Ionic liquids for Microwave-assisted Processing of Biomass Waste

by

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I, Ozunimi Lilian Iti declare that this thesis is my own work and that the work of other authors has been referenced.

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Abstract

The use of biomass as fuels, feedstock and materials has gained recognition in recent years. Developing sustainable solvents for biomass processing and recovery remains a challenge of the chemical industry. Room temperature ionic liquids have been designed for application in biomass waste recovery. Their polarities have been determined and it was found that protic alkylammonium ionic liquids have high α and β values. A comparison of the Kamlet Taft properties with that of alkylimidazolium ionic liquids shows that polarities can be expanded by changing the functionalities on the anion and cation. The stabilities of ammonium ionic liquids as shown by thermogravimetric analysis are lower than their imidazolium counterparts. All ionic liquids have been found to heat up appreciably under microwave irradiation. Their effectiveness as solvents for carbohydrates and biomass has been examined. It was found that the solubility of carbohydrates by ionic liquids is dependent on the polarity of the ionic liquids and other factors such as temperature and the presence of water. High α **HBD** ability and high β **HBA** ability were found to promote solubility of glucose and sucrose in ionic liquids, while high β and low α were found to promote cellulose solubility. A novel extraction protocol for the delignification of lignocellulosic biomass wastes under microwave irradiation has been designed that can reduce the amount of waste effluents produced from the process.

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In loving memory of

My parents; Taiwo Lilian and Thomas Ibitimi

and my brother, Ayibaemi.

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Abbreviations and Symbols

AcO	Acetate
Amim	1-allyl-3- methylimidazolium
BF_4	Tetrafluoroborate
C	Speed of light
C_2mim	1-ethyl-3-methylimidazolium
C_2OHmim	1-(1-hydroxybutyl)-3methylimidazolium
C_3mim	1-propyl-3-methylimidazolium
C_3Omim	1-(1-methoxyethyl)-3-methylimidazolium
C_4mim	1-butyl-3-methylimidazolium
C_6mim	1-hexyl-3-methylimidazolium
C_8mim	1-octyl-3-methylimidazolium
$CDCl_3$	Deuterated Chloroform
Cl	Chloride
D_2O	Deuterated Water
DMSO	Dimethyl Sulfoxide
DN/AN	Donor Number/Acceptor Number

DSC	Differential Scanning Calorimetry
EPA/EPD	Electron Pair Acceptor/Donor
E_T	Transition Energy
E_T^{30}	Empirical solvent polarity parameter, based on the absorption of Reichardt's dye
E_{NR}	Nile Red Transition Energy
FTIR	Fourier-Transform Infra-red
Gly	Glycolate
H	Planck's constant
$H_2N(CH_2CH_2OMe)_2$	Bis-2-methoxyethylammonium
H_2PO_4	Dihydrogen Phosphate
HBA/HBD	Hydrogen Bond Acceptor/Donor
Kcal	Kilo calories
kJ	Kilo joules
IL	Ionic Liquid
MAE	Microwave Assisted Extraction
MeOD	Deuterated Methanol
Mol	Moles
N_A	Avogadro's number
$NHMe_2Et$	Dimethylethylammonium
$NHMe_2EtOH$	Dimethylethanolammonium
NTf_2	Bistrifluoromethylsulfonylimide

OH	Hydroxyl
PF_6	Hexafluorophosphate
PPM	Parts Per Million
PrO	Propionate
S	second
SEM	Scanning Electon Microscopy
T_b	Boiling point
T_c	Devitrification temperature
T_g	Glass transition
TGA	Thermogravimetrical Analysis
T_m	Melting Point
TSIL	Task Specific Ionic Liquid
T_v	Temperature of Complete Volatilisation
α	Hydrogen Bond Donor Acidity
β	Hydrogen Bond Acceptor Basicity
λ_{max}	Wavelength of Maximum Absorption
π^*	Dipolarity/Polarisability
^oC	Degrees Celsius

Chapter 1 Introduction

1.1 Background

The use of biomass and biomass residues in productive applications has gained importance in recent years. Many of these efforts have been geared towards biomass use as a fuel, feedstock or material. There are environmental, legislative, economic and social drivers contributing towards the increase in biomass applications in industry. Although biomass is a renewable resource, the sustainability of increased virgin biomass use is questionable considering the large volumes of biomass wastes already being produced annually from industrial, commercial and domestic applications in Europe and North America, plus the burden on land use for non-food agriculture. Recovering biomass wastes instead of discarding them is at the top of the waste hierarchy and has already gained momentum in certain industrial sectors including the paper industry.

The recovery of paper for reuse has remained very high in recent years. According to the Food and Agricultural Organisation, production of paper and paperboard in Europe for 2008 was 112.7 million tonnes out of which, recovered paper was approximately 58 million tonnes.[1]

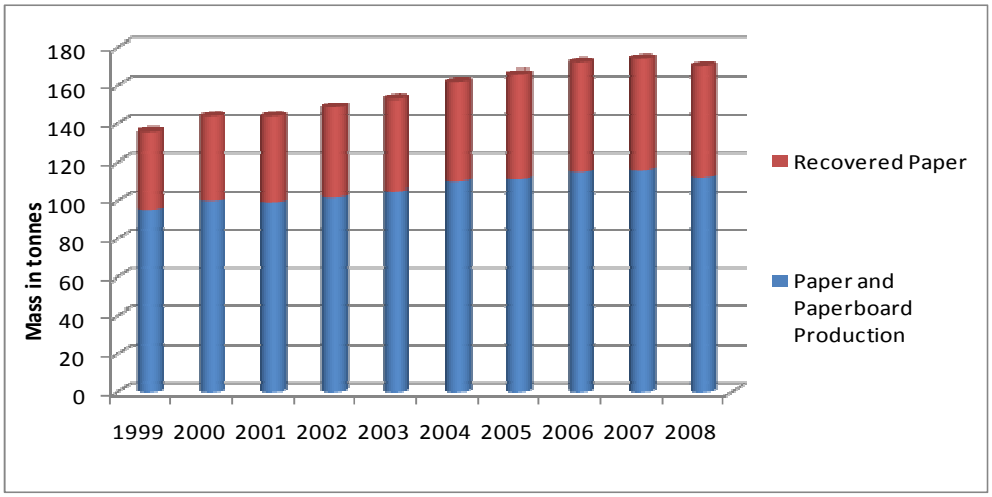


Figure 1.1: Mass of Paper and Paperboard produced and recovered (source, FAOSTAT).[1]

The recovery of biomass wastes and their use in various industrial and commercial applications can reduce the burden on natural resources, recover their economic value and help industries stay within legislative boundaries.

The Framework Directive on Waste governs waste legislation in Europe.[2] It includes two categories of directives: those setting requirements for the permission and operation of waste disposal facilities, and those dealing with disposal options for specific types of waste.[2] According to the European Landfill Directive (1999/31/EC), biodegradable municipal waste going to landfills must be reduced to 35 % of the total amount (base year 1995) by 2016. Biomass falls under biodegradable municipal wastes and can include food and kitchen wastes, garden wastes and paper. Furthermore, Directive 2004/12/EC amending Directive 94/62/EC on Packaging and Packaging Waste specifies a minimum recycling target of 60% on paper and board packaging. The ability of the paper industry to meet the stringent demands of today's legislation and stay economically relevant lies in the technical options

available for waste recovery. The challenge in processing biomass involves developing environmentally-benign chemicals and solvents, reducing the number of processing steps and also to minimise waste production. The most costly part of biomass processing can be the pre-treatment or delignification stages.[3] The waste paper industry relies heavily on strong acids and bases, large amounts of water and various chlorinated compounds for processing biomass.

1.2 Motivation

Ionic liquids have gained growing attention in recent years as sustainable solvents in a wide range of applications. Their low vapour pressures give them advantage over volatile organic compounds such that their emission from chemical processes can be better controlled. They can be used as ideal substitutes in conventional separation techniques and extractions because of their stability, low volatility and adjustable miscibility and polarity.[4] It has been shown that ionic liquids can dissolve cellulose, lignin and wood and the bio-molecules regenerated using non-solvents like water and ethanol without derivatisation.[5-9] It has been suggested that ionic liquids dissolve these bio-molecules by disrupting their extensive hydrogen bonding networks, thus allowing for dissolution.[7] There has been growing interest in the use of microwave irradiation for biomass processing in ionic liquids.[7, 10, 11] Microwave heating, as an alternative to conventional heating technique, has been proved to be more rapid, uniform and efficient.[12] Ionic liquids are ideal solvents for microwave applications because of their high ionic conductivities and efficient absorption of microwave energy.[13] Microwave energy has been used as a pre-treatment step before the delignification of wood in **[C_2mim][AcO]**.[11]Although the authors did not exploit the use of microwave energy in the delignification process itself, the potential exists for shortening delignification times using

microwave heating. Alkylimidazolium ionic liquids of the carboxylate, chloride and phosphate anion have been shown to be good solvents for cellulose and wood.[6, 7, 14] Alkylammonium ionic liquids are cheaper and more readily available than their imidazolium counterparts. They could therefore make ideal sustainable alternative solvents in the delignification of lignocellulosic wastes.

1.3 Scope and Objectives of Thesis

The research reported in this thesis investigates the use of ionic liquids as sustainable solvents in processing carbohydrates and biomass. Its main objectives are to design ionic liquids that can dissolve carbohydrates with varying complexities at high concentrations, to determine the effects of these ionic liquids on the recovered carbohydrates and to develop a microwave-assisted delignification process utilising an alkylammonium acid-base ionic liquid.

Bronsted acid-base ionic liquids can be prepared by the controlled combination of a protic acid and an organic base.[15] Since many delignifaction procedures rely on the use of organic bases and acids for delignification and lignin recovery respectively, the potential exists to develop a process that utilises the starting acid or base material of an acid-base ionic liquid thereby reducing the waste and high treatment costs associated with delignification processes that use bases or acids completely different from the pulping solvent.

In Chapter 2, the synthesis and characterisation of alkylammonium and imidazolium ionic liquids is discussed, including their adequate purification for solvatochromic investigations.

Chapter 3 investigates the polarity of the ionic liquids using Kamlet-Taft Solvatochromic dyes in UV spectroscopy. The properties required for different anion and cation types, to be classed as good solvents for a range of carbohydrates is examined via Kamlet Taft descriptors.

Biomass extractions are often done at high temperatures, thus Chapter 4 examines the thermal stability of ionic liquids and explores the suitability of microwave conductivity as a tool in biomass processing.

The effect of various alkylammonium ionic liquids on carbohydrates is dealt with in the first part of Chapter 5. After this, the quantitative and qualitative characterisation of a molded paper waste sample, using standard acid-insoluble (Klason) Lignin Test, Ashing, TGA and FTIR analysis is shown. An extraction protocol is designed using the selected ionic liquid with its conjugate acid and base in a bid to optimise solubility and recovery of a delignified cellulose fraction with reduced inorganic content. This part also shows characterisation of the fractions recovered from the extractions based on referencing with FTIR spectra of the waste sample, Klason Lignin (from the waste sample) and characteristic peaks and shoulders of Cellulose, Lignin and Hemicellulose.

The thesis concludes with an assessment of the suitability of acid-base ionic liquids for biomass extractions based on the findings of the study, suggestions for future work and further applications of the results.

Chapter 2 Synthesis and Purification of Ionic Liquids

2.1 Introduction to Ionic Liquids

Ionic liquids are liquids that consist only of ions. They should be differentiated however from molten salts. While molten salts have high melting points, ionic liquids are generally liquid at low temperatures (<100 **ºC**).[16]

The development of ionic liquids dates back to 1914 when ethylammonium nitrate was first synthesised.[17] By the 1950s, the first ionic liquids containing chloroaluminate ions were developed at the Rice Institute in Texas for use in electroplating. More research mainly focusing on electrochemical applications resumed in the 1970s.

Research in ionic liquids received a substantial boost by the work of Wilkes's group when they synthesised ionic liquids with significantly enhanced stability against hydrolysis for example low melting tetrafluoroborate melts,[18] which in contrast to chloroaluminate ionic liquids, offered high tolerance versus functional groups which opened up a much larger range of applications especially for transition metal catalysis.

Ionic liquids possess physical properties that make them interesting as potential solvents for synthesis. Some of these properties are listed below.[19]

a) They are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought into the same phase.

b) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet non-coordinating solvents.

c) They are immiscible with a variety of organic solvents and provide a non-aqueous, polar alternative for two-phase systems.However, hydrophobic ionic liquids can also be used as immiscible polar phases with water.

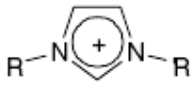
d) Ionic liquids have low volatility, hence environmental contamination via evaporation is not a problem and they may be used in high-vacuum systems. They can therefore be easily separated from other more volatile solvents.

e) They can be designed for specific tasks. The physical and chemical properties of ionic liquids can be specifically varied over a wide range by the selection of suitable cations and anions. The possibility arises to optimize the ionic reaction medium for a specific application by stepwise tuning the relevant solvent properties through the introduction of functional groups that can convey desirable properties on the whole ionic liquid. This is why they have been referred to as ‘designer solvents’.

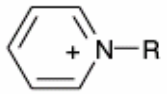
f) Since ionic liquids are quite different from molecular solvents, the outcome of their reactions is not always known. They can provide unique solvent effects for chemical reactions.

2.2 Synthesis and Purification of Ionic Liquids

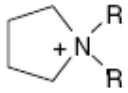
Most ionic liquids consist of a large sterically bulky cation associated with a weakly co-ordinating inorganic or organic anion. Some typical cations used in the formation of ionic liquids are shown (Figure 1.1).



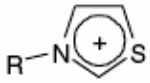
N, N, Dialkylimidazolium



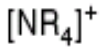
N-Alkylpyridinium



N,N-Dialkylpyrrolidinium



N-Alkylthiazolium



Tetraalkylammonium



Tetraalkylphosphonium

Figure 2.1: Typical cations used in ionic liquid synthesis.

Ionic Liquids of both the dialkylimidazolium and alkylammonium type are prepared in this study. Some typical anions used in this work are shown below.

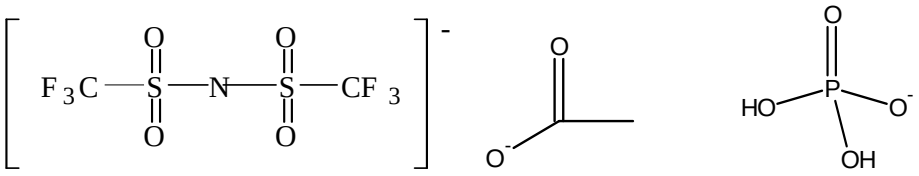


Figure 2.2: Ionic Liquid Anions used in this study

2.2.1 Synthesis of Imidazolium Ionic Liquids

The method used for synthesising Imidazolium ionic liquids involves two steps.

1. The first step is the alkylation of the required imidazole derivative via the amine group. This is achieved quite easily, using a slight molar excess of the alkyl halide. This step is done at low temperatures (<50 **ºC**) over 5 days to avoid colour in the final product.

2. The second step involves anion exchange usually with the corresponding alkali metal salt of the anion required. This gives the product and an alkali metal halide, which is slightly soluble in the ionic liquid.

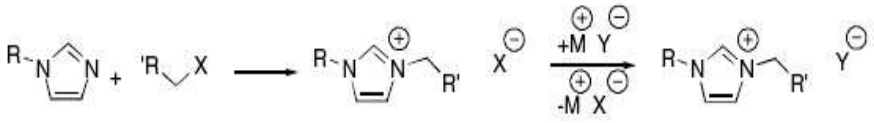


Figure 2.3: Synthesis of alkylimidazolium ionic liquids.

2.2.1.1 Test for Chloride

The ionic liquid is required halide free so as to avoid interference with reactions and analyses. Thus, the product is washed several times with water to generate a halide-free ionic liquid and the chloride content tested by precipitation with $AgNO_3$, which is sensitive to chloride. A white precipitate is formed on adding 2-3 drops of 0.1M $AgNO_3$ to the ionic liquid, signifying the presence of chloride. The ionic liquid is washed several times with water till no precipitate is detected on testing with $AgNO_3$.

This method overall is time-consuming but it results in a very pure and colourless product, suitable for use in solvatochromic measurements.

2.2.2 Synthesis of Alkylammonium Ionic Liquids

The alkylammonium ionic liquids are made from readily available starting materials and are therefore typically cheaper than the imidazolium ones.

Two methods were employed in synthesising alkylammonium ionic liquids in this thesis.

a) For the secondary and tertiary amines, equimolar amounts of the acid were added dropwise while stirring to the appropriate amine contained in a round-bottom flask over ice. The reaction is very exothermic, therefore the temperature of the reaction has to be kept lower than 40 **ºC**. Where inorganic acids are used, the reaction is very aggressive and thus the acid has to be added carefully and very slowly.

b) For the quaternary ammoniums, cation exchange was done with the appropriate organic acid with water as a by-product.

The resulting product was then washed several times with diethylether to remove excess amounts of acid or base. Unlike the imidazolium ionic liquids, stirring these ionic liquids in charcoal and passing through a bed of silica did not decolourise them, therefore care was taken to choose starting materials that were stable after distillation and remained colourless when stored in a nitrogen-filled flask. After trials, it was found that these ionic liquids have lower vapour pressures than their imidazolium counterparts and as such many cannot be dried at high temperatures for extended periods under vacuum. The **ILs** made from tertiary amines and monoprotic acids were most likely to decompose after heating under vacuum. Heating under vacuum was only carried out for such ionic liquids at low temperatures and for short periods. They were therefore freeze-dried as part of the purification process. Chapter 4 deals with the stability of these ionic liquids.

The general schemes for preparation of alkylammonium **ILs** are given in Scheme 2.1

a) $NR_3 + HX \rightarrow HNR_3^+ {}^- X$

b) $[NR_4]^+OH + HCOOR^1 \rightarrow [NR_4]^+{}^-OOCR^1 + H_2O$

Scheme 2.1 : General Schemes for Synthesis of Alkylammonium Ionic Liquids

Where **X= H_2PO_4** and **$RCOO^-$** and R= **H** or Alkyl

2.3 Experimental

2.3.1 General

All procedures involving oxygen and moisture-sensitive materials were conducted under dry nitrogen conditions using standard Schlenk techniques or manipulated in a nitrogen atmosphere glove box.

Reagents were purchased from Aldrich, Fischer Scientific or Acros Organics unless otherwise stated. Lithium bis(trifluoromethylsulfonyl)imide was purchased from Solvent Innovation GmbH and Choline hydroxide from Alfa Aesar. All solvents and reagents were freshly distilled and dried using standard procedures before use, except where otherwise stated.

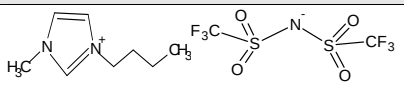
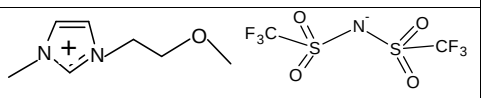
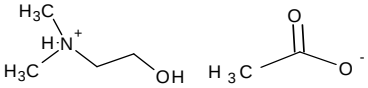
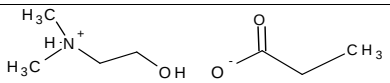
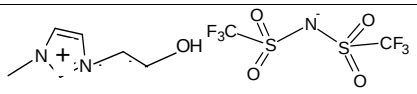
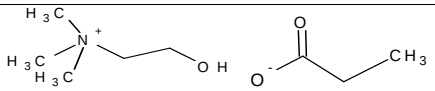
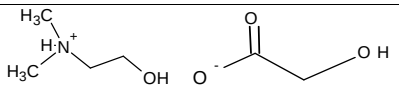
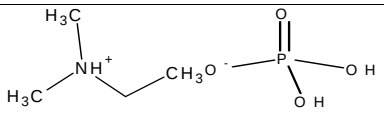
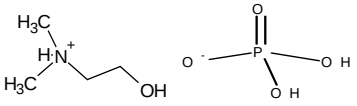
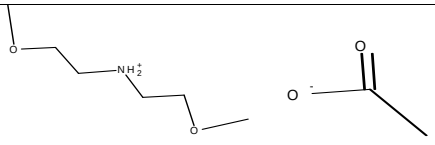
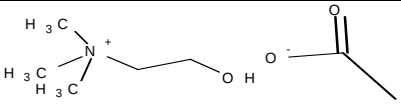
2.3.2 Analytical

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 400MHz Bruker DRX spectrometer. Chemical shifts are reported in ppm(versus tetramethylsilane) and coupling constants in Hz. FAB Mass spectra were recorded on a VG AutoSpec-Q mass spectrometer.

2.3.3 Synthesis and Characterisation

The structures of the ionic liquids synthesised in this Chapter are shown in the table below. The number notation used for each ionic liquid in the table is used in the rest of the thesis to represent the ionic liquid.

Table 2.1: Numbers and structures of ionic liquids synthesised

Number	Ionic Liquid	Structure
IL1	**[C_4mim][NTf_2]**	
IL7	**[C_3Omim][NTf_2]**	
IL8	**[$NHMe_2EtOH$][AcO]**	
IL9	**[$NHMe_2EtOH$][PrO]**	
IL10	**[C_2OHmim][[NTf_2]**	
IL11	**[Choline][PrO]**	
IL18	**[$NHMe_2EtOH$][Gly]**	
IL19	**[$NHMe_2Et$][H_2PO_4]**	
IL20	**[$NHMe_2EtOH$][H_2PO_4]**	
IL21	**[$H_2N(CH_2CH_2OMe)_2$][AcO]**	
IL22	**[Choline][AcO]**	

2.3.3.1 Synthesis of 1-butyl-3-methylimidazolium chloride [C_4mim][Cl]

A flask containing 1-methylimidazole (50 ml, 0.63 mol) and toluene (30 ml) was cooled in an ice bath and chlorobutane (72 ml, 0.693 mol) added dropwise under N_2 , while stirring. The solution was allowed to cool to room temperature, then heated at 45˚C until the mixture became turbid. It was then heated for a further 48hrs. The toluene phase was decanted after cooling, from the resultant pale yellow, viscous liquid, which crystallised on cooling. The product was recrystallised several times with ethyl acetate, from the minimum amount of acetonitrile. The solid was then washed with ethyl acetate (3x30) ml and dried *in vacuo* for 8 hrs to give white crystals of [C_4mim][Cl].

^{1}H NMR: δ_H (ppm, $CDCl_3$): 9.84 (1H, s, NCHN), 7.32 and 7.16 (2H,s, NC<u>H</u>C<u>H</u>N), 3.84(2H, t, ^3J = 7.3 Hz, N-CH_2-), 3.61 (3H, s, N-CH_3), 1.53(2H, m, N-CH_2-C<u>H</u>$_2$-), 0.87 (2H, m, N-CH_2-CH_2-C<u>H</u>$_2$-), 0.48 (3H, t, ^3J = 7.4 Hz, N-CH_2-CH_2-CH_2- C<u>H</u>$_3$).

MS: m/z (FAB$^+$): 83, ([Hmim]$^+$, 32%) and 139 ([C_4mim]$^+$, 100%).

MS: *m*/*z* (FAB$^-$) : 383, [(C_4mim)$_2Cl_3$]$^-$, 20 %; 209, [(C_4mim)Cl_2]$^-$, 100 %; 35,

2.3.3.2 Synthesis of 1-(1-hydroxybutyl)-3-methylimidazolium chloride, [C_4OHmim][Cl]

A flask containing 1-methylimidazole (75 ml, 0.94 mol) and toluene (50 ml) was cooled in an ice bath and 4-chloro-1-butanol (103 ml, 1.034 mol) added dropwise under N_2 , while

stirring. The solution was allowed to cool to room temperature, then heated at 45˚C until the mixture became turbid. It was then heated for a further 48hrs. The toluene phase was decanted after cooling, from the resultant yellow viscous liquid, which remained liquid even after cooling. The product was washed several times with ethyl acetate (4x20) ml and dried *in vacuo* for 8 hrs to give the yellow viscous liquid, [C_4OHmim]Cl.

^{1}H NMR: δ_H (ppm, DMSO- d^6): 9.63 (1H, s, NCHN), 7.94 and 7.87 (2H,m, NCHCHN), 4.22 (2H, t, ^3J = 7.2 Hz, N-CH_2-), 3.89 (3H, s, N-CH_3), 3.32 (2H, t, ^3J = 6.28Hz, N-CH_2-CH_2-CH_2-CH_2-), 1.77 (2H, m, N-CH_2-CH_2-), 1.31 (2H, m, N-CH_2-CH_2-CH_2-).

^{1}C NMR: δ_C (ppm, DMSO- d^6): 137.13 (s, N_2CH), 124.0 and 122.73 (s, 2NCH)60.19 (s, CH_2OH), 49.08 (s, N-CH_2-), 36.19 (s, N-CH_3), 29.25 (s, N-CH_2-CH_2- CH_2-), 26.92(s, N-CH_2-CH_2-).

2.3.3.3 Synthesis of 1-(1-hydroxyethyl)-3-methylimidazolium chloride, [C_2OHmim][Cl].

A flask containing 1-methylimidazole (75ml, 0.63mol) and toluene (50ml) was cooled in an ice bath and 2-chloroethanol (69.3ml, 0.693 mol) added dropwise under N_2 , while stirring. The solution was allowed to cool to room temperature, then heated at 45˚C until the mixture became turbid. It was then heated for a further 48hrs. The toluene phase was decanted after cooling, from the resultant pale yellow, viscous liquid, which crystallised on cooling. The product was recrystallised several times with ethyl acetate, from the minimum amount of acetonitrile. The solid was then washed with ethyl acetate (3x30) ml and dried *in vacuo* for 8 hrs to give white crystals of [C_2OHmim]Cl.

^{1}H NMR: δ_H (ppm, DMSO- d^6): 9.22 (1H, s, NCHN), 7.78 and 7.73 (2H, m, NCHCHN), 5.42 (1H, t, ^{3}J = 5.4Hz, N-CH_2-CH_2-OH), 4.24 (2H, t, ^{3}J = 5.2 Hz, N-CH_2-), 3.88 (3H, s, N-CH_3), 3.72 (2H, m, N-CH_2-CH_2-OH)

^{1}C NMR: δ_C (ppm, DMSO- d^6): 137.34: (s, N_2CH), 123.76 and 123.13 (s, 2NCH), 59.75 (s, CH_2-OH), 52.02 (s, N-CH_2-), 36.12 (s, N-CH_3).

2.3.3.4 Synthesis of 1-(1-methoxyethyl)-3-methylimidazolium chloride, [C_3Omim]Cl

A flask containing 1-methylimidazole (77.3 ml, 0.94 mol) and toluene (75 ml) was cooled in an ice bath and 2-chloroethylmethyl ether (98.3 ml, 1.04 mol) added dropwise under N_2 , while stirring. The solution was allowed to cool to room temperature, then heated at 45˚C until the mixture became turbid. It was then heated for a further 48hrs. The toluene phase was decanted after cooling, from the resultant clear viscous liquid, which crystallised on cooling. The product was recrystallised several times with ethyl acetate, from the minimum amount of acetonitrile. The solid was then washed with ethyl acetate (2x30) ml and dried *in vacuo* for 8 hrs to give white crystals of [C_3Omim]Cl.

^{1}H NMR: δ_H (ppm, $CDCl_3$): 10.31 ((1H, s, NCHN), 7.55 and 7.52 (2H, m, NCHCHN), 4.48 (2H, t, ^{3}J = 4.63 Hz, N-CH_2-), 3.99 (3H, s, N-CH_3), 3.65 (2H, t, ^{3}J = 4.83 Hz, N-CH_2-CH_2-O), 3.24 (3H, s, O-CH_3).

^{1}C NMR: δ_C (ppm, $CDCl_3$): 137.58 (s, N_2CH), 122.95 and 122.92 (s, 2NCH), 70.1 (s, O-CH_3), 58.75 (s, N-CH_2-$\underline{C}H_2$-O), 49.47 (s, N-CH_2-), 36.31 (s, N-CH_3).

MS: *m/z* (FAB$^+$): $[(C_3Omim)_2Cl]^+$, (317: 32%), $[C_3Omim]^+$, (141:100%).

2.3.3.5 Synthesis of 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide

In a flask, Lithium *bis*(trifluoromethylsulfonyl) imide (51.3g, 0.179 mol) was added to a solution of $[C_4mim]Cl$ (40g, 0.177 mol) in dichloromethane. The resulting suspension was allowed to stir under nitrogen for 48 hrs. Cannula filtration and subsequent rinsing of the residual salt with dichloromethane (2 x 30) ml gave a colourless liquid, which was further diluted and washed with aliquots of water (3 x 20ml) until chloride free as indicated by precipitation with $AgNO_3$ solution. The liquid was dried in vacuo for 4 hrs and filtered through a short pad of neutral alumina (length = 1-2 cm) after being treated with charcoal. The resulting colourless liquid was dried thoroughly in vacuo at 80 **ºC** for a further 8 hrs to afford $[C_4mim][NTf_2]$.

^{1}H NMR: δ_H (ppm, $CDCl_3$): 8.74 (1H, s, N_2CH), 7.29 and 7.26 (2H,s, 2NCH), 4.18 (2H, t, ^3J = 7.1 Hz, N-CH_2-), 3.93 (3H, s, N-CH_3), 1.84 (2H, m, N-CH_2-CH_2-),1.35 (2H, m, N-CH_2-CH_2-CH_2-), 0.95 (3H, t, ^3J = 7.4 Hz, N-CH_2-CH_2-CH_2- CH_3).

^{1}C NMR: δ_C (ppm, $CDCl_3$): 136.01(s, N_2CH), 124.53 and 123.63 (s, 2NCH), 114.96 (q, ^1J = 321.1 Hz, CF_3), 49.90 (s, N-CH_3), 36.27 (s, N-CH_2-), 31.88 (s, N-CH_2-$\underline{C}H_2$-), 19.28 (s, N-CH_2-CH_2-$\underline{C}H_2$-), 13.16 (s, N-CH_2-CH_2-CH_2- $\underline{C}H_3$).

MS: *m/z* (FAB+) MS: 558, $[(C_4mim)_2(NTf)_2]^+$, 1 %; 139, $[(C_4mim)]^+$, 100 %.

MS: *m/z* (FAB-) MS: 699, $[(C_4mim)(NTf_2)_2)]^-$, 8 %; 280, $[NTf_2]^-$, 92 %.

2.3.3.6 Synthesis of 1-(1-hydroxybutyl)-3methylimidazolium bis(trifluoromethylsulfonyl)imide

In a flask, Lithium *bis*(trifluoromethylsulfonyl) imide (150.2g, 0.689 mol) was added to a solution of $[C_4OHmim]Cl$ (130g, 0.682 mol) in dichloromethane. The resulting suspension was allowed to stir under nitrogen for 48 hrs. Cannula filtration and subsequent rinsing of the residual salt with dichloromethane (2 x 30) ml gave a colourless liquid, which was further diluted and washed with aliquots of water (3 x 20) ml until chloride free as indicated by precipitation with $AgNO_3$ solution. The liquid was dried in vacuo for 4 hrs and filtered through a short pad of neutral alumina (length = 1-2cm) after being treated with charcoal. The resulting colourless liquid was dried thoroughly in vacuo at 80 ˚C for a further 8 hrs to afford $[C_4OHmim]$ $[NTf_2]$.

