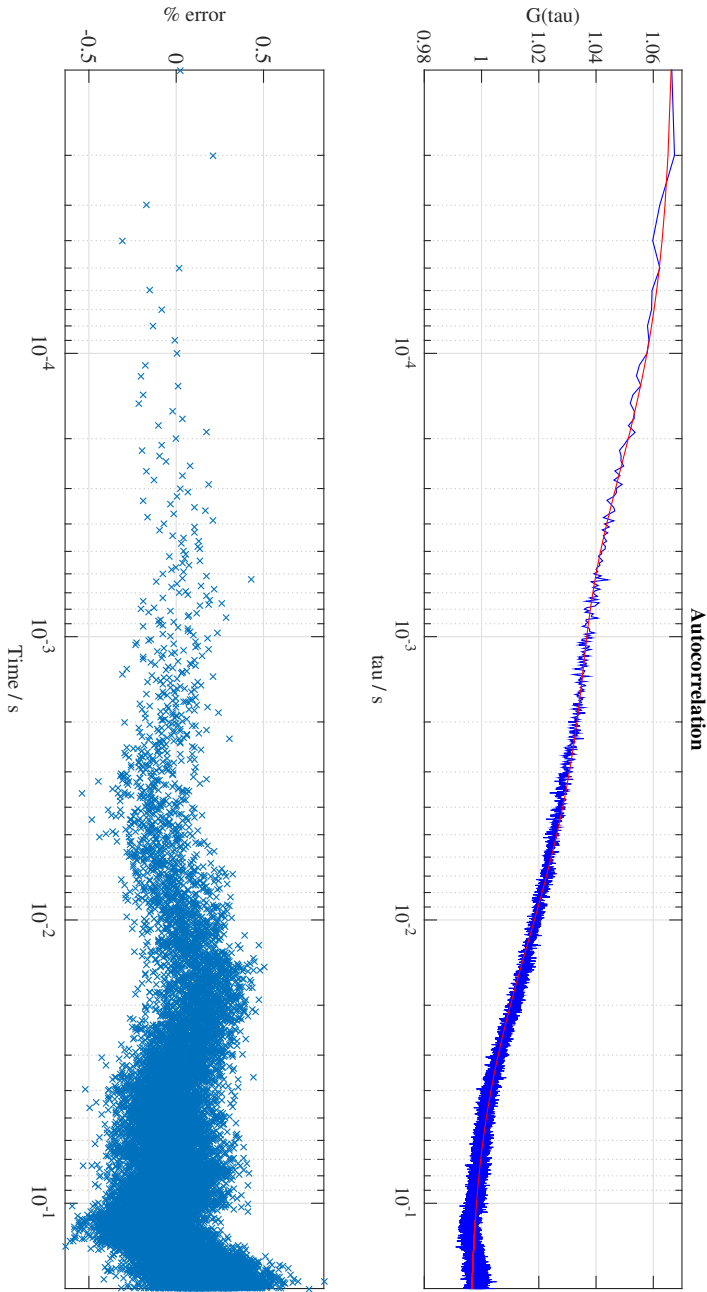


**Figure B.0.7** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_1pyrr][NTf_2]$ , pre applied field, at the surface.

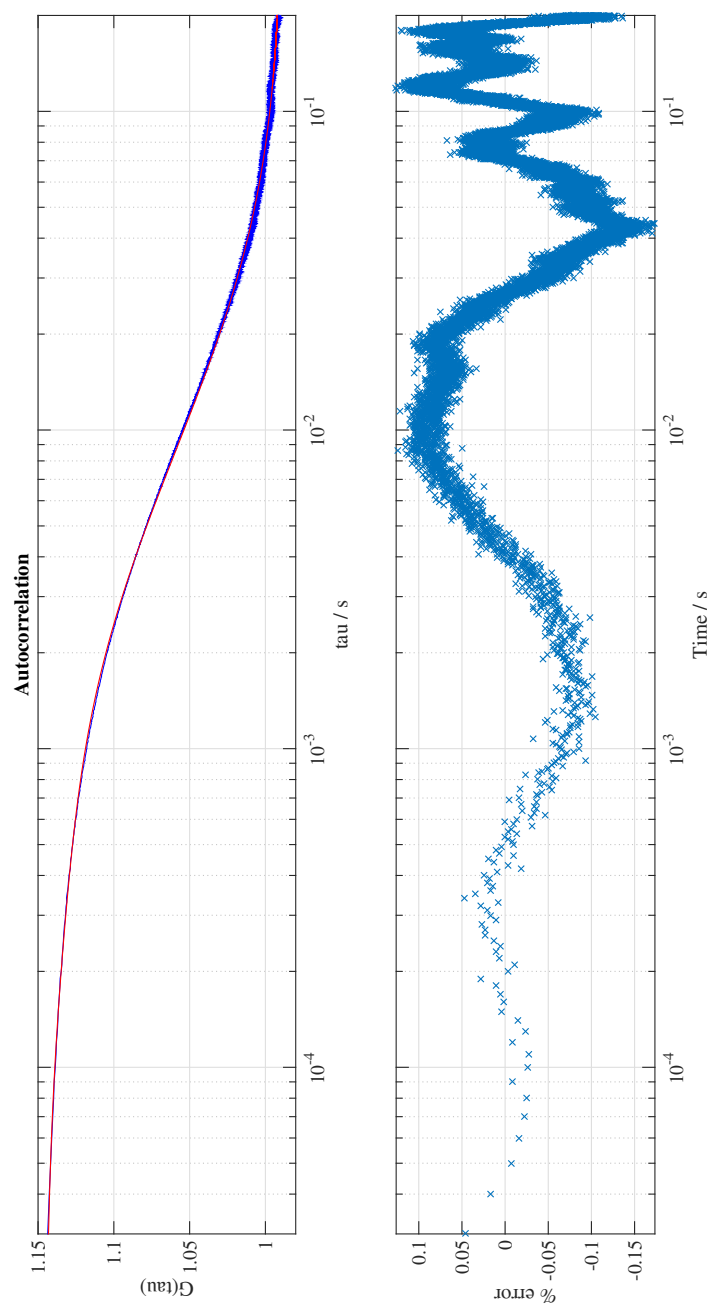


**Figure B.0.8** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[\text{C}_4\text{C}_1\text{pyrr}][\text{NTf}_2]$ , with a +3 V applied field, at the surface.

