TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

REGENERATION OF IONIC LIQUIDS FROM WASTE SOLUTIONS OF CELLULOSE VALORISATION PROCESSES

IOONILISTE VEDELIKE TAASTAMINE TESLLUSLOOSI VALORISEERIMISPROTSESSIDE JÄÄTMELAHUSTEST

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Tallinn 2022

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Department of Materials and Environmental Technology

THESIS TASK

Student: Annika Aguraiujua, 204731KVEM

Study programme, KVEM12/20 – Technology of Wood, Plastic and Textiles

main speciality: 1 – wood technology

Supervisor(s): Illia Krasnou, Researcher, +37258389514

Thesis topic:

Regeneration of ionic liquids from waste solutions of cellulose valorisation processes

Iooniliste vedelike taastamine teslluslòosi valoriseerimisprotsesside jäätmelahustest

Thesis main objectives:

1. Develop a method for ionic liquid cleaning.
2. Develop a method for ionic liquid regeneration.
3. Develop a technique for quality control.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Study of different cleaning menthods: extraction, carbon washing. Quality control by rheology.	31.05.2021
2.	Distillation of solvents from ionic liquid waste solutions, quality control by NMR.	19.12.2021
3.	Study of water effects on ionic liquid, quality control by NMR, writing master thesis.	15.05.2022

Language: English **Deadline for submission of thesis:** 24.05.2022

Student: Annika Aguraiuja 24.05.2022

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CONTENTS

PREFACE

The main aim of this study is to develop a method for the recycling of the ionic liquid 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]), a novel ionic liquid with good cellulose solvation properties. The ionic liquid has been used in cellulose valorisation processes and this study is part of the larger RESTA10 project "Chemical valorisation of cellulose in an environment of ionic liquids" where ionic liquids are used in the preparation of thermoplastic cellulose derivatives. The project has been financed by the Estonian Research Council and is conducted at Tallinn University of Technology in the Department of Materials and Environmental Technology.

In this work, several recycling processes (liquid-liquid extraction, distillation, activated carbon and phase separation techniques) of ionic liquids are studied and applied to [mTBNH][OAc]. Each recycling process's effectiveness is evaluated and processes showing potential for recycling were studied by FT-IR, rheology, and proton NMR. The quantitative method of determining the ionic liquids purity after recycling was developed using proton NMR.

I would like to thank my supervisor Dr Illia Krasnou for supporting, guiding, and supervising this work and allowing me to reach my goals. Additionally, I would like to thank PhD student Nutan Savale for sending samples to NMR for analysis.

Keywords: ionic liquid, cellulose, recycling, green chemistry, Master's thesis.

List of abbreviations and symbols

ABS	Aqueous Biphasic System
AC	Activated Carbon
DP	Degree of Polymerisation
FT-IR	Fourier-transform infrared spectroscopy
IL	Ionic liquid
NMR	Nuclear Magnetic Resonance
rpm	Rotations per minute
SCF	Supercritical fluid
ScCO2	Supercritical carbon dioxide
VMD	Vacuum membrane distillation
[APPH][OAc]	3-(aminopropyl)-2-pyrrolidonium acetate
[Amim][Cl]	1-allyl-3-methylimidazolium chloride
[Bmim] BF_4	1-Butyl-3-methylimidazolium Tetrafluoroborate
[Bmim][PF6]	1-butyl3-methylimidazolium hexafluorophosphate
[Bmim]Cl	1-butyl-3-methylimidazolium chloride
[Bmim]$FeCl_4$	1-butyl-3-methylimidazolium tetrachloroferrate
[C2mim][Cl]	1-ethyl-3-methylimidazolium chloride
[DBNH][OAc]	1,5-diazabicyclo[4.3.0]non-5-enium acetate
[mTBDH][OAc]	7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate
[mTBNH][OAc]	5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate
[Omim]PF_6	1-octyl-3-methylimidazolium hexafluorophosphate
5-HMF	5-hydroxymethylfurfural

1. INTRODUCTION

Wood is a material abundant in nature, consisting mostly of cellulose, hemicelluloses, and lignin (Ramage et al., 2017). Cellulose is a simple biopolymer, consisting of glucose molecules that are connected by a β-1,4-glycosidic bond. Each glucose molecule on the cellulose chain contains three free hydroxyl groups, which form both intra- and intermolecular hydrogen bonds (Hauru, 2017). Cellulose and its derivatives are in use in many industries such as veterinary foods, wood and paper, fibres and clothes, cosmetics, and pharmaceutical industries (Shokri & Adibkia, 2013).