^{1}H NMR: δ_H (ppm, DMSO- d^6): 9.09 (1H, s, N_2CH), 7.74 and 7.73 (2H,m, 2NCH), 4.18 (2H, t, ^3J = 7.2, N-CH_2-), 3.85 (3H, s, N-CH_3), 1.84 (2H, m, N-CH_2-C$\underline{H}_2$-), 1.39 (2H, N-CH_2-CH_2- C$\underline{H}_2$-),

^{1}C NMR: δ_C (ppm, DMSO- d^6): 136.26 (s, N_2CH), 124.0 and 122.66 (s, 2NCH)115.13 (q, ^1J = 321.3 Hz, CF_3), 60.37 (s, CH_2OH), 49.221 (s, N-CH_2-), 36.09 (s, N-CH_3), 29.21 (s, N-CH_2-CH_2- $\underline{C}H_2$-), 26.85 (s, N-CH_2-$\underline{C}H_2$-).

2.3.3.7 Synthesis of 1-(1-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

In a flask, Lithium *bis*(trifluoromethylsulfonyl) imide (124.43g, 0.57 mol) was added to a solution of $[C_2OHmim]Cl$ (100g, 0.56 mol) in dichloromethane. The resulting suspension was allowed to stir under nitrogen for 48 hrs. Cannula filtration and subsequent rinsing of the residual salt with dichloromethane (2 x 30)ml gave a colourless liquid, which was further diluted and washed with aliquots of water (3 x 20ml) until chloride free as indicated by precipitation with $AgNO_3$ solution. The liquid was dried in vacuo for 4 hrs and filtered through a short pad of neutral alumina (length = 1-2cm) after being treated with charcoal. The resulting colourless liquid was dried thoroughly in vacuo at 80 ˚C for a further 8 hrs to afford $[C_2OHmim]$ $[NTf_2]$.

^{1}H NMR: δ_H (ppm, DMSO- d^6): 9.09 (1H, s, N_2CH), 7.72 and 7.69 (2H, m, 2NCH), 4.36 (2H, t, ^3J = 4.9, N-CH_2-), 3.87 (3H, s, N-CH_3), 3.67 (2H, m, C$\underline{H}_2$OH), 3.38 (1H, s, $CH_2O\underline{H}$),

^{1}C NMR: δ_C (ppm, DMSO- d^6): 136.26 (s, N_2CH), 124.0 and 122.66 (s, 2NCH)115.13 (q, ^1J = 321.3 Hz, CF_3), 60.37 (s, CH_2OH), 49.221 (s, N-CH_2-), 36.09 (s, N-CH_3), 29.21 (s, N-CH_2-CH_2- $\underline{C}H_2$-), 26.85 (s, N-CH_2-$\underline{C}H_2$-).

2.3.3.8 Synthesis of 1-(1-methoxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

In a flask, Lithium *bis*(trifluoromethylsulfonyl) imide (187.1g, 0.858mol) was added to a solution of $[C_3Omim]Cl$ (120g, 0.85 mol) in dichloromethane. The resulting suspension was allowed to stir under nitrogen for 48 hrs. Cannula filtration and subsequent rinsing of the residual salt with dichloromethane (2 x 30) ml gave a colourless liquid, which was further diluted and washed with aliquots of water (3 x 20) ml until chloride free as indicated by precipitation with $AgNO_3$ solution. The liquid was dried in vacuo for 4 hrs and filtered through a short pad of neutral alumina (length = 1-2 cm) after being treated with charcoal. The resulting colourless liquid was dried thoroughly in vacuo at 80˚C for a further 8 hrs to afford $[C_3Omim]$ $[NTf_2]$.

^{1}C NMR: δ_C (ppm, DMSO- d^6): 137.16(s, N_2CH), 123.64and 122.93 (s, 2NCH)115.12 (q, ^1J = 321.3 Hz, CF_3), 69.88 (s, CH_3O), 58.24 (s, O-CH_2-), 49.18 (s, N-CH_2-), 35.92 (s, N-CH_3),

2.3.3.9 Synthesis of Bis(2-methoxyethyl)ammonium acetate

To a flask over ice containing Bis(2-methoxyethyl)amine (100ml, 0.68mol), glacial acetic acid (38.9ml, 0.68mol) was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting yellow ionic liquid was washed with diethyl ether (2 x 40) ml dried at 30 **ºC** under vacuum for 2 hours to remove excess diethyl ether. The ionic liquid was freeze dried under vacuum before use.

^{1}H NMR: δ_H (ppm, DMSO- d^6): 7.59 (s, 3H, NH_2), 3.44 (t, *J* = 5.5 Hz, 4H, 2N-CH_2), 3.25 (s, 6H, O-CH_3), 2.78 (t, *J* = 5.5 Hz, 4H, 2O-CH_2), 1.83 (s, 3H, C-CH_3).

^{1}C NMR: δ_C (ppm, DMSO- d^6): 173.28 (s, COO), 70.48 (s, 2 N$\underline{C}H_2$), 58.39 (s, 2OCH_3), 48.29 (s, 2OCH_2), 22.04 (s, OCH_3).

MS: *m/z* (ESI-TOF+) MS : 134, $[H_2N(MeOCH_3)_2]^+$ 100%

2.3.3.10 Synthesis of N,N-dimethylethanolammonium Acetate

To a flask over ice containing N,N-dimethylethanolamine (18g, 0.2 mol), acetic acid (11.6g, 0.2 mol) was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting colourless ionic liquid was washed with diethyl ether (2 x 40) ml dried at 30 **ºC** under vacuum for 2 hours to remove excess diethyl ether. The ionic liquid was freeze dried under vacuum before use.

^{1}H NMR: δ_H(ppm, MeOD): 5.15 (s, 2H, NCH_2), 3.92 – 3.81 (m, 2H, NCH_2), 3.26 – 3.15 (m, 2H, NCH_2), 2.88 (s, 6H, 2CH_3), 1.95 (s, 3H, OCH_3)

^{1}C NMR: δ_C(ppm, MeOD): 177.78 (s, COO), 59.05 (s,N- 2CH_3), 55.31 (OCH_2), 41.66 (s, NCH_2), 21.94 (s, $\underline{C}H_3COO$).

2.3.3.11 Synthesis of N,N-dimethylethanolammonium Propionate

To a flask over ice containing N,N-dimethylethanolamine (70.96g, 0.8 mol), propionic acid (58.97g, 0.8 mol) was added slowly. The reaction was allowed to stir under nitrogen for 12

hours. The resulting colourless ionic liquid was washed with diethyl ether (2 x 40) ml dried at 30 **ºC** under vacuum for 2 hours to remove excess diethyl ether. The ionic liquid was freeze dried under vacuum before use.

^{1}H NMR: δ_H(ppm, DMSO- d^6): 7.01 (s, 2H, NCH_2), 3.55 (t, 2H, NCH_2, *J*=5.9Hz), 2.59 (t, 2H, OCH_2, *J* = 6.4Hz), 2.35 (s, 6H, $2NCH_3$), 2.11(q, 2H, $C\underline{C}H_2$, *J* = 7.6Hz) , 0.96 (t, 3H, $C\underline{C}H_3$, *J* = 7.6Hz).

^{1}C NMR: δ_C (ppm, DMSO- d^6): 177.46 (s, COO), 60.65 (s, N-$2CH_3$), 57.27 (s, O-CH_2), 44.51 (s, NCH_2), 28.20 (s, $C\underline{C}H_2$), 10.63 (s, $C\underline{C}H_3$).

2.3.3.12 Synthesis of N,N-dimethylethylammonium Glycolate

To a flask over ice containing N,N-dimethylethylamine (68g, 0.93 mol), glycolic acid (70.7g, 0.93 mol) in water solution was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting colourless ionic liquid was dried at 60 **ºC** under vacuum for 6-12 hours to remove excess water.

^{1}H NMR: δ_H(ppm, DMSO- d^6): 3.84 (s, 6H, $N2CH_3$), 3.01 (q, 2H, NCH_2, *J* = 7.3 Hz), 2.67 (s, 2H, OCH_2O), 1.16 (t, 3H, $C\underline{H}_3CH_2$, *J* = 7.3 Hz).
^{1}C NMR: (ppm, DMSO- d^6): 175.21 (s, COO), 60.11 (s, $N2CH_3$), 51.79 (s, CH_2OH), 41.83 (s, NCH_2), 9.65 (s, $\underline{C}H_3CH_2$).

MS: *m/z* (LSIMS-): 75-$[OHCH_2COO]^-$ 36%, 133-$[H_2NCH_2CH_2][OHCH_2CO]^-$100%
MS: *m/z* (LSIMS+): 74-$[HNCH_2CH_2]^+$100%

2.3.3.13 Synthesis of N,N-dimethylethylammonium Dihydrogenphosphate

To a flask over ice containing N,N-dimethylethylamine (81.6g, 1.12 mol), phosphoric acid (109.3g, 1.12 mol) in water solution was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting colourless ionic liquid was dried at 70 **ºC** under vacuum for 6-12 hours to remove excess water.

^{1}C NMR: δ_C (ppm, DMSO- d^6): 51.89 (s, N2CH_3), 41.87 (s, NCH_2) , 9.70 (s, $\underline{C}H_3CH_2$).

^{31}P NMR: δ_P (162Hz, ppm, DMSO- d^6): 1.07, (PO_4)

MS: *m/z* (LSIMS-) : 97- $[H_2PO_4]^-$ 55%, 79-$[PO_3]^-$ 100%

2.3.3.14 Synthesis of N,N-dimethylethanolammonium Dihydrogenphosphate

To a flask over ice containing N,N-dimethylethanolamine (106.4g, 1.19 mol), phosphoric acid (117g, 1.19 mol) in water solution was added slowly. The reaction was allowed to stir under Nitrogen for 12 hours. The resulting colourless ionic liquid was dried at 70 **ºC** under vacuum for 6-12 hours to remove excess water.

^{1}C NMR: δ_C (ppm, D_2O): 58.40 (s, CH_2OH), 54.84 (s, NCH_2), 42.64 (s, N2CH_3).

^{31}P NMR: δ_P (162Hz, ppm, DMSO- d^6): 0.86, (PO_4)

MS: *m/z* (LSIMS-): 97- $[H_2PO_4]^-$ 65%, 79-$[PO_3]^-$ 100%

2.3.3.15 Synthesis of Choline Acetate

To a flask over ice containing Choline Hydroxide (59.7g, 0.54 mol), Glacial Acetic acid (32.54g, 0.54 mol) was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting colourless ionic liquid was washed with diethyl ether (2 x 40) ml and was dried at 60 **ºC** under vacuum for 6-12 hours to remove excess water.

^{1}H NMR: δ_H (ppm, MeOD): 4.03 (s, 2H, C$\underline{H}_2$OH), 3.53 (s, 2H, C$\underline{H}_2$CH$_2$OH), 3.26 (9 H, s, N-3CH$_3$), 1.91 (s, 3H, CH_3CO).

^{1}C NMR: δ_C (ppm, MeOD): 177.87 31 (s, CO), 67.67 (s, CH$_2$N), 55.65 (s, CH$_2$OH), 53.36 (s, N-3CH$_3$), 22.86 (s, $\underline{C}H_3$CO).

MS: *m/z* (LSIMS+): 104-[N(CH$_3$)$_3$(CH$_2$)$_2$)OH]$^+$100%

2.3.3.16 Synthesis of Choline Propionate

To a flask over ice containing Choline Hydroxide (50.4g, 0.42 mol), Propionic acid (34g, 0.42 mol) was added slowly. The reaction was allowed to stir under nitrogen for 12 hours. The resulting colourless ionic liquid was washed with diethyl ether (2 x 40) ml and was dried at 60 **ºC** under vacuum for 6-12 hours to remove excess water.

^{1}H NMR: δ_H(ppm, MeOD): 4.12 – 3.92 (m, 2H, N-CH$_2$), 3.56 – 3.45 (m, 2H, O-CH2), 3.23(s, 9H, N3CH$_3$), 2.19 (q, CCH$_2$, J = 7.6 Hz, 2H), 1.11 (t, CCH$_3$, J = 7.6 Hz, 3H).

^{1}C NMR: δ_C (ppm, MeOD): 179.31 (s, CO), 67.66 (d, *C*H2N) , 55. 70 (s, *C*H_2OH), 53.33 (t, N-3CH_3), 28.59 (s, <u>*C*</u>H_2CO), 9.02 (s, <u>*C*</u>H3CH2).

MS: *m/z* (LSIMS+): 104-$[N(CH_3)_3(CH_2)_2)OH]^+$100%

MS: *m/z* (LSIMS-): 73- $[H_3CCH_2COO]^-$ 72%

Chapter 3 Polarity

3.1 Introduction[20-24]

Majority of chemical reactions are carried out in the liquid phase using solvents. It has long been known that the choice of a solvent can influence the rate of a reaction. Solvents have been classified by various methods. They have been classified based on their macroscopic physical constants such as boiling point, vapor pressure, density, cohesive pressure, index of refraction, relative permittivity, thermal conductivity, surface tension, etc. They have also been classified based on their chemical constitution e.g. molecular or ionic in structure.

From the molecular-microscopic point of view, a solvent consists of individual, mutually interacting solvent molecules, characterized by molecular properties such as dipole moment, electronic polarisability, hydrogen-bond donor (**HBD**) and hydrogen-bond acceptor (**HBA**) capability, electron-pair donor (EPD) and electron-pair acceptor (EPA) capability, etc. These properties determine the concept of 'polarity'. Polarity is easier defined in such qualitative terms. Most quantitative definitions make use of the dielectric constant which cannot be measured for ionic liquids since they are not non-conducting.[24] IUPAC recommends a precise definition for polarity as follows:

That the polarity is the sum of all possible, non-specific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute.[25]

To design solvents with good properties for dissolving cellulose or other biomass, their polarities and in effect hydrogen bonding properties have to be known.

3.2 Measuring Polarity

Physical constants are not adequate for measuring polarity since they do not take into account most of the interactions happening at the molecular level. Other ways of measuring polarity have involved spectroscopic parameters of solvent polarity, derived from solvent-sensitive standard compounds absorbing radiation in spectral ranges corresponding to UV/Vis, IR, ESR, and NMR spectra.

The first comprehensive solvent scale constructed using a dye was the Kosower scale in 1958.[23] it was based on the the longest wavelength intermolecular charge transfer transition of 1-ethyl-4-methoxycarbonylpyridinium iodide. This scale was flawed because of its inability to measure very polar solvents as the peak measured moves under a much stronger $\pi \rightarrow \pi^*$ transition. Many different polarity scales exist, which are commonly used including the Y, Z, E_T^{30}, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, $\boldsymbol{\pi^*}$, DN and AN scales. The most commonly measured ones are the Dimroth et al; E_T^{30} and the Kamlet-Taft; $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\pi^*}$ scales. These are the ones used for measuring the polarities of ionic liquids in this thesis.

3.2.1 The E_T Scale

The E_T^{30} scale was proposed by Dimroth *et al* in 1963 as an empirical measure of polarity based on the pyridinium-N-phenoxide betaine dye[20], otherwise known as Reichardt's dye (Figure 3.1).

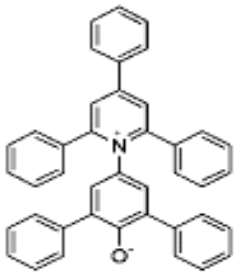


Figure 3.1: **Reichardt's dye, 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinium) phenolate.**

The major advantage over Kosower's dye is that the solvatochromic absorption is at longer wavelengths[20] since Reichardt's dye exhibits the largest solvatochromic range known, with a shift of about 500nm on going from a polar solvent (λ_{max} = 453nm in water) to non-polar solvent (λ_{max} = 925 nm) in hexane). The wavelength maximum of the spectral component with the longest wavelength for intermolecular charge-transfer $\pi \rightarrow \pi^*$ is represented by λ_{max} (Figure 3.2). The calculation of E_T^{30} is based on Equation 3.1.

$$E_T^{30} = \frac{h \times c \times N_A}{\lambda_{max}} = \frac{28592}{\lambda_{max}}$$

Equation 3.1: Calculation of E_T^{30} where *h* is Planck's constant, *c* is the speed of light and N_A is Avogadro's number.

According to Equation 3.1, the E_T^{30} value for a solvent is simply defined as the transition energy of the dissolved betaine dye measured in kcal/mol.

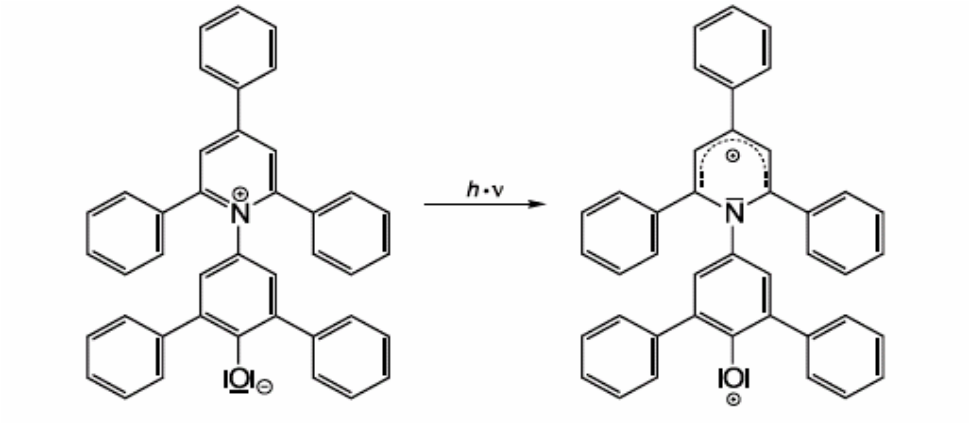


Figure 3.2: π→π* absorption band for Reichardt's dye.

As a result of its large hypsochromic shift, Reichardt's dye is very sensitive to variations in its immediate solvent environment and the E_T^{30} values provide an excellent and very sensitive characterization of the polarity of solvents, high E_T^{30} values corresponding to high solvent polarity.[20] Since E_T^{30} uses S.I. units, it is difficult to use and the use of normalised E_T^N values was introduced. They are defined according to Equation 3.2, using water and tetramethylsilane (TMS) as extreme reference solvents.

$$E_T^N = \frac{E_{T\ (solv)}^{30} - E_{T\ (TMS)}^{30}}{E_{T\ (water)}^{30} - E_{T\ (TMS)}^{30}} = \frac{E_{T\ (solv)}^{30} - 30.7}{32.4}$$

Equation 3.2: Calculation of E_T^N

The extensive delocalization of the positive charge on the pyridinium nitrogen through the ring system leads to λ_{max} being susceptible to changes in dipolar and polarization interactions, while the localized negative charge on the phenolic oxygen leads to changes in λ_{max} based on the Lewis acidity of the solvent and its hydrogen bonding ability. Thus, Reichardt's dye is more suitable as a measure of a range of different interactions important to reaction solvent effects.

The major limitation of the E_T^{30} values is the fact that they cannot be measured for acidic solvents such as carboxylic acids. Addition of traces of an acid to solutions of the betaine dye immediately changes the colour to pale yellow due to protonation at the phenolic oxygen atom of the dye. The protonated form no longer exhibits the long wavelength solvatochromic absorption band. The lipophilic stain, Nile Red (see Figure 3.3) is stable in very strong acids and exhibits large shifts in the wavelength of its maximum absorption allowing subtle changes in solvent strength to be quantified.[26] It has thus been a useful alternative for calculating the transition energies of solvents, especially those that are sufficiently acidic to protonate Reichardt's dye.[26, 27]

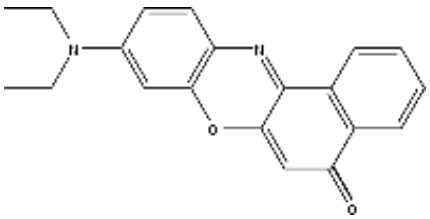


Figure 3.3: Nile Red

Nile Red is positively solvatochromic; therefore, when dissolved in increasingly polar media, the wavelength of its visible absorption maximum (λ_{max}) moves to longer wavelengths (lower energies).[27]

The solvatochromic comparison method was constructed by Kamlet and Taft in 1976[21, 22] based on UV-VIS spectra of solvatochromic compounds. They produced a β-scale of solvent **HBA** basicities, an ***α***-scale of solvent **HBD** ability and a ***π****-scale of solvent dipolarity/polarisability. The measures of ***β*** and ***α*** are determined mainly by the energies of the longest wavelength absorption carefully selected probe solutes in different solvents.

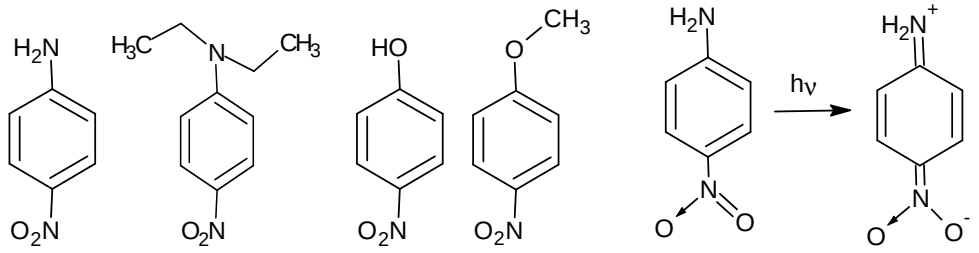
The values were used to create a *linear solvation energy relationship* shown in Equation 3.3

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi*$$

Equation 3.3: The Kamlet-Taft Linear Solvation Energy Relationship.

3.2.2 The β Scale

The ***β*** scale of hydrogen bond acceptor basicities is measured via comparison of the λ_{max} values for a pair of homomorphic dyes. The principle lies in the ability of both members of the pair to act as **HBA** substrates (at the nitro oxygen), with only one able to act as a **HBD** substrate in **HBA** solvents. The various dyes used in the measurements are shown in Figure 3.4.



(1) (2) (3)

Figure 3.4: **Homomorphic dye pairs; (1) 4-nitroaniline/*N,N*-diethyl-4-nitroaniline and (2) 4-nitrophenol/4-nitroanisole and (3) the origin of the solvatochromic transition.**

The homomorphic pair used in this report is the 4-nitroaniline/*N,N*-diethyl-4-nitroaniline dye pair.

Kamlet and Taft compared the υ_{max} values for the electronic transition of the homorphic pair 4-nitroaniline/*N,N*-diethyl-4-nitroaniline in different solvents. The plot of the data showed good linear regression shown in Equation 3.4.

$$\nu_{\text{4-nitroaniline}} = 1.035\nu_{\textit{N,N}\text{-diethyl-4-nitroaniline}} + 2.64$$

Equation 3.4: Regression equation for 4-nitroanline and N,N-diethyl-4-nitroaniline in non-HBA solvents.

Where ν in kilo Kaysers is defined by Equation 3.5, below.

$$\nu = \frac{1}{\lambda_{max} \times 10^{-4}}$$

Equation 3.5: **Relationship between υ and λ.**

The enhanced solvatochromic shift ($-\Delta\Delta\nu$) obtained due to the **HBD** ability of a solvent is given by Equation 3.6.

$$-\Delta\Delta\nu = \nu_{\text{4-nitroaniline}}\,(\text{calcd}) - \nu_{\text{4-nitroaniline}}\,(\text{obsd})$$

Equation 3.6: **Calculation of the enhanced solvatochromic shift due to the HBD ability of a solvent.**

Inserting Equation 3.4 into Equation 3.6 and then normalising to the strong **HBA** solvent used (hexamethylphosphoric amide, β=1), a measure of the **HBA** ability of a solvent (β) is obtained (Equation 3.7).

$$\beta = \frac{1.035\,\nu_{\text{N, N – diethyl – 4 – nitroaniline}} + 2.64 - \nu_{\text{4 – nitroaniline}}}{2.80}$$

Equation 3.7: **Calculation of normalised HBA ability of a solvent**

3.2.3 The α Scale

Kamlet and Taft constructed the ***α***-scale of solvent **HBD** acidities, a measure of the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The method used was similar to that used for the ***β*** scale.

A plot of υ_{max} values for Reichardt's dye against υ_{max} values for 4-nitroanisole in different solvents gave the corresponding linear regression. They normalised to obtain an ***α*** value of 1 for methanol (a strong **HBD** solvent). An enhanced solvatochromic shift ($-\Delta\Delta\nu$) was obtained and an equation to calculate the ***α***-value was obtained (Equation 3.8).

$$\alpha = \frac{\nu_{4\text{ - nitroaniso le}} + \nu_{\text{Reichardt}} - 74.58}{6.24}$$

Equation 3.8: **Calculation of the normalised HBD of a solvent.**

3.2.4 The π Scale*

Kamlet and Taft constructed the ***π**** scale, based on the average of the solvatochromic behaviour of a large number of indicators.

The ***π**** scale was constructed with the objective of serving as an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric constant.

The linear solvation energy relationship in Equation 3.7 was used to relate the υ_{max} values for each individual dye with ***π****. Therefore, assuming XYZ is the υ_{max} for a particular dye in a given solvent and this dye is a non-**HBD**/**HBD** solute (i.e. a=b=0), then υ_0 replaces XYZ_0 in the equation and Equation 3.9 is obtained.

$$\nu_{\max} = \nu_0 + s\pi^*$$

Equation 3.9: General equation for the dipolarity/polarisability of a solvent.

Where s and υ_0 are dependent on the dye being used and are obtained from correlations between υ_0 and ***π****.

3.3 Polarity and Solvation in Ionic Liquids

The solvation properties of ionic liquids can be varied by changing the nature of the ions in the ionic liquid. Miscibility with water can be varied from complete miscibility to low miscibility, by changing the anion from, for example, $Cl^-$to $[NTf_2]^-$.[24] The lipophilicity of the ionic liquid can also be varied by the degree of cation substitution with alkyl substituents. Hydrophobic ionic liquids can thus be used to design aqueous/IL biphasic systems. Ionic liquids also undergo π→π or C–H→π interactions, which increase their affinity for aromatic compounds.

Solvent properties are characterized by hydrogen-bond donation from the cation to polar or dipolar solutes and hydrogen-bond accepting functionality in the anion. These properties can also be varied by changing the cation substituents or the anion. Simple molecular solvents (hexane, for example) are limited in the number and types of solvation interactions possible with dissolved molecules.[28] More complex solvents with increased functionalities however, will have additional interactions with dissolved molecules.

Ionic liquids are very complex solvents. Given their structure and diversity of functionality, they are capable of most types of interactions (e.g., dispersive, *ð-ð*, n-*ð*, hydrogen bonding, dipolar, ionic/charge-charge). Thus, the range of solvent-solute interactions possible in ionic liquids is wider than that of molecular solvents. This wide range of interactions, especially hydrogen bonding can be exploited in the dissolution of complex and simple sugars. The use of various ionic liquids for the dissolution of simple and complex carbohydrates including glucose,[29, 30] sucrose,[30] starch, lignin and cellulose[5, 7, 10, 30-32] has been reported. Ionic liquids

with anions having high hydrogen bond accepting (**HBA**) properties were found to be better solvents for sugars and wood than those having low **HBA** properties.[7, 33] These **HBA** and **HBD** properties are investigated in this chapter using solvatochromic methods.

Several authors have investigated the polarities of ionic liquids using the α, β and π^* scales of the Kamlet-Taft solvatochromic method.[5, 6, 34-39] In addition to the analysis of general solvent-solute interactions,[34, 40] the influence of water,[36, 39] functionality[36, 37, 41] and also separation properties[38] have been investigated using the Kamlet-Taft method.

A wide range of possible solvent-solute interactions have been suggested for dialkylimidazolium ionic liquids as shown in Figure 3.5.[40] This further illustrates the usefulness of multi-parameter approaches to solvent polarity since the betaine dye alone cannot register all the possible interactions.

The work of Crowhurst et al[34] showed that ionic liquids are polar solvents, which under the right conditions can act as both hydrogen bond donors and hydrogen bond acceptors. They found π^* values to be generally high across ionic liquids and suggested that this parameter is the least easy to manipulate whereas since α and β vary more widely with the selection of the ions composing the ionic liquid, they can be deliberately manipulated.

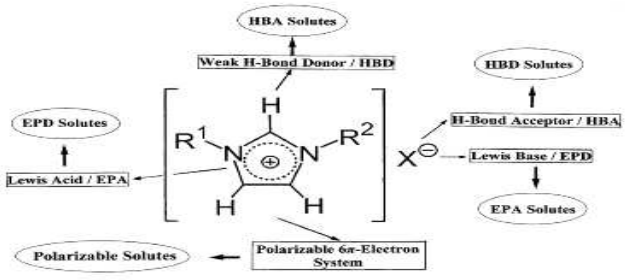


Figure 3.5: Possible intermolecular solute–solvent interactions with 1,3-dialkylimidazolium- based ionic liquids as solvents. Solvent properties in rectangles; solute properties in ellipses.[40]

Dzyuba and Bartsch found that the substitution of functional groups in the X position of 1-X-3-methylimidazolium bis(trifluoromethylsulfonyl) imides can markedly expand the polarity range for such ionic liquids.[36]

It has also been observed that polarity measurements determined for the same ionic liquid by different research groups can sometimes differ considerably.[40] These differences have been attributed to traces of polar impurities like chloride since chloride salts are intermediates in alkylimidazolium ionic liquid synthesis. The chloride salts themselves have been reputed to be good solvents for cellulose dissolution.[7, 42-45]

The disadvantages in using chloride salts for cellulose processing however, is that they have high melting points and viscosities, thereby raising the temperatures at which dissolution must be carried out. At such high temperatures, unwanted side reactions could occur. Their high affinity for water also means that special conditions may need to be created to limit the presence of water during the dissolution process. Designing halide-free ionic liquids for cellulose dissolution and investigating their polarities is therefore necessary. The presence of chloride in ionic liquids synthesised via a chloride intermediate may lend a false polarity to the ionic liquid and any cellulose dissolution achieved may actually be as a result of the chloride impurity.

The alkylammonium carboxylate ionic liquids used here have been prepared in one step without a chloride intermediate. Few[37, 38] studies have been done on the polarities of alkylammonium carboxylates. Since the carboxylate anions of these ionic liquids are the conjugate bases of weak acids, they could have high **HBA** basicities. High hydrogen bond

basicity is necessary to dissolve cellulose, in order to weaken the intermolecular and intramolecular hydrogen bonds of the cellulose chains.[6, 10]

3.4 Polarity Measurements of Ionic Liquids

Polarity measurements were done on 2 separate ionic liquid sets; a set of alkylimidazolium ionic liquids with **–OH** and **–O** functionality and a set of alkylammonium ionic liquids with **–OH** functionality. The aim was to investigate **HBA** basicity of the respective carboxylate anions and test the effects of the above functional groups on ionic liquid polarisabilities and hydrogen bond donor and acceptor properties, comparing for both sets of ionic liquids.

3.4.1 Chemical and reagents

2,6-Diphenyl-4-(2,4,6-triphenyl-N-pyridino)phenolate (Reichardt's dye) was used as received from Aldrich. *N,N*-diethyl-4-nitroaniline was purchased from Frinton laboratories and used without further purification. 4-Nitroaniline was purchaed from Fluka. Dichloromethane was obtained from BDH.

3.4.2 Instrumental

3.4.2.1 UV-Vis spectra

UV spectra were recorded using a Perkin Elmer Lambda 2 spectrophotometer, calibrated to ± 0.2 nm using a holmium oxide standard. All spectra were obtained at 25 °C with an accuracy of ≥ 0.5 nm and using 1 cm zirconium cells. Measurements were taken between 800 and 200 nm.

3.4.3 Methodology

Quartz cuvettes were filled with the solution mixture under nitrogen. The blank was made using a 'wet' sample of the ionic liquid. Spectra were used only if the absorption of the λ_{max} peak was greater than 0.2 and less than 1.