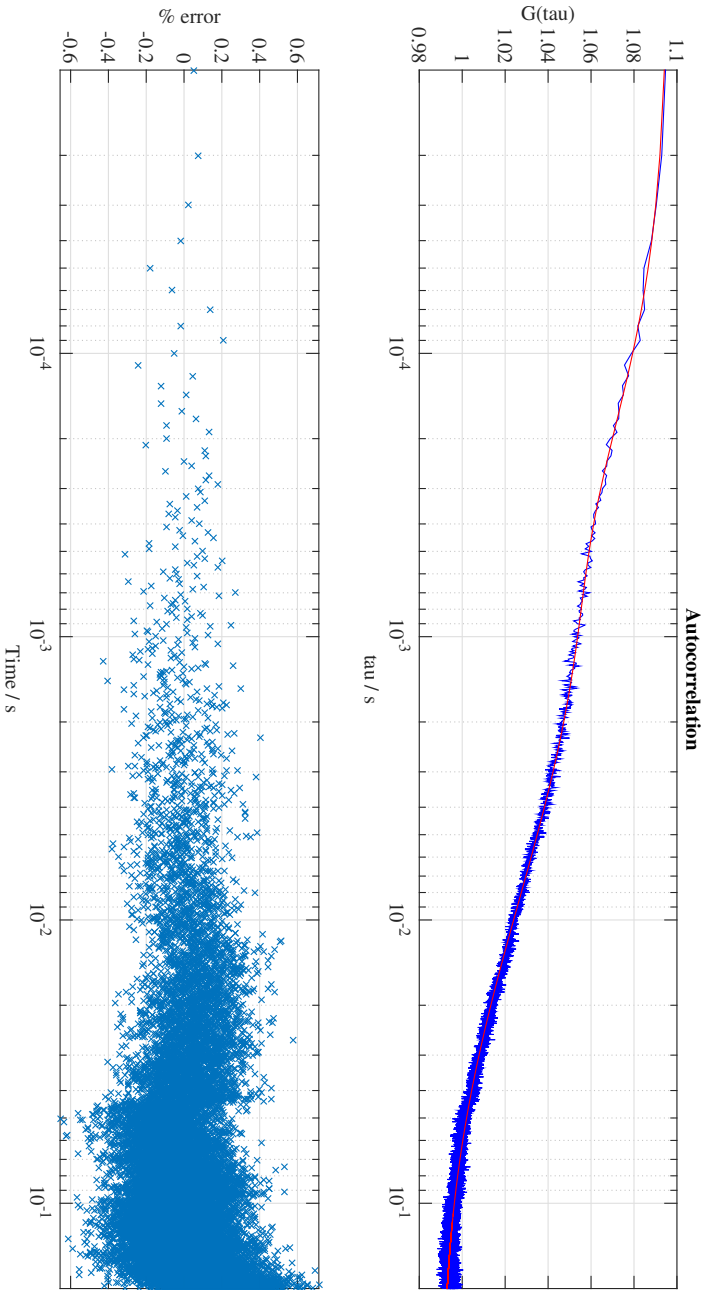


**Figure B.0.9** – Autocorrelation curve (Top - blue line), estimated fit (Top - red line) and the associated percentage error for  $[C_4C_1pyrr][NTf_2]$ , post applied field, at the surface.

| Determined Fit Parameters for the Autocorrelation Curve                              |                       |                        |       |                  |                       |       |
|--------------------------------------------------------------------------------------|-----------------------|------------------------|-------|------------------|-----------------------|-------|
|                                                                                      | $\tau_D$              | $\frac{z_0}{\omega_0}$ | $N$   | Background Corr. | $\tau_T$              | $F_T$ |
| Water, Pre applied field, Bulk                                                       | $1.92 \times 10^{-4}$ | 463.15                 | 0.45  | -0.0065          | $3.54 \times 10^{-5}$ | 0.098 |
| Water, +3 V applied field, Bulk                                                      | $1.71 \times 10^{-4}$ | 8.13                   | 0.30  | -0.0149          | $3.06 \times 10^{-5}$ | 0.050 |
| Water, Post field, Bulk                                                              | $1.97 \times 10^{-4}$ | 6.36                   | 0.31  | -0.0120          | $4.12 \times 10^{-5}$ | 0.080 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], Pre applied field, Surface    | $6.99 \times 10^{-3}$ | 499.83                 | 4.56  | -0.0047          | $2.85 \times 10^{-4}$ | 0.826 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], +3 V applied field, Surface   | $4.00 \times 10^{-2}$ | 0.33                   | 6.37  | -0.0116          | $1.50 \times 10^{-4}$ | 0.057 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], Post field, Surface           | $3.03 \times 10^{-2}$ | 0.37                   | 6.78  | -0.0150          | $1.17 \times 10^{-4}$ | 0.050 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], Pre applied field, Bulk       | $8.00 \times 10^{-2}$ | 503.23                 | 5.71  | -0.0086          | $3.24 \times 10^{-4}$ | 0.549 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], +3 V applied field, Bulk      | $6.70 \times 10^{-2}$ | 0.26                   | 3.92  | -0.0237          | $4.18 \times 10^{-4}$ | 0.152 |
| [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ], Post applied field, Bulk      | $6.00 \times 10^{-2}$ | 0.26                   | 4.20  | -0.0226          | $3.36 \times 10^{-4}$ | 0.121 |
| [C <sub>4</sub> C <sub>1</sub> pyrr][NTf <sub>2</sub> ], Pre applied field, Surface  | $1.82 \times 10^{-2}$ | 1.00                   | 13.93 | -0.0044          | $2.51 \times 10^{-4}$ | 0.385 |
| [C <sub>4</sub> C <sub>1</sub> pyrr][NTf <sub>2</sub> ], +3 V applied field, Surface | $8.78 \times 10^{-2}$ | 0.34                   | 5.88  | -0.0236          | $3.60 \times 10^{-4}$ | 0.339 |
| [C <sub>4</sub> C <sub>1</sub> pyrr][NTf <sub>2</sub> ], Post applied field, Surface | $8.32 \times 10^{-2}$ | 0.23                   | 9.48  | -0.0109          | $1.97 \times 10^{-4}$ | 0.326 |

**Table B.0.1** – Determined autocorrelation curve fit parameters for Chapter 5, Section 5.2.2.



# Appendix C

## MATLAB<sup>®</sup> Code

### C.1 Fluorescence Correlation Spectroscopy

The MATLAB<sup>®</sup> code provide (see Sections C.1.1 & C.1.2) was used for the fitting of the recorded autocorrelation curves, detailed in Chapter 5, to the autocorrelation model:

$$G(\tau) = \frac{1}{N} \left(1 + \frac{\tau}{\tau_D}\right)^{-1} \left(1 + \frac{\tau}{K^2 \tau_D}\right)^{-\frac{1}{2}} \left[ F_T \exp\left(-\frac{\tau}{\tau_T}\right) + (1 - F_T) \right] + DC$$

where,  $N$  is the average number of probe molecules (fluorescent molecules) within the observation volume,  $\tau_D$  is the molecular diffusion time (also known as the correlation time),  $F_T$  is the “triplet fraction”, i.e. the proportion of the diffusing molecules which spend time in the triplet state,  $\tau_T$  is the associated triplet crossing diffusion time,  $DC$  is the value when  $\tau \rightarrow \infty$  (which is typically  $DC = 1$ ) i.e. baseline offset,  $K = \frac{z_0}{\omega_0}$  where  $z_0$  is the  $\frac{1}{e^2}$  radii in the direction of the optical axis and  $\omega_0$  is the  $\frac{1}{e^2}$  radius perpendicular to the optical axis.