Cellulose needs to be extracted from biomass and valorised for many of its end uses. More than 90% of the world's biomass is in wood lignocelluloses. Environmental and energy problems related to fossil fuels are increasing the demand for the efficient use of this biomass. (Ohno & Miyafuji, 2014)

Current processes which are used to make useful products out of cellulose include acid hydrolysis, enzymatic saccharification, and pyrolysis. These processes however require extreme conditions with high temperatures and pressures. Due to these extreme conditions, the current processes used to modify cellulose are not considered environmentally friendly and do not make cellulose valorisation better than the use of fossil fuels. (Ohno & Miyafuji, 2014)

Cellulose cannot be dissolved in water or other conventional organic solvents therefore it is necessary to find a way to dissolve cellulose in an effective and environmentally friendly way. Ionic liquids are salts, which are in the liquid state at 100 °C or at below temperatures. They are called "green solvents" as they have negligible vapour pressure, are non-flammable and recyclable. Additionally, it has been found that imidazolium-based ionic liquids can dissolve cellulose very well, which is why ionic liquids are being looked at as a possible media for cellulose modification. (Ohno & Miyafuji, 2014)

However, unfortunately, the cost of ionic liquids is high, which limits its application in industry and ionic liquids commercialisation. The cost of ionic liquids can be lowered by gathering ionic liquid lifetime and recyclability data such as degree of sensitivity to contaminants and ionic liquids rejuvenation/recycling processes. To make ionic liquids economically viable, long-term stability and recyclability are crucial. (*Ionic Liquid Commercialization*, 2004)

This thesis concentrates on methods used to clean and regenerate ionic liquids and applying those methods to the ionic liquid 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]) which has been used in cellulose valorisation processes. Several methods are tested, and the efficiency of each method analysed by rheology, FT-IR (Fourier-transform infrared spectroscopy) and/or NMR (Nuclear Magnetic Resonance). The quality of the recycled ionic liquid has been studied by proton NMR and its ability to dissolve cellulose after recycling processes by rheology.

2. LITERATURE OVERVIEW

2.1 Ionic liquids

Ionic liquids (ILs) are salts which have a melting point below 100 °C (Welton, 1999). Two classes of ionic liquids exist: aprotic and protic ILs. Aprotic ionic liquids are considered the conventional type of ionic liquids and they consist of a bulky organic cation (e.g., imidazolium) and an anion (e.g., Cl$^-$). Common cations and anions of ionic liquids are shown in figure 2.1.1. Protic ionic liquids however are made via a proton transfer from a Bronsted acid to a Bronsted base (Peric et al., 2013).

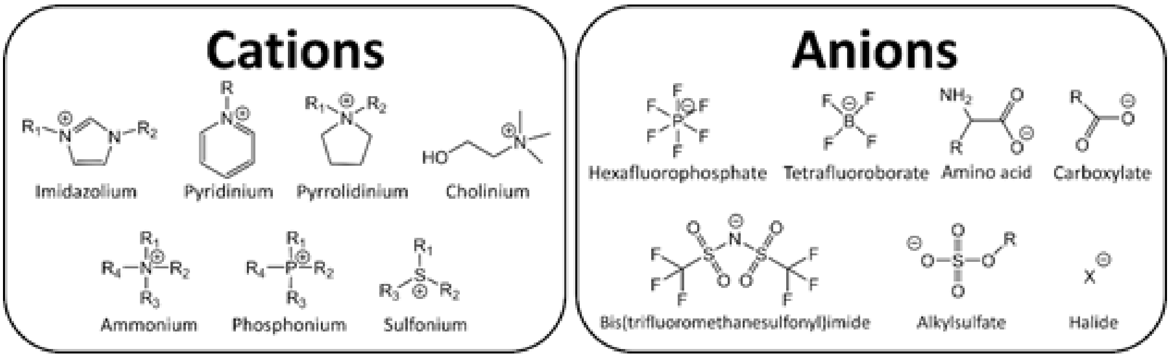


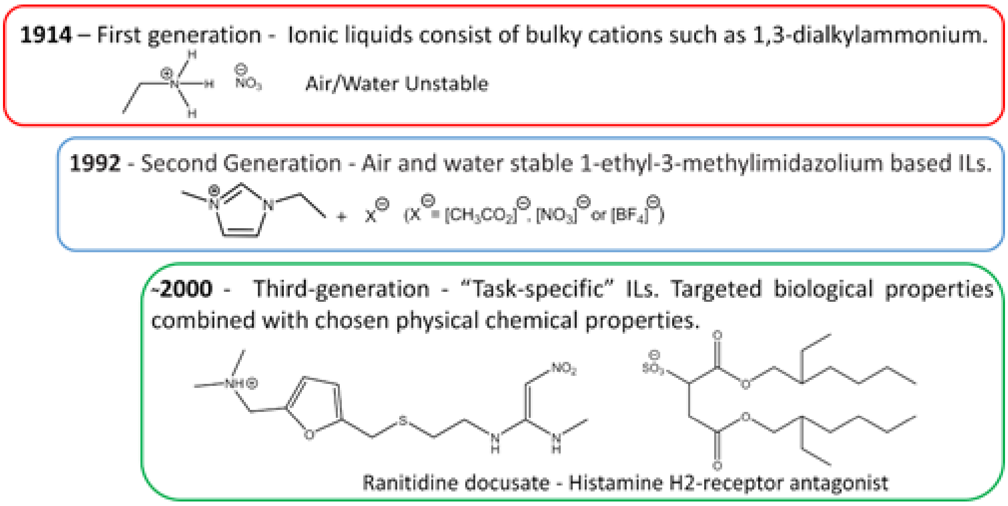
Figure 2.1.1. Common cations and anions of ionic liquids. (Silva et al., 2020)