3.4.3.1 Addition of Reichardt's dye (For Alkylimidazolium Ionic Liquids)

1.0 ml of the ionic liquid was dried under vacuum at 50 ºC for 5-8 hours. A solution of the Reichardt's dye was made under nitrogen using 0.0025g of dye in a 5 ml volumetric flask with freshly distilled DCM. 0.5 ml of the dye solution was added to the ionic liquid (under nitrogen) and the DCM removed under vacuum. If the blue colour persisted, it was left under vacuum for 2 hours before measurement but if it became colourless, the addition process was repeated as many times as necessary. Re-addition was usually not necessary in samples that were base-washed.

3.4.3.2 Base Washing of Ionic Liquids (For Alkylimidazolium Ionic Liquids)

A mixture of ionic liquid and DCM (1:4 ratio) was washed with aliquots of aqueous KOH (pH 9-10, 5x 1ml), then distilled water (5x1ml). The DCM layer was then concentrated on a rotary evaporator and dried under vacuum at 50 ºC for 48 hours.

3.4.3.3 Addition of N,N-diethyl-4-nitroaniline to Samples (For Alkylimidazolium Ionic Liquids)

As section 3.4.3.1 but with the dye solution containing 0.0044g of N,N-diethyl-4-nitroaniline and in a 25ml volumetric flask, using DCM as solvent. Roughly 0.4ml of the solution was added to the ionic liquid sample before drying under vacuum. No colour change was observed after addition to the ionic liquid and only one addition was necessary in all cases.

3.4.3.4 Addition of 4-Nitroaniline (For Alkylimidazolium Ionic Liquids)

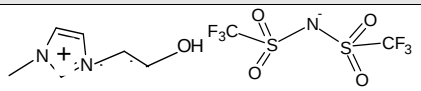
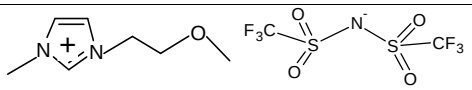
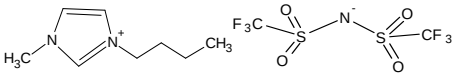
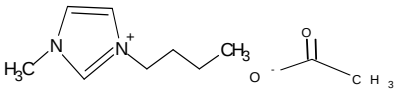
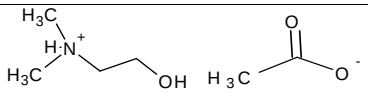
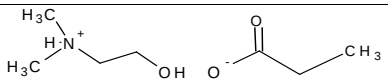
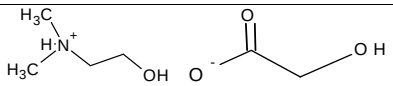
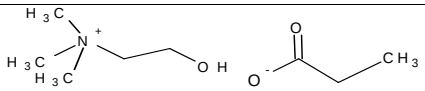
As described in section 3.4.3.3 but using 4-nitroaniline instead. A yellow colour was observed on addition.

3.4.3.5 Addition of All Dyes to Alkylammonium Ionic Liquids

Since all the dyes dissolve in the alkylammonium ionic liquids appreciably, the prescribed amounts of dyes in the previous sections were added to the neat dried ionic liquids before measurement and because all measurements were done at 25 **ºC**, this restricted the investigation to those ionic liquids that were sufficiently liquid at 25 **ºC**. Therefore, the polarities of the dihydrogenphosphate ionic liquids and the dimethylethanol ammonium acetate were not measured. Where the absorbance at λ_{max} was above 1, the mixture was diluted with more **IL** till it was below 1.

0.0025g of Nile Red was added to dimethylethanolammonium glycolate, since it did not give an absorption spectrum for Reichardt's dye. Polarity measurements were carried out on the ionic liquids in the following table.

Table 3.1: Set of Alkylimidazolium and Alkylammonium Ionic Liquids Measured

Ionic Liquid	Structure
[C_2OHmim][[NTf_2]	
[C_3Omim][NTf_2]	
[C_4mim][NTf_2]	
[C_4mim][AcO]	
[$NHMe_2$EtOH][AcO]	
[$NHMe_2$EtOH][PrO]	
[$NHMe_2$EtOH][Gly]	
[Choline][Pro]	

3.4.4 E_T Measurements

Earlier work had investigated the polarities of alkylimidazolium ionic liquids with **–OH** and **–O** functionalities. Addition of the dye gave coloured samples which were used in obtaining the various spectra. λ_{max} values were calculated using Origin.

The λ_{max} values of the respective ILs in Reichardt's dye were in the range of 472 to 555 as shown in Table 3.2. The ILs with λ_{max} values around 550 showed a purple colour on addition of the dye while those with λ_{max} values below 500 were orange in colour. Repeated additions of the dye to **IL18** resulted in a pale yellow colour and did not yield any absorption within its spectrum. This means that protonation of the dye occurred by an available proton on the IL. This proton could be available from excess acid in the system or from the **–OH** group on the alkyl side chain. The UV absorption in Nile red was measured for **IL18**.

Table 3.2: Characteristics of selected ionic liquids in Reichardt's Dye.

Ionic Liquid	Dye	Colour Change	λ_{max}/nm
IL10	Reichardt's	Purple	550
IL7	Reichardt's	Purple	549
IL1	Reichardt's	Purple	555
IL8	Reichardt's	Orange	497
IL9	Reichardt's	Orange	472
IL18	Nile Red	Red	586
IL11	Reichardt's	Purple	555

Since both dimethylethanolammonium acetate and propionate gave an absorption spectrum, this means that the presence of a proton directly bonded to the nitrogen atom on the alkylammonium cation alone was not sufficient to protonate the betaine dye. However, the presence of a hydroxyl group on the side chain of either the cation or anion appears to favour protonation the most. This suggests that a hydroxyl proton on either the cation or anion has a stronger attraction for the phenolic oxygen atom of the dye.

The E_T^{30} and E_T^{N} values were calculated using the Equation 3.1 and Equation 3.2.

Nile Red molar transition energy ($\mathbf{E_{NR}}$) values are calculated using the equation below

$$E_{NR} = \left(\frac{hcN_A}{\lambda_{max}}\right) \times 10^6$$

Equation 3.10: where *h* is Planck's constant, *c* is the speed of light and N_A is Avogadro's number.

This equation was used to calculate the E_{NR} values in Table 3.4 based on the corresponding λ_{max} values measured.

From Table 3.3, it can be seen that the replacement of a proton on the ammonium nitrogen with a methyl group increases the wavelength of maximum absorption and gives the resulting alkylammonium **IL** polarity similar to its imidazolium counterparts.

Table 3.3: Reichardt Wavelengths and E_T values for various ionic liquids.

Ionic Liquids	Molecular Weight	λ_{max}/ nm	E_{30} E_T /kcalmol^{-1}	E_N E_T
IL10	280.15	550.45	51.94	0.66
IL7	421.28	549.40	52.04	0.66
IL1	419.36	554.50	51.56	0.64
IL8	149.18	497.00	57.53	0.83
IL9	163.21	472.00	60.58	0.92
IL11	177.24	555.00	51.52	0.64

Table 3.4 compares the λ_{max} value of **IL18** with that of other ionic liquids and shows their corresponding E_{NR} values and that of water and 2-aminoethanol.

Table 3.4: Wavelengths of maximum absorption and Nile Red Excitation Energies for Ionic Liquids

Ionic Liquids	λ_{max}/nm	E_{NR}/ kJ mol^{-1}
[C_3mim][NTf_2]	547.50[36]	218.4
IL1	548.70[27]	218.0[27]
IL7	561.00[36]	213.2
IL10	566.00[36]	211.3
IL18	586.00	204.1
Water	-	201.7[27]
2-aminoethanol	-	214.5[27]

Although these values do not give an absolute idea of the polarities, we can deduce the relative polarity of **IL18** to the other ionic liquids**.**

IL18 is shown to be more polar than all the other ionic liquids and water but less polar than 2-aminoethanol. Considering that water has a high ***α*** value of **1.17**, we could also expect a similar value from this ionic liquid if it did not protonate the betaine dye. 2-aminoethanol would certainly be expected to have a higher ***α*** value than that of ethanol, which is **0.86**[20] since it has more acidic protons caused by the withdrawing amino-group attached to **C-2**. We may therefore say that this is a highly polar ionic liquid with strong **HBD** acidity.

3.4.5 π Measurements*

The ***π**** measurements were made using the dye N,N- diethyl-4-nitroaniline as the indicator.

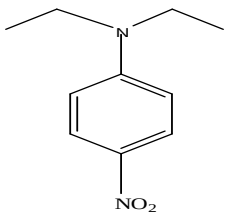


Figure 3.6 Structure of N,N-diethyl-4-nitroaniline dye

The UV spectra were obtained in the same way as the Reichardts' for both the alkylimidazolium and alkylammonium **ILs**. All the ionic liquids turned a bright yellow colour on addition of the N,N-diethyl-4-nitroaniline dye. The value for ***π**** was calculated using the equation below

$$\pi^* = 0.314(27.52 - \nu_{N,N-diethyl-4-nitroaniline})$$

Equation 3**.11: Calculation of π* using N,N-diethyl-4-nitroaniline dye.**

It has been shown that π^* measurements using various dyes are generally high across ionic liquids.[34]

Table 3.5: π*measurements for various ionic liquids.

Ionic Liquid	π^*
IL10	0.99
IL7	0.99
IL1	0.98
[C_4mim][HCOO]	1.03[6]
[C_4mim][AcO] (IL15)	0.99
[C_4mim][PrO]	0.96[6]
[C_4mim][BuO]	0.94[6]
[C_4mim][PeO]	0.91[6]
IL8	0.98
IL9	0.93
IL18	1.09
IL11	1.02

All the ionic liquids investigated here have high π^* values greater than 0.9. Crowhurst *et al* previously found that π^* values depend on anion type, with **[NTf_2]** anions having the lowest values. However, the results of this work show that both the cation and anion can affect π^*. The high π^* values for the alkylammonium ionic liquids are evidence of the formation of ionic polar species, having surprisingly comparable dipolarities as the imidazolium ionic liquids, since we expect excesses of acid and base in the alkyammonium **ILs**. Increasing the chain length of the carboxylate anion of the alkylammonium **ILs** decreased their π^* values.

This agrees with previous work[6] studying the polarities of a range of alkylimidazolium **ILs** with carboxylate anions having varying alkyl chain lengths, where π^* was also shown to decrease with increasing chain length. This could be attributed to the negative charge becoming more spread out across the methylene groups as the chain increases and thus less available to interact with the solute probe. The presence of a hydroxyl group on the alkyl side chain of the anion however, increased the dipolarity due to the **–OH** group causing increased attraction between the anion and cation.

Polarities of concentrations of **IL8** with excess amounts of acid and base were measured. It was expected that these new compounds would possess reduced π^* values since there would be reduced attraction between the anion and cation caused by the amounts of free acid and base. The reverse was however the case. All the compounds made with excess acid and base had higher π^* values than the 1:1 compound.

Table 3.6: Kamlet Taft Values for various concentrations of IL8

IL Concentration	π^*	α	B
Equimolar	0.9827	0.9960	0.7538
5% Excess Acid	1.0014	0.8038	0.8258
10% Excess Acid	1.0199	0.9174	0.7337
5% Excess Base	1.0014	0.9827	0.7081
10% Excess Base	1.0567	0.9056	0.6904

This could be as a result of excess amounts of acid and base present in the equimolar mixture at the end of the reaction, reacting with acid (or base) added and moving the

equilibrium towards the formation of the neutral ionic liquid by mopping up excess base (or acid) and therefore giving higher polarities or **π*** values.

3.4.6 *The α Measurements*

The ability of the Ionic Liquids to donate protons in a solvent-to-solute hydrogen bond were calculated using the ***α* -scale**. This scale is based on the E_T^{30} values obtained from the absorption of Reichardt's dye and the **π*** values from the absorption of the N,N-diethyl-4-nitroaniline dye. Reichardt's dye can register effects arising from solvent dipolarity, hydrogen bonding, and Lewis acidity, with the greatest contribution coming from the hydrogen bond donor property of the solvent. [21]

The hydrogen bond donor acidity of ionic liquids, ***α*** has previously been found to be strongly cation dependent, mainly due to the ring hydrogens. [34] This work aims to investigate the hydrogen bond donating properties of the ionic liquid by adding the hydroxyl functionality on the side chain on both the cation and anion.

The ***α*** values were calculated using already measured E_T^{30} and **π*** values, using the equation derived by Kamlet and Taft (Equation 3.12).

$$\alpha = 0.0649E_T^{30} - 2.03 - 0.72\pi^*$$

Equation 3.12: Calculation of *α*

The hydrogen bond donor acidities of the imidazolium ionic liquids shown in Table 3.5 are around 0.6. It has been reported that substitution of the imidazolium ring proton with an alkyl group reduces the hydrogen bond donor ability.[34] The N-protons on the ammonium cation, like the ring protons should also have a weak **HBD** ability. Therefore, substituting the N-proton with a methyl group allows us to independently measure the **HBD** ability of the hydroxyl group on the side chain.

Table 3.7: *α* values for ionic liquids.

Ionic Liquids	***A***
IL10	0.63
IL7	0.63
IL1	0.61
IL15	0.55[6]
IL8	1.00
IL9	1.23
IL11	0.58

The alkylammonium **ILs** with a proton attached to the nitrogen atom both have very high ***α*** values; 1 for **IL8** with the value increasing to 1.2 when the chain on the anion is lengthened by one methylene group. Replacing the cation proton with a methyl group in **IL11** halves that value. We see here strong effects on ***α*** by the cation and smaller effects by the anion. The work of Ohno and Fukaya on alkylimidazoilum carboxylates[6] did not show a regular trend for ***α*** with increasing chain length on the anion.

3.4.7 <u>The β Measurements</u>

The Kamlet and Taft ***β*** measurement makes use of a homomorphic pair of dyes, one of which has already been used in the ***π**** scale. The set used in this study is the aniline pair of dyes comprising N,N-diethyl-4-nitroaniline and 4-nitroaniline.

A B

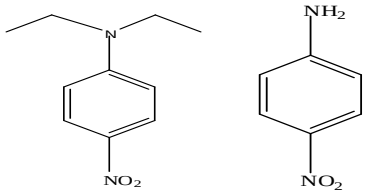


Figure 3.7: Aniline dye pair. A: N,N-diethyl-4-nitroaniline. B: 4-nitroaniline.

The dyes were added to the ionic liquids in the same way as described previously. The Kamlet and Taft derived equation for the aniline pair was used to calculate ***β*** *in* Equation **3**.13.

$$\beta = \frac{1.035\nu_{N,N-diethyl-4-nitroaniline} + 2.64 - \nu_{4-nitroaniline}}{2.80}$$

Equation 3**.13: Calculation of *β* using aniline pair of dyes.**

Previous work has found ***β*** for imidazolium **ILs** to be generally anion dependent.[34] This work investigates the effect of hydrogen donating and accepting functional groups of the cation and anion of the **ILs** on their overall hydrogen bond accepting properties. High ***β***

values of ionic liquids have been reported as being important for the dissolution of cellulose and other carbohydrates.[5, 6, 14, 33] Since β is anion dependent, it has also been suggested that the solubility of carbohydrates in ionic liquids is dependent on the nature of the anion. Basic ionic liquids with dicyanamide,[46] carboxylate,[6, 14, 37, 38] phosphate,[5] phosphonate[5] and chloride[7, 43-45] anions have been reported as good solvents for carbohydrates.

The Imidazolium ionic liquids of the $\mathbf{NTf_2}$ anion studied here (Table 3.8) all have low β values around 0.2, making them unsuitable as solvents for carbohydrates. Changing the anion to acetate increases the β value more than four times to 1.09 as this is a smaller anion with the charge spread over fewer atoms. Keeping this same anion and moving to the dimethylethanolammonium cation, the β value reduces to 0.75.

Table 3.8: β values for ionic liquids.

Ionic Liquids	B
IL10	0.231
IL7	0.226
IL1	0.243
IL15	1.090
IL8	0.750
IL9	0.770
IL18	0.430
IL11	0.920

Thus, we begin to see cation effects on β, albeit smaller. This could be attributed to competition of the protons on the cation against the **HBD** solute probe for the **HBA** centre of the anion. For the imidazolium cation, there is no proton directly bonded to a nitrogen atom. Lengthening the alkyl chain on the anion by one methylene group also increases β slightly and substituting the N-proton of the cation with a methyl group brings the β back up to 0.92. The substitution of a methyl proton on the acetate anion with **–OH** also reduces β from 0.75 to 0.43. This shows that the presence of a hydroxyl group on the side chain of the anion has a larger effect on β than the presence of a hydroxyl group on the side chain of the cation.

3.5 Ideal Polarity Characteristics for Carbohydrate Dissolving Solvents

To select suitable characteristics for solvents for carbohydrates, a comparison is done on Kamlet-Taft properties of conventional solvents used for carbohydrate dissolution. Kamlet-Taft values for solvents commonly used for glucose, sucrose, starch and cellulose are given in Table 3.9. Water is known to be a good solvent for glucose and sucrose, yet has an α value of 1.16, thus a high **HBD** ability does not seem to hinder dissolution of the simpler carbohydrates. This is probably due to less hydrogen bonding in the simple sugars and thus availability of oxygen atoms to form hydrogen bonds with the solvent protons. In addition, the moderate β of water is sufficient to dissolve glucose and sucrose. It may be therefore that a high β value is not needed at all for an ionic liquid designed to dissolve simple carbohydrates.

Table 3.9: Kamlet Taft Properties of some conventional solvents for carbohydrates

Solute	Molecular Solvent	Kamlet Taft Properties		
		π^*	α	β
Glucose, Sucrose	**Water**[34]	1.13	1.16	0.5
Starch	**Dimethylsulfoxide**	1.00	0	0.76
Cellulose	**N,N-dimethylacetamide***[47]	0.88	0	0.78
Cellulose	**N,N-dimethylacetamide/7.5% LiCl***[47]	0.65	0.46	2.00

*** Measured using different set of dyes from this study**

A solvent often used for dissolving cellulose fibres is N,N-dimethylacetamide. The pure solvent has a β value of 0.78 and an α value of 0. This solvent is best as a solvent for cellulose when mixed with Lithium Chloride at a concentration of 8% of the Lithium Chloride. At this concentration, β is as high as 2, and α is still moderate at 0.46. Although trying to achieve a solvent with a β value as high as this may be difficult without adding chloride, it is clear that the higher the β value, the better for cellulose dissolution. I would say, that in addition to high β values, low to moderate α values are also necessary for good solubility, since high α values means that there could be competition between hydrogen bonding between the anion and cellulose, with strong **HBD** functional groups on the cation. Dimethylsulfoxide (**DMSO**) is often the solvent of choice for derivatisation of starch. From Table 3.9, we can see again a high β value and α **HBD** acidity of 0 for **DMSO**. It is not known from literature what range the **HBD** acidity of an ionic liquid should be in, to dissolve starch. Comparing these values with those of the ionic liquids previously reported to dissolve carbohydrates especially cellulose appreciably, all have not only high β values but also low to moderate α values.[5, 6, 14]Table 3.10 shows the values for a range of ionic

liquids. Ionic Liquids **12, 13, 14, 15, 16** and **17** have all been reported to dissolve cellulose at appreciable concentrations.[5-7, 14]

Table 3.10: Comparison of Kamlet-Taft values for a diverse range of ionic liquids

Number	IL	π^*	α	β
IL1	**$[C_4mim][NTf_2]$**	0.98	0.61	0.24
IL2	**$[C_4mim][PF_6]$**[48]	1.03	0.63	0.41
IL3	**$[C_4mim][BF_4]$**[48]	1.05	0.63	0.38
IL4	**$[C_4mim][TfO]$**[48]	1.01	0.63	0.46
IL5	**$[C_4mmim][NTf_2]$**[48]	1.01	0.38	0.24
IL6	**$[C_4mmim][BF_4]$**[34]	1.08	0.40	0.36
IL7	**$[C_3Omim][NTf_2]$**	0.99	0.63	0.23
IL8	**$[NHMe_2EtOH][AcO]$**	0.98	1.00	0.75
IL9	**$[NHMe_2EtOH][PrO]$**	0.93	1.23	0.77
IL10	**$[C_2OHmim][NTf_2]$**	0.99	0.63	0.23
IL11	**[Choline][PrO]**	1.02	0.58	0.92
IL12	**$[C_4mim]Cl$**[14]	1.14	0.44	0.84
IL13	**[Amim]Cl**[14]	1.17	0.46	0.83
IL14	**[Amim][HCOO]**[14]	1.08	0.48	0.99
IL15	**$[C_4mim][AcO]$**[6]	0.99	0.55	1.09
IL16	**$[C_2mim][(meO)_2PO_2]$**[5]	1.06	0.51	1.00
IL17	**$[C_2mim][MePO_3Me]$**[5]	1.04	0.50	1.07
IL18	**$[NHMe_2EtOH][Gly]$**	1.09	-	0.43

All of these ionic liquids have not only high ***β*** values but also low to moderate ***α*** values. A plot of ***β*** as a function of ***α*** for the ionic liquids in Table 3.10 shows the correlation of high ***β*** with low ***α*** values for the cellulose solvating ionic liquids.

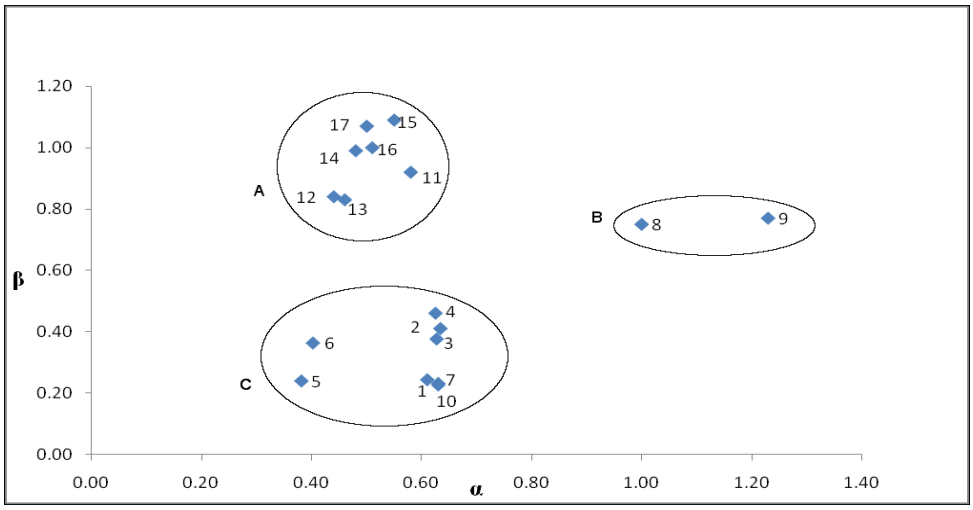


Figure 3.8: *β* plotted as a function of *α* and predicting correlation for solubility of carbohydrates

Thus, those ionic liquids that fit into circle A, could be classified as good solvents for carbohydrates, those in circle B may be poor solvents for complex carbohydrates but good solvents for simple carbohydrates due to their very high ***α*** values and those in circle C with both low to moderate ***β*** and ***α*** values would be either poor solvents or non-solvents for carbohydrates.

From the above results, we can assume that, of the ionic liquids measured for this study, **11** would be a promising candidate as a solvent for cellulose since it has a high ***β*** value of 0.92 and a moderate ***α*** value of 0.58. Ionic liquids **8** and **9** are unlikely to be good solvents for cellulose but are basic enough to dissolve simpler carbohydrates. Based on the results, **11**

may also be a good solvent for starch. I would not expect **1**, **7** or **10** to dissolve any carbohydrates appreciably.

3.6 Conclusions

The π^* dipolarity values are generally high across ionic liquids. Increasing the length of a side chain on the anion of an ionic liquid can slightly reduce the dipolarity. The results of this chapter agree that α is largely cation dependent, however an ionic liquid set with basic anions substituted with acidic functional groups but countered with much less acidic cations than the ones used here would be more suitable to test anion effects on **HBD** acidity.

Where a very acidic proton on the cation is replaced by a methyl group, there can be a substantial cation effect on the **HBA** basicity of an ionic liquid, β. Thus, reducing the acidity of the cation can also increase the basicity of the ionic liquid as a whole. The basicity of the ionic liquid is perhaps better described as dependent on the different functionalities on the anion and cation rather than only the anion as a whole.

Highly basic anions may not be necessary for dissolution of simple carbohydrates. Ionic liquids with high β values and low to moderate α values should be better solvents for cellulose and other complex carbohydrates. Chapter 5 will review solubility studies of carbohydrates and show results of solubility tests of carbohydrates with varying complexities, in the ionic liquids measured here, where a more conclusive statement can be made on the effects of ionic liquid polarity on solvation of carbohydrates.

Chapter 4 Thermophysical Properties of Ionic Liquids

Before designing a solvent as a separation medium in any process there has to be a fundamental understanding of the physical and chemical properties of the solvent.[49] Ideal physical properties would include thermal stability for high temperature separations, a wide liquid range[24], low viscosity to facilitate mixing and a large difference in density in comparison to other process solvents to aid phase separation.[49]

Such physical properties are related to the mechanics and engineering components associated with a process.[49]

This chapter will focus on some general physical properties of ionic liquids that make them good solvents and show the physical characteristics of the ionic liquids studied. Reference will be made to imidazolium ionic liquids and ammonium ionic liquids in general.

4.1 Thermal Decomposition Temperatures and Phase Transitions

Melting points, glass-transition temperatures, and thermal decomposition temperatures are needed to set the feasible temperature operating range for a particular fluid.[50]

4.1.1 Melting Points and Glass Transitions

The liquid range of ionic liquids can be much greater than that found in molecular solvents. For example, water has a liquid range of 100 **ºC** (0 to 100 **ºC**) and dichloromethane has one of 145 **ºC** (-95 to 40 **ºC**)[24], whereas the ionic liquid **IL1** has a liquid range of more than 400 **ºC** (-4 to 440 **ºC**).[51] The solid–liquid transition temperatures of ionic liquids can (ideally) be below ambient and as low as –100 **°C**. The most efficient method for measuring the transition temperatures is differential scanning calorimetry (DSC).[24] Several authors have reported melting points[49, 51-53] and glass transition temperatures[49, 52, 54] of ionic liquids. The lower liquid limit of ionic liquids is defined by their melting points.[55] Melting points are typically difficult to measure[49, 55] because of supercooling.[53, 55]

Glass Transition, T_g gives a representation of the cohesive energy of the sample, with low cohesive energies corresponding to low T_g values.[56]Low T_g values are a good indication that the ionic liquid is likely to have desirable physicochemical properties such as low viscosity and high ionic conductivity.[56]

Fredlake *et al*[50] identified 3 types of thermal behaviour for imidazolium-based ionic liquids. The first class involves imidazolium ionic liquids having a distinct freezing point on cooling and a distinct melting point on heating. These kinds of ionic liquids will readily crystallise and not form glasses. [C_4mim][TfO] was shown to have this kind of behaviour.

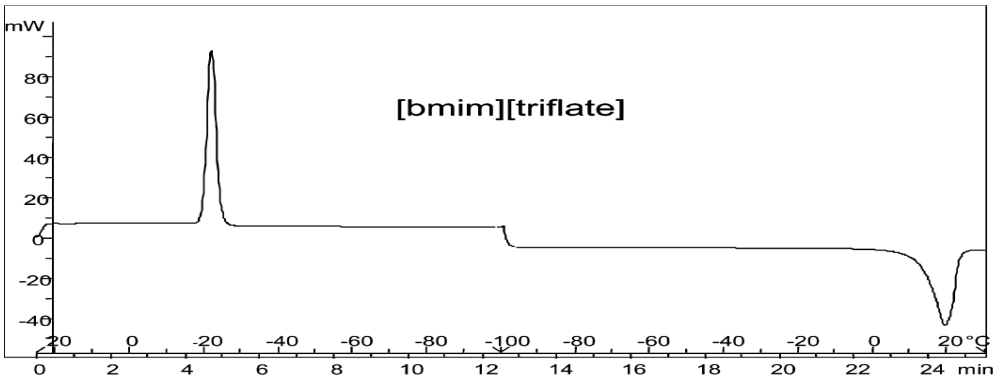


Figure 4.1: DSC scan for [C_4mim][TfO], showing a distinct freezing point upon cooling and a distinct melting point upon heating.[50]

The second class exhibits no true phase transitions but only the formation of an amorphous glass on cooling and reformation of the liquid on heating. Such ionic liquids have no melting or freezing points but only glass transitions as shown for **IL3**.

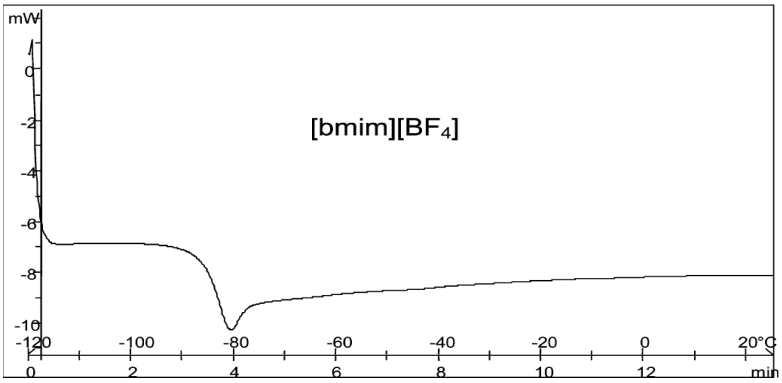


Figure 4.2: DSC scan for IL3, showing only a glass transition around -85 °C.[50]

The third class of imidazolium ionic liquids exhibits liquid subcooling to a glass state but on heating to temperatures above the glass transition, T_g the liquid crystallises at the point T_c

and as it is heated further, it melts at T_m. This is shown in the DSC scan of **IL1** in **Figure 4.3**.

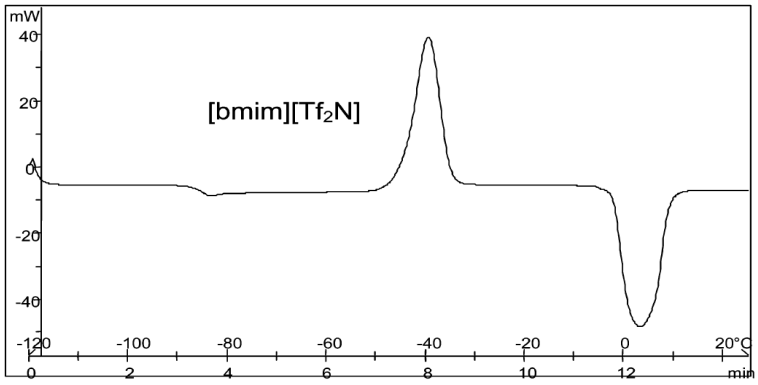


Figure 4.3: DSC scan for IL1, showing a glass-transition temperature, followed by a cold crystallization and a melting transition.[50]

Changes in the imidazolium ring substitution patterns can have significant effects on the melting points of imidazolium salts, beyond those anticipated by simple changes in symmetry or hydrogen bonding interactions.[24]

Dzyuba and Bartsch[57] investigated the influence of 1-alkyl-(aralkyl) group and anion variation on the phase transitions, density, viscosity, and surface tension of a selection of 1-alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluoromethylsulfonyl)imides. They reported lower phase transition temperatures for [C_n-mim][NTf_2] ionic liquids when compared to [C_n-mim][PF_6] ionic liquids. This suggests a strong anion effect on physical properties of ionic liquids although the authors also reported a decrease in phase transition temperatures with increase in *n* for [$Ph(CH_2)_n$-mim][PF_6] but a corresponding increase with increase in *n* for [$Ph(CH_2)_n$-mim][NTf_2].