### C.1.1 Autocorr.m

```

1
2 clear all; close all; warning off;
3
4 set(0, 'defaultfigurecolor', {[] 1, 1, 1 {]});
5
6  \%\%\%Fits autocorrelation function including triplet ...
   contribution
7  but
8
9  \%\%\%ignoring surface contributions
10
11  \%\%\%\%\% PARAMETERS \%\%\%\%\%
12
13  file = '/Users/Alastair/Desktop/For Processing/20141114/...
        BmimNTf2\_Pos3V.Fcs';
14
15  filename='BmimNTf2\_Pos3V.Fcs'
16
17  Res = 10e-6;
18
19  StAuto = 30e-6; \% time: start of fit (s)
20
21  EnAuto = 2e-1; \% time: end of fit (s)
22
23  Type = 2;
24
25  \%\%\%\%\% Fitting Parameters \%\%\%\%\%
26
27  startingB(1) = 5e-2; \% Td (s)
28
29  lb(1) = 4e-2; ub(1) = 6e-2;
30
31  startingB(2)=0.01; \% R/d
32
33  lb(2) = 0; ub(2) = 1000;
34

```

```

35 startingB(3)= 7; \% N
36
37 lb(3) = 6; ub(3) = 8;
38
39 startingB(4)=1; \% bkg
40
41 lb(4) = -1.1; ub(4) = 1.1;
42
43 startingB(5) = 8e-5; \% Tb
44
45 lb(5) = 10e-6; ub(5) = 1e-3;
46
47 startingB(6) = 0.1; \% F Proportion of time molecules spend in ...
    the
48 triplet state.
49
50 lb(6) = 0; ub(6) = 0.2;
51
52 \% startingB(7) = 1e-3; \% Tf
53
54 \% lb(7) = 1e-5; ub(7) = 1e-1;
55
56 \% \% \% \% \% second comp \% \% \% \% \%
57
58 \% startingB(8) = 0.1; \% Td (s)
59
60 \% lb(8) = 1e-4; ub(8) = 1;
61
62 \%
63
64 \% startingB(9)=6; \% N
65
66 \% lb(9) = 1; ub(9) = 20;
67
68 \% startingB(5) = 4e-3; \% Tb
69
70 \% lb(5) = 1e-8; ub(5) = 1e-2;
71
72 \%

```

```

73
74  \% startingB(6) = 0.5; \% F
75
76  \% lb(6) = 0; ub(6) = 1;
77
78  \% \% \% \% \% end \% \% \% \% \%
79
80  {[ ]data FitParam3D{ ]] = Routine3D(file,StAuto,EnAuto,startingB,...
      ub,lb,Type,
81  Res, filename);
82
83  output\_file\_name = {[ ]filename 'autocor.mat' ]];
84
85  save(output\_file\_name)
86
87  \% FitParamAll3D(:,i) = FitParam3D'
88
89  \%FitParam3D = {[ ]diff\_time rad\_dep numb bkg Tb F{ ]];
90
91  \% {[ ]data TwocomFitParam3D{ ]] = Routine2com3D(file,StAuto,...
      EnAuto,startingB,ub,lb,Type,
92  Res);
93
94  \% FitParam2comAll3D(:,i) = TwocomFitParam3D'
95
96  \%FitParam3D = {[ ]diff\_time rad\_dep numb bkg Tb F{ ]];
97
98  \%{[ ]data FitParam2D{ ]] = Routine2D(file,StAuto,EnAuto,...
      startingB,ub,lb,Type);
99
100  \%FitParam2D = {[ ]diff\_time numb bkg Tb F{ ]];
101
102  \%{[ ]data FitParam1D{ ]] = Routine1D(file,StAuto,EnAuto,...
      startingB,ub,lb,Type);
103
104  \% \%FitParam1D = {[ ]diff\_time numb bkg Tb F{ ]];
105
106  \%{[ ]data FitParam1DFlow{ ]] = Routine1DFlow(file,StAuto,EnAuto,...
      startingB,ub,lb,Type,

```

```
107 Res);  
108  
109 \%{{data FitParam3DFlow{}} = Routine3DFlow(file,StAuto,EnAuto,...  
    startingB,ub,lb,Type,  
110 Res);  
111  
112 \%FitParam1DFlow = {{Td r/d numb bkg Tf{}}};
```

### C.1.2 Routine3D.m

```

1
2 function {[]data FitParam3D{}} = Routine3D(file,StAuto,EnAuto,...
    startingB,ub,lb,Type,Res,
3 filename);
4
5 raw = importdata(file);
6
7 \%raw = Original.data;
8
9 tol = 1e-9;
10
11 auto = raw(:,Type);
12
13 AutoCorTi = {[]1:length(auto){}}'{'*}Res;
14
15 Low = dsearchn(AutoCorTi,StAuto);
16
17 High = dsearchn(AutoCorTi,EnAuto);
18
19 AutoCorTi = AutoCorTi(Low:High);
20
21 auto = auto(Low:High);
22
23 figure(1)
24
25 subplot(2,1,1)
26
27 semilogx(AutoCorTi,auto,'b'); axis tight;
28
29 ylabel('G(tau)'); xlabel('tau (s)'); title('Autocorrelation');
30
31 set(gca,'Ylim',[[]0.98 1.14{[]}])
32
33 hold on;
34
35 \% Call fitting

```

```
36
37 options=optimset
38
39 ('Display','on','TolX',tol,'MaxFunEvals',10000,'MaxIter',10000,...
    'LargeScale','off');
40
41 AutoCorrVar = fmincon
42
43 ('autofn',startingB,{{}},{{}},{{}},{{}},lb,ub,{{}},...
    options,AutoCorTi,auto);
44
45 diff\_time = AutoCorrVar(1); \%diffusion time
46
47 rad\_dep = AutoCorrVar(2); \% radius /depth
48
49 numb= AutoCorrVar(3);\% number of molecules
50
51 bkg = AutoCorrVar(4);
52
53 Tb= AutoCorrVar(5);\% number of molecules
54
55 F = AutoCorrVar(6);
56
57 k = 1 + (AutoCorTi./diff\_time);
58
59 l = 1 + (AutoCorTi./diff\_time/rad\_dep/rad\_dep);
60
61 sec = sqrt(l);
62
63 m = (1./(k.*sec)).*(1-F+F*exp(-AutoCorTi./Tb));
64
65 AutoCorFit1 = 1+(1/(numb)).*m +bkg;
66
67 AutoCorFit = AutoCorFit1;\% + AutoCorFit2;
68
69 semilogx(AutoCorTi,AutoCorFit,'r');
70
71 subplot(2,1,2)
72
```

```

73 resA = (auto-AutoCorFit)./auto{*}100;
74
75 subplot(2,1,2)
76
77 semilogx(AutoCorTi,resA,'x'); axis tight;
78
79 ylabel('\% error')
80
81 xlabel('Time (s)')
82
83 saveas(gcf, {[]filename 'autocor.fig'[]});
84
85 FitParam3D = {[]diff\_time rad\_dep numb bkg Tb F[]};
86
87 w = 568e-9;
88
89 Td1 = AutoCorrVar(1);
90
91 D1 = w\textasciicircum{}2./(4{*}Td1); \%m2/s
92
93 D1 = D1 \%m2/s \%100{*}100 cm2/s
94
95 Td2 = AutoCorrVar(1);
96
97 D2 = w\textasciicircum{}2./(4{*}Td2); \%m2/s
98
99 D2 = D2 \%m2/s \%100{*}100 \%cm2/s
100
101 \%AutoCorrVar
102
103 data = {[]AutoCorTi auto AutoCorFit1[]];

```

## C.2 Theoretical modelling - electrolyte ion (carrier) diffusion across interfaces

The following code was that produced in Chapter 6 and is based upon a split-step integration scheme.

### C.2.1 Split-step model

```

1
2 function varargout = liqliqinterfaces(varargin)
3
4  \% LIQLIQINTERFACES M-file for liqliqinterfaces.fig \% ...
   LIQLIQINTERFACES,
5  by itself, creates a new LIQLIQINTERFACES or raises the ...
   existing \%
6  singleton{*}. \% \% H = LIQLIQINTERFACES returns the handle to ...
   a new
7  LIQLIQINTERFACES or the handle to \% the existing singleton{*}....
   \%
8  \% LIQLIQINTERFACES('CALLBACK',hObject,eventData,handles,...) ...
   calls
9  the local \% function named CALLBACK in LIQLIQINTERFACES.M with...
   the
10 given input arguments. \% \% LIQLIQINTERFACES('Property','Value...
   ',...)
11 creates a new LIQLIQINTERFACES or raises the \% existing ...
   singleton{*}.
12 Starting from the left, property value pairs are \% applied to ...
   the
13 GUI before liqliqinterfaces\_OpeningFcn gets called. An \% ...
   unrecognized
14 property name or invalid value makes property application \% ...
   stop.
15 All inputs are passed to liqliqinterfaces\_OpeningFcn via ...
   varargin.