There are four main reasons why ionic liquids are increasingly being used as a solvent during chemical synthesis. Firstly, ionic liquids are good solvents for a variety of compounds (both organic and inorganic) and allow for the solvation of unusual reagent combinations in the same phase. Secondly, they compose of ions, which allows them to be highly polar but at the same time a noncoordinating solvent. Thirdly, they are often immiscible with many organic solvents, allowing for interesting two-phase systems. Lastly, ionic liquids are non-volatile, which means they can be used under a high vacuum, without containment problems. (Welton, 1999)

The discovery of ionic liquids is controversial, some consider the first ionic liquid as ethylammonium nitrate ([EtNH$_3$][NO$_3$]) discovered by Paul Wielden in 1914 whilst others consider the first ionic liquid as ethanolammonium nitrate, which was synthesised by Gabriel and Weiner in 1888. The debate stems from the fact that Wielden's ionic liquid had a melting point of 13 – 14 °C whilst Gabriel's discovered compound had a melting point of 50 °C, which is higher than room temperature. Nevertheless, these ionic liquids are considered the first generation of ionic liquids, which were unstable in both air and water environments. (Silva et al., 2020)

The second generation of ionic liquids was prepared by Wilkes and Zaworotko in 1992. These were based on the 1-ethyl-3-methylimidazolium cation and anions such as

$[CH_3CO_2]^-$, $[NO_3]^-$ and $[BF_4]^-$. This generation of ionic liquids was air and water stable and therefore easier to handle, which is why research of ionic liquids, and their properties have become more common in the last 25 years. The third generation of ionic liquids was developed as "task-specific" ionic liquids and stemmed from functionalized imidazolium-based ILs synthesised by Ann Visser which were capable of extracting heavy metals such as Hg^{+2} from aqueous solutions. Thus, the third generation of ionic liquids are modified for their desired applications. The first, second and third generation of ionic liquids is shown in figure 2.1.2.(Silva et al., 2020)


1914 – First generation - Ionic liquids consist of bulky cations such as 1,3-dialkylammonium.

Air/Water Unstable

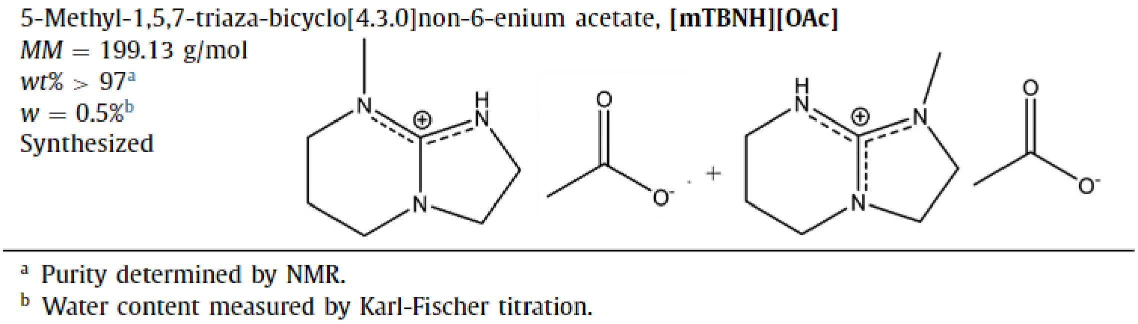
1992 - Second Generation - Air and water stable 1-ethyl-3-methylimidazolium based ILs.

~2000 - Third-generation - "Task-specific" ILs. Targeted biological properties combined with chosen physical chemical properties.