Variation of the alkyl chain length can cause significant changes in melting points and in the tendency of the ionic liquids to form glasses on cooling.[24, 57] Holbrey and Seddon[58] reported a reduction in the melting points of a series of 1-alkyl-3-methylimidazolium tetrafluoroborates with increase in substituent length of the alkyl chain on position *N*-3. An increase in melting points was observed on increasing the alkyl chain lengths further than *n* = 8-10. This has been attributed to *van der Waals* interactions between the long hydrocarbon chains contributing to local structure by induction of microphase separation between the covalent, hydrophobic alkyl chains and charged ionic regions of the molecules.[24] The investigations of Huddleston *et al* on imidazolium ionic liquids also support this theory. Variations in the length of the 1-alkyl chain have been shown to have a larger effect on the phase transitions for $[C_n\text{-mim}][PF_6]$ than for $[C_n\text{-mim}][NTf_2]$.[57]

Increased branching of alkyl substituents on imidazolium ionic liquids have been shown to increase their melting points.[52, 53] T_g values of branched tetrafluoroborate and chloride-containing ionic liquids were reported to be 10-15 **ºC** higher than for their linear analogues.[52] The effects of branching on phase transitions have been attributed to changes in efficiency of the crystal packing as free rotation volume decreases and atom density is increased.[24]

There has been recent interest in the thermal behaviour of non-imidazolium containing ionic liquids.[54, 59-61]Ammonium ionic liquids have been classified as protic ionic liquids since they are synthesised by transfer of a bronsted acid to a bronsted base.[56, 62]Angell and co-workers[62, 63] have classified ionic liquids as good, poor, superionic and non-ionic based on the classical Walden rule (See **Figure 4.4**). The Walden rule relates the ionic mobilities (represented by the equivalent conductivity $\Lambda\left(\Lambda = F\sum_1 U_i Z_i\right)$ to the fluidity $\phi\left(\varphi = \eta^{-1}\right)$ of

the medium through which the ions move. If the liquid can be well represented as an ensemble of independent ions then the Walden plot will correspond closely with the ideal line.[62] This means that in the absence of any ion-ion interactions, the slope should be unity. They established the position of the ideal line in **Figure 4.04** using aqueous KCl solutions at high dilutions.

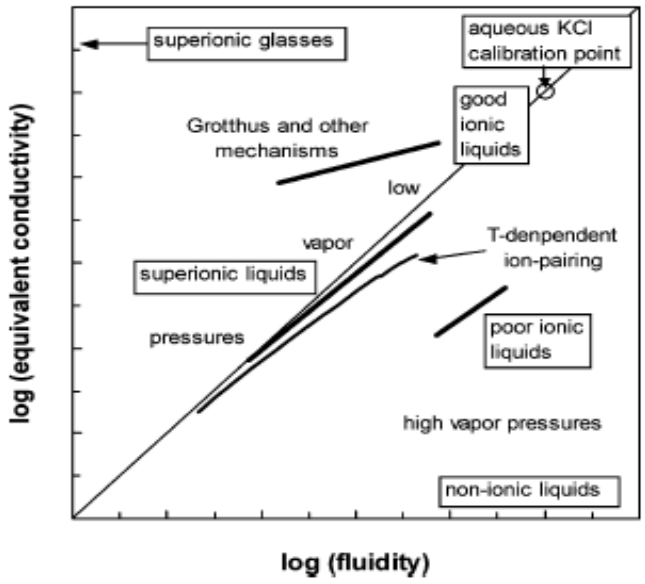


Figure 4.4Classification diagram for ionic liquids, based on the classical Walden rule, and deviations there from.[62]

Good ionic liquids are expected to have the conductivity increase directly related to the increase in fluidity, and to have negligible vapour pressure.[56] Protic ammonium ionic liquids with their low conductivities and higher vapour pressures were thus further classified as poor ionic liquids.[62]

Luo *et al*[59] have reported the DSC plots of a series of trialkylammonium and amide containing ionic liquids. The anions studied were the bis(trifluoromethylsulfonyl)imide ($[NTf_2]^-$) and the bis(perfluoroethylsulfonyl) imide ($[BETI]^-$). All ammonium ionic liquids gave heat absorption peaks corresponding to their melting points. Melting points were correlated to alkyl chain length and decreased with increase in chain length from n = 3-8. Some of the ionic liquids gave exothermic peaks which could be assigned to the crystallization point but most did not show any glass transition points. The $[NTf_2]^-$ ionic liquids showed lower heat absorption temperatures than the $[BETI]^-$ ionic liquids.

DSC scans for the amide-containing ionic liquids did not give much information but some showed broad peaks around -80 to -50 **ºC** corresponding to glass transition points similar to the plot for **IL3** in **Figure** 4.02 above. The authors suggested that the lack of any real melting points indicate that these amide-based ionic liquids are highly disordered.

Yuan *et al*[54] reported wide temperature ranges for a series of hydroxyl ammonium ionic liquids with formate, acetate and lactate anions. All but one of these ionic liquids were liquid at room temperature and showed distinct glass transition points.

Melting points appeared to increase with increasing substitution on the anions with the lactate ionic liquids having higher melting points than the acetate and formate ionic liquids respectively. No clear cation effect was shown in the results.

Greaves *et al*[56] investigated the physicochemical properties of 25 protic ammonium ionic liquids prepared by the stoichiometric combination of a bronsted acid and an amine. Most of the samples were liquid below 100 **ºC**. Many did not show the combination of T_g, T_c, and T_m. The glass transition showed clear trends with changes in the structure of the cation and anion, with T_g increasing slowly with increasing alkyl chain length, and increasing by a

larger amount with the substitution of a hydroxyl group. Smaller anions and anions with shorter alkyl chains were also shown to lead to lower T_g values. The authors did not find any correlation of ion structure with melting points or crystallization points. Samples containing an inorganic anion were however more likely to be solid at room temperature than those containing an organic anion. They found that the solid samples did not show T_g or T_c thermal transitions on their DSC traces unless the samples were preheated to above T_m. They also showed that the crystallization is an exothermic process, whereas melting is endothermic and found a weak correlation between increasing T_m with increasing endothermic enthalpy for this phase transition.

Belieres and Angell[63] studied a wide range of ammonium formates, nitrates, tetrafluoroborates, triflates, methanesulfonates, hydrogen sulfates, fluorohydrogenphosphates and dihydrogenphosphates.

They reported glass transitions which were higher for dihydrogen phosphate, fluorohydrogenphosphate, methanesulfonates, hydrogensulfates and nitrate containing salts than for formates.[63] This shows a trend for inorganic anions to have higher glass transitions. Glass transitions were not detected for the triflate and tetrafluoroborate salts investigated and only a few crystallisation points T_C were detected across all the compounds.[63]

Ohno and co-workers[37] have synthesised a suite of ionic liquids composed of only biomaterials and carried out a systematic study of their thermal transitions. The ionic liquids studied were choline salts with acetate, propionate, glycolate, benzoate, tiglate, H-succinate, H-malate, H-tartrate, H-fumarate and H-maleate anions. The Differential Scanning Calorimetry analysis of the ionic liquids showed that **[Choline][AcO]** gave a T_m of 51 **ºC**

while its glycolate analogue gave a melting point of 38 **ºC**. They attributed the low melting point of the glycolate to the attractive property of the hydroxyl group on the glycolate anion and its assymetrical structure.[37] No peaks were observed corresponding to melting and freezing behaviour for the **[Choline][PrO]** and **[Choline][tiglate]** ionic liquids possibly as a result of the asymmetric structure of their anions causing poor packing of the ions.[37]

4.1.1.1 Thermal Stability

The thermal stability of solvents is a valuable property when designing extraction protocols that require heating. Since ionic liquids have negligible vapour pressures, the upper limit of their liquid range is bound by the decomposition temperature.[24] Most imidazolium ionic liquids begin to decompose around 400 **°C** with minimal vapour pressure below their decomposition temperature, as determined by thermal gravimetric analyses.[49] In most cases, decomposition occurs with complete mass loss and volatilization of the component fragments.[24]

Belieres and Angell[63] have reported that for protic ionic liquids formed with low-energy proton transfers, the weight loss begins at the boiling point and for those formed with high-energy proton transfer, boiling would only occur at very high temperatures and is thus pre-empted by decomposition. Salts formed by proton transfers that are weak will not form liquids with uniform charge distributions hence their Walden plots will fall below the ideal line, and their vapour pressures will not be very low.[62]

The decomposition temperatures of imidazolium ionic liquids have been shown to follow the general order $Cl^- < [BF_4]^- \sim [PF_6]^- < [NTf_2]^-$ meaning that ionic liquids containing weakly coordinating anions are most stable to high-temperature decomposition.[24, 49, 51, 53, 58] The onset of decomposition temperatures has also been shown to decrease as anion hydrophilicity increases.[53]

Ngo *et al*[53] have shown that thermal stability has a strong dependence on both cation and anion structure. They observed that thermal decomposition is endothermic with the inorganic anions and exothermic with the organic anions investigated. The substitution of hydrogen with an alkyl group on the imidazolium ring has been shown to increase stability.[53, 59] This effect appears to increase with the C-2 hydrogen due to its higher acidity.[49, 53] The length of the alkyl chain however, has not shown any strong effects on thermal stability.[49, 59]

Luo *et al* have suggested that mass transport and evaporation play a small part in determining decomposition temperatures when they found that increasing the size of their TGA sample mass from 10 mg to 30 mg lead to an increase of the onset decomposition temperature (T_{onset}) by 10 **ºC** at 10 **ºC**/min scan rate. They observed that decreasing the heating rate by a factor of 10 also induced a large decrease (about 40 **ºC**) of the onset decomposition temperature. Imidazolium $[PF_6]^-$ salts are strongly affected by pan composition displaying as much as 100 **ºC** lower thermal stability in the presence of aluminium compared to alumina.[53]

Halide anions can dramatically reduce the thermal stability and reduce the onset of decomposition to at least 100 **°C** below the corresponding ionic liquids with non-halide anions.[53]Thus, it can be deduced that the presence of chloride impurities can reduce the thermal stability of ionic liquids.

The ammonium ionic liquids used in this study are prepared by the proton transfer from a bronsted acid to an amine, thus removing the problem of chloride impurities.

The thermal behaviour of ammonium ionic liquids depends on whether they have an inorganic or organic anion.[56] The ammonium ionic liquids with inorganic anions have higher decomposition temperatures than those with organic anions.[56, 59]

Luo *et al*[59] in their comparison of ammonium-based $[NTf_2]^-$ and $[BETI]^-$ ionic liquids with their imidazolium-based counterparts, found that the ammonium-based ionic liquids had decomposition temperatures of about 100 **ºC** lower than the imidazolium ionic liquids. They attributed the lower thermal stability to the ability of the ammonium ionic liquids to have a reverse proton transfer reaction to form their respective acid and amine starting materials. They also reported that the thermal stability of the ammonium-based ionic liquids showed no correlation with the length of the alkyl chains on the cations. They however found that the ionic liquids with the $[NTf_2]^-$ anion had decomposition temperatures about 20 **ºC** higher than those with the $[BETI]^-$ anion, thus showing correlation between their thermal stability and anion type.

Greaves *et al*[56] in their study on the thermal properties of 25 protic ammonium ionic liquids with both organic and inorganic anions, found that many of the samples began to lose weight even at ambient temperatures. They attributed this weight loss to evaporation and found that it was most notable in the case of the formate ionic liquids.

They found that the salts containing inorganic anions had greater thermal stability than those containing organic anions. The authors did not find peaks corresponding to the boiling

points of the ionic liquid precursors and thus concluded that the protic ionic liquids were not reforming the acid and base via proton transfer.

Belieres and Angell[63] in their work on protic ammonium salts showed that the boiling points T_b and thermal decompositions T_{dec} of formates and methanesulfonates respectively, generally increase with increasing molecular weight.[63] The thermal stabilities of the nitrate, tetrafluoroborate, triflate and methanesulfonate salts were higher than that of the salts with organic anions[63] agreeing with the work of Greaves *et al* above.

Zhao *et al*[30] have compared the decomposition temperatures in air of **IL15** with that of its ethyl analogue, [Me(OEt)$_2$-Et-Im], [Me(OEt)$_3$-Et-Im], [Me(OEt)$_4$-Et-Im], [Me(OEt)$_2$-Et$_3$N] and [Me(OEt)$_3$-Et$_3$N][AcO]. The decomposition point for **IL15** was 4 **°C** lower than that for [C$_3$mim][AcO] and increasing the -OEt substitution on both the methyl group on the imidazolium and the methyl group on the ammonium nitrogen, had little or no effect on the decomposition temperatures. This suggests a strong anion effect on decomposition temperatures for [AcO] ionic liquids.

The TGA studies on choline salts done by Ohno and co-workers showed the range of temperature for 5% weight loss (T_{dec}) to be 184–223 **°C**.[37] The decomposition temperatures varied considerably from anion to anion, thereby showing a correlation with anion type. There was however no clear correlation with molecular weights.

4.1.1.2 Isothermal Stability

Care needs to be taken when using decomposition temperatures of ionic liquids as a basis for planning thermal extraction protocols. Isothermal studies on ionic liquids have shown decomposition temperatures of ionic liquids lower than results obtained previously under normal TGA conditions.[64, 65]

The long-term thermal behavior of [C_4mim]Cl and [C_6mim]Cl ionic liquids have been investigated[64] using isothermal TGA studies for 15 hours with argon purge at 150 mL/min. The isothermal TGA studies showed that [C_4mim]Cl and [C_6mim]Cl ionic have substantial (15 h) long-term thermal stability up to 160 ◦C. Thereafter, they found that the ionic liquids lose weight progressively. They used a pseudo-zero-order rate law to determine the kinetics of isothermal decomposition of ionic liquids in the temperature range of 150–200 ◦C. Activation energies for decomposition of [C_4mim]Cl and [C_6mim]Cl determined using Arrhenius relation were 121 and 117 kJ/mol, respectively.

Ammonium ionic liquids have been shown to be less thermally stable than their imidazolium counterparts. Microwaves can be used to shorten the extraction times of processes using ammonium ionic liquids or indeed imidazolium ones where necessary.

4.2 Microwave Conductivity

The use of microwave technology dates back to the design of a fixed frequency microwave generator called the magnetron[66] during the Second World War. It was developed as part of the drive to enhance RADAR technology. By the 1950's, domestic and industrial microwaves began to appear on the U.S. market and their use for heating food became more widespread by the 70's and 80's.

Although the application of microwave technology in Inorganic Chemistry has been known since the 1970's,[67] its application to reduce reaction time in organic reactions was first reported in 1986.[68, 69]

4.2.1 Microwave Theory and Background

Microwave heating exploits the ability of some substances to convert electromagnetic energy into thermal energy.[66] The microwave region of the electromagnetic spectrum lies between the infra-red region and the radiofrequency region (**Figure** 4.05). The wavelength of the region ranges from 1mm to 1m corresponding to frequencies of between 300 MHz and 300 GHz.[66] Microwave ovens operate at a frequency of 2450 MHz, corresponding to a wavelength of 12.2cm or at 900 MHz(33.3cm).[66]

This frequency is fixed for most domestic and industrial microwaves in order to avoid interference with telecommunications and RADAR transmissions. At 2450MHz, only rotation of molecules will occur, resulting in an energy release of 0.23 kcal/mol.[66] Thus, the

oscillatory motion causes collisions with surrounding molecules and a resultant release of thermal energy into the medium.[70]

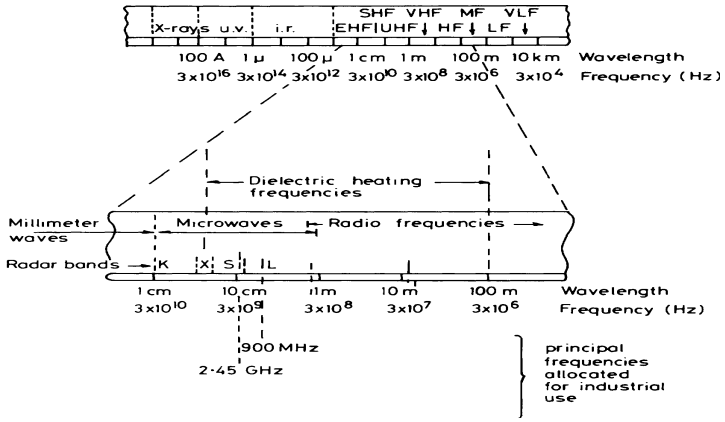


Figure 4.5: The Electromagnetic Spectrum indicating the important microwave frequencies for dielectric heating.[66]

4.2.1.1 Microwave Heating

Microwave radiation like all other electromagnetic radiations is made up of two components, a magnetic field component and an electric field component. The component responsible for dielectric heating is the electrical component.[71] This heating effect produced by the electric field is due to its ability to exert a force on charged particles.[66] There are two mechanisms available for the explanation of dielectric heating by microwave radiation, dipole rotation and ionic conduction.[71]

a) Dipole Rotation

A substance possessing a dipole moment in the region of an electric field, will attempt to align itself to the applied electric field by rotating (See **Figure** 4.06).[71] If the frequency of irradiation is too low, the molecule rotates in phase with the electric field and gains some energy, but the overall heating effect is quite small.



Figure 4.6: Dipolar molecules rotating to align themselves with the field.[71]

On the other hand, if the frequency is too high, the molecules cannot respond to the electric field fast enough and no rotation occurs. When a microwave frequency is applied, the time in which the field changes is about the same as the response time of the molecules.[66] The frequency is however not high enough for the rotating molecule to precisely follow the field, so as the dipole attempts to re-align itself with the electric field, the field is already changing and it generates a phase difference between its own alignment and that of the dipole.[71] The resulting phase difference, δ, generates a component $I \sin \delta$, in phase with the electric field (**Figure 4.7b**). Resistive heating known as dielectric loss occurs and causes energy to be absorbed from the electric field.[72]

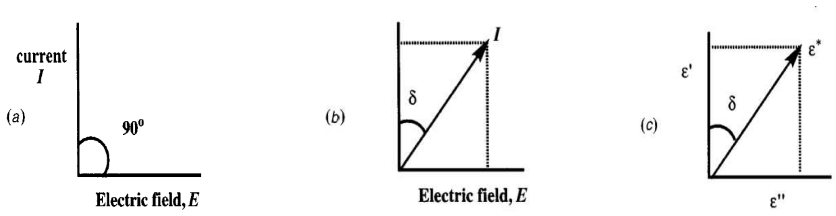


Figure 4.7: Phase diagrams for (*a*) an ideal dielectric where the energy is transmitted without loss; (*b*) where there is a phase displacement δ and the current acquires a component *I* x sin δ in-phase with the voltage and consequently there is a dissipation of energy. In (*c*) the relationship between ε*, ε′ and ε″ is illustrated; tan δ = ε″ / ε′[72]

This loss angle, δ (**Figure 4.7**c) shows the ability of a substance to convert electromagnetic energy into thermal energy at a given frequency and temperature and is usually defined as its tangent.[66, 71]

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Equation 4.1: Relationship between the dielectric constant and the dielectric loss.

ε' is the relative permittivity or dielectric constant, a measure of the ability of a molecule (or assembly of molecules) to be polarised by an electric field.[73] ε'' is the dielectric loss, which indicates the ability of a medium to convert dielectric energy into heat. For materials with comparable ε′, and for low values of *tan δ*, this relationship can provide a convenient method for comparing the efficiency of conversion of microwave energy into thermal energy. Therefore, a material with a higher loss tangent will be expected to absorb more

microwave heat if irradiated at the same power and for the same period of time as one with a similar dielectric constant.[71] Take ethanol and acetone for example, both solvents have comparable dielectric constants ε_s (Table 4.1)[71] If they are both heated at the same radiation power and for the same period of time, the final temperature will be much higher in ethanol than in acetone (**Figure 4.8**). At room temperature and under the influence of a static electric field, ε', is equal to the dielectric constant, ε_s.[71]

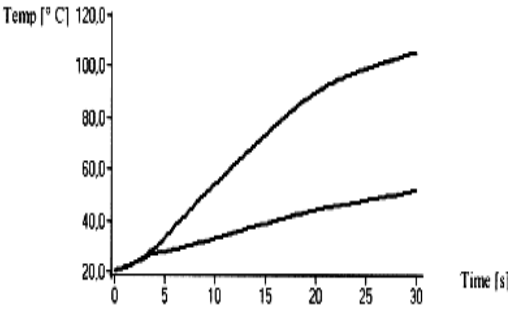


Figure 4.8: The temperature increase of ethanol and acetone, respectively, at 150W microwave irradiation. The upper curve represents ethanol the lower plot represents acetone.[71]

Although *tan* δ is a helpful parameter for comparing the heating rates of a range of compounds having similar chemical and physical characteristics more complex expressions, which take into account the complexity of the electric field patterns, the heat capacities of the compounds and their densities, are required in order to calculate these heating rates reliably.

Table 4.1: Dielectric constants and loss tangent values for some common solvents.[71]

Solvent	Dielectric Constant ε'	Loss Tangent *tan* δ
Hexane	1.9	-
Benzene	2.3	-
Carbon Tetrachloride	2.2	-
Chloroform	4.8	-
Acetic Acid	6.1	0.091
Ethyl Acetate	6.2	0.174
THF	7.6	0.059
Methylene Chloride	9.1	0.047
Acetone	20.6	0.042
Ethanol	24.6	0.054
Methanol	32.7	0.941
Acetonitrile	36	0.659
Dimethylformamide	36.7	0.062
DMSO	47	0.161
Formic Acid	58	0.722
Water	80.4	0.123

The relationship between the relaxation time, τ and the permitivitties, ε' and ε'' as shown by Gabriel *et al*[72] has been used to explain these complexities. The relaxation time is the time taken for one molecule to return to 36.8% of its original situation when the electric field is switched off.[71] It is temperature dependent and decreases as the temperature is increased. Both ε' and ε'' are dependent on τ, therefore the ability of a solvent to convert microwave energy into heat, will be determined not only by the frequency but also by the temperature.

b) Ionic Conduction

Ionic conduction occurs when there are charged species present in a solution. If a solution containing ions or even a single isolated ion with a hydrogen bonded cluster in the sample, is under the influence of an electric field, the ions will move through the solution resulting in expenditure of energy due to an increased collision rate, converting the kinetic energy to thermal energy(**Figure 4.9**).[71]



Figure 4.9: Charged particles in a solution will follow the applied electric field**.**

Thus, if two samples containing distilled water and tap water, respectively, are heated in a single mode microwave cavity at a fixed radiation power and for a fixed time, the final temperature will be higher in the tap water sample(**Figure 4.10**).[71]

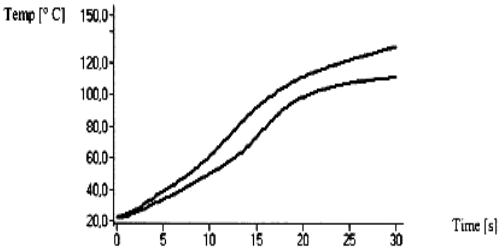


Figure 4.10: **The temperature increases of distilled water and tap water, respectively, at 150W microwave irradiation. The upper curve represents tap water and the lower curve represents distilled water.**

In the above example, the heat generated by the conduction mechanism due to the presence of ions adds to the heat produced through the dipolar mechanism, resulting in a higher final temperature in the tap water. In general, with regards to heat-producing capacity, ionic conduction is a much stronger interaction than dipole rotation.

4.2.1.2 Microwave Effects

Since the introduction of microwave-assisted organic synthesis in 1986, there has been a debate on what actually alters the outcome of the synthesis.[71] The debate centres on whether the outcome is simply as a result of the thermal heat generated by microwave irradiation, or if there are "specific microwave effects". Specific microwave effects are claimed when the outcome of synthesis performed using microwave heating is different from that obtained using conventional heating apparatus. Loupy *et al* have reported regio-selectivity in the solvent-free phenacylation of 1,2,4-triazole under microwave irradiation.[74] They proposed that specific microwave effects could be expected for polar mechanisms, when the polarity is increased during the reaction from ground state to transition state, thus lowering the activation energy.

Some authors have attributed specific microwave effects to thermal effects occurring as a result of superheating.[71] Stuerga *et al* have associated reaction specificities in the sulfonation of naphthalene with control of very high heating rates.[75]

4.2.1.3 Instrumentation

There are two types of microwave reactors currently available, multimode and mono-mode reactors. In the so-called multimode instruments (similar to domestic ovens), the microwaves that enter the cavity are reflected by the walls and the load over the typically large cavity. In most instruments a mode stirrer ensures homogeneity of the field distribution.[76] In the much smaller mono-mode cavity, the electromagnetic irradiation is directed through an accurately designed rectangular or circular wave guide onto the reaction vessel mounted at a fixed distance from the radiation source, thus creating a standing wave. The key difference between the two types of reactor systems is that whereas in multimode cavities several reaction vessels can be irradiated simultaneously in multi-vessel rotors, in mono-mode systems only one vessel can be irradiated at the time.

Many of the early experiments in microwave-assisted organic synthesis were carried out in domestic microwave ovens. In such ovens, the irradiation power is generally controlled by on/off cycles of the magnetron (pulsed irradiation), and it is usually difficult to monitor the reaction temperature in a reliable way. This makes reproducibility of the reaction conditions very difficult. Today, most commercially available microwave reactors for synthesis now feature built-in magnetic stirrers, direct temperature control of the reaction mixture with the aid of fiber-optic probes or IR sensors, and software that enables temperature/pressure control by regulation of microwave power output.[76]Large scale batch and continuous multimode ovens are now available and single mode microwave ovens with options for batch or continuous processing have been designed for specific research purposes.[73]

4.2.2 Microwave-Assisted Organic Syntheses (MAOS)

Microwave heating is very convenient to use in organic synthesis, because the heating is instantaneous, very specific and there is no contact required between the energy source and the reaction vessel.[71]

Microwave-assisted organic syntheses were first reported in 1986. Gedye *et al* employed microwave irradiation in acid hydrolysis, oxidation and esterification reactions.[68] Soon after, Giguere *et al* reported Diels Alder and Claisen reactions carried out under microwave energy.[69] These early experiments were done in domestic microwaves, in sealed vessels.

In more recent times, microwave heating has been carried out under controlled conditions using dedicated microwave reactors. Solution-phase *Heck* Reactions have been successfully carried out by MAOS.[77-79] The *Suzuki* Reaction (palladium-catalysed cross-coupling of aryl halides with boronic acids) is probably one of the most versatile and commonly used cross-coupling reactions in modern organic synthesis.[80] Carrying out high-speed *Suzuki* reactions under controlled microwave conditions can be considered almost a routine synthetic procedure today.[79] Countless other organic reactions, as reviewed by Kappe have been carried out under microwave reaction including *Sonogashira*, *Negishi*, *Ullmann* condensations, asymmetric allylic alkylations, nucleophilic aromatic substitutions and numerous transition-metal-mediated processes.[76]

4.2.3 Microwave-Assisted Extractions (MAE)

Sophisticated analytical procedures are available today that would detect very low quantities of individual contaminants and compounds of special interest or value. Sample preparation is a critical step in chemical and biochemical analyses, usually being the slowest step in the analysis.[81] The aim of sample preparation is that the components should be extracted from complex matrices with less time and energy consumption but with the highest efficiency and reproducibility.

Extraction is one of the least evolved steps in analytical procedure.[82] One of the most commonly used techniques today, Soxhlet extraction, was developed by F. Soxhlet in 1879.[83] The technique involves repeated percolation of the sample with recondensed vapours of the solvent being used and is one of the most used techniques for extraction of organic contaminants.[82] Problems of large quantities of solvent, often toxic and the need for faster extractions, led to the introduction of supercritical fluid extraction.[84] This method is however limited by high costs and selectivity, which requires advanced optimisation.[82]

The extraction of organic compounds by microwave irradiation was first reported by Ganzler *et al* in 1986.[85] They used microwave irradiation in the extraction of various compounds including pyrimidine glucosides, gossypol, crude fat and pesticides from different sources (fava beans, cottonseed, food and soil samples). The emergence of commercial microwave systems which are specifically designed for extraction is rather recent, and has encouraged renewed interest in the technique. This interest has been mainly focused on the extraction of organic compounds from environmental matrices.[82]

Several reviews have been published on MAE from environmental matrices. Letellier *et al* have reviewed the extraction of pesticides, herbicides, PAHs, PCBs from soils, sediments, sludge and water.[82] Kaufmann *et al* have reviewed the application of MAE to natural product extraction from various plant materials.[70] The application of MAE in extraction of pollutants from environmental matrices in general has also been extensively reviewed.[86]

4.2.4 Ionic Liquids as solvents in Microwave-assisted Organic Syntheses and Extractions.

Ionic liquids interact very efficiently with microwaves through conduction and are rapidly heated without any significant pressure increase because of their negligible vapour pressure.[87] Therefore, safety problems arising from over-pressurisation of heated sealed reaction vessels can be minimised.

The use of ionic liquids as solvents in MAOS has gained considerable attention in recent years. Palladium-catalysed Heck arylations have been successfully carried out in **IL2** under controlled microwave conditions, in reduced time.[88]

The Beckmann rearrangement of ketoximes in the presence of 5% mol of H_2SO_4 in **IL2** has been carried out under microwave energy.[89]

Arfan and Bazureau have also reported mild and efficient esterification reactions of carboxylic acids with *neo*-pentanol using task-specific ionic liquids with hydrogen sulphate counter-anions under solvent-free microwave irradiation.[90]

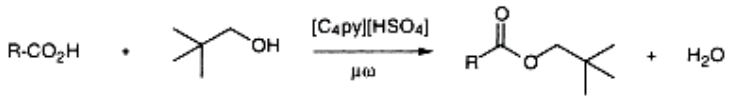


Figure 4.11: General scheme for Preparation of esters from *neo*-pentanol 3 and acids in $[C_4py][HSO_4]$ as catalyst under microwave irradiation.[90]

Other authors have employed ionic liquids as co-solvents or doping agents to improve the heating ability of non-polar solvents in microwaves.[87, 91, 92]

Ionic liquids themselves have been synthesised using microwave energy. Varma and Namboodiri were the first to prepare ionic liquids under solvent-free microwave irradiation using household ovens.[93, 94] These reactions were carried out in open vessels using a large excess of haloalkanes. Other authors have reported preparations in sealed vessels using more dedicated microwave instruments, thus preventing reactant loss and achieving better reproducibility.[95, 96] Deetlefs and Seddon reported reduction in conventional reaction times of up to 70% and comparable yields.[95]

4.3 Thermophysical Properties and Microwave Conductivity Profiles of Ionic Liquids

DSC scans of 7 ammonium ionic liquids in the temperature range -60 to 100 **°C** were taken using a Perkin Elmer Diamond Differential Scanning Calorimeter at a heating rate of 10 **°C**/min. Both the cations and anions used in synthesising the ionic liquids were varied to investigate the effect of increased substitution on the cation and anion and the effect of the presence of a hydroxyl group on the anion. The ionic liquids studied were of the acetate, propionate, glycolate and dihydrogenphosphate anions.

4.3.1 Glass Transitions and Melting Points

Table **4.2** shows the phase transitions for the respective ionic liquids. All but one of the ionic liquids was liquid at room temperature although the dihydrogen phosphates were extremely viscous. The ionic liquids gave higher glass transitions than 1-alkyl-3-methylimidazolium salts, which are typically in the region between -90 and -70**°C**.[24] These ammonium salts vitrified between -60 and -30**°C**. They did not show the combination of T_g, T_c, and T_m agreeing with the work of Greaves *et al*[56], although they reported lower T_g values in general for their ammonium ionic liquids. They did however report a trend for the presence of hydroxyl group to increase the T_g; this may account for the higher T_g values observed here. The dimethylethylhydroxyl acetate and propionate did not show any transitions at all in the scan range, suggesting that they may depict glass transitions lower than -60**°C**. The corresponding glycolate gave a higher glass transition of -37**°C** as a result

of increased attraction from the hydroxyl group on the anion and increase in asymmetry, thereby increasing the cohesive energy. Thus, the absence of a glass transition for **IL19** could also be attributed to the absence of a hydroxyl group on the cation. Only the dihydrogenphosphate ionic liquids showed devitrification temperatures in the heating step again showing a greater affinity to form a more ordered system. This is shown in the comparison of DSC scans of the diethylethanolammonium dihydrogenphosphate and glycolate ionic liquids in Figure **4.12**.