```

```

16  \% \% {*}See GUI Options on GUIDE's Tools menu. Choose \...
    textquotedbl{}GUI
17  allows only one \% instance to run (singleton)\textquotedbl{}. ...
    \%
18  \% See also: GUIDE, GUIDATA, GUIHANDLES
19
20  \% Edit the above text to modify the response to help ...
    liqliqinterfaces
21
22  \% Last Modified by GUIDE v2.5 11-Feb-2015 07:29:32
23
24  \% Begin initialization code - DO NOT EDIT gui\_Singleton = 1; ...
    gui\_State
25  = struct('gui\_Name', mfilename, ... 'gui\_Singleton', gui\...
    _Singleton,
26  ... 'gui\_OpeningFcn', @liqliqinterfaces\_OpeningFcn, ... 'gui\...
    _OutputFcn',
27  @liqliqinterfaces\_OutputFcn, ... 'gui\_LayoutFcn', {[{}]} , ...
    ... 'gui\_Callback',
28  {[{}]}); if nargin && ischar(varargin\{1\}) gui\_State.gui\...
    _Callback
29  = str2func(varargin\{1\}); end
30
31  if narginout {[}varargout\{1:nargout\}{]} = gui\_mainfcn(gui\...
    _State,
32  varargin\{:}\}); else gui\_mainfcn(gui\_State, varargin\{:}\}); ...
    end
33  \% End initialization code - DO NOT EDIT end
34
35  \% --- Executes just before liqliqinterfaces is made visible. ...
    function
36  liqliqinterfaces\_OpeningFcn(hObject, eventdata, handles, ...
    varargin)
37  handles.output = hObject; guidata(hObject, handles); \% UIWAIT ...
    makes
38  liqliqinterfaces wait for user response (see UIRESUME) \% ...
    uiwait(handles.figure1);
39  end
40

```

```

41  \% --- Outputs from this function are returned to the command ...
    line.
42  function varargout = liqliqinterfaces\_OutputFcn(hObject, ...
    eventdata,
43  handles) varargout{1\} = handles.output; end
44
45  function diffLHSpos\_Callback(hObject, eventdata, handles) end
46
47  \% --- Executes during object creation, after setting all ...
    properties.
48  function diffLHSpos\_CreateFcn(hObject, eventdata, handles) if ...
    ispc
49  \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
50  set(hObject,'BackgroundColor','white'); end end
51
52  function diffRHSpos\_Callback(hObject, eventdata, handles) end
53
54  \% --- Executes during object creation, after setting all ...
    properties.
55  function diffRHSpos\_CreateFcn(hObject, eventdata, handles) if ...
    ispc
56  \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
57  set(hObject,'BackgroundColor','white'); end end
58
59  function diffLHSneg\_Callback(hObject, eventdata, handles) end
60
61  \% --- Executes during object creation, after setting all ...
    properties.
62  function diffLHSneg\_CreateFcn(hObject, eventdata, handles) if ...
    ispc
63  \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
64  set(hObject,'BackgroundColor','white'); end end
65
66  function V0\_Callback(hObject, eventdata, handles) end
67

```

```

68  \% --- Executes during object creation, after setting all ...
    properties.
69  function V0\_CreateFcn(hObject, eventdata, handles) if ispc ...
        \&\& isequal(get(hObject,'BackgroundColor'),
70  get(0,'defaultUicontrolBackgroundColor')) set(hObject,'...
        BackgroundColor','white');
71  end end
72
73  \% --- Executes on button press in calculate. function ...
    calculate\_Callback(hObject,
74  eventdata, handles) set(handles.stopexec,'Value',0.0) set(...
        handles.calculate,'String','Working...')
75  drawnow; {[ ]dummy{}}=liqliqcalc(hObject, eventdata, handles); ...
        set(handles.calculate,'String','Calculate')
76  drawnow; end
77
78  function maxx\_Callback(hObject, eventdata, handles) end
79
80  \% --- Executes during object creation, after setting all ...
    properties.
81  function maxx\_CreateFcn(hObject, eventdata, handles) if ispc ...
        \&\&
82  isequal(get(hObject,'BackgroundColor'), get(0,'...
        defaultUicontrolBackgroundColor'))
83  set(hObject,'BackgroundColor','white'); end end
84
85  function xrange\_Callback(hObject, eventdata, handles) end
86
87  \% --- Executes during object creation, after setting all ...
    properties.
88  function xrange\_CreateFcn(hObject, eventdata, handles) if ispc...
        \&\&
89  isequal(get(hObject,'BackgroundColor'), get(0,'...
        defaultUicontrolBackgroundColor'))
90  set(hObject,'BackgroundColor','white'); end end
91
92  function diffRHSneg\_Callback(hObject, eventdata, handles) end
93

```

```

94  \% --- Executes during object creation, after setting all ...
    properties.
95  function diffRHSneg\_CreateFcn(hObject, eventdata, handles) if ...
        ispc
96  \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
        defaultUicontrolBackgroundColor'))
97  set(hObject,'BackgroundColor','white'); end end
98
99  function maxt\_Callback(hObject, eventdata, handles) end
100
101  \% --- Executes during object creation, after setting all ...
    properties.
102  function maxt\_CreateFcn(hObject, eventdata, handles) if ispc ...
        \&\&
103  isequal(get(hObject,'BackgroundColor'), get(0,'...
        defaultUicontrolBackgroundColor'))
104  set(hObject,'BackgroundColor','white'); end end
105
106  function {[]dummy{}}=liqliqcalc(hObject, eventdata, handles)
107
108  Vstore={[]0,0{}}; Jstore={[]0,0{}};
109
110  \%print('test.jpg'); tempinK=300.0;
111
112  F=96368.0; R=8.31174; beta=F/(R{*}tempinK);
113
114  \%NB a constant permittivity of 2.5 is assumed for both liquids...
        \%couplingcoeff=str2double(get(handles.couplingcoeff,'...
        String'));
115  \%couplingcoeff=1.0;
116
117  \%fieldcarriercoupling=get(handles.fieldcarriercoupling,'Value...
        ');
118  dirlabel={[]'/Users/Alastair/Desktop/SplitStep/',datestr(now...
        ,30){}};
119  set(handles.cdirlabel,'String',dirlabel) mkdir({[]dirlabel{}}) ...
        fileout
120  = fopen({[]dirlabel,'/simdat.dat'{}},'a');
121