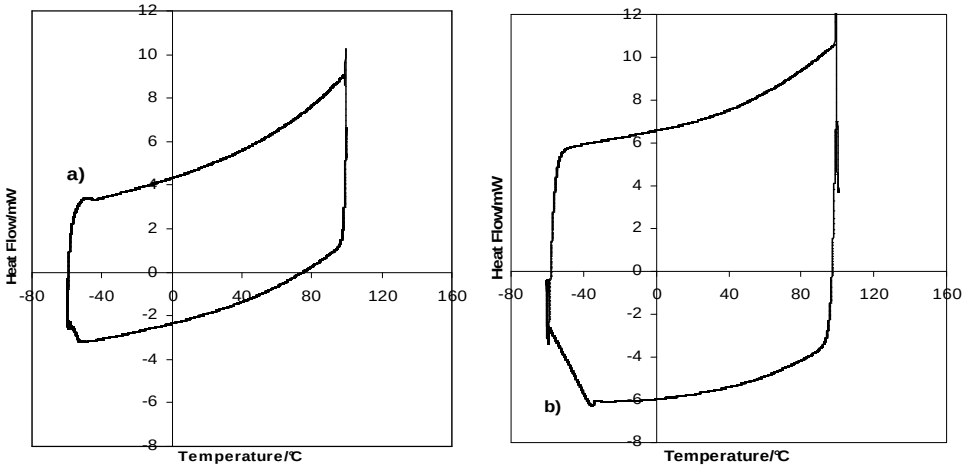


Figure 4.12: a) DSC Plot of diethylethanolammonium dihydrogen phosphate showing T_g in cooling step and T_c in heating step. b) DSC Plot of diethylethanolammonium glycolate showing only T_g in cooling step.

Only Choline Propionate showed a distinct melting point at -3°**C**, with a sharp endothermic peak, likely due to a higher purity than the other ionic liquids studied. This is not surprising since the higher thermal stability of this particular **IL** compared to **IL8** and **IL9**, meant that it could withstand further purification at elevated temperatures, *in vacuo* to reduce its water content. Even though choline acetate is a solid at room temperature, it did not yield a

melting point in its DSC scan. This IL has earlier been reported to have a melting point of 51°**C**.[37]

Table 4.2: Phase Transitions of the Selected Ionic Liquids Including Their Glass Transition (T_g), Devitrification Temperature (T_c), and Melting Point (T_m)

Ionic Liquids	**Molecular Weight**	**Physical State**	T_g/°C	T_c/°C	T_m/°C
IL8	149.18	L	n.d.[a]	n.d.	n.d.
IL9	163.21	L	n.d.	n.d.	n.d.
IL18	165.19	L	-37	n.d.	n.d.
IL19	171.13	L	n.d.	-49	n.d.
IL20	187.13	L	-52	-45	n.d.
IL22	163.21	S	-35	n.d.	n.d.
IL11	177.24	L	n.d.	n.d.	-3

[a] Not detected.

It should be noted that there was a direct correlation of the presence of phase transitions in the DSC scans with increased thermal stability (Table **4.2**) of the **IL**s. Thus, the reduced thermal stability of the tertiary ammonium based acetate and propionate meant an inability to withstand further purification at higher temperatures resulting in higher impurities and possibly contributed to the absence of phase transitions. There were no clear trends on effect of alkyl substitution on glass transitions and melting points.

4.3.2 Thermal Properties

DTA/TGA experiments were performed using a simultaneous thermal analyser STA 1500 (Rheometric Scientific) designed to give TGA weight loss and energy changes arising from weight loss. The use of DTA in addition to DSC was to enable the measurement of boiling points of the protic ionic liquids, which cannot be determined using standard DSC. Samples were weighed and placed in unsealed alumina crucibles and heated from room temperature to 450 **°C** under N_2 atmosphere and with a heating rate of 5 **°C**/min. The dihydrogenphosphate ionic liquids were heated up to 1000 **°C**.

4.3.2.1 Boiling Points and Ionicity

The ΔpK_a is derived from the difference in aqueous solution pK_a values for the respective acid and base starting materials. In aqueous solutions, the free energy driving the transfer may be obtained from data on the work of transfer of protons from acid to water, and from water to base, respectively.[62] The ΔpK_a values can give a relative measure of how complete the proton transfer is from acid to base to form a neutral ionic species,[62, 97, 98] although it is not clear how relevant the aqueous pK_a values used, are to acid-base equilibria in non-aqueous ionic liquids.[99] Table **4.3** shows ΔpK_a, boiling points T_b, temperatures of complete volatilisation T_v and molecular weights of the respective ionic liquids.

Table 4.3: Thermal Properties of Ionic Liquids

Ionic Liquids	Molecular Weight	ΔpK_a	T_b/°C	T_v/°C
IL8	149.18	4.5	86.88	127.36
IL9	163.21	4.4	96.07	135.16
IL18	165.19	5.4	-	349.45
IL19	171.13	7.9	-	949.72[a]
IL20	187.13	7.1	-	914.63[a]
IL22	163.21	-	155.7	232.48
IL11	177.24	-	160.01	234.78

[a]: T_v taken at 90% volatilisation.

ΔpK_a values for alkylammonium ionic liquids with organic anions have been reported to be between 4 and 7 and that for inorganic ionic liquids between 8 and 12.[99] The ΔpK_a values in Table 4.3 suggest that the inorganic acid based ionic liquids have a stronger tendency towards the ionised forms than the organic ionic liquids. Values are not given for the choline **ILs** since they are not formed by proton transfer from acid to base. There is general agreement that for the truly protic **ILs** (i.e. excluding the choline ILs), the temperature of volatilisation is higher for ionic liquids with greater ΔpK_a, therefore we can conclude that the more complete the proton transfer is from acid to base to form the IL, the higher the temperature needed to pull the cation and anion apart and reform the starting materials.

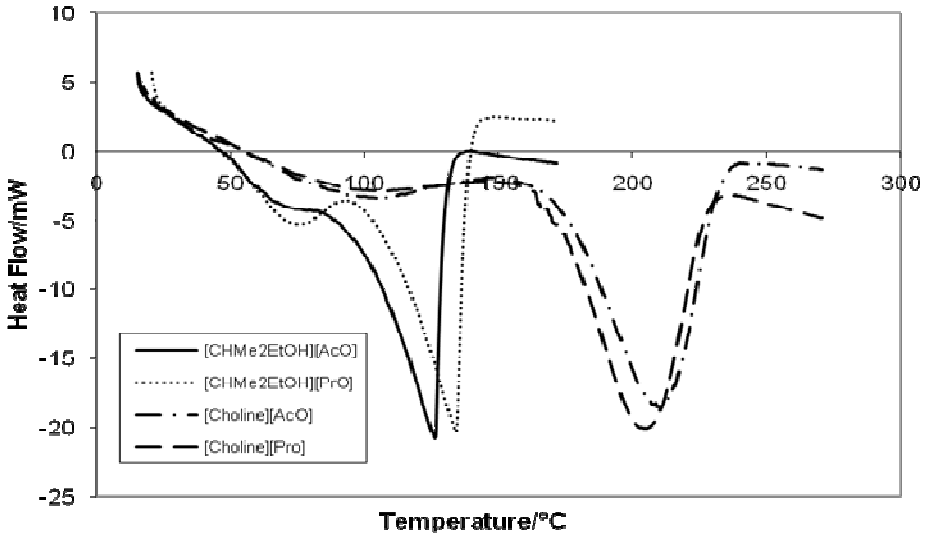


Figure 4.13: Heat Flow Scan showing T_b for Acetate and Propionate Ionic Liquids

The [AcO] and [PrO] ionic liquids gave distinct boiling point signals T_b shown by a sharp endothermic displacement.[62, 100]This displacement in the case of the dimethylethanol based **ILs,** signifies the relocation of the proton on the acid[63] hence the pronounced sharpness of this endothermic peak. For the glycolate ionic liquid and the dihydrogen phosphate ones, decomposition occurred before boiling. The absence of a proton on the cations of the choline based **ILs** is sufficient enough to raise their boiling points by up to 70 **ºC**. This is because the removal of a proton from the cation to reform the acid and base starting materials is easier for the dimethylethanol **ILs**, whereas for the Choline **ILs**, there is no proton on the cation and the removal of a methyl group will not form the initial starting materials.

4.3.2.2 Weight Loss and Decomposition

Although the work of Zhao *et* al[30] suggested only a weak cation effect on decomposition rates of acetates on lengthening the alkyl chain, it is shown here that the replacement of a

proton with an alkyl group clearly gives a marked increase in thermal stability and thus increases the volatilisation temperature. This is because the proton on the cation is easily removed to reform the acid and base starting materials. Weak endothermic peaks were observed for all the [AcO] and [PrO] ionic liquids (see **Fig 4.13**) probably corresponding to the removal of water or excess acid/base[15] in the system. Weight loss at ambient temperatures corresponding to evaporation was evident for most of the ionic liquids but more marked for those with tertiary amines and organic acids as starting materials. Those ionic liquids having inorganic anions clearly showed a higher thermal stability than those with organic anions as observed previously.[56, 97] Their boiling points were preceded by decomposition as is customary[56] for ionic liquids containing inorganic anions. They showed a series of thermal transitions, suggesting the presence of several phases within the system.

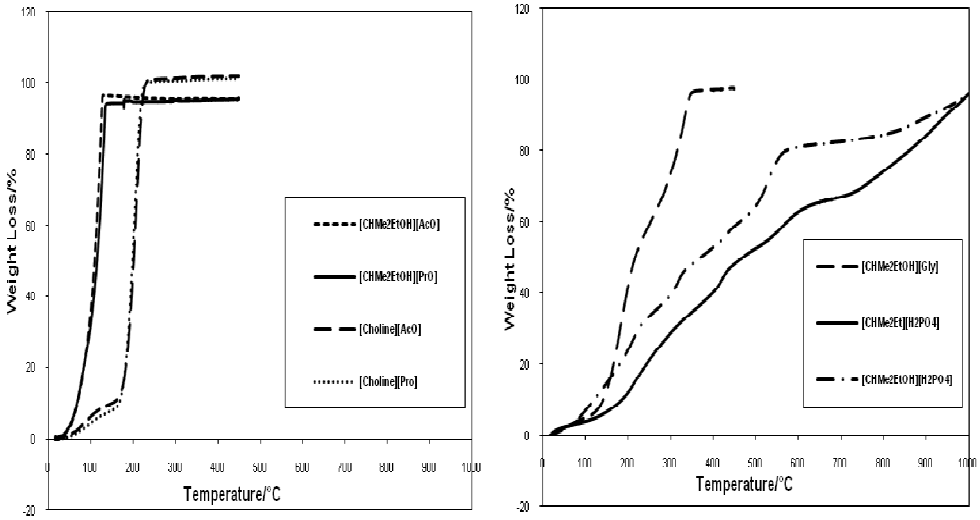


Figure 4.14: Weight loss diagrams for selected ionic liquids

Substitution of the proton on the the dimethylethanolammonium cation with another methyl group increased the thermal stability substantially and increased T_v by about 100 **ºC**.

Lengthening the alkyl group on the anion side chain by one carbon also increases the volatilisation temperature but by a much smaller magnitude.

The replacement of a proton on the methyl group of the acetate anion, with an **–OH** group increased the thermal stability significantly and the resulting glycolate anion ionic liquid also showed a series of thermal transitions (decompositions) preceding its boiling point. This suggests that the presence of an **–OH** group on the anion also contributes to a higher thermal stability. This is probably due to the **-OH** group causing increased attraction of the anion to the cation making it more difficult to split the **IL** and reform its starting materials. Greaves *et al*[56] in their work on the physicochemical properties of a series of 25 protic ionic liquids and protic fused salts, also reported higher decomposition points for their glycolate ionic liquids than the respective acetate counterparts.

From the results shown above, the **IL8** and **IL9** on the strength of thermal properties alone, would be poor solvents for biomass processing due to their inability to withstand high temperatures without decomposition. The corresponding Choline **ILs** would make better solvents due to their higher thermal stability although the acetate with its high melting point would require operating temperatures close to the maximum 120 **ºC** employed for this study. Their lower implied glass transitions should also result in lower viscosities and higher ionic conductivities. The microwave conductivities of the ionic liquids are studied in the next section to investigate the suitability of this mode of heating to speed up the biomass processing rates.

4.3.3 Dielectric Heating Profile of Ionic Liquids

The use of ionic liquids in microwave-assisted syntheses and extractions has been reported in recent publications.[88-90, 101, 102] The tuneable properties of ionic liquids, wide liquid range and high thermal stability make them suitable candidates as solvents in microwave-assisted processes. Their low vapour pressure is desirable to prevent pressure build-up in reaction vessels leading to explosions.[89] As stated earlier, microwaves couple directly with ions, via ionic conduction and polar molecules, via dipole rotation. Thus, the presence of ions and polar molecules in a substance is essential for dielectric heating to occur. Ionic liquids are entirely made up of ions and are also polar molecules, so they make ideal solvents for microwave irradiation.[13] This section aims to investigate the heating behaviour of various ionic liquids in microwaves as a tool in optimising experimental conditions in microwave extractions involving ionic liquids.

8 ml of the ionic liquids studied were irradiated with microwave energy to investigate their heating rates, in a Multiwave® 3000 V1.52 (Anton Paar, GmbH) multimode-microwave oven at 200W power setting in closed vessels. The temperature was recorded with a fibre-optic sapphire sensor inside the sample. All measurements were repeated 5 times and a ^{1}H NMR spectrum was taken between each run. The ionic liquids were heated up to 100 ˚**C** and the time achieved at 80 ˚**C** was recorded to avoid power cut-offs from the microwave. Plot of the results showed a curved temperature-time dependency for each of the ionic liquids studied. An example is shown below (**Fig 4.15**).

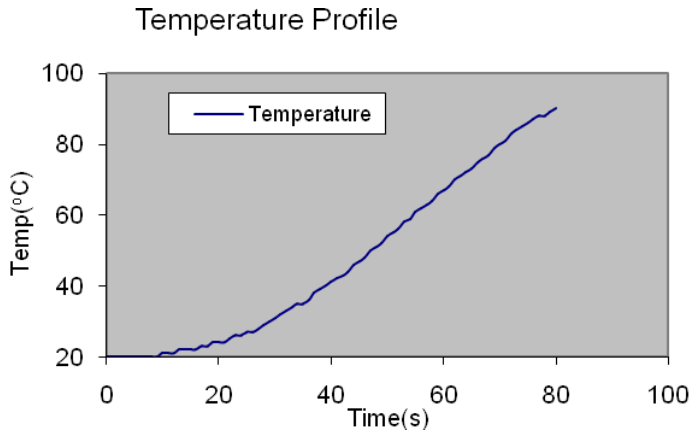


Figure 4.15: Temperature profile for [C_4mim][NTf_2] when heated from 20 to 80 °C.

The temperature profiles of the ionic liquids remained the same within 5% error even after the 5th run and the errors were largely due to the heating not starting at the same temperature when the runs were repeated. The best values were reported to take into account the temperature at which each run started.

The heating behaviour of ionic liquids under microwave irradiation has been studied.[13] Microwave heating times are determined by ionic conductivity and dipole relaxation times. Relaxation times generally increase with viscosity as expressed by Debye, in the following equation for a spherical molecule of radius *r* rotating in a viscous continuum

$$\tau = 4\pi r^3 \eta / kT$$

Equation 4.2: The relationship between viscosity and relaxation time.

This clearly shows a direct relationship between relaxation times and viscosity and an inverse relationship with temperature. Relaxation times will decrease with increasing

temperature. Thus, the rate of dielectric heating for any material should increase as higher temperatures are achieved.

4.3.3.1 Dielectric Heating Profiles of Imidazolium Ionic Liquids

The methyl imidazolium ionic liquids studied were derivatives of the form in **Fig 4.16.**

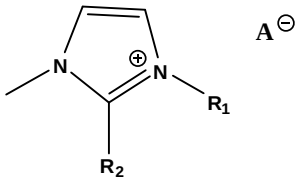


Figure 4.16: Alkylimidazolium ionic liquid. A: NTf_2, TfO, PF_6, BF_4 and SbF_6.

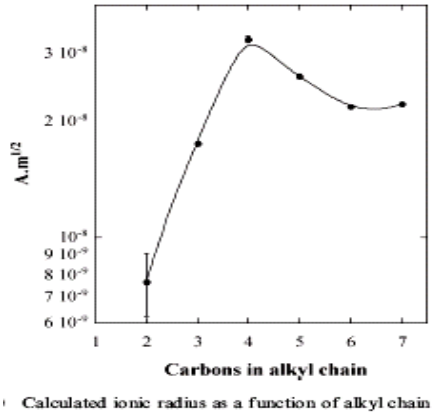
Dzyuba and Bartsch have shown that viscosities of ionic liquids increase with increase in alkyl chain length on the ring nitrogen.[103]

Results show a trend for the heating time of the bis (trifluoromethylsulfonyl) imide ionic liquids to increase with increase in viscosity and chain length of the alkyl substituent from 4 to 8 carbons.

Table 4.4: **Comparison of heating times of selected imidazolium ionic liquids.**

R1	R2	A ⊖	Molecular Weight	Time 20-80˚C
Ethyl	**H**	**NTf_2**	391.31	72
Butyl	**H**	**NTf_2**	419.36	70
Butyl	**Methyl**	**NTf_2**	433.39	79
Hexyl	**H**	**NTf_2**	447.42	77
Octyl	**H**	**NTf_2**	475.47	84
EtOMe	**H**	**NTf_2**	421.28	84
Butyl	**H**	**TfO**	288.29	76
Butyl	**H**	**PF_6**	284.18	81
Butyl	**H**	**BF4**	226.02	74
Butyl	**H**	**SbF6**	374.95	72

The heating time on increase from 2 to 4 carbons however, shows the reverse trend and this agrees with work previously reported by Hoffman et al, showing a decrease in heating times from 40 to 140 **˚C** on increase in chain length from 1 carbon to 4 carbons.[13]



Calculated ionic radius as a function of alkyl chain length.

Figure 4.17: Calcualted ionic radii as functions of alkyl chain length.[104]

Previous reports have been made of an increase in ionic radii of imidazolium salts up to 4 carbons and a subsequent decrease above 4 carbons, possibly due to increased intramolecular attractions(Fig 4.17).[104] The value for **[C_4m_2im][NTf_2]** is slightly higher than that for **[C_6mim][NTf_2]**. This may be due to the extra methyl group being on C-2 rather than the N-1. The difference in heating times for **[C_4mim][PF_6]** and **[C_4mim][BF_4]** are very different in the Hoffman study. This could be attributed to a dramatic effect of the presence of water on the viscosity of **[C_4mim][PF_6]**,[105] bearing in mind that the rate of change in temperature of a substance irradiated with microwave energy, increases with increase in temperature. Heating times for the same cation, 1, butyl-3-methylimidazolium shows no obvious trends in heating times.

4.3.3.2 Dielectric Heating Profiles of Ammonium Ionic Liquids

The dielectric heating profiles of ammonium ionic liquids have been investigated. The effect on heating times of replacing the proton on the ammonium cation with a methyl group was investigated and the effect of hydroxyl groups on both the anion and cation was also studied. The heating times for the ammonium ionic liquids investigated are shown in **Table 4.5**. All the ionic liquids heat up appreciably under microwave irradiation. Repeated irradiation under microwave energy did not change the chemical structure of the ionic liquids. ^{1}HNMR spectroscopy showed the same peaks at the same frequencies before the first irradiation. The acetate and propionate ionic liquids gave heating times of between 74 and 81 seconds. They heated up faster under microwave irradiation than the glycolate and dihydrogen phosphate ionic liquids. Substituting the proton on the cations with and alkyl group increased the heating time for both acetate and propionate ionic liquids. Increasing the chain length of the

alkyl chain on the anion also led to longer heating times however, the replacement of the proton with an additional methyl group on the cations increased the heating times of the ionic liquids to a greater extent than lengthening the chain on the anion.

Table 4.5: Microwave Heating Times of Alkylammonium Ionic Liquids

Ionic Liquids	Molecular Weight	Time (20-80˚C)/S
IL8	149.18	74
IL9	163.21	76
IL22	163.21	80
IL11	177.24	81
IL18	165.19	87
IL19	171.13	131
IL20	187.13	166

The glycolate counterpart of the dimethylethanol ammonium **ILs**, **IL18** gave a longer heating time than both the acetate and propionate ones, an effect of introducing an **–OH** group on the alkyl side chain.

The presence of an **–OH** group on the cation also has a large effect on the microwave conductivity, which agrees with previous reports that functional groups with the ability to form hydrogen bonds have a strong influence on microwave relaxation times. For the dihydrogen phosphate ionic liquids, substituting a proton on the ethyl side chain for an **–OH** group increased the conduction by up to 35 seconds. The effect of the **–OH** group is largely due to enhanced attraction created between the anion and cation, making the IL more tightly held together and hence more ionic in character. The increased ionicity however, rather than

favouring increased conduction, does the reverse. This suggests that microwave conduction is more efficient for single charged species than for neutral ionic species. This greater neutrality of the hydrogen phosphate ionic liquids makes them more resistant to microwave energy and therefore they gave heating times well above 120 seconds. The dihydrogen phosphates, **IL20** and **21**. do not lie along the straight line, reflecting their much higher stabilities and the fact that T_v was taken at 90% decomposition. These results agree with the thermal stabilities of the ionic liquids, where replacing the protons on the cation also increases the stability of the ionic liquid to a much larger extent than lengthening the chain on the anion by one methylene group; therefore, microwave conductivity of **ILs** is also dependent on their thermal stability and the time taken for the ionic liquids to reach 80 **ºC,** increases with increasing thermal stability (See **Fig 4.19**).

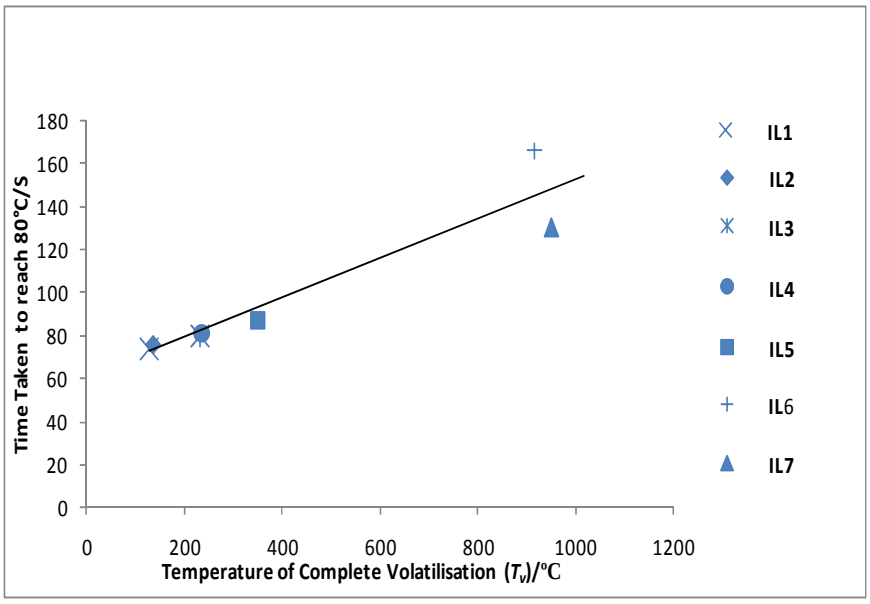
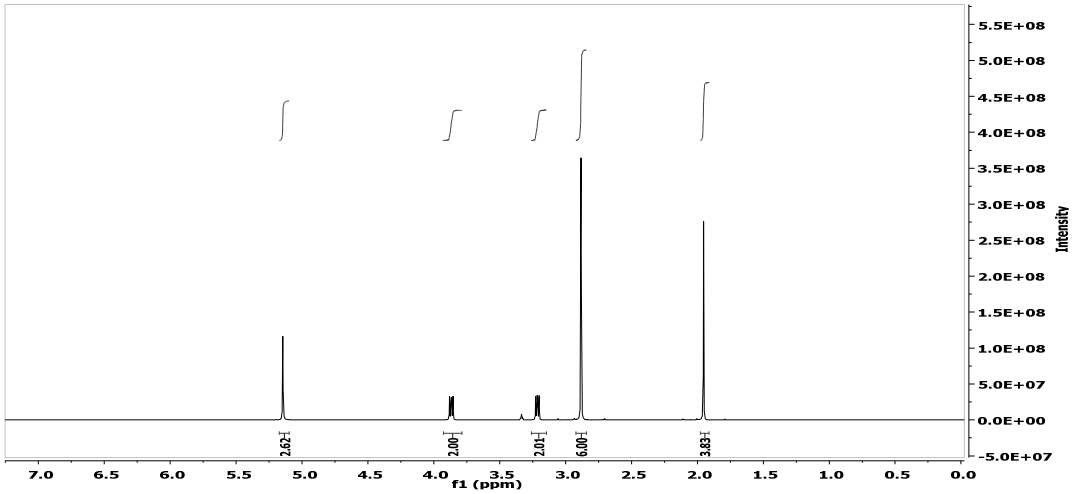


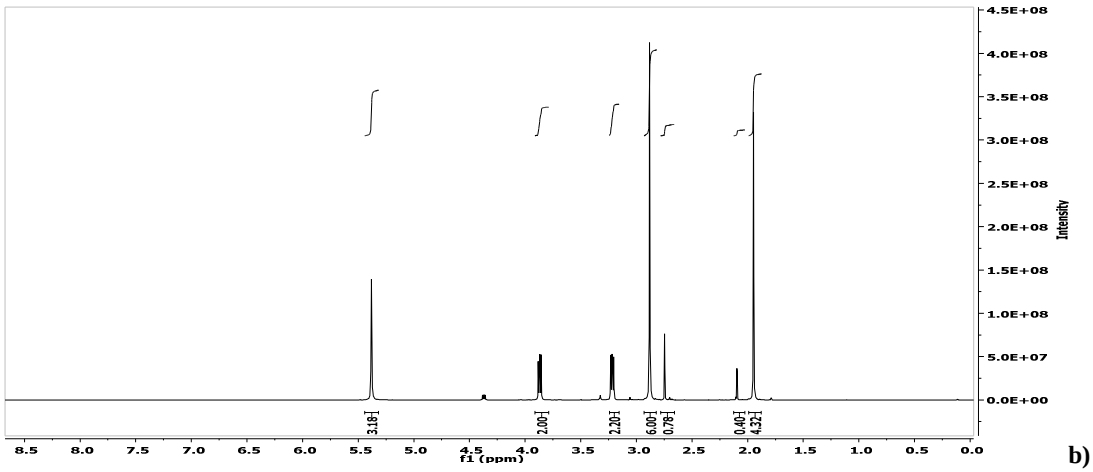
Figure 4.19: Plot of Tv vs. Microwave Conductivity Time

From the above results, the microwave stability of the anions can be summarised as:

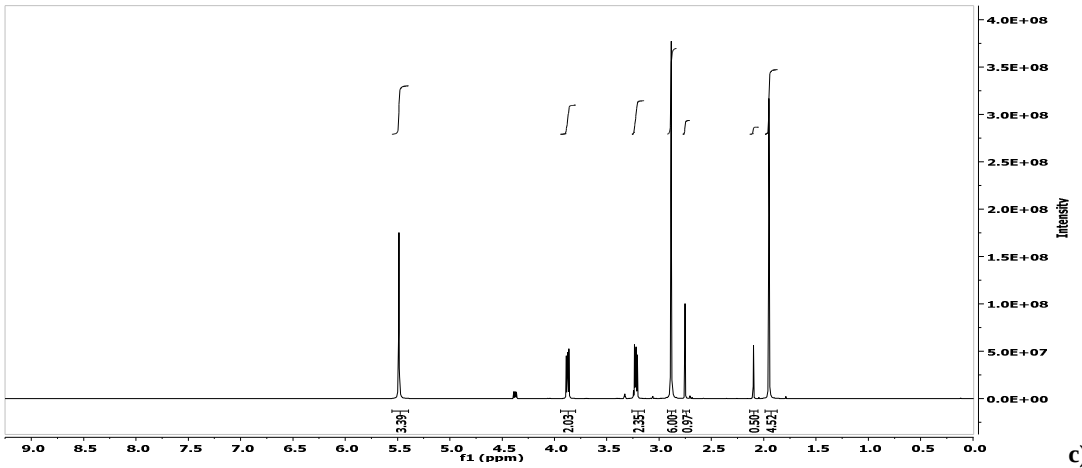
[H_2PO_4] > [Gly] > [Pro] > [AcO]



a)



b)



c)

Figure 4.20: **^{1}HNMR spectra for Dimethylethanolammonium Acetate after a) 1st Microwave Irradiation b)3rd Microwave Irradiation and c) 5th Microwave Irradiation**

The ^{1}H NMR spectra of all the ionic liquids treated with microwave irradiation showed the chemical shifts and integrations (for the peaks not undergoing fast exchange of protons) as the untreated samples with very slight excess of starting material after the 3rd scan. Figure 4.20 shows the ^{1}H NMR spectra of dimethylethanolammonium acetate after the 1st, 3rd and 5th scan under microwave irradiation. After the 1st scan, the chemical shifts remain the same as those for an untreated sample of dimethylethanolammonium acetate, while from the 3rd scan, small amounts of acid begin to show up. The integrals for the methyl group proton on the acetate anion and the acetic acid are in the ratio of 12:1 for the 3rd time of microwave irradiation. This ratio is increased to 9:1 after the 5th scan, showing that the acid is increasing in the system. Thus, we can say that the alkylammonium ionic liquids can be used up to 3 times under microwave irradiation and still retain their chemical properties. Recycling of the ionic liquids with slight excess of acid or base can be done using diethyl ether as extractant or by regenerating the ionic liquids with the required base or acid.

4.4 Conclusions

Alkylammonium ionic liquids have lower T_g values than imidazolium ionic liquids and do not show a combination of glass transitions, melting points and crystallization points under differential scanning calorimetry. The presence of hydroxyl groups on the anion increases the cohesive energy of the ionic liquid and results in higher glass transition temperatures and higher thermal stability. There are no obvious trends on the effect of change in alkyl substitution on glass transitions, however. The thermal stabilities of alkylammonium ionic liquids are dependent on the nature of substitution on both the cation and anion. The

presence of hydroxyl groups on both the anion and cation will increase stability due to greater cohesive energy and substituting the proton on the cation for a methyl group also increases the thermal stability. Incomplete transfer of the proton of the acid starting material to the base to form the ionic liquid favours shorter microwave heating times, therefore designing ionic liquids with higher thermal stability for use in microwave applications is not necessarily advantageous especially if irradiation is carried out within a closed system with sealed sample tubes. Since the presence of hydroxyl groups on the anion increased the microwave conductivity time, this should be taken into consideration when designing ionic liquids for biomass processing, since the presence of hydroxyl groups could favour dissolution in the ionic liquid. Where increased hydrogen bonding favours biomass dissolution, it does not however favour faster heating times. This is attributed to the hydrogen bonding causing restriction on rotational freedom. We have investigated the thermal stabilities of alkylammonium ionic liquids, showing that they begin to boil even at temperatures below 100 **ºC** and are therefore not particularly suited for biomass processing using conventional heating. Alkylammonium ionic liquids heated with microwave energy on the other hand can be heated up to the same temperature several times and still retain the same chemical and thermal properties. The nature of the acid-base ionic liquids means that even where some evaporation has occurred, the ionic liquid could be easily regenerated by addition of small amounts of acid or base starting material, or recycled using diethylether.

The next chapter will look at dissolution rates of biomass samples in the ionic liquids being studied and explore the use of microwave assisted extraction for biomass processing using ionic liquids.

Chapter 5 Ionic Liquids for Biomass Processing

5.1 Carbohydrates in Ionic Liquids

There has been keen interest in recent years on the application of ionic liquids in carbohydrate chemistry.[46, 106] The use of carbohydrates as inexpensive and renewable feedstock for the chemical and allied industries has been hampered by the low solubility of underivatised carbohydrates in almost any solvent but water.[46] The properties of ionic liquids that make them most appealing for biomass processing are their wide liquid range, high thermal stability, recyclability and the potential to fine-tune their properties by varying the cations and anions used in syntheses.

The solvation properties of ionic liquids can be varied by changing the nature of the ions in the ionic liquid. Miscibility with water can be varied from complete miscibility to low miscibility, by changing the anion from, for example, $Cl^-$to $[NTf_2]^-$.[107, 108]

The lipophilicity of the ionic liquid can also be varied by the degree of cation substitution with alkyl substituents. Hydrophobic ionic liquids can thus be used to design aqueous/IL biphasic systems. Ionic liquids also undergo $\pi\rightarrow\pi$ or C–H$\rightarrow\pi$ interactions, which increase their affinity for aromatic compounds. Solvent properties are characterized by H-bond donation from the cation to polar or dipolar solutes and H-bond accepting functionality in the anion. These properties can also be varied by changing the cation substituents or the anion. Simple molecular solvents (hexane, for example) are limited in the number and types of solvation interactions possible with dissolved molecules.[107, 109] More complex solvents

with increased functionalities however, will have additional interactions with dissolved molecules.

Ionic liquids are very complex solvents. Given their structure and diversity of functionality, they are capable of most types of interactions (e.g., dispersive, *ð-ð*, n-*ð*, hydrogen bonding, dipolar, ionic/charge-charge). Thus, the range of solvent-solute interactions possible in ionic liquids is wider than that of molecular solvents.

Although as far back as 1931 Charles Graenacher patented solutions of cellulose in pyridinium salts (mainly chlorides) in the presence of nitrogen containing bases,[110] these pyridinium salts were however not reported under the umbrella of ionic liquids. The Sheldon group was the first to point out the potential for biotransformations in ionic liquids when they reported lipase-catalysed reactions in **IL3** and **IL2**.[111] Solubility studies of various carbohydrates have since been carried out. Most of these studies attempt to dissolve the carbohydrates while heating and stirring.

The Rogers' group was one of the earliest to carry out comprehensive work on carbohydrate dissolution in ionic liquids.[7, 31, 112] They reported the dissolution of cellulose in varying concentrations in Br^-, Cl^-, $[BF_4]^-$, $[SCN]^-$ and $[PF_6]^-$ ionic liquids under conventional heating conditions and microwave heating.[7] Solubilities of up to 10% in **[C_4mim]Cl** at 100 **ºC** and up to 25% under microwave heating were achieved.

It has been suggested that solvation in ionic liquids is anion dependent.[46, 108] Liu et al compared the solubilities of glucose, sucrose, lactose and cyclodextrin in a range of ionic liquids and found that those containing the dicyanamide anion dissolved glucose more than an order of magnitude better than those of the tetrafluoroborate anion.[46] The ability to form hydrogen bonds with complex bio-molecules is considered the primary mechanism of carbohydrate solubility in ionic liquids.

McFarlane and co-workers attributed the high solubility of carbohydrates in dicyanamide ionic liquids to the H-bond acceptor properties of the dicyanamide anion.[113] Remsing et al also confirmed interaction of chloride ions of **[C_4mim]Cl** with the cellulose -OH groups in a 1:1 stoichiometry using ^{13}C and $^{35/37}Cl$ NMR relaxation measurements[114] and molecular dynamics simulation of β-D-glucose in 1,3-dimethylimidazolium chloride (**[MMIM]Cl**) also suggested hydrogen bonding between chloride anions and hydroxyl groups.[29, 115]
The regio-selective transesterifications of D-glucose and cellulose have been carried out in ionic liquids.[30] Acetate ionic liquids were synthesised, that were capable of dissolving carbohydrates without denaturing the lipase.

Phosphate and phosphonate anion containing ionic liquids have also been reported to dissolve microcrystalline cellulose (MCC) under mild conditions.[5]

It is evident that a wide range of carbohydrates will be dissolved by chloride salts.[7, 42, 115] However, most chloride salts are solid at room temperature, while the liquid ones are of too high a viscosity to make good solvents.[14] Indeed the presence of chloride impurity in other ionic liquids is undesirable and may be corrosive. As mentioned in **Chapter 2**, ionic liquids

synthesised from carboxylic acids, given their wide range of choice have been known to be of low viscosity.[116]

It is evident that the dissolution of cellulose in ionic liquids has received wide attention.[7, 10, 44-46, 112, 114, 117] This is because cellulose as the most abundant organic polymer on earth, can be used in a variety of physical and chemical processes to fabricate new materials.[5]

However, few studies have been done on the solubility of starch in ionic liquids. Biswas *et al* found starch and zein protein to be soluble in **[C_4mim]Cl** and **[C_4mim][dca]** at 80 **ºC**.[118] Amylose has also been found to be soluble in **[Amim][HCOO]** at a concentration of about 18%wt[14] when dissolved at 60 ºC and in **[C_4mim][dca]**[46] at about 4gL^{-1} when dissolved at 25 ºC.

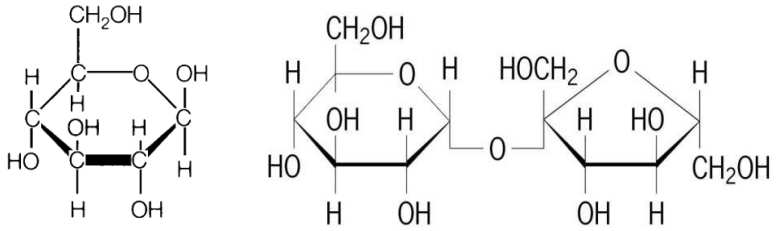
5.2 Solubility Tests of Carbohydrates in Selected Ionic Liquids

The aim of this section is to investigate the solubility of various carbohydrates in ionic liquids and the effects of different cation and anion combinations on carbohydrate solubility.

5.2.1 Types of Carbohydrates

The solutes used in this study were glucose, sucrose, starch and cellulose. They were chosen in increasing order of complexity to enable the classification of ionic liquids in order of their ability to dissolve the solutes.

D-glucose, being the most abundant monosaccharide in nature[119], has been chosen here for investigation. Glucose is a 6-carbon monosaccharide consisting of a single polyhydroxy aldehyde unit.[119]



A **B**

Figure 5.1: Structures of simple sugars used in solubility tests. A: Glucose, B: Sucrose

Sucrose was chosen since it is a disaccharide and therefore higher in complexity than glucose. It is made up of D-glucose and D-fructose covalently joined together. Sucrose is obtained from two sources, in the tropics from sugar cane and in the temperate zone from sugar beet.[120]

The configuration and conformation of sucrose, as determined by x-ray crystallography[121], neutron diffraction[122], ^{1}H[123, 124] and ^{13}CNMR.[124, 125] show that all hydroxyl groups except O-4 are involved in hydrogen bonding, two of them intramolecular (as in Figure 5.2).

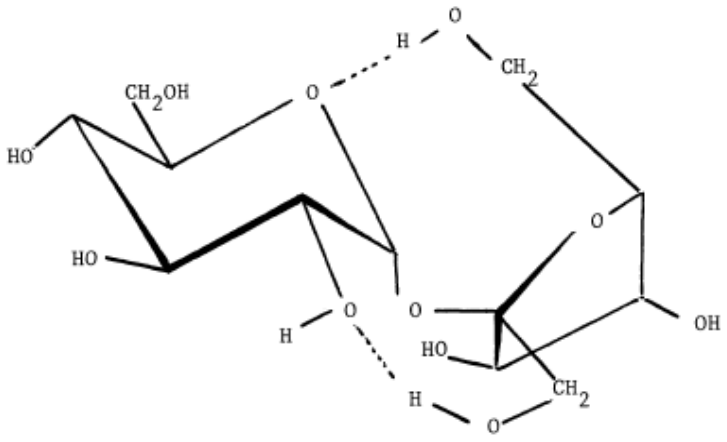


Figure 5.2: Structure of sucrose showing intramolecular hydrogen bonds.[120]

Thus, any solvent used to dissolve sucrose, would have to have functional groups that can interact with O-4 or break some of the intramolecular and intermolecular hydrogen bonds of the sucrose molecule. It is not surprising then that the solubility of sucrose in ionic liquids has been reported to be much less than that of glucose.[46]

Sucrose solubility in non-aqueous solvents is known to be generally lower than in water and it does not dissolve in non-polar solvents.[126]

Starch is the most important storage polysaccharide in plant cells and consists of two types of glucose polymers; amylose and amylopectin.[119] The former consists of long, unbranched chains of n-glucose residues connected by (**α1→4**) linkages varying in molecular weight from a few thousand to more than a million while the latter also has a high molecular weight but is highly branched.[119] The glycosidic linkages joining successive glucose residues in amylopectin chains are (**α1→4**), while the branch points occurring every 24 to 30 residues are (**α1→6**) linkages.[119]

Starch molecules are heavily hydrated, because they have many exposed hydroxyl groups available to hydrogen-bond with water. These hydroxyl groups should also be available to hydrogen-bond with hydroxyl-containing or oxygen-containing ionic liquids.

Cellulose, $\mathbf{(C_6H_{10}O_5)_n}$ is a fibrous, tough, water-insoluble substance found in the cell walls of plants, especially in stalks, stems, trunks, and all woody plant matter.[119] It can be extracted from wood and cotton.[45]

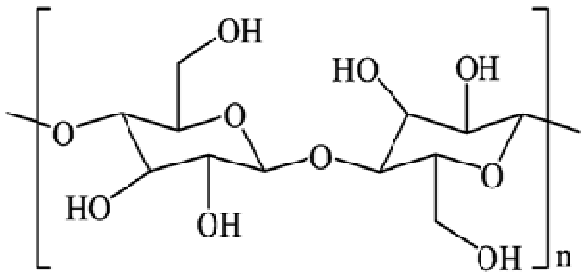


Figure 5.3: Structure of Cellulose monomers

The cellulose molecule, like amylose is a linear, unbranched homopolysaccharide, consisting of 10,000 to 15,000 D-glucose units. However, the glucose residues in cellulose are linked by **(β1→4)** glycosidic bonds, whereas those of amylose are linked by **(α1→4)** bonds.[119]

The most stable three-dimensional structure for the **(α1→4)** -linked chains of starch is a tightly coiled helix, which is stabilized by interchain hydrogen bonds; the average plane (determined by x-ray diffraction) of each residue along the amylose chain forms a 60º angle with the average plane of the preceding residue, therefore the helical structure has six residues per turn.[119] For cellulose however, the most stable conformation is that in which

each chair is turned 180º relative to its neighbours, resulting in a straight, extended chain and thus having all its **-OH** groups available for hydrogen bonding with neighbouring chains.[119] A network of interchain and intrachain hydrogen bonds can then be formed by several chains lying side by side and producing straight, supramolecular fibers of high tensile strength, a property of cellulose that has made it a very useful material for centuries.[119] Thus, cellulose is the starting material for a variety of products, including cellophane, rayon, cellulose acetate, carboxymethyl cellulose, and many more which are used for a large number of industrial applications, e.g. fibres, tissues, and paper.[45] In such materials, since there is already extensive hydrogen bonding between the molecules of cellulose, the capacity for new hydrogen bond formation is low and thus the water content is low.[119] This also means that any solvent that is intended to dissolve cellulose must be able to break these chains of cellulose, freeing up some **–OH** groups to hydrogen bond with its polar functional groups. Thus, the conditions necessary for dissolving cellulose would be quite different from those needed to dissolve starch, which has more available **–OH** groups for hydrogen bonding.

5.2.2 Effects of Solvent Type on Solubility

Solubility tests of glucose, sucrose, starch and cellulose were carried out in various ionic liquids. Initial work on the solubility of these carbohydrates in bistrifluromethylsulfonyl imides achieved little or no solubility. This could be attributed to the low ***β*** **HBA** properties of these ionic liquids, and agrees with other reports[30] on imidazolium NTf_2 ionic liquids. The work was continued with the carboxylate ionic liquids and a comparison done on all the ionic liquids as solvents for carbohydrates.

5.2.2.1 Instrumentation and Materials

Glucose and sucrose were obtained from Riedel-de-Haen. Potato Starch was obtained from Fluka, Alkali Lignin and Cellulose fibres from Sigma Aldrich. Except where mentioned, all dissolution experiments and extractions were carried out on a Carousel Reaction Station with reflux head. Microwave-assisted extractions were carried out in a domestic microwave. FTIR scans were taken with a Perkin Elmer FT-IR 100 Spectrometer. SEM images were taken using a JEOL 840A Scanning Electron Microscope operated at an acceleration voltage of 20keV. TGA was performed using a Rheometric Scientific STA 1500 simultaneous thermal analyser.

5.2.2.2 Comparison of Glucose and Sucrose Solubility in Ionic Liquids

D-glucose powder and sucrose granules both obtained from Riedel-de-Haen were added to 1-2ml of dry ionic liquids and stirred at room temperature till a clear solution was formed, and then further solute was added till saturation or till stirring was no more possible. Where solubility did not occur at the first concentration, more ionic liquid was added till a clear solution was observed.

a) **b)**

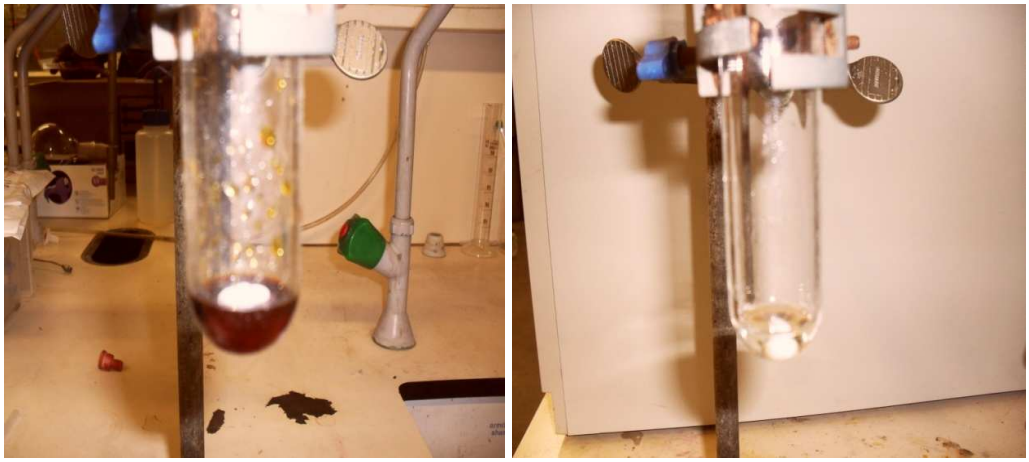


Figure 5.4: Pictures of glass vessels containing a) glucose and b) sucrose in IL8 ionic liquid.

Dissolution was very slow for both glucose and sucrose. Concentrations below 20% generally dissolved within 12 hours but once the concentration of sugar was increased up to 20% and above, dissolution became even slower and took between 72 and 96 hours to dissolve completely. This can be attributed to the low temperature of operation, with dissolution being very dependent on stirring. Hence, higher concentrations could not be dissolved once the solution could no longer be stirred. The ionic liquids became coloured as the glucose powder dissolved in them, however this colour change was not observed with the sucrose solutions.

The solubility test results showed a trend for higher solubility of glucose than sucrose in the same liquid. This was consistent for the acetate, propionate and glycolate ionic liquids studied and counters the work of Zhao et al, where they observe identical solubility of glucose and sucrose in **[Me(OEt)$_3$-Et$_3$N][AcO]**.

Table 5.1 : Solubility of glucose and sucrose in Ionic liquids

Solute	Ionic Liquids	Solubility(%w/w)	Temperature(ºC)
Glucose	**[C_2mim][AcO]**	60[30]	60
	[Me(OEt)$_3$-Et-Im][AcO]	80[30]	60
	[Me(OEt)$_3$-Et$_3$N][AcO]	16[30]	60
	IL21	37	25
	IL8	33(40)*	25(60)*
	IL9	25	25
	IL18	7	25
	IL19	*Insoluble*	60
	IL20	*Insoluble*	60
	IL11	20	25
Sucrose	**IL15**	*Insoluble*	25
	[Me(OEt)$_3$-Et$_3$N][AcO]	16[30]	60
	IL21	11	25
	IL8	18	25
	IL9	10	25
	IL18	3	25
	IL19	*Insoluble*	60
	IL20	*Insoluble*	60
	IL11	*Insoluble*	25

* Brackets used to depict solubility at 40 **ºC**.

The effect of increased hydrophobicity on moving from acetate to propionate was seen in the reduced solubility of both glucose and sucrose in the propionate ionic liquids. Although this result is contrary to the **HBA** basicity values for the dimethylethanolammonium acetate and propionate, since the latter has a slightly higher value, it is probably countered by its significantly higher **HBD** acidity. The solubility of glucose is lower in choline propionate than in the protic ionic liquids and sucrose does not dissolve at all. This suggests that a high **HBD** ability is good for glucose and sucrose dissolution. This also explains why **IL21** dissolved more glucose than the other alkylammonium ionic liquids despite the 2 protons attached to its cation nitrogen. The dihydrogen phosphates are poor solvents for both glucose and sucrose. This could be attributed to the hydroxyl groups on the anion causing intramolecular hydrogen bonding in the ionic liquid and making the **HBA** centre unavailable for interacting with the solute molecule**.**

5.2.2.3 Solubility of Starch in Ionic Liquids

Solutions of Potato starch were made in 1-2 ml of ionic liquid in reaction tubes with reflux heads. Samples were first stirred at room temperature for 1 hour and concentrations were increased gradually when dissolution occurred by addition of more solute or reduced at saturation, by addition of more ionic liquid. Where no signs of dissolution occurred, the temperature was increased to 40 **ºC** and held for 2 hours. Thereafter, temperature increases were at 10 **ºC** intervals and held for 2 hours to a maximum of 90 **ºC**. Maximum temperatures were chosen based on temperatures normally used for dissolution of starch in DMSO.

Table 5.2: Solubility of starch in ionic liquids and DMSO

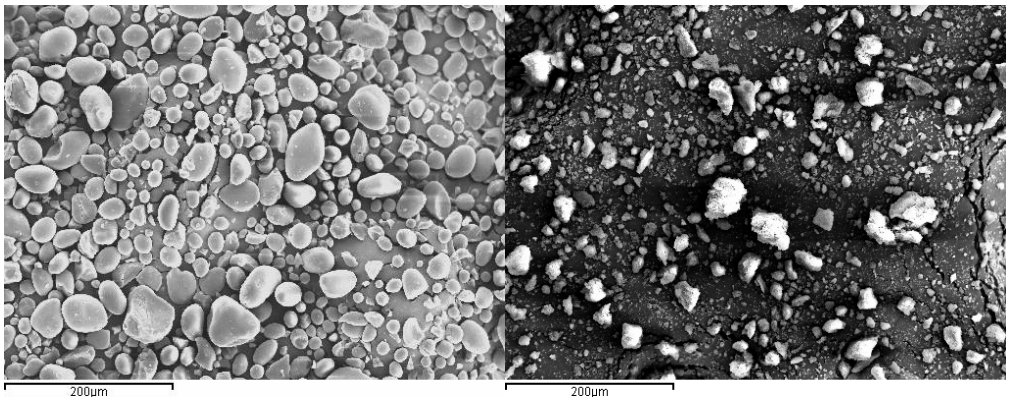
Solute	Ionic Liquids	Solubility %w/w	Temperature
Starch	**DMSO**	10	80
	[C_4mim]Cl	15[118]	80
	[C_4mim][dca]	10[118]	90
	IL15	10	90
	IL8	15	80
	IL9	14	90
	IL18	15	90
	IL19	*Insoluble*	90
	IL20	*Insoluble*	90
	IL11	7.5	120

Starch is not soluble in most organic solvents. It is only soluble in dimethyl sulfoxide, although it gelatinises in water at high temperatures. 10%w/w starch dissolved in DMSO at 80 **ºC**. Starch dissolved in most of the ionic liquids within 2 hours of heating at the dissolution temperature. The solubility of starch in most of the ammonium ionic liquids compares favourably with its solubility in **DMSO**, **[C_4mim]Cl, IL15** and **[C_4mim][dca]**. Substituting the N-proton with a methyl group reduces the solubility of starch in the ionic liquid and increases the required operating temperature by 30 **ºC**. This suggests that the mechanism of solvation is not only via hydrogen bonding with the ionic liquid anion but that the N-proton also participates in the solvation process. Therefore, a high **HBD** ability does not hinder dissolution. There are no other obvious trends with respect to solubility and the Kamlet Taft properties of these ionic liquids.

It has been previously suggested that DMSO needs a small amount of water to help in the solvation of dispersed starch polymers.[127, 128] In addition, although a 1:1 solution of **[C_4mim][$MeSO_4$]** and water dissolved 10%w/w of starch at 90 **ºC** and dry **[C_4mim][$MeSO_4$]** dissolved the same amount of starch at 100 **ºC**, when dissolution of 5%w/w of starch in this ionic liquid was attempted under vacuum at 90 **ºC** to reduce any slight amount of water present in the ionic liquid, dissolution did not occur. Thus, like DMSO the presence of water in some ionic liquids also aids the dissolution of starch granules. It is important to note that water has a high $\boldsymbol{\alpha}$ value and as such would increase the **HBD** ability of the DMSO solution.

5.2.2.3.1 Effects of Solvents on Morphology of Starch

The starch samples were regenerated from ionic liquid solutions by precipitation with methanol. The recovery amount was over 80% for all of the ionic liquids except choline propionate at 33% and N,N-dimethylethanol glycolate, where recovery was only 22%. The effect of ionic liquids on starch morphology was studied using electron microscopy. All regenerated starch samples were pre-dried in a vacuum oven at 40 **ºC**. All samples were coated in gold using an Emitech Gold Sputter machine.



a) **b)**

Figure 5.5: Scanning Electron Micrographs of a) Untreated Potato Starch and b) Potato Starch regenerated from DMSO.

Dissolution of potato starch in DMSO at high temperature causes fracture of the starch granules. The mechanism is similar with the alkylammonium propionate ionic liquids where fracture of the granules also occurs but with larger particles, suggesting that these solvents are slightly less aggressive solvents for starch than DMSO.

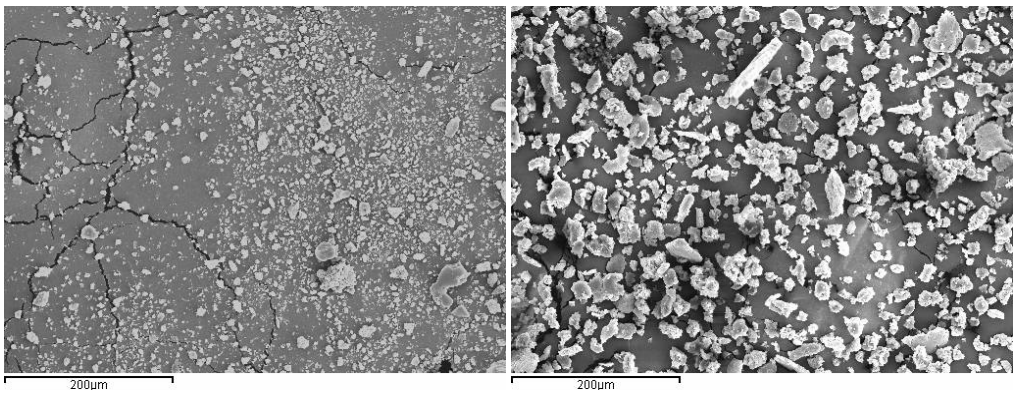


Figure 5.6: Scanning Electron micrographs of Starch regenerated from IL8 and IL9

The undissolved samples regenerated from dihydrogen phosphate ionic liquids and dried in the same manner show that the starch granules remain intact, although there is a small amount of etching of the granule surfaces. This confirms that the granule disintegration is not simply as a result of heat but also of chemical activity from the solvents.

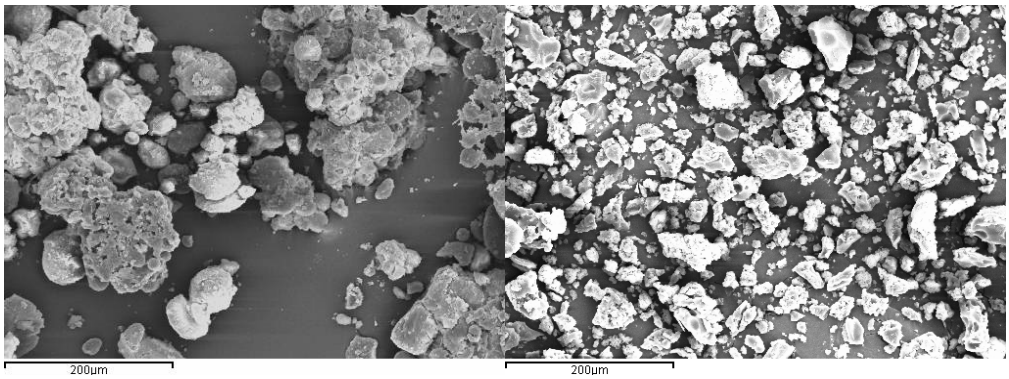


Figure 5.7: Scanning Electron micrographs of starch regenerated from a) IL18 and Choline propionate.

The effect of dimethylethanolammonium glycolate on the morphology of the starch granules was markedly different. Although the granules were fragmented, agglomeration of the granule pieces occurred.

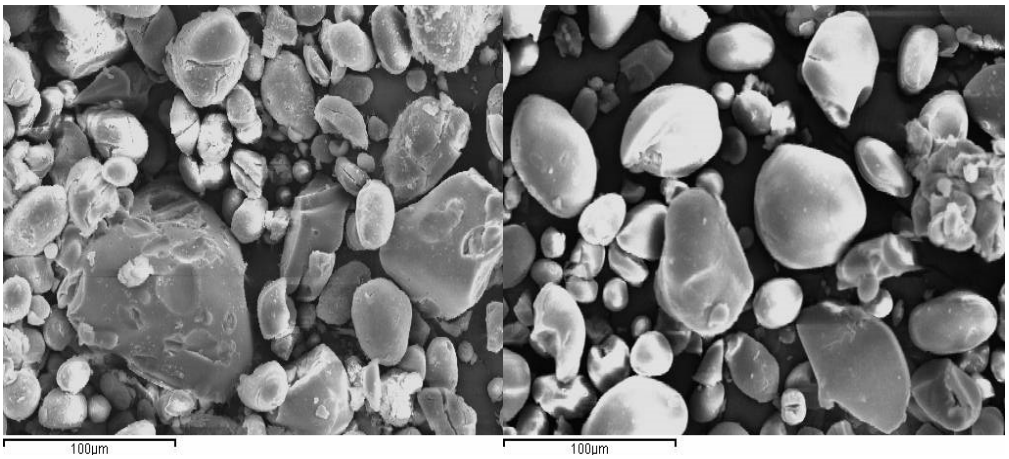


Figure 5.8: Scanning Electron micrographs of undissolved starch recovered from N,N- dimethylethanol ammonium and N,N-dimethylethyl dihydrogenphosphate ionic liquids.

5.2.2.4 Solubility of Cellulose in Ionic Liquids

Cellulose fibres obtained from Aldrich were added to 1-2 ml of ionic liquid in reaction tubes with reflux heads. Samples were first stirred at room temperature for 1 hour and concentrations were increased gradually when dissolution occurred by addition of more solute or reduced at saturation, by addition of more ionic liquid. Where no signs of dissolution occurred, the temperature was increased to 40 **ºC** and held for 2 hours. Thereafter, temperature increases were at 10 **ºC** intervals and held for 2 hours to a maximum of 120 **ºC**. Maximum temperatures were chosen based on temperatures normally used for dissolution of cellulose in N-methylmorpholine-N-oxide (NMMO) solvent system for regenerating cellulose fibres, which uses operating temperatures of between 80 and 130 **ºC**.[129] All experiments for cellulose were carried out in sealed glass vessels under a water vacuum.

Table 5.3: Showing Solubilities of cellulose in ionic liquids at various temperatues

Solute	Ionic Liquids	Solubility %w/w	Temperature
Cellulose	**IL1**	*Insoluble*	120
	IL10	*Insoluble*	120
	IL7	*Insoluble*	120
	[C_4mim]Cl	10^7	100
	[Amim]Cl	10^{14}	100
	[Amim][HCOO]	10^{14}	60
	IL15	10	60

	$[C_4mim][Me_2PO_4]$	3	55
	$[C_4mim][MeSO_4]$	3	100
	$[Me(OEt)_3\text{-}Et_3N][AcO]$	10^{30}	110
	IL8	*Insoluble*	120
	IL9	*Insoluble*	120
	IL18	*Insoluble*	120
	IL19	*Insoluble*	120
	IL20	*Insoluble*	120
	IL22	>1%	120
	IL11	3	120
	IL11*	5	140 Watt

*Microwaved at 140 Watt for 60 seconds

Where dissolution occurred, an orange-brown solution was formed which did not precipitate after cooling. The **$[NTf_2]$** anion ionic liquids generally did not dissolve cellulose, even where **HBA** functionality was introduced on the alkyl side chain of the cation. This reflects their low **HBA** $\boldsymbol{\beta}$ values. The imidazolium chloride ionic liquids have been reported to dissolve 10%w/w of cellulose, reflecting their high $\boldsymbol{\beta}$ values. Cellulose solubility was further tested in imidazolium ionic liquids with the **IL15, $[C_4mim][Me_2PO_4]$** and **$[C_4mim][MeSO_4]$** anions. The **IL15 IL** dissolved 10% while the other 2 **ILs** dissolved 3% w/w of cellulose. It is important to note the low temperature of dissolution of cellulose in **$[C_4mim][Me_2PO_4]$**. The cellulose dissolved in **$[C_4mim][MeSO_4]$** resulted in a cloudy solution and the fibres could not be regenerated and recovered. This suggests degradation of the cellulose fibres making it an unacceptable solvent for cellulose.

The alkylammonium ionic liquids with high α values, as expected did not dissolve cellulose. This could be attributed to the acidic proton on the cation interfering with hydrogen bonding between the anion and the cellulose **–OH** groups. This proton has been replaced with a methyl group in choline propionate, thus decreasing the α value and increasing the β value. Thus, 3% of cellulose dissolves in the ionic liquid within 2 hours.

Microwave heating can speed up the reaction times and also increase the concentration of dissolved solutes in ionic liquids.[7] Heating cellulose in choline propionate at 140 Watt increased the solubility to 5%.

5.2.2.4.1 *Effect of Water on Solubility of Cellulose*

0.06g of cellulose was added to a weighed 75% solution of **IL15** in water and heated under vacuum to remove the water present. Once dissolution occurred, the viscous solution formed was allowed to cool and the amount of water removed was determined gravimetrically. The resultant solution was found to have 16% of water present. This is in contrast to reports by other authors[7] that more than 1% added water causes precipitation of dissolved cellulose. The addition of water to ionic liquid solutions during microwave heating is beneficial for sufficient wetting of the fibres and to control the rate of heating of the ionic liquids.