```

```

122 numpts=1024; fprintf(fileout, 'numpts= %g \textbackslash{}r', ...
    numpts);
123
124 V1=str2double(get(handles.V1, 'String')); fprintf(fileout, '...
    Voltage
125 V1(V)= %g \textbackslash{}r', V1);
126
127 V2=str2double(get(handles.V2, 'String')); V2=get(...
    handles.sliderV2, 'Value');
128 set(handles.cvolts, 'String', {[ ]'Voltage V2(V)', num2str(V2){ ]}); ...
    fprintf(fileout, 'Voltage
129 V2(V)= %g \textbackslash{}r', V2);
130
131 diffLHSpes=str2double(get(handles.diffLHSpes, 'String')); ...
    fprintf(fileout, 'Positive
132 ion diffusion coefficient for LHS= %g \textbackslash{}r', ...
    diffLHSpes);
133
134 diffLHSneg=str2double(get(handles.diffLHSneg, 'String')); ...
    fprintf(fileout, 'Negative
135 ion diffusion coefficient for LHS= %g \textbackslash{}r', ...
    diffLHSneg);
136
137 diffRHSpes=str2double(get(handles.diffRHSpes, 'String')); ...
    fprintf(fileout, 'Positive
138 ion diffusion coefficient for RHS= %g \textbackslash{}r', ...
    diffRHSpes);
139
140 diffRHSneg=str2double(get(handles.diffRHSneg, 'String')); ...
    fprintf(fileout, 'Negative
141 ion diffusion coefficient for RHS= %g \textbackslash{}r', ...
    diffRHSneg);
142
143 xrange=str2double(get(handles.xrange, 'String')); fprintf(...
    fileout, 'xrange=
144 %g \textbackslash{}r', xrange);
145
146 minx=-xrange/2.0; maxx=-minx;
147

```

```

148 \%V0=str2double(get(handles.V0,'String')); \%fprintf(fileout,'...
    Voltage
149 applied= \%g \textbackslash{}r',V0);
150
151 maxt=str2double(get(handles.maxt,'String')); fprintf(fileout,'...
    Maximum
152 time= \%g \textbackslash{}r',maxt);
153
154 numtsteps=str2double(get(handles.numtsteps,'String')); fprintf(...
    fileout,'Number
155 of time steps= \%g \textbackslash{}r',numtsteps);
156
157 \% start solving the equations here and work with molar ...
    concentrations
158 \%backconc=1.0; \%backconc=0.01; backconc=str2double(get(...
    handles.backconc,'String'));
159 fprintf(fileout,'backconc(M)= \%g \textbackslash{}r',backconc);...
    x=linspace(minx,maxx,numpts);
160 phi=linspace(0,0,numpts); V=linspace(0,0,numpts); numpoints=64;...
    xpoints=linspace(minx,maxx,numpoints);
161
162 nlpos=backconc.*ones(1,numpts); nlneg=backconc.*ones(1,...
    numpts);
163
164 kplus=str2double(get(handles.kplus,'String')); fprintf(fileout,...
    'kplus=
165 \%g \textbackslash{}r',kplus); kminus=str2double(get(...
    handles.kminus,'String'));
166 fprintf(fileout,'kminus= \%g \textbackslash{}r',kminus); \%...
    leftconcpos=2.0{*}backconc./(kplus+1.0);
167 \%rightconcpos=kplus.*leftconcpos; \%rightconcneg=2.0{*}...
    backconc./(kminus+1.0);
168 \%leftconcneg=kminus.*rightconcneg;
169
170 hold(handles.potential,'off'); hold(handles.carriers,'off'); ...
    numtsteps=str2double(get(handles.numtsteps,'String'));
171 fprintf(fileout,'numtsteps= \%g \textbackslash{}r',numtsteps); ...
    dt=maxt/numtsteps;
172 tplots=str2double(get(handles.tplots,'String'));

```

```

173
174 fprintf(fileout, 'Time between plots(s)= %g \textbackslash{}r', ...
    tplots);
175 numplots=floor(maxt./tplots); plotstep=floor(numtsteps./...
    numplots);
176
177 if (plotstep<1) plotstep=1; end \%plotstep=10;
178
179 \%potential of left hand electrode is defined as V1;
180
181 k=0; timenow=0.0; while ((get(handles.stopexec, 'Value')==0) ...
    \&\&(timenow<=maxt))
182 \%get(handles.stopexec, 'Value') k=k+1; timenow=timenow+dt; set(...
    handles.ctime, 'String', {[ ]'Time', num2str(timenow), '
183 (s) ' [ ]})
184
185 Vinterface=phi(numpts/2); Vinterface=0.0;
186
187 zi=1.0; {[ ]noutpos, Joutpos{ ]}=diffuse\_with\_milsom\_boundary\_...
    \_conditions\_mod(kplus{*}exp(beta{*}Vinterface), backconc, x, ...
    nlpos, numpts, phi, diffRHSpos, diffLHSpos, dt, tempinK, zi);
188 zi=-1.0; {[ ]noutneg, Joutneg{ ]}=diffuse\_with\_milsom\_boundary\_...
    \_conditions\_mod(kminus{*}exp(-beta{*}Vinterface), backconc, x...
    , nlneg, numpts, phi, diffRHSneg, diffLHSneg, dt, tempinK, zi);
189 nlpos=noutpos; nlneg=noutneg;
190
191 rho=noutpos-noutneg; zerofield=get(handles.zerofield, 'Value'); ...
    V1=str2double(get(handles.V1, 'String'));
192 \%fprintf(fileout, 'Voltage V1(V)= %g \textbackslash{}r', V1);
193
194 V2=str2double(get(handles.V2, 'String')); V2=get(...
    handles.sliderV2, 'Value');
195 set(handles.cvolts, 'String', {[ ]'Voltage V2(V) ', num2str(V2) [ ]});...
    \%fprintf(fileout, 'Voltage
196 V2(V)= %g \textbackslash{}r', V2); if (zerofield==1) {[ ]V{ ]}=...
    potzerofieldmod(x, rho, V1, numpts);
197 else {[ ]V{ ]}=pot4amod(x, rho, V1, V2, numpts); end ...
    fieldcarriercoupling=get(handles.fieldcarriercoupling, 'Value...
    ');

```

```

198 if (fieldcarriercoupling==1) phi=V; else phi=0.0{*}V; end
199
200 if (k==plotstep{*}floor(k/plotstep))
201
202   \%plot(handles.potential,x,V,'g'); \%xlabel(handles.potential,'...
      Position(m)');
203   \%ylabel(handles.potential,'Potential(V)'); \%drawnow dx=x(2)-x...
      (1);
204   posrat=nlpos(numpts/2)./nlpos(numpts/2+1); negrat=nlneg(numpts...
      /2)./nlneg(numpts/2+1);
205   poscarrierratio=[] 'Positive carrier density boundary ratio=',...
      num2str(posrat){}];
206   negcarrierratio=[] 'Negative carrier density boundary ratio=',...
      num2str(negrat){}];
207   set(handles.negcarrierratio,'String',negcarrierratio); set(...
      handles.poscarrierratio,'String',poscarrierratio);
208
209   plotcurrent=get(handles.plotcurrent,'Value'); if (plotcurrent...
      ==0)
210     \%eps0=8.854e-12; \%R=8.31174; \%F=96368.0; \%ld=sqrt(eps0.*)...
      R.*}tempinK./(backconc.*}(zi{*}F).\textasciicircum{2}));
211     \%figure(10); \%plot(x./ld,nlpos./backconc,'b'); hold on \%plot...
      (x./ld,nlneg./backconc,'r');
212     \%xlabel('Position(m)'); \%ylabel('Relative ionic concentration...
      (no
213     units)'); \%hold off \%drawnow {[{}phisteady,npossteady,...
      nnegsteady{]}=steadystate(xpoints,backconc,kplus);
214     steady=get(handles.steadystate,'Value'); plot(handles.potential...
      ,1e9.*}x,1e3.*}V,'--k','LineWidth',1);
215     xlabel(handles.potential,'Position(nm)','FontSize',19); ylabel(...
      handles.potential,'Potential(mV)','FontSize',19);
216     hold(handles.potential,'on') if (steady==1) plot(...
      handles.potential,1e9.*}xpoints,1e3.*}phisteady,'ok','...
      LineWidth',2,...
217     'MarkerEdgeColor','k',... 'MarkerFaceColor',[.49 1 .63{}],.....
      'MarkerSize',5);
218   end
219

```

```

220 drawnow plot(handles.carriers,1e9.*x(1:numpts/2),nlpos(1:...
    numpts/2),'-k','LineWidth',1);
221 hold on \% -k = black, solid plot(handles.carriers,1e9.*x(1:...
    numpts/2),nlneg(1:numpts/2),'--k','LineWidth',1);
222 \% --k = black, dashed plot(handles.carriers,1e9.*x(numpts...
    /2+1:numpts),nlpos(numpts/2+1:numpts),'-k','LineWidth',1);
223 hold on \% -k = black, solid plot(handles.carriers,1e9.*x(...
    numpts/2+1:numpts),nlneg(numpts/2+1:numpts),'--k','LineWidth...
    ',1);
224 \% --k = black, dashed if (steady==1) plot(handles.carriers,1E9....
    .*xpoints(1:numpoints/2),nnegsteady(1:numpoints/2),'ok','...
    LineWidth',2,...
225 'MarkerEdgeColor','k',... 'MarkerFaceColor',{[] .49 1 .63[]},.....
    'MarkerSize',5);
226 plot(handles.carriers,1E9.*xpoints(1:numpoints/2),npossteady...
    (1:numpoints/2),'ok','LineWidth',2,...
227 'MarkerEdgeColor','k',... 'MarkerFaceColor',{[] .49 1 .63[]},.....
    'MarkerSize',5);
228 plot(handles.carriers,1E9.*xpoints(numpoints/2+1:numpoints),...
    nnegsteady(numpoints/2+1:numpoints),'ok','LineWidth',2,...
229 'MarkerEdgeColor','k',... 'MarkerFaceColor',{[] .49 1 .63[]},.....
    'MarkerSize',5);
230 plot(handles.carriers,1E9.*xpoints(numpoints/2+1:numpoints),...
    npossteady(numpoints/2+1:numpoints),'ok','LineWidth',2,...
231 'MarkerEdgeColor','k',... 'MarkerFaceColor',{[] .49 1 .63[]},.....
    'MarkerSize',5);
232 end hold(handles.carriers,'on') xlabel(handles.carriers,'...
    Position(nm)','FontSize',19);
233 ylabel(handles.carriers,'Ion concentration(mmole)','FontSize'...
    ,19);
234 drawnow if (get(handles.holdprevious,'Value')==0) hold(...
    handles.potential,'off')
235 hold(handles.carriers,'off') end
236
237 else
238
239 jposLHS=-diffLHSpos.*((nlpos(2:numpts/2)-nlpos(1:numpts/2-1))...
    ./dx+....

```

```

240 0.5.*}(nlpos(2:numpts/2)+nlpos(1:numpts/2-1)).*}beta.*}(phi...
    (2:numpts/2)-phi(1:numpts/2-1))./dx);
241
242 jposRHS=-diffRHSpos.*}((nlpos(numpts/2+2:numpts)-nlpos(numpts...
    /2+1:numpts-1))./dx+....
243 0.5.*}(nlpos(numpts/2+2:numpts)+nlpos(numpts/2+1:numpts-1))....
    .*}beta.*}(phi(numpts/2+2:numpts)-phi(numpts/2+1:numpts-1))...
    ./dx);
244
245 jnegLHS=-diffLHSneg.*}((nlneg(2:numpts/2)-nlneg(1:numpts/2-1))...
    ./dx-....
246 0.5.*}(nlneg(2:numpts/2)+nlneg(1:numpts/2-1)).*}beta.*}(phi...
    (2:numpts/2)-phi(1:numpts/2-1))./dx);
247
248 jnegRHS=-diffRHSneg.*}((nlneg(numpts/2+2:numpts)-nlneg(numpts...
    /2+1:numpts-1))./dx-....
249 0.5.*}(nlneg(numpts/2+2:numpts)+nlneg(numpts/2+1:numpts-1))....
    .*}beta.*}(phi(numpts/2+2:numpts)-phi(numpts/2+1:numpts-1))...
    ./dx);
250 plot(handles.carriers,[[]x(1:numpts/2),x(numpts/2+1:numpts)...
    {}],[[]Joutpos(1:numpts/2),Joutpos(numpts/2+1:numpts){}],'-k...
    ','LineWidth',1);
251 hold(handles.carriers,'on'); plot(handles.carriers,[[]x(1:...
    numpts/2),x(numpts/2+1:numpts){}],{[]Joutneg(1:numpts/2),...
    Joutneg(numpts/2+1:numpts){}], '--k','LineWidth',1);
252 plot(handles.carriers,[[]x(1:numpts/2),x(numpts/2+1:numpts)...
    {}],[[]Joutpos(1:numpts/2),Joutpos(numpts/2+1:numpts){}]...
253 -{[]Joutneg(1:numpts/2),Joutneg(numpts/2+1:numpts){}], 'g', '...
    LineWidth',1);
254 set(handles.ccurrent,'String',[[]'Current(units?)=',num2str(...
    Joutpos(1)-Joutneg(1)){}])
255 if(get(handles.cgrabdata,'Value')==1) Vstore={[]Vstore,V2{}} ...
    Jstore={[]Jstore,Joutpos(1)-Joutneg(1){}}
256 figure(20) size(Vstore) size(Jstore) plot(Vstore,Jstore) set(...
    handles.cgrabdata,'Value',0)
257 end xlabel(handles.carriers,'Position(microns)','FontSize',19);...
    ylabel(handles.carriers,'Current','FontSize',19);
258 xlabel(handles.carriers,'Position(m)'); ylabel(handles.carriers...
    , 'Current (A) ');

```

```

259 if (get(handles.holdprevious,'Value')==0) hold(handles.carriers...
    , 'off');
260 end plot(handles.potential,1e6.*x,1e3.*V,'k','LineWidth',1)...
    ; xlabel(handles.potential,'Position(microns)','FontSize'...
    ,19);
261 ylabel(handles.potential,'Potential(mV)','FontSize',19); ...
    drawnow
262
263 end end
264
265 end fclose(fileout); dummy=1;
266
267 end
268
269 function {[V]}=potzerofieldmod(x,rho,V1,numpts) \%x contains ...
    the
270 position vector and rho the corresponding charge density \%V1 ...
    is potential
271 on the left hand boundary \%V2 is the potential on the right ...
    hand
272 boundary \%An even mesh containing numpts data points is ...
    assumed.
273
274 F=96368.0; perm=2.5; eps0=8.854E-12; \%assumes an even mesh dx=...
    x(2)-x(1);
275 Q1=-F.*rho.*dx.\textasciicircum{ }2/(perm.*eps0); r=Q1; a=...
    rho.*0.0;
276 b=a; c=a; \%Set up the finite difference matrix for i=1:numpts ...
    if
277 ((i>1)\&\&(i<numpts)) a(i)=1.0; b(i)=-2.0; c(i)=1.0;
278
279 end if (i==1) \%This sets the potential to V1 at the first ...
    boundary
280 a(i)=0.0; b(i)=1.0; c(i)=0.0; r(i)=V1; end \% if (i==2) \% \% ...
    This
281 sets the field to zero at the first boundary \% a(i)=-1.0; \% b...
    (i)=1.0;
282 \% r(i)=0.0; \% end
283