5.2.2.4.2 *Effect of Ionic Liquids on Morphology of Regenerated Cellulose Fibres*

Cellulose fibres were regenerated from the ionic liquids by flushing with generous amounts of water. The resultant fibres were scanned by SEM to investigate the effect of the solvents on fibre structure and morphology.

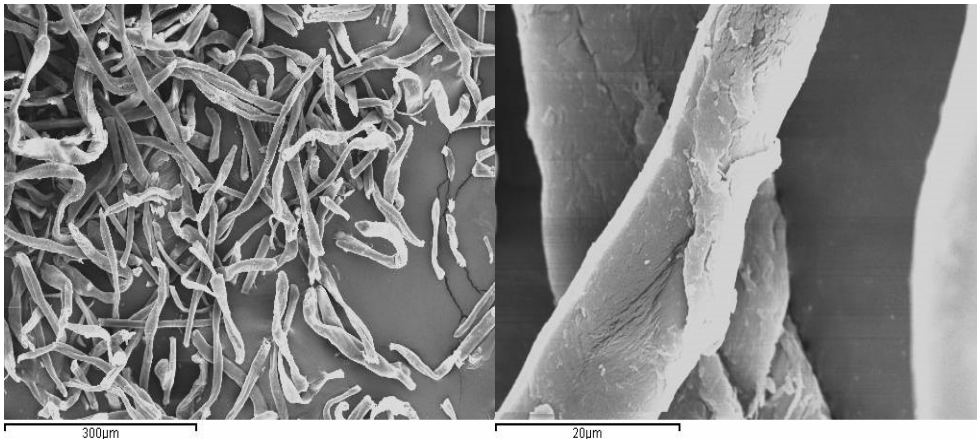


Figure 5.9: Untreated long fibres of cellulose at 300µm and 20µm.

Untreated cellulose fibres are shown above, with the macrofibrils well separated. A closer image of a fibril shows the surface free of any deep trenches although, there are thin lines and boundaries. The cellulose samples that dissolved in the ionic liquids showed varying dramatic changes in morphology.

Cellulose regenerated from the 2 imidazolium ionic liquids showed a flattening of the macrofibrils. **IL15** caused flaking and disintegration of the surface. **[C_4mim][Me_2PO_4]** however, caused a smoother surface with the fibre lines visible within the sheet-like matrix. The regenerated cellulose from choline **ILs** retained more of their fibre structure although there were also deeper grooves and etching on the fibre surface than when untreated.

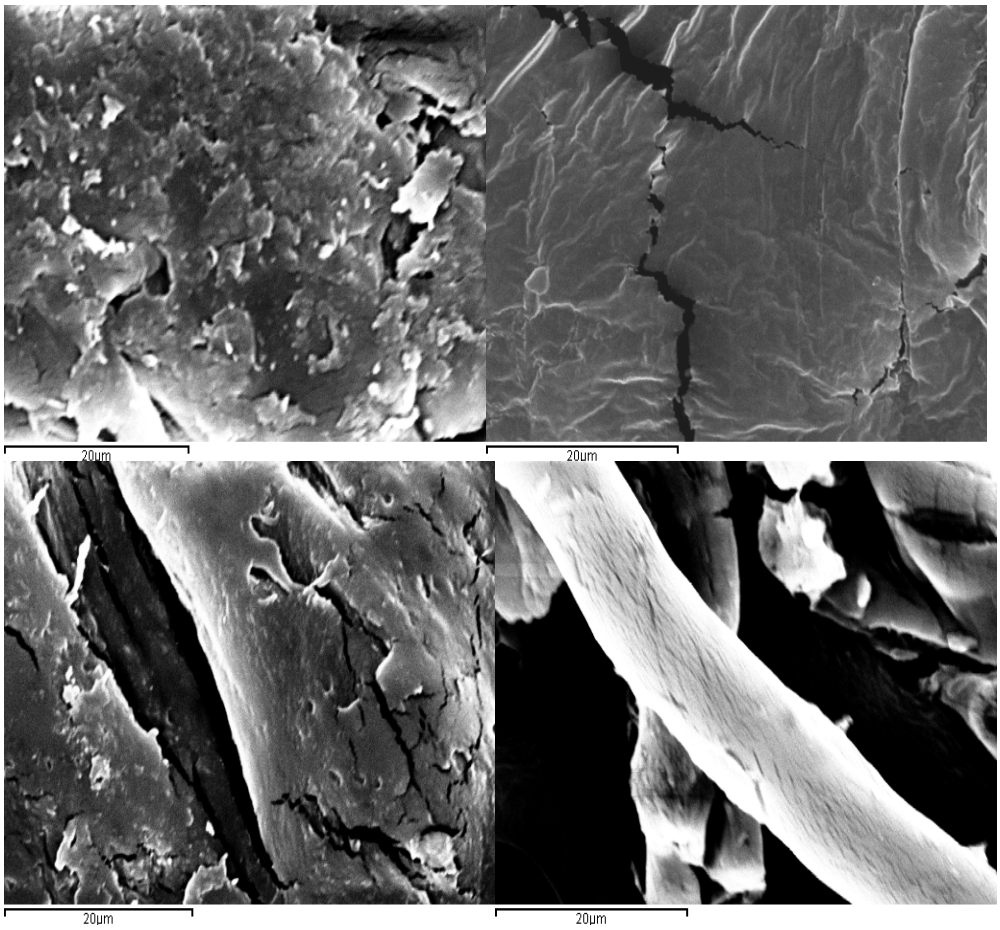
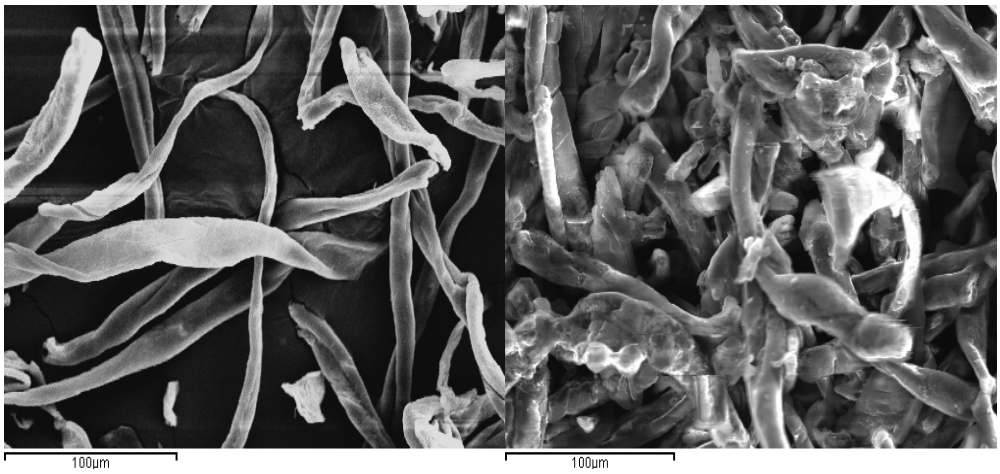


Figure 5.10: Clockwise from top left, regenerated cellulose from IL15, [C_4mim][Me_2PO_4], IL22 and IL11.

5.2.2.4.3 *Effect of Microwave Energy on Cellulose Morphology*

The effect of microwave energy on the morphology of cellulose was investigated by scanning cellulose regenerated from **IL1** after conventional heating and microwave heating. An ionic liquid with a very low $\boldsymbol{\beta}$ value was purposely chosen since there would be minimal interaction between the ionic liquid and cellulose molecule. The regenerated macrofibrils after conventional heating retained their normal size and morphology as untreated cellulose.

Cellulose heated in the ionic liquid under microwave energy however, clearly showed swelling of the fibres. Thus, there is a possible microwave effect on cellulose in ionic liquids.



a) **b)**

Figure 5.11: Images of cellulose regenerated from IL1 after a) conventional heating and b) microwave heating.

This finding also depicts the usefulness of microwave energy in biomass pre-treatment. It could be especially useful with swelling solvents where the retention of the cellulose fibres is important, since many cellulose solvents will deform and flatten the fibres.

5.3 Ionic liquids as Solvents for Biomass Extractions and Waste Recovery

Designing environmentally benign separation processes has become increasingly important in the development of clean manufacturing processes.[130] Ionic liquids have been described as ideal substitutes for organic solvents in separations and extractions because of their stability, low volatility and adjustable miscibility and polarity.[4] The hydrophilicity and hydrophobicity of the ionic liquid can be controlled by varying the nature of the cation and anion.[49] Thus, Task Specific Ionic Liquids (TSIL) can be designed to have special functionalities with selectivity for a particular solute.

The use of **ILs** for separating organics from oil and gas produced water has been reported.[131] The distribution coefficients of typical organic contaminants (hexanoic acid, 1-nonanol, toluene, acetic acid, and cyclohexanone), between water and ionic liquids were measured. The authors found that ionic liquids could be effective in the selective removal of particular contaminants in produced water, and remain blind to other constituents such as paraffinic organic compounds.

Imidazolium ionic liquids have also been examined as alternative solvents for the separation of amino acids from aqueous media.[132] It was found that **[C_6mim][BF_4]** and **[C_8mim][BF_4]** ionic liquids may be adapted to liquid-liquid recovery process of some amino acids from aqueous media, and L-tryptophan can be effectively separated from fermentation broth in a multiple step process using **[C_6mim][BF_4]** as an extractant. Electrostatic interactions between the cation form of the amino acids and the anion of the ionic liquids are suggested to be responsible for a high degree of extraction at low pH.

The potential use of ionic liquids as extractants in the recovery of butanol has been investigated.[133] The distillation of butanol from biofuel fermentation broth by distillation is uneconomical. Pervaporative Butanol recovery from 1 wt% aqueous solution and **[C_8mim][PF_6]** was carried out using a polydimethylsiloxane membrane. Butanol–water ratio in the permeate was close to Butanol–water ratio in ionic liquid feed, suggesting that the membrane did not improve the separation.

Ionic liquids have received attention in recent years as solvents for biomass processing[134-137] and extraction of lignin from wood.[11, 138]

Eucalyptus grandis, southern pine, and Norway spruce thermomechanical pulp were pre-treated with **[Amim]Cl** and hydrolysed to glucose.[137] It was found that an increase in the wood density decreased the efficiency of the pretreatment, whereas extended pulverization periods decreased the yield of the regenerated wood after the **IL** pre-treatment, with more glucose being released during the enzymatic hydrolysis.

The dissolution of oak, ponderosa pine, smooth sumac, grape stem, flax shives, and triticale straw in **[C_4mim]Cl** under microwave irradiation has been reported.[136] 5% of the wood samples completely dissolved in the ionic liquid after 60 seconds of irradiation.

The dissolution and partial delignification of Southern Yellow Pine and Red Oak in **[C_2mim][AcO]** has been reported.[11] It was shown to be a better solvent than **[C_4mim]Cl** for the dissolution of wood. The authors used a 1:1 v/v of acetone and water for the regeneration process. 59% of the holocellulose (*i.e.*, the sum of cellulose and hemicellulose) in the

original wood was recovered in the cellulose-rich reconstituted material; whereas 31% and 38% of the original lignin was recovered. The recovery of the lignin was optimised by adjusting the pH of the washing to 2–3, using concentrated H_2SO_4, although it was mentioned that this would be problematic when recycling the ionic liquid.

Lignocellulosic biomass comprises cellulose, lignin and hemicelluloses. Although cellulose is only made up of glucose monomers, hemicelluloses can be made up of different D-pentose monomers with xylose normally being most abundant.

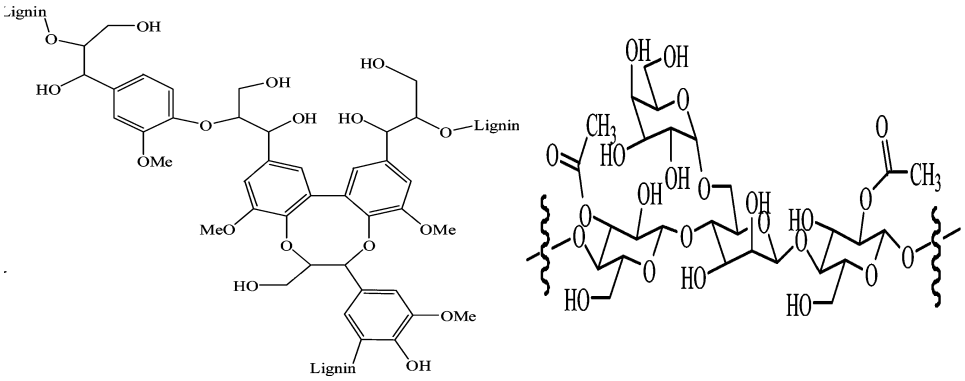


Figure 5.12: Representative Structure of Lignin (left) and Hemicellulose (right)[11]

Unlike cellulose, it is a branched polymer made up shorter chains. Lignin is a rigid polymer derived from phenylalanine and tyrosine. It has a complex structure, which is difficult to characterise and as such not well understood. Cellulose and hemicelluloses occur bound in lignin within biomass.

Biomass is easier utilised after delignification or reduction of total lignin content. This separation is not only useful in the paper industry but also in processing biomass for

hydrolysis to ethanol and other chemicals. The main focus of the pulp and paper industry is in this separation of lignin from the cellulose rich fraction of biomass.

The separation of cellulose from the hemicelluloses and lignin matrix is illustrated in the diagram below.

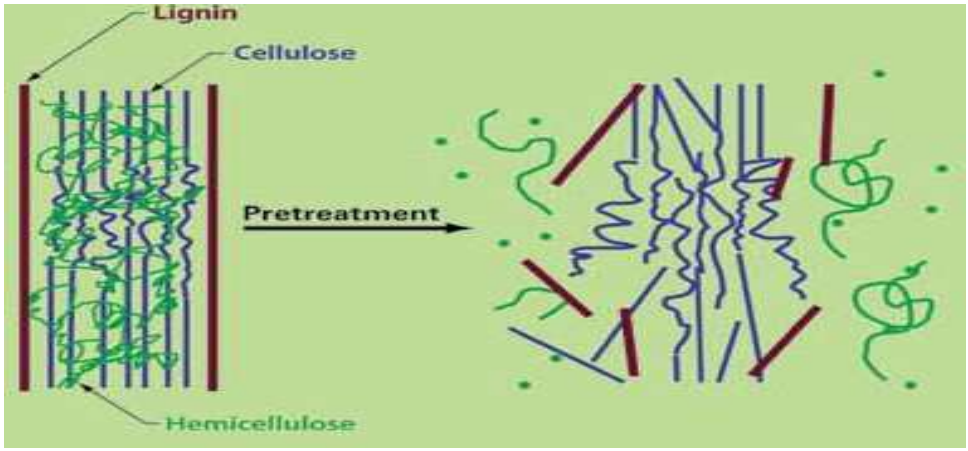


Figure 5.13: Pre-treatment of biomass frees cellulose from the lignocellulosic matrix.[139]

5.3.1 Pulping Processes in the Pulp and Paper Industry

Wood pulp used for manufacturing paper is produced by mechanical or chemical pulping. Mechanical pulp is produced by using large, rotating grinding roller stones to break up small bolts of wood.[140] The process does not separate lignin from cellulose, thus the quality of paper produced is low. This low grade paper is used for making newspapers, catalogs, paperboard, etc. The mechanical pulp fibres are often mixed with varying amounts of

chemical pulps to enhance the strength of the resulting paper. Types of mechanical grounding processes include groundwood, pressurised groundwood, refiner mechanical and thermomechanical processes. Chemical pulping involves cooking debarked and chipped wood in solutions of various chemicals, screening to remove any uncooked chips, and washing to remove the cooking "liquor." After this, the pulp is bleached to increase its purity, brightness, and whiteness depending on the final application. The process actually separates useable cellulose fibres from the lignin. As a result, chemical pulping yields higher quality (strength and permanence) pulps albeit of lower yields (45-55 percent) than mechanical pulps.[140, 141] Chemical pulping processes include the *Kraft* process, *Sulfite* process, semi-chemical process and solvent or organosolv processes. A short overview of the various chemical pulping processes is given below.

5.3.1.1 Kraft Process

The most commonly used of the chemical pulping processes is called the *Kraft* process.[142] It is an improvement of the *Soda* process, so called because wood chips are cooked in a solution of sodium hydroxide (caustic soda) at a pH of 12.[142] The conventional *Kraft* process is an alkaline process performed in an aqueous solution of delignification agents, NaOH and Na_2S, at the cooking temperature of 155–175 **°C** for a given duration, dependent on the type of raw material being delignified.[143] After pulping, lignin is degraded into smaller alkali-soluble fragments, mainly through the cleavage of ***α***- and β-aryl ether bonds. Any residual lignin after the process is stopped is removed using bleaching agents like elemental chlorine, chlorine dioxide, peroxide or ozone. Disadvantages include the expense of building mills (due to the special metals necessary to handle the temperatures, pressures, and caustic chemicals), low yields, and odours.[140]

5.3.1.2 Sulfite Process[140]

This process, dating from the 1870s, cooks chips in acid conditions in a solution of sulphur dioxide in water. The sulfur dioxide combines with lignin, and both are removed by the addition of a base (e.g. ammonium, sodium, or magnesium). Sulfite pulps are not as strong as kraft so are not used in strength applications, but their good sheet formation, softness, bulk, and absorbency make them suited to tissue and

sanitary papers. Unbleached sulphite is brighter than unbleached kraft and thus can be used where high brightness is not required. Sulfite pulp is now being bleached with oxygen, peroxide, or ozone.

5.3.1.3 Semi-chemical[140]

The process was developed in the 1920s for hardwoods and results in a lower quality paper with high yield (60-80 percent). It involves cooking wood chips in a mild chemical environment followed by mechanical defibrating. The pulp thus produced is characterized by intermediate strength and good stiffness and has been widely used for corrugating media.

5.3.1.4 Organosolv Processes

Solvent pulping was first patented in 1931 as the Kleinert ethanol process.[140] It involves using organic solvents to separate lignocellulosic biomass into its constituents, thus replacing water in the system. Advantages of solvent pulping include advantages include lower capital costs, operating costs comparable to *Kraft*, easily bleached pulps, high yield, recovery of by-products (lignins and sugars), sulfur and chlorine free operations, low water

use, and low effluent **BOD** and toxicity. Numerous organic solvents have been used for organosolv processes.[144] These include methanol, ethanol, amines, amine oxides, organic acids, peroxyacids, dioxane, etc. They are mostly used in conjunction with catalysts like hydrochloric acid, sulphuric acid, calcium or magnesium chlorides, anthraquinone, manganese complexes, etc. Solvent pulping can also be carried out in combination with other pulping processes.

5.3.2 Paper Wastes

Paper, as a major product of the forestry industry is widely used by society and therefore is a major source of municipal and commercial waste. The main source of fibre used in paper production is lignocellulosic biomass obtained from wood, waste paper and agricultural fibres. Waste paper is composed of previously used and discarded paper or paperboard products, which both contain cellulose fibres that can be subsequently combined with other inputs to manufacture paper, paperboard, or other wood-fibre-based products.

Molded paper products are generally made from recovered newspapers or paperboard. Thus, they are mainly composed of mechanical pulps. They have been defined by The Wiley Encyclopedia of Packaging Technology as

"Three-dimensional packaging and food-service articles that are manufactured by forming from an aqueous slurry of cellulosic fibers into discrete products on screened, formaminated molds in a process analogous to continuous-sheet cylinder-board paper making".[145]

Preparing waste paper for reuse involves repulping the paper and removing any ink, adhesives, and other contaminants which were introduced during the manufacture or use of the initial product. [140]The growth and sustainability of waste paper use is dependent on the technical availability of methods to process and reduce contaminants in waste paper.[146]

Recovering molded paper wastes for conversion to higher quality paper can be carried out using a chemical pulping process. The remainder of this chapter looks at the feasibility of designing a pulping or delignification process for a molded paper waste sample involving a modified solvent (ionic liquid) pulping process in alkaline conditions.

5.3.3 Characterisation of a Molded Paper Waste Sample

Samples of waste molded paper egg boxes used were supplied by Dispak Limited, Melksham (Wiltshire, England). Characterisation of the sample was done using standard methods.



a) **b)**

Figure 5.14: Pictures of a) cut pieces and b) shredded molded paper waste

5.3.3.1 Moisture Determination

Dry matter content (92.6 wt %) was determined by drying a portion of the sample at 105 **ºC**±2 **ºC** till constant mass according to standard procedures.[147]

5.3.3.2 Preparation of Waste Sample

Representative samples of each egg-box were collected and ground to obtain fibres. The rough fibres were passed through a stack of sieves and fibres smaller than 425µ were collected.

5.3.3.3 Determination of Inorganic Content by Ashing

Residual ash (14.5 wt %) was determined by igniting representative sections of the whole sample at 525 **ºC** in a muffle furnace for 3 hours according to standard procedures.[148]

5.3.3.4 Determination of acid-insoluble Lignin

Lignin (21.8 wt %) was defined as acid-insoluble lignin using 72% H_2SO_4 according to standard methods[149] and corrected for ash in lignin by igniting in a muffle furnace at 525 **ºC** for 3 hours as above.

5.3.3.5 Thermogravimetric Analysis

Weight loss curves of the biomass waste sample, commercial samples of cellulose, xylan and lignin were compared along with other biomass residues. The samples were scanned with a constant heating rate of 20 **ºC**/min in air. The characteristics of biomass samples can vary considerably depending on their source.[150] Comparison of the weight loss curves for paper waste, commercial cellulose and lignin are shown. The commercial cellulose sample has its main weight loss temperatures between 310 and 376 **ºC** corresponding to about 81% sample weight. Comparing with the curve for commercial lignin, the remaining roughly 14% of the commercial cellulose sample corresponds with the decomposition band for lignin. Lignin is known to decompose in a wider temperature range than other biomass components,[150] 88% shown here to decompose between 256 and 591 **ºC**. Xylan is representative of hemicelluloses and has been shown to have a devolatilization temperature of between 253 and 308 **ºC**.[150]

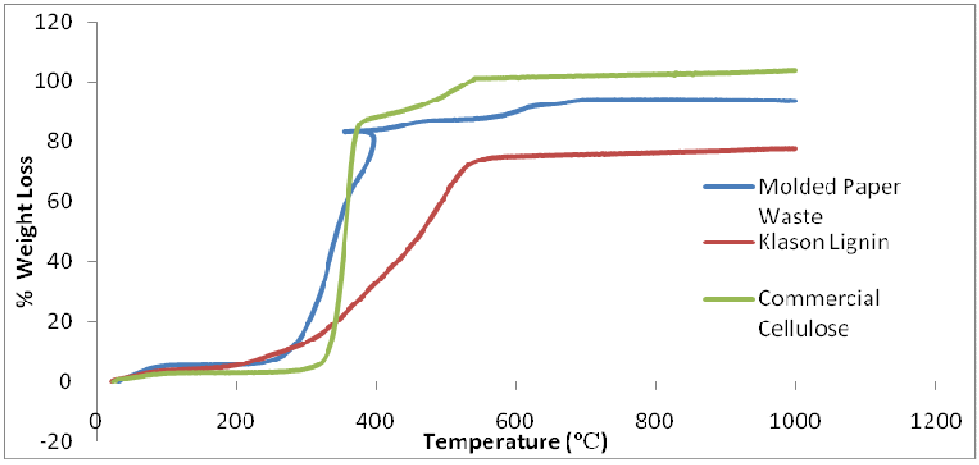


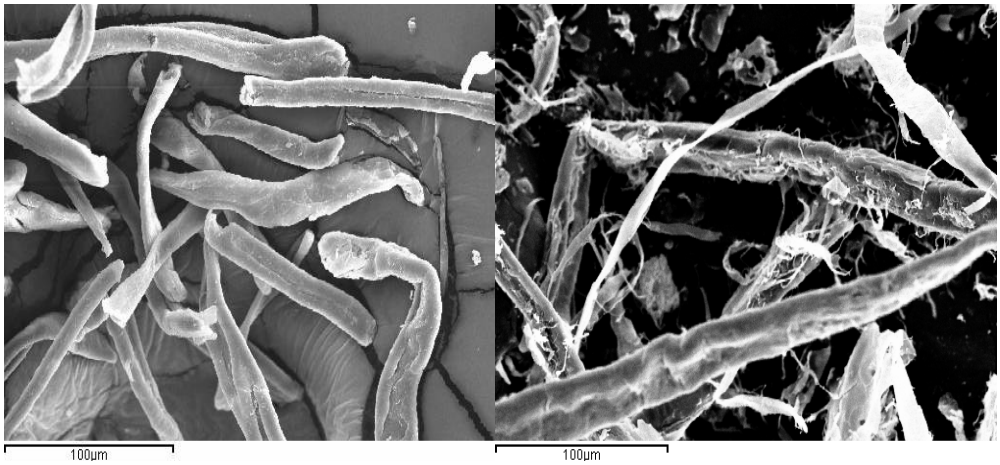
Figure 5.15: Comparison of Weight Loss Scans for Molded Paper Waste, its Klason Lignin and Commercial Cellulose.

Thus, the decomposition range for the waste sample between 262 and 363 **ºC** should account for both hemicelluloses and cellulose, with the hemicelluloses making up less than 20% of the sample. The remaining significant weight loss step between 529 and 363 **ºC** (roughly 23% of sample weight) would account for lignin. This lies close to the 21.8% klason lignin measured. The start of the weight loss for lignin is taken from the weight loss of this klason lignin which begins at 529 **ºC**.

Thus, we can estimate a cellulose content of 30-40%. Additional slow weight loss to above 700 **ºC** is typical of the decomposition of inorganics,[150] of which calcium carbonate is used as filler in the paper industry.[151]

5.3.3.6 Morphology

The morphology of the molded paper waste was studied using SEM. Micrographs of sections of the waste paper sample were taken under the same conditions in section 5.2. A comparison is made with a micrograph of pure cellulose.



a) **b)**

Figure 5.16: Images of a) pure cellulose fibres and b) a molded waste paper sample.

The pure cellulose fibres show their characteristic slightly ridged surfaces. The molded paper waste sample has longer fibres, signifying that it has undergone less cutting in the refiner stage. Thin wisps of hemicellulose and lignin matrix are also visible in the image.

5.3.3.7 FTIR Analysis

Scans were taken of the waste sample and reference samples of lignin and cellulose. The plots of the waste sample alone against reference samples of cellulose and lignin are shown below.

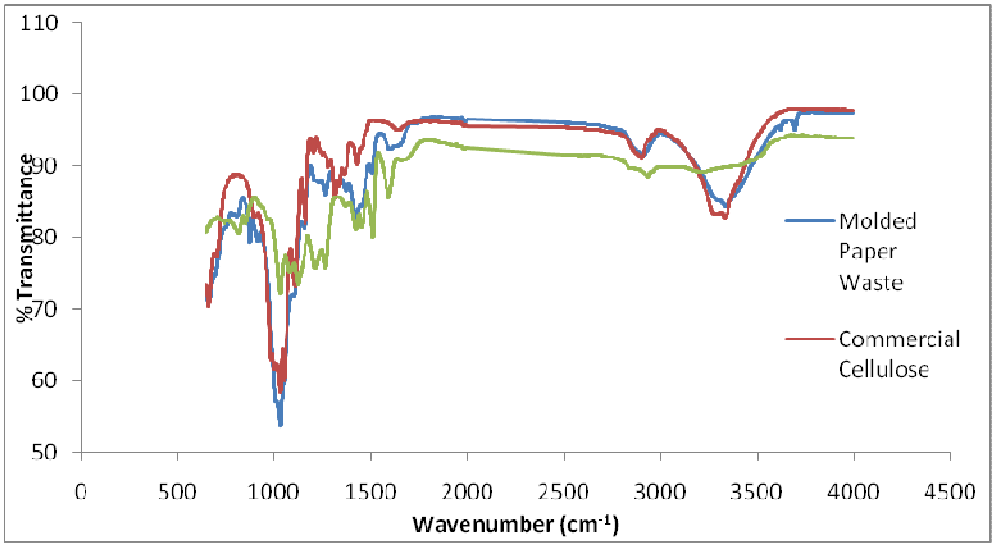


Figure 5.17: IR plots of a molded paper waste sample, commercially obtained cellulose and lignin.

Comparing the scans and also reference data for hemicelluloses,[152] it was found that the commercial cellulose sample had characteristic peaks at 887, 1434 and 1642. These peaks were found in the molded paper waste sample at 903, 1437 and 1621. The lignin sample had characteristic peaks at 1704, 1599, 1514 and 821. Other smaller peaks were at 1457, 1430, 1271, 1222 and 1035. The main peaks due to lignin were found in the

molded paper waste sample at 1694, 1609, 1518 and 829. Overlap of some of the lignin and cellulose peaks in the waste sample caused shifting of some of their characteristic peaks. Table 5.5 shows the characteristic peaks of pure cellulose, lignin and the molded paper waste sample with suggested peaks assignments compared to work reviewed by *Adapa et al.*[152]

Table 5.4: Peak Assignments for a Molded Paper Waste Sample, Cellulose and Lignin

Wavenumber (cm^{-1})	**Pure Lignin**	**Pure Cellulose**	**Molded Paper Waste**	**Peak Assignments[152]**
1700-1650	1704	-	1694(Lignin)	
1650-1600	1599	1642	1651(Hemicellulose), 1609(Lignin), 1621(Cellulose)	1600-1610 – aromatic skeletal vibration; 1651 – carbonyl stretching conjugate with aromatic rings
1600-1550	-	-	1567 (Hemicellulose)	1595 – aromatic skeletal vibrations plus C=O stretch
1550-1500	1514	-	1518 (Lignin)	1510 – strong ring stretching (aromatic lignin), 1513 – aromatic C=C stretch
1500-1450	1457	-	-	C-H deformation (methyl and methylene)
1450-1400	1430	1434	1437(Cellulose),	1420 – weak C-O stretching; 1430 – CH2 in-plane bending vibrations

1400-1350	1372	1375	1388	Weak C-O stretching
1350-1300	-	1321, 1342	1345(Cellulose)	1335 – weak C-O stretching
1300-1250	1274	1300	1284	
1250-1200	-	1234	1247(Hemicellulose)	1246 – weak C-O stretching Hemicelluloses
1200-1150	-	1166	1166(Cellulose)	Glycosidic linkage; C-O-C ring vibrational stretching
1150-1100	1110, 11	1114	1114	1125/1110 – C-O and C-C ring vibrational stretching
1100-1050	1072	1062	1061	1078 – β(1-3) polysaccharide
1050-1000	1034	-	1039	1035 – C-O, C=C and C-C-O vibrational stretching, 1045 – C-OH bending
1000-950	988	-	-	991 – β-glucan
950-900	-	-	-	
900-850	865	899	899	8 95 – β-1-4 linkage, 900 – anti-symmetric out-of-plane ring stretch of amorphous cellulose
850-800	822	-	-	

They reported that characteristic peaks of hemicellulose (xylan) were at 1646, 1563, 1044 and 899 cm^{-1}. The peaks due to hemicelluloses found in the waste paper sample were instead at 1651, 1567, 1057, and 903.

5.3.4 Solubility of Molded Waste Paper in Selected Ionic Liquids

Prior to solubility tests on waste paper, a mixture of lignin and cellulose was dissolved in choline propionate to test the possibility of selectively extracting lignin from the mixture.

A mixture of lignin and cellulose containing 60% lignin and 40% cellulose was prepared. 6%w/w of this mixture dissolved in 3 ml of choline propionate at 120 **ºC** within 3 hours. Recovery of the cellulose was carried out by precipitating in 70% ethanol solution, which is the optimum ethanol concentration[153] for lignin retention in the filtrate. After washing 3 times with ethanol solution, the cellulose fraction was dried and weighed. 87.5% of cellulose was recovered from this lignocelluloses mixture.