```

```

284 if (i==numpts) \% This sets the field to zero at the second ...
    boundary,
285 but leaves the potential at the boundary undefined b(i)=1.0; a(...
    i)=-1.0;
286 r(i)=0.0; end end \%V=(potmat\textbackslash{}Q1')'; V=tridiag(a...
    ,b,c,r,numpts);
287 end
288
289 function {[ ]nout,Jout{ ]}=diffuse\_with\_milsom\_boundary\_...
    \_conditions\_mod(kplus,backconc,x,nin,numpts,phi,diffRHS,...
    diffLHS,dt,tempinK,zi)
290 \%nin is the density of negatively charged carriers \%pin is ...
    the density
291 of positively charged carriers \%phi is the potential \%nout ...
    and pout
292 are the carrier densities after diffusion F=96368.0; R=8.31174;...
    beta=zi.{*}F/(R{*}tempinK);
293
294 dx=x(2)-x(1);
295
296 aa=zeros(1,numpts); bb=zeros(1,numpts); cc=zeros(1,numpts);
297
298 aco=zeros(1,numpts); bco=zeros(1,numpts); dphidx=zeros(1,numpts...
    );
299 Jout=zeros(1,numpts);
300
301 Δ=diffRHS./diffLHS;
302
303 S=zeros(1,numpts);
304
305 \%Calculate the derivative of the potential for i=2:numpts ...
    dphidx(i)=(phi(i)-phi(i-1))./dx;
306 end \%Assume the field is constant near the boundary dphidx(1)=...
    dphidx(2);
307
308 \%Setup the current coefficients for the transport calculation ...
    for
309 i=2:numpts if (i<numpts/2+1) aco(i)=(diffLHS./dx-beta./2.0{*}...
    diffLHS.{*}dphidx(i));

```

```

310 bco(i)=(-diffLHS./dx-beta./2.0{*}diffLHS.*}dphidx(i)); end if ...
    (i>numpts/2+1)
311 aco(i)=(diffRHS./dx-beta./2.0{*}diffRHS.*}dphidx(i)); bco(i)...
    =(-diffRHS./dx-beta./2.0{*}diffRHS.*}dphidx(i));
312 end if (i==numpts/2+1) alpha=(kplus+kplus.*}beta./2.0.*}...
    dphidx(i).{*}dx+Δ-Δ.*}beta./2.0.*}dphidx(i).{*}dx);
313 gamma=kplus./alpha; aco(i)=(2.0.*}(1.0-gamma).{*}diffLHS./dx-...
    gamma.*}beta.*}diffLHS.*}dphidx(i));
314 bco(i)=(-2.0.*}gamma.*}Δ.*}diffLHS./dx-gamma.*}Δ.*}beta....
    {*}diffLHS.*}dphidx(i));
315 end end
316
317 \% The i=1 boundary condition assumes a fixed carrier density ...
    \% The
318 i=numpts boundary condition assumes zero current. \%diffmatrix=...
    zeros(numpts,numpts);
319
320 for i=1:numpts if (i==1) S(i)=backconc; bb(i)=1.0; end if (i==...
    numpts)
321 S(i)=backconc; bb(i)=1.0; end if ((i\textasciitilde{}}=1)\&\&(i\...
    textasciitilde{}}=numpts))
322 \%diffmatrix(i,i)=Q(i)-C(i)+2; \%diffmatrix(i,i-1)=B(i)-1; \%...
    diffmatrix(i,i+1)=-B(i)-1;
323 \%aa(i)=-aco(i).{*}dt./(2.0.*}dx); \%bb(i)=1.0-(bco(i)-aco(i...
    +1)).{*}dt./(2.0.*}dx);
324 \%cc(i)=bco(i+1).{*}dt./(2.0.*}dx); \%S(i)=nin(i)+(nin(i-1)...
    {*}aco(i)+nin(i).{*}(bco(i)-aco(i+1))-nin(i+1).{*}bco(i+1))....
    {*}dt./(2.0.*}dx);
325 \%Jout(i)=aco(i).{*}nin(i-1)+bco(i).{*}nin(i); aa(i)=-aco(i)./2...
    .0;
326 bb(i)=dx./dt-(bco(i)-aco(i+1))./2.0; cc(i)=bco(i+1)./2.0; S(i)=...
    dx./dt.*}nin(i)+(nin(i-1).{*}aco(i)+nin(i).{*}(bco(i)-aco(i...
    +1))-nin(i+1).{*}bco(i+1))./2.0;
327 Jout(i)=(aco(i).{*}nin(i-1)+bco(i).{*}nin(i)).{*}dt./dx;
328
329 end end
330
331 Jout(1)=Jout(2); Jout(numpts)=Jout(numpts-1); nout=tridiag(aa,...
    bb,cc,S,numpts);

```

```

332
333 end
334
335 function numtsteps\_Callback(hObject, eventdata, handles) end
336
337 % --- Executes during object creation, after setting all ...
    properties.
338 function numtsteps\_CreateFcn(hObject, eventdata, handles) if ...
    ispc
339 \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
        defaultUiControlBackgroundColor'))
340 set(hObject,'BackgroundColor','white'); end end
341
342 function {[]V{}}=pot4amod(x,rho,V1,V2,numpts) \%x contains the ...
    position
343 vector and rho the corresponding cahрге density \%V1 is ...
    potential
344 on the left hand boundary \%V2 is the potential on the right ...
    hand
345 boundary \%An even mesh containing numpts data points is ...
    assumed.
346
347 F=96368.0; eps0=8.854E-12; perm=2.5; \%assumes an even mesh dx=...
    x(2)-x(1);
348 Q1=-F.*rho.*dx.\textasciicircum{}2/(perm.*eps0); a=zeros...
    (1,numpts);
349 b=zeros(1,numpts); c=zeros(1,numpts); \%set up the finite ...
    difference
350 matrix for i=1:numpts if ((i>1)\&\&(i<numpts)) a(i)=1.0; b(i)...
    =-2.0;
351 c(i)=1.0; end if (i==1) b(i)=1.0; Q1(i)=V1; end if (i==numpts) ...
    b(i)=1.0;
352 Q1(i)=V2; end end V=tridiag(a,b,c,Q1,numpts); end
353
354 function kplus\_Callback(hObject, eventdata, handles) end
355
356 % --- Executes during object creation, after setting all ...
    properties.

```

```

357 function kplus\_CreateFcn(hObject, eventdata, handles) if ispc ...
    \&\&
358 isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
359 set(hObject,'BackgroundColor','white'); end end
360
361 function kminus\_Callback(hObject, eventdata, handles) end
362
363 \% --- Executes during object creation, after setting all ...
    properties.
364 function kminus\_CreateFcn(hObject, eventdata, handles) if ispc...
    \&\&
365 isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
366 set(hObject,'BackgroundColor','white'); end end
367
368 \% --- Executes on button press in fieldcarriercoupling. ...
    function
369 fieldcarriercoupling\_Callback(hObject, eventdata, handles) end
370
371 function couplingcoeff\_Callback(hObject, eventdata, handles) ...
    end
372
373 \% --- Executes during object creation, after setting all ...
    properties.
374 function couplingcoeff\_CreateFcn(hObject, eventdata, handles) ...
    if
375 ispc \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
    defaultUicontrolBackgroundColor'))
376 set(hObject,'BackgroundColor','white'); end end
377
378 function V1\_Callback(hObject, eventdata, handles) end
379
380 \% --- Executes during object creation, after setting all ...
    properties.
381 function V1\_CreateFcn(hObject, eventdata, handles) if ispc ...
    \&\& isequal(get(hObject,'BackgroundColor'),
382 get(0,'defaultUicontrolBackgroundColor')) set(hObject,'...
    BackgroundColor','white');