The solubility of the waste paper was tested in **IL22** and **IL11**. 3% w/w of waste paper was soluble in **IL11**. Microwave irradiation of the solution also dissolved 3% of the waste paper. Although prior solubility test of lignin and cellulose mixture in the ionic liquid resulted in the mixture dissolving and the cellulose was recovered, selective recovery of any of the biomass components of the waste from the **IL** was not achieved. However, the TGA scan of the recovered waste sample after microwave irradiation in the **IL** showed that there was probably some rupturing of the lignocellulosic matrix.

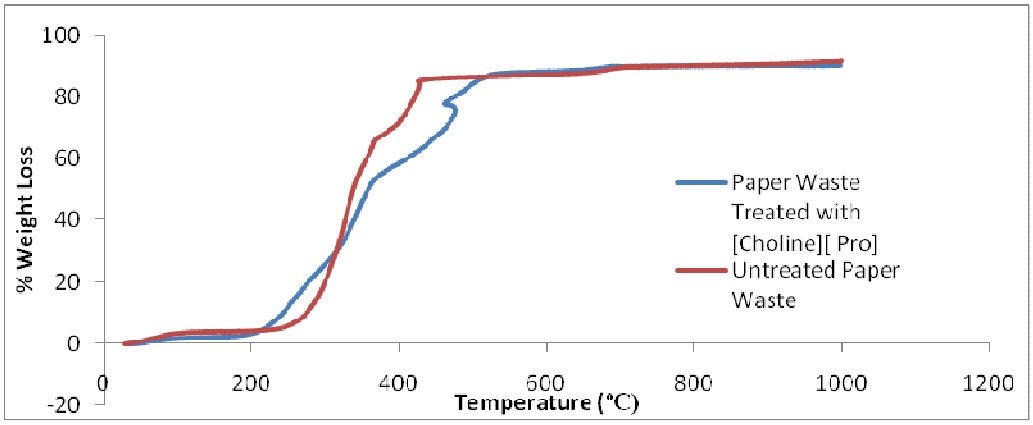


Figure 5.18: Comparison of TGA Weight Loss Curves for Untreated Paper Waste and Paper Waste Treated with Choline Propionate under microwave irradiation

Figure 5.18 shows comparative weight loss scans of untreated molded paper waste and waste paper treated with choline propionate under microwave irradiation. The treated paper showed more distinct weight loss steps for the different biomass components than the untreated waste. There is a clear weight loss step for hemicelluloses between 299 and 220 **ºC** corresponding to about 19% reduction in weight. Furthermore, the weight loss step for lignin shifted to between 474 and 409, corresponding to about 14% of the waste sample.

Most common pre-treatment or delignification methods for lignocellulosics have to break the lignin barrier and free the cellulose fibres from lignin and hemicellulose, as shown in Figure 5.13 and further work to recover the lignin and other extractives is done. These methods include acid and base pre-treatment method, steam explosion and hot water treatment. The most effective for recovering lignin are acid-base pre-treatments, although these tend to use very strong acids and base, requiring neutralisation and resulting in large volumes of salt waste. Since the main solvent used in this study is a salt, an *in-situ* acid-base extraction process can be designed that utilises the ionic liquid starting materials, with excess base to improve delignification and excess acid to enhance recovery of lignin. Thus

any neutralisation can be done to result in the ionic liquid itself as a product, which can then be recycled back into the process. This process would use the ionic liquid as primary solvent, reducing the amount of water needed in the extraction process and therefore lower energy costs for water removal.

5.3.5 Extraction Protocol for Delignification of a Lignocellulosic Biomass Waste

5.3.5.1 Development

Since both the *Soda* and *Kraft* processes employ alkali as delignification agents,[142, 143] experiments were carried out to test the effect of addition of **[Choline]OH** to the ionic liquid to aid delignification. Pulping experiments were carried out at 110 **ºC** in **[Choline]OH** (as supplied in 54% w/w water) alone. Varying concentrations of **IL11** and **[Choline]OH** mixtures were also used to test the effect on pulping of adding **[Choline]OH** to the ionic liquid. After pulping, the cellulose-rich fraction was precipitated using 70% ethanol, since this has been evaluated as the optimum concentration[153] for lignin retention in the filtrate. Filtration was carried out using glass crucibles and the biomass dried in a vacuum oven at 60 ºC for 4 hours before analysis.

Pulping with **[Choline]OH** alone, the black liquor was formed in 2 hours and the molded paper sample precipitated using 70% ethanol. Only 33% of the original sample was recovered after precipitation, however 16% of the lignin fraction was recovered.

FTIR analysis of the molded paper sample recovered showed that the extraction was not selective enough for lignin and much of the hemicellulose was degraded in the process of extraction. The characteristic hemicellulose peak at 1044 cm^{-1} is completely gone from the IR scan and so also are most of the shoulders and small peaks between 900 and 1124 cm^{-1} signifying degradation in the cellulose portion.

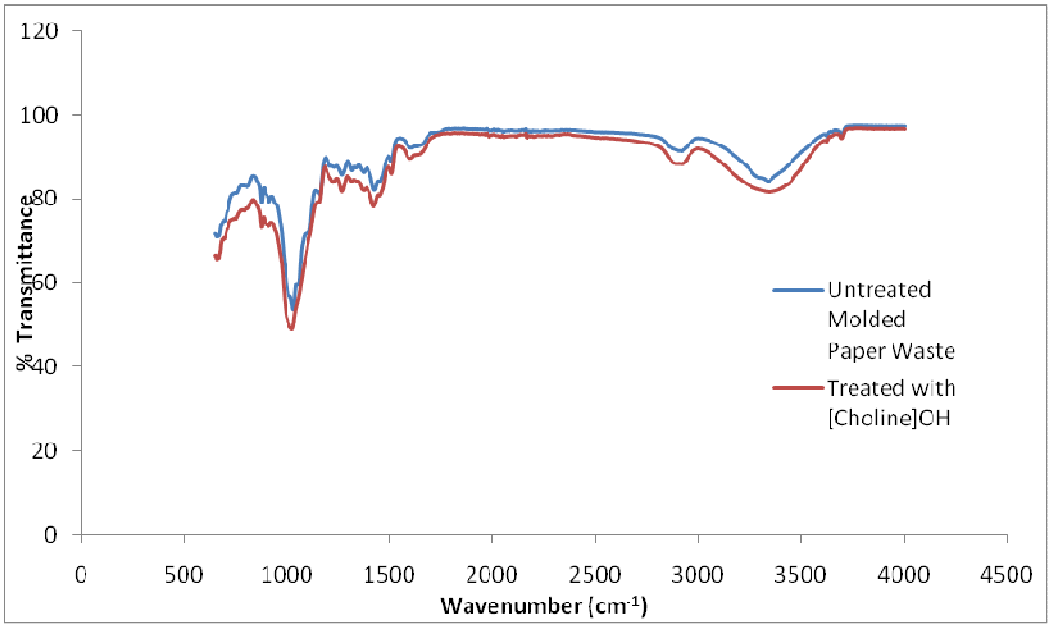


Figure 5.19: Comparison of FTIR scans of untreated waste paper and waste paper treated with [Choline]OH

The main advantages of hemicellulose retention in pulp are increase in pulp yield and increase in pulp strength.[154] This invariably leads to lower costs and increased economic margins. The presence of high hemicellulose content in the pulp helps to increase the ability of the fibres to attract and to retain water in the fiber wall.[155] This improves the fibre swelling, brings weakening in the microfibril linkages in the cell wall, and favours the pulp refining.[155]

Further experiments were carried out with mixtures of 90%, 92%, 94%, 96% and 98% **IL11** with **[Choline]OH** to determine if the addition of small amounts of **[Choline]OH** to the ionic liquid would aid the formation of black liquor, signifying the removal of lignin from the lignocellulosic pulp. All the mixtures formed a black liquor after heating for 2 hours at 110 **ºC**. The mixture containing 90% of the ionic liquid was chosen as the solvent for the extraction protocol, to allow for more water in the system (5.4%), which aids the thorough wetting of the fibres.

An extraction protocol using the constituent acid and base of the ionic liquid has been developed. This method makes it possible for excess acid or base used to be recycled back to form the ionic liquid solvent, thus reducing waste effluent. The steps in this extraction protocol are outlined below.

Step 1: The molded paper waste was shredded, dried and sieved as described in section 5.3.2.2.

Step 2: 0.2g of the waste paper was cooked in 4ml of the ionic liquid-base solution for 2 hours at 110 **ºC** with the formation of black liquor.

Step 3: The resulting pulp was washed in a beaker with copious amounts of 70% ethanol, retaining the lignin in the filtrate. The pH of the filtrate measured with a pH metre was 12.4.

Step 4: The resulting pulp was washed several times with 70% ethanol and dried under vacuum at 60 **ºC** for 4 hours before analysis.

Step 5: Lignin precipitation is often achieved by acidifying the black liquor to a pH less than 4.[156]Thus, the black liquor was acidified with propionic acid to pH 3.9 and the lignin fraction collected after filtration.

Step 6: The spent ionic liquid solution was neutralised with **[Choline]OH** and dried under vacuum.

The steps after pulping for the recovery of the cellulose pulp, lignin fraction and ionic liquid are further elaborated in subsequent sections.

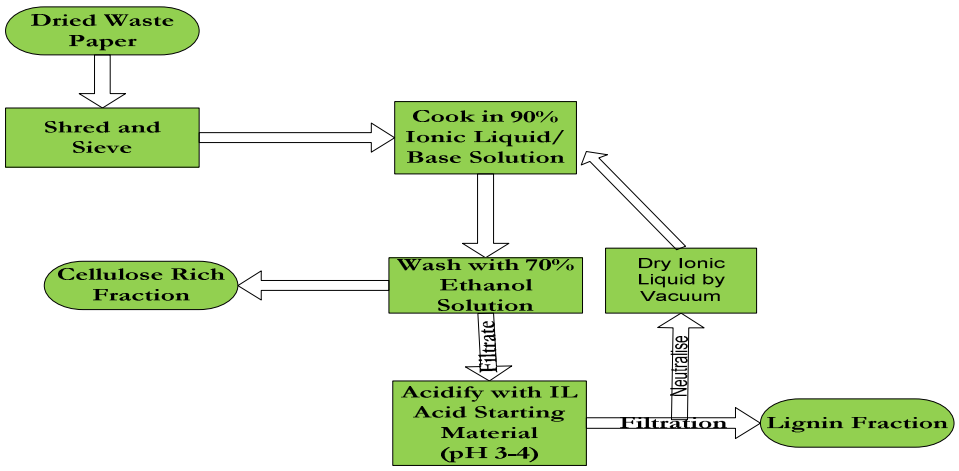


Figure 5.20: Extraction protocol utilising acid and base components of an alkylammonium acid-base ionic liquid.

The extraction process is shown in the diagram above. The use of 90% of the ionic liquid in its constituent base, **[Choline]OH** enhances the delignification of the biomass waste. Microwave heating was employed to reduce cooking times and optimise the extraction

process. Heating was carried out in open vessels at 140 Watt at 10 second intervals. Complete dissolution was achieved in 90 seconds, forming a black liquor.

5.3.5.2 Recovery of the Cellulose Rich Biomass

The cellulose rich fraction was recovered from the black liquor formed by precipitation with 70% ethanol in water in a large beaker. This concentration of ethanol is necessary for optimum lignin retention in the filtrate.[153] Filtration was carried out using glass crucibles and the biomass dried in a vacuum oven at 60 **ºC** for 4 hours before analysis. 0.13g of the pulp was recovered, corresponding to 65% pulp recovery.

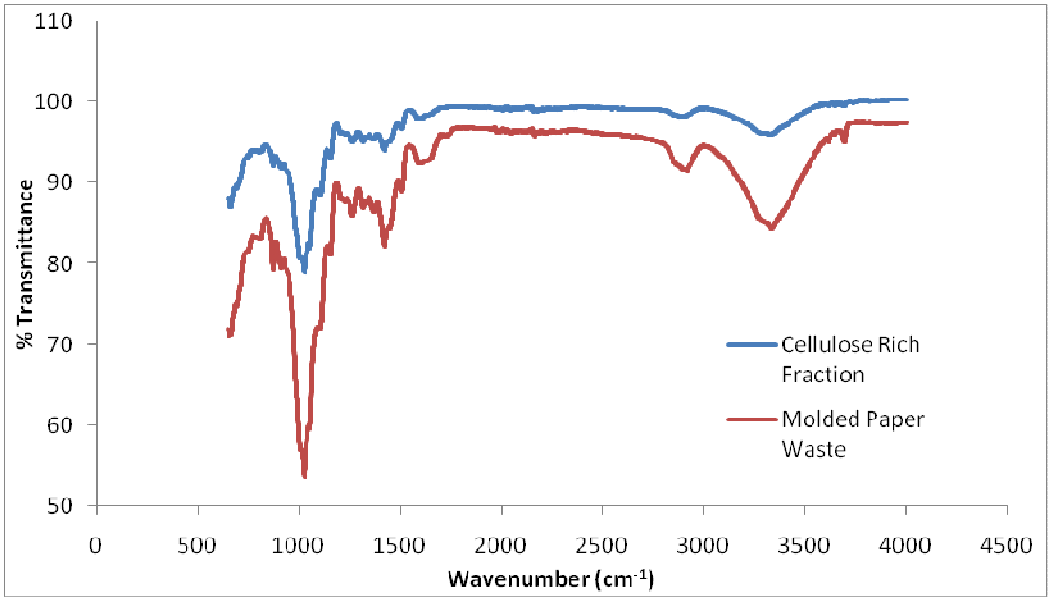


Figure 5.21: Comparison of FT-IR Scans for Untreated Molded Paper Waste and the Treated Cellulose Rich Fraction.

The FT-IR scan of the recovered waste paper compared to the untreated waste showed that there was reduction in the intensity of characteristic peaks due to lignin at 1694, 1609, 1518

and 829 and a slight shift of the peaks towards the right. The characteristic hemicellulose peak at 1044 cm^{-1} is still present, showing that when the biomass is pulped with the ionic liquid as base solvent, more pulp is recovered and more of the hemicellulose portion is retained in the recovered pulp. The small peaks between 700 and 850 cm^{-1} due to inorganics (most likely $CaCO_3$) were also largely reduced.

Comparing the pulp yield of 65% when the ionic liquid mixture was used with the pulp yield of 33% when only **[Choline]OH** was used in pulping, it is evident that using the ionic liquid mixture is beneficial because it aids the retention of the holocellulose portion in the pulp, resulting in higher pulp yield while the presence of **[Choline]OH** in the mixture aids in the delignification process.

The TGA weight loss curve of the sample after treatment showed a weight loss of about 10 % between 529 and 373 **ºC**. Thus, the waste sample was successfully delignified from 23% lignin to 10% lignin. It is noted that complete delignification did not occur, however the delignification of wood in the Kraft process is about 50%.[157]

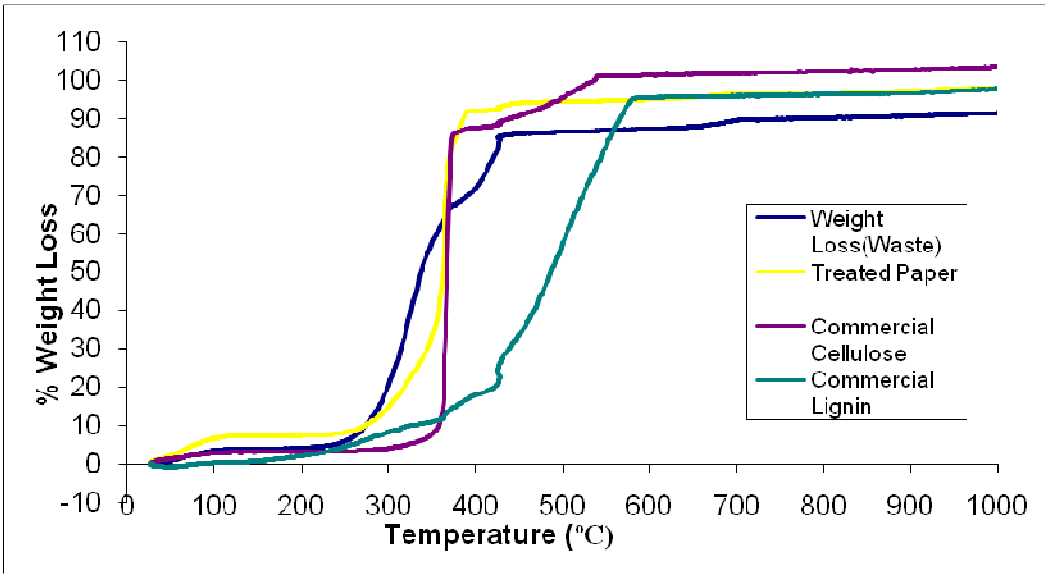


Figure 5.22: Comparison of %Weight Loss for Untreated Waste, Treated Waste Paper, Commercial Cellulose and Lignin.

The steady slope showing weight loss between 360 and 220 **ºC**, shows that there is retention of hemicellulose in the waste sample, as a removal of all the hemicelluloses would have resulted in a sharp downward weight loss with little slope as given by the commercial cellulose sample.

5.3.5.3 Recovery of Lignin Fraction

The lignin fraction in ionic liquid and ethanol was acidified dropwise with its constituent acid, propionic acid till pH 3-4. The pH was recorded with a pH meter. The pH at the beginning of the acidification process was 12.4. As the pH increased, the black liquor became lighter in colour. The acidification was stopped at pH 3.9 and the liquor centrifuged for 5 minutes at 10000 rpm, then filtered by ultra-filtration through a self-cleaning filter with a nominal rating of 5-15 k Dalton and 0.2-0.02μm pore size. 0.004g of lignin was recovered from the pulping of 0.2g of molded paper waste which is equal to 2% recovery of lignin. The recovery of lignin is much lower than the 31% reported by Sun *et al*[11] from **[C_2mim][AcO]**, but they utilised a strong acid (H_2SO_4) to reduce the pH to 2-3 and enhance lignin recovery. Furthermore, the presence of H_2SO_4 in the filtrate would make recovery of the ionic liquid difficult. They also used **DMSO** to reduce the viscosity of the solution in the pulping process and considering that **DMSO** has an α of 0 (lower than **[C_2mim][AcO]**), it is very likely that it contributed to the dissolution.

FT-IR scans of the recovered lignin fraction, klason lignin of the paper waste and commercial lignin are compared below.

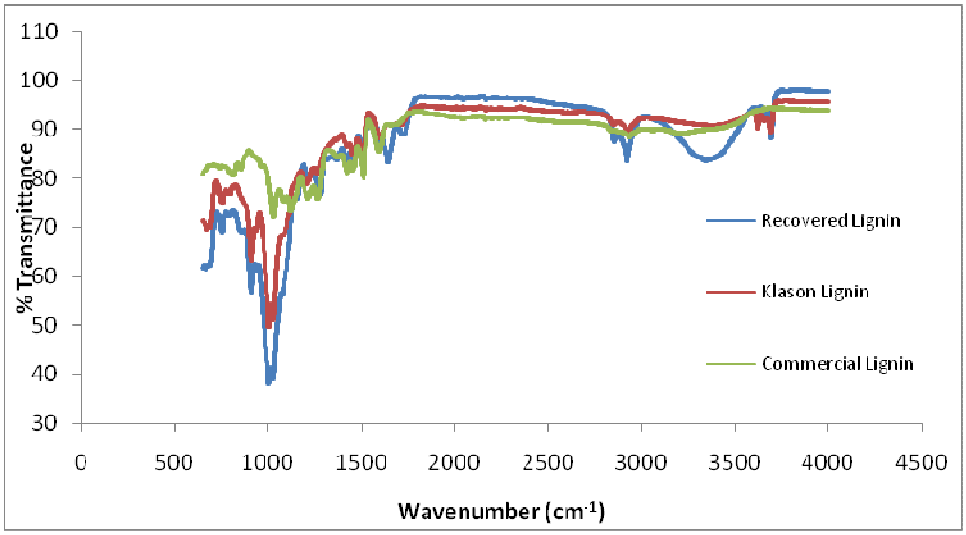


Figure 5.23: Comparison of FTIR scans of recovered lignin with the acid-insoluble lignin of the waste sample and commercial lignin.

The FT-IR scan of the recovered lignin fraction was almost identical to the klason lignin of the waste sample. The main difference was in the **–OH** stretching peak possibly due to water which was between 3000 and 3600 cm^{-1}. The hemicelluloses peak around 1000 cm^{-1} was also retained in the lignin fraction.

5.3.5.4 Recovery of Choline Propionate

The choline propionate filtrate was dried under vacuum at 60 **ºC** for 8 hours to evaporate the water and ethanol present. ^{1}H NMR of the ionic liquid showed the same peaks due to the ammonium cation and propionate anion. The triplet at 1.1 ppm representing the methyl end group on the propionate anion has a higher integration (more than twice the integration) than the singlet representing the 3 methyl groups on the cation, showing that there is a large amount of excess propionic acid in the **IL**. The recovery of the **IL** to its neutral form can be

done by reaction of the recovered form with choline hydroxide and monitoring the integration of singlet at 3.21 ppm.

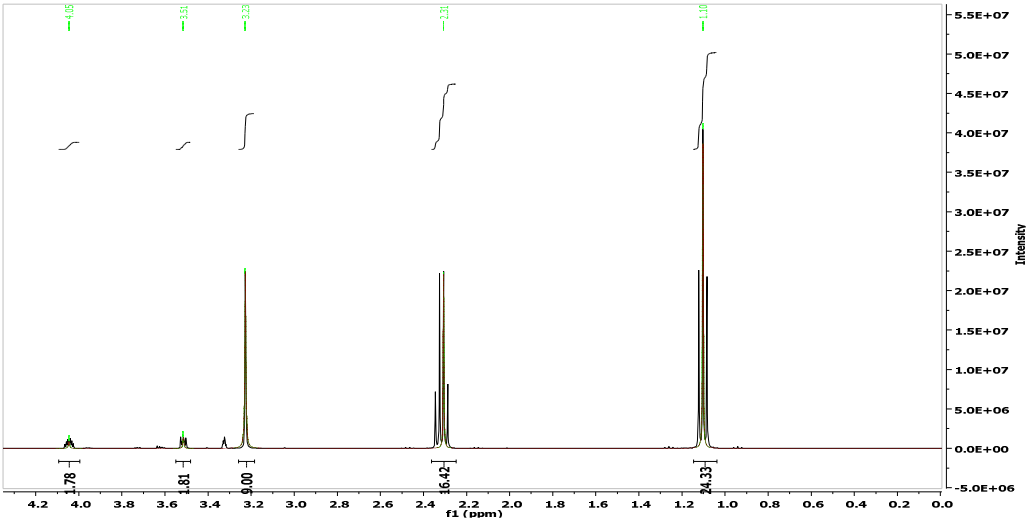


Figure 5.24: ^{1}H NMR of choline propionate showing excess acid in the system.

There were no additional peaks in the spectrum except a small peak for water at 3.3 ppm, suggesting that a poor filtration method contributed to the loss of lignin from the extraction.

5.3.5.5 Effect of Extraction Process on Molded Paper Morphology

SEM micrographs of the recovered waste sample showed that the fibres aggregated, although the fibre structure is still partially retained in contrast to other reports[7, 11] where a more homogenous structure was formed after treatment with imidazolium ionic liquids. This effect of alkylammonium ionic liquids on cellulose morphology may be useful in textile applications, where the retention of natural fibre structure could be beneficial.

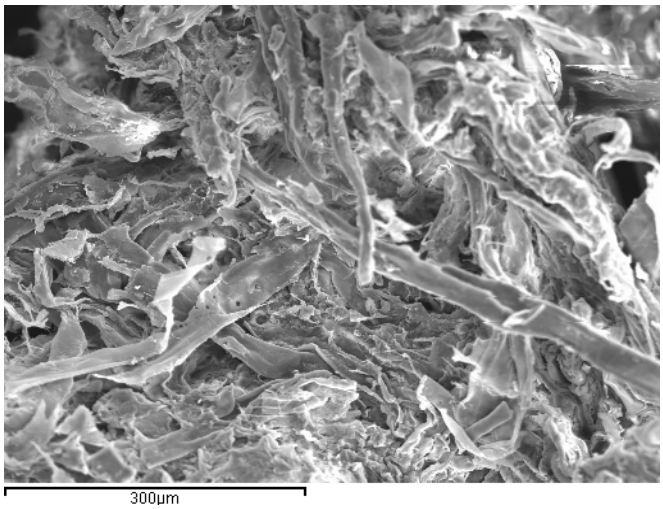


Figure 5.25: SEM micrograph of regenerated biomass waste fibres

5.4 Conclusions

The solubility of glucose, sucrose, starch and cellulose in ionic liquids has been investigated. The effects of the different cation and anion types on the solubility of the various sugars, was also investigated based on the Kamlet Taft Properties reported in Chapter 3.

Glucose and sucrose dissolved appreciably in most of the ionic liquids. Solubility in the alkylammonium acetates and propionates was comparable to solubility in **[C_2mim][AcO]**. It was found that the solubility of glucose was higher than the solubility of sucrose in the ionic liquids studied. This is expected since sucrose is a disaccharide and higher energy would be required to break the glycosidic linkage between its constituent glucose and fructose molecule. Furthermore, sucrose molecules undergo intramolecular hydrogen bonding. High α values of the alkylammonium ionic liquids conferred by a proton on the cation appeared to enhance solubility in contrast to cellulose where this property directly impedes solubility.

Starch dissolved appreciably in alkylammonium carboxylates. The solubility was also comparable to that of DMSO and other alkylimidazolium ionic liquids with high β values. The reduction in α by replacing the proton on the dimethylethanolammonium cation to form the choline cation resulted in a reduction in solubility. Thus, a higher α does not impede solubility as long as β is sufficiently high. Thus, designing an ionic liquid solvent for starch to mirror the zero α value of DMSO is not necessary and in fact, is probably not beneficial since DMSO requires a slight amount of water to aid dissolution as the added water would confer a higher α on the ionic liquid solution.

SEM results showed that like DMSO, disintegration of starch granules occurs on dissolution in ionic liquids.

All alkylammonium **ILs** with a proton on the cation did not dissolve cellulose. **IL11** with its moderate α and high β value successfully dissolved cellulose at 120 **ºC.** Solubility was lower in the alkylammonium **ILs** than in the imidazolium chlorides and carboxylates but irradiation under microwave energy improved the solubility. It was found that dissolved cellulose in **IL15** can contain up to 16% of water without precipitation, in contrast to reports by other authors.[7] It was also found that ionic liquids dissolve cellulose, flattening the fibres and distorting the morphology, although there is less distortion of the fibres with the alkylammonium **ILs**.

A molded paper waste sample was characterised using standard gravimetric, heating methods and FT-IR. The sample was found to have a high lignin content of more than 20%. Delignification of the lignocellulosic waste sample by **IL11** to 10% lignin content was achieved. An extraction protocol utilising the acid and base starting materials was

successfully developed, which enabled the recovery of a lignin fraction from the treated waste. The delignified waste fraction retained some of the hemicellulose content. The recycling of the ionic liquid after neutralisation of the solution back into the extraction process would minimise waste effluent.

Chapter 6 Assessment and Future Work

Alkylammonium room temperature ionic liquids that dissolve carbohydrates appreciably have been designed. Their chemical and physical properties have been investigated. Protic alkylammonium ionic liquids have high α and β values, yet are good solvents for glucose and sucrose. It was found that they have low thermal stability and thus cannot withstand the high temperatures needed for some biomass processing applications. They are therefore not suitable as solvents for the more complex carbohydrates which need a high amount of energy to break their extensive inter and intramolecular hydrogen bonding.

This thesis showed that non-protic alkylammonium ionic liquids are good solvents for glucose, sucrose, starch and cellulose. Their high β values and moderate α values make them good solvents for cellulose. The removal of a proton from the cation however, reduces the solubility of glucose and sucrose in these ionic liquids, suggesting that a high α is beneficial for glucose and sucrose solubility. Whereas other authors[14, 46] have reported solubility of carbohydrates in general to be favourable in ionic liquids with basic anions, this work has shown that solubility of simple carbohydrates is also cation dependent and that high α can be beneficial for glucose and sucrose solubility. This finding is supported by the fact that water, the common solvent for glucose and sucrose has a very high α value of 1.16 and a moderate β of 0.5. Further work in this area can involve designing **ILs** with moderate β and high α and testing the solubility of simple carbohydrates in those ionic liquids.

It has been shown that microwave conductivity can be used to speed up the extraction process for lignocellulosic wastes in ionic liquids and improve the extraction efficiency. A microwave effect on the morphology of the lignocellulosic waste sample was also observed, when treated with **IL1.** Heating the cellulose fibres in **IL1** by microwave energy caused swelling of the fibres, as compared to conventional heating. Thus, the thesis has in addition, shown the potential of microwave heating as a pre-treatment method for biomass processing. It could especially be useful as pre-treatment before enzymatic hydrolysis since swelling the fibres could open up the lignocellulosic matrix enough for the enzymes to gain access.

The protic dihydrogenphosphate ionic liquids have a high stability but they are not carbohydrate solvents. They may find use in high temperature applications requiring high **HBD** ionic liquids. Although the use of choline propionate as solvent for lignocellulosic biomass has been achieved, future work in this area should examine the design of non-protic alkylammonium ionic liquids with hydrogen bond accepting constituents on the cation, like ethoxy-groups to further reduce the $\boldsymbol{\alpha}$ value and increase $\boldsymbol{\beta}$. This is likely to result in higher dissolution rates for cellulose or lignocelluloses.

The delignification of a biomass sample was successfully achieved using a mixture of the ionic liquid and its constituent base, **[Choline]OH**. This process is an improvement on conventional organosolv processes since it is less aggressive on the hemicellulose portion of the biomass and this particular quality is conveyed by the presence of the ionic liquid. The pulp yield from the process using the **IL** mixture was also double that of when **[Choline]OH** alone was used as the pulping solvent.

The process developed can be useful in the reduction of waste from delignification processes. Excess amounts of amine can be used to improve the delignification efficiency where needed, while excess amount of the starting acid would be used to optimise the recovery of lignin. Neutralisation of any excess acid with the starting base would produce more ionic liquid to be channelled back into the extraction process, thus reducing the large volumes of salt waste that are typical of lignocellulosic processing plants.

Although the recovery of lignin in this work was low compared to the results by Sun *et al* in **[C_2mim][AcO]**, they utilised **DMSO** and **H_2SO_4** in the solubilisation and delignification processes respectively, which is not very different from the status quo in biomass processing. The use of **H_2SO_4** would also cause problems in the solvent recovery stage, whereas, with the ionic liquid mixture used in this thesis, the potential is there to recover the solvent and regenerate with the starting base. Other authors[8] have reported the delignification of woods of varying hardness in **[C_4mim]Cl**. 5 wt% suspensions of dried and finely divided wood chips in a solution of the IL and 15 wt% DMSO-d_6 were stirred at 100 ºC for periods ranging from 2 to 24 h. Their pulp yields of 30-60% were lower than the yield from the process reported in this thesis and they made no effort to recover the lignin from their filtrates.

In future, designing a cation-anion pair with high ***β*** and a stronger conjugate acid would also optimise the delignification process developed, if the pH of the black liquor could be reduced to 2-3. This would result in higher lignin recovery from the liquor.

The optimisation of the filtration method for recovering lignin from the black liquor would be another step in increasing the lignin yield, which would in turn reduce the amount of waste effluent produced from the process.

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