```

```

383 end end
384
385 function V2\_Callback(hObject, eventdata, handles) end
386
387 % --- Executes during object creation, after setting all ...
      properties.
388 function V2\_CreateFcn(hObject, eventdata, handles) if ispc ...
      \&\& isequal(get(hObject,'BackgroundColor'),
389 get(0,'defaultUicontrolBackgroundColor')) set(hObject,'...
      BackgroundColor','white');
390 end end
391
392 function {[u]} = tridiag(a,b,c,r,N) \% Function tridiag: \% ...
      Inverts
393 a tridiagonal system whose lower, main and upper diagonals \% ...
      are
394 respectively given by the vectors a, b and c. \% r is the ...
      righthand
395 side, and N is the size of the system. The result is placed in ...
      u.
396 \% (Adapted from Numerical Recipes, Press et al. 1992) u=b.{*}0...
      .0;
397 gamma=b.{*}0.0; if (b(1)==0) fprintf(1,'Reorder the equations ...
      for
398 the tridiagonal solver...') pause end beta = b(1) ; u(1) = r(1)...
      /beta
399 ; \% Start the decomposition and forward substitution for j = ...
      2:N
400 gamma(j) = c(j-1)/beta ; beta = b(j)-a(j){*}gamma(j) ; if (beta...
      ==0)
401 fprintf(1,'The tridiagonal solver failed...') pause end u(j) = ...
      (r(j)-a(j){*}u(j-1))/beta
402 ; end \% Perform the backsubstitution for j = 1:(N-1) k = N-j; ...
      u(k)
403 = u(k)-gamma(k+1){*}u(k+1) ; end end
404
405 function {[X]}=PENTA(N,E,A,D,C,F,B) \% Taken from http://...
      www.math.uakron.edu/~textasciitilde{}kreider/anpde/...
      Anpde.html

```

```

406
407  \% RESULTS: matrix has 5 bands, EADCF, with D being the main ...
      diagonal,
408  \% E and A are the lower diagonals, and C and F are the upper ...
      diagonals.
409
410  \% E is defined for rows i = 3:N, but is defined as E(1) to E(N...
      -2)
411  E=E(3:N); \% A is defined for rows i = 2:N, but is defined as A...
      (1)
412  to A(N-1) A=A(2:N); \% D is defined for rows i = 1:N \% C is ...
      defined
413  for rows i = 1:N-1, but the last element isn't used C=C(1:N-1);...
      \%
414  F is defined for rows i = 1:N-2, but the last 2 elements aren't...
      used
415  F=F(1:N-2);
416
417  \% B is the right-hand side \% X is the solution vector
418
419  for I=2:N-1 XMULT=A(I-1)./D(I-1); D(I)=D(I)-XMULT{*}C(I-1); C(I...
      )=C(I)-XMULT{*}F(I-1);
420  B(I)=B(I)-XMULT{*}B(I-1); XMULT=E(I-1)./D(I-1); A(I)=A(I)-XMULT...
      {*}C(I-1);
421  D(I+1)=D(I+1)-XMULT{*}F(I-1); B(I+1)=B(I+1)-XMULT{*}B(I-1); end...
      XMULT
422  = A(N-1)./D(N-1); D(N)=D(N)-XMULT{*}C(N-1); X(N)=(B(N)-XMULT{*}...
      B(N-1))/D(N);
423  X(N-1)=(B(N-1)-C(N-1){*}X(N))/D(N-1); for I=N-2:-1:1 X(I)=(B(I)...
      -F(I){*}X(I+2)-C(I){*}X(I+1))/D(I);
424  end end
425
426  \% --- Executes on button press in stopexec. function stopexec\...
      _Callback(hObject,
427  eventdata, handles) set(handles.stopexec,'Value',1.0) set(...
      handles.calculate,'String','Calculate')
428  drawnow; end
429

```

```

430  \% --- Executes on button press in plotcurrent. function ...
      plotcurrent\_Callback(hObject,
431  eventdata, handles) end
432
433  \% --- Executes on button press in zerofield. function ...
      zerofield\_Callback(hObject,
434  eventdata, handles) end
435
436  function {[phi,npos,nneg{}}=steadystate(x,backconc,...
      boundarycarrierratio)
437  eps0=8.854e-12; R=8.31174; F=96368.0; TempinK=300.0; zi=1.0; ...
      perm=2.5;
438  ld=sqrt(perm{*}eps0.*R.*TempinK./(backconc.*(zi{*}F)).\...
      textasciicircum{2}));
439  qzero=sqrt(boundarycarrierratio); phi0=(R.*TempinK)/(zi{*}F)...
      {*}log(qzero);
440  etar=sqrt(2).{*}atanh(sqrt(qzero));
441
442  qeta=tanh(-1.0/sqrt(2.0).{*}((x./ld)+etar)).\textasciicircum...
      {}2; phi=R.*TempinK./(zi.*F).{*}log(qeta);
443  npos=backconc.*exp(zi.*F./(R.*TempinK){*}phi); nneg=...
      backconc.*exp(-zi.*F./(R.*TempinK){*}phi);
444
445  phil=phi-2.0{*}phi0; phi2=-fliplr(phi); nneg1=fliplr(npos); ...
      npos1=fliplr(nneg);
446  nneg(x<0)=backconc; phi(x>0)=phil(x>0); phi(x<0)=phi2(x<0);
447
448  nneg(x<0)=nneg1(x<0); npos(x<0)=npos1(x<0); end
449
450  function backconc\_Callback(hObject, eventdata, handles) end
451
452  \% --- Executes during object creation, after setting all ...
      properties.
453  function backconc\_CreateFcn(hObject, eventdata, handles) if ...
      ispc
454  \&\& isequal(get(hObject,'BackgroundColor'), get(0,'...
      defaultUiControlBackgroundColor'))
455  set(hObject,'BackgroundColor','white'); end end
456

```

```

457  \% --- Executes on button press in steadystate. function ...
      steadystate\_Callback(hObject,
458  eventdata, handles) end
459
460  \% --- Executes on button press in dumpgraphs2. function ...
      dumpgraphs2\_Callback(hObject,
461  eventdata, handles) handles.exportFigure = figure; replotAxis(...
      handles.carriers);
462  figure(handles.carriers); end
463
464  \% --- Executes on button press in dumpgraphs3. function ...
      dumpgraphs3\_Callback(hObject,
465  eventdata, handles) handles.exportFigure = figure; replotAxis(...
      handles.potential);
466  figure(handles.potential); end
467
468  function tplots\_Callback(hObject, eventdata, handles) end
469
470  \% --- Executes during object creation, after setting all ...
      properties.
471  function tplots\_CreateFcn(hObject, eventdata, handles) if ispc...
      \&\&
472  isequal(get(hObject,'BackgroundColor'), get(0,'...
      defaultUiControlBackgroundColor'))
473  set(hObject,'BackgroundColor','white'); end end
474
475  \% --- Executes on button press in holdprevious. function ...
      holdprevious\_Callback(hObject,
476  eventdata, handles) end
477
478  \% --- Executes on slider movement. function sliderV2\_Callback...
      (hObject,
479  eventdata, handles) end
480
481  \% --- Executes during object creation, after setting all ...
      properties.
482  function sliderV2\_CreateFcn(hObject, eventdata, handles) if ...
      isequal(get(hObject,'BackgroundColor'),

```

```
483 get(0, 'defaultUicontrolBackgroundColor') set(hObject, '...  
    BackgroundColor', {[].9  
484 .9 .9{}}); end end  
485  
486 \% --- Executes on button press in cgrabdata function cgrabdata...  
    _Callback(hObject,  
487 eventdata, handles) end
```