Ranitidine docusate - Histamine H2-receptor antagonist

Figure 2.1.2. The first, second and third generation of ionic liquids and their time of discovery. (Silva et al., 2020)

This master's thesis focuses on the ionic liquid 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]), a novel ionic liquid developed and produced by Liuotin Group OY in Helsinki, Finland. The chemical structure of the ionic liquid is shown in figure 2.1.3. The ionic liquid is a 50:50 mixture of 5- and 7-methyl isomers(*Ionic Liquids and Superbases on Offer from Liuotin.Com*, n.d.), which the structural difference comes from the mTBN superbase. The difference is in the location of the double bond and thus the location of the methyl group.(Martins et al., 2022)


5-Methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate, **[mTBNH][OAc]**
$MM = 199.13$ g/mol
$wt\% > 97^a$
$w = 0.5\%^b$
Synthesized

[a] Purity determined by NMR.
[b] Water content measured by Karl-Fischer titration.

Figure 2.1.3. Chemical structure and properties of 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]). (Martins et al., 2022)

The recycling of the ionic liquid 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) has been studied by Parviainen et al. The ionic liquid had been used in the Ioncell-F process. The studied ionic liquid is similar in structure to [mTBNH][OAc] and [mTBDH][OAc]. However, concerns have been raised regarding the thermal and hydrolytic stability of the ionic liquid during recovery (Parviainen et al., 2015).

In the study performed by Parviainen et al., it was determined that the ionic liquid hydrolyses when in contact with water at elevated temperatures. The study involved the synthesis of ionic liquid, cellulose solvation, and recovery of the ionic liquid by a high vacuum rotary evaporator for 2 hours at 60 °C at 1-3 mbar. Lastly, the ionic liquid was studied by ^{1}H NMR. (Parviainen et al., 2015)

It was discovered that 6.0 - 13.6 mol% of hydrolysis occurred per cycle of dissolution. The fifth cycle was the last cycle that was capable of dissolving the cellulose completely. Dissolution properties were lost at 41.5-54.9 mol% degree of hydrolysis, which is equal to the water content of 4.1-5.4 wt% in pure ionic liquid. Figure 2.1.4. shows the effect of ionic liquid hydrolysis per dissolution cycle on the recovery of the ionic liquid. (Parviainen et al., 2015)

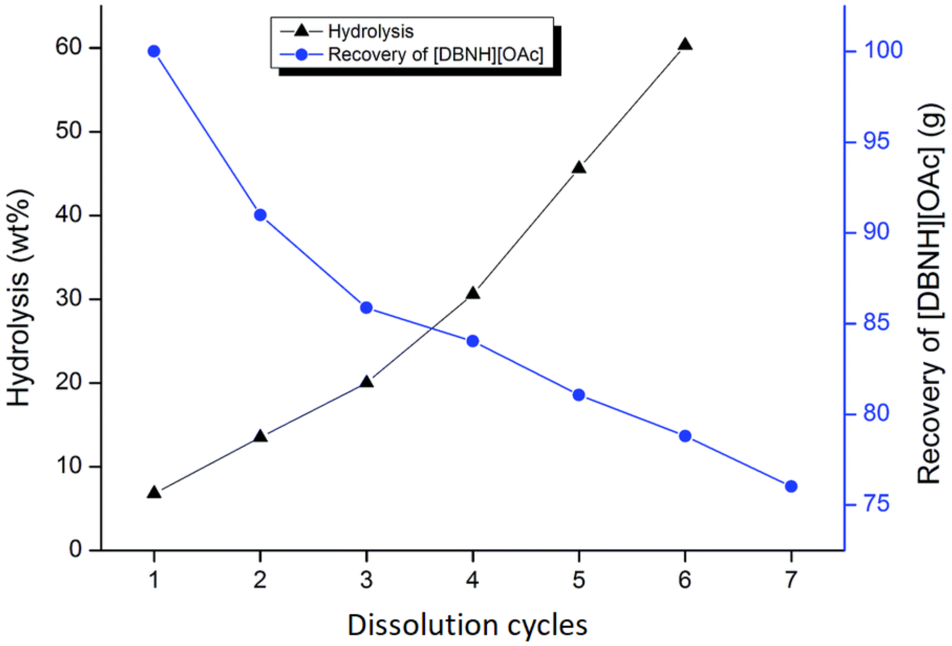


Figure 2.1.4. The increase in the hydrolysis of the ionic liquid [DBNH][OAc] compared with the recovery of ionic liquid by mass. The higher the hydrolysis, the lower the recovery. (Parviainen et al., 2015)

The process solvent itself had an average recovery rate of 95.6%, however, the solvent does contain the initial and its hydrolysis products. The average loss of mass was determined as 2.5g for each cycle. NMR analysis showed that [DBNH][OAc] undergoes hydrolysis in an aqueous environment at elevated temperatures producing 3-(aminopropyl)-2-pyrrolidonium acetate ([APPH][OAc]) as shown in figure 2.1.5. The hydrolysis is confirmed by the C7 signals for [DBNH][OAc] and [APPH][OAc] which do not overlap with any other signals; thus, integrals of the C7 signals were used to determine the rate of hydrolysis as 6.0 - 13.6 mol% per cycle.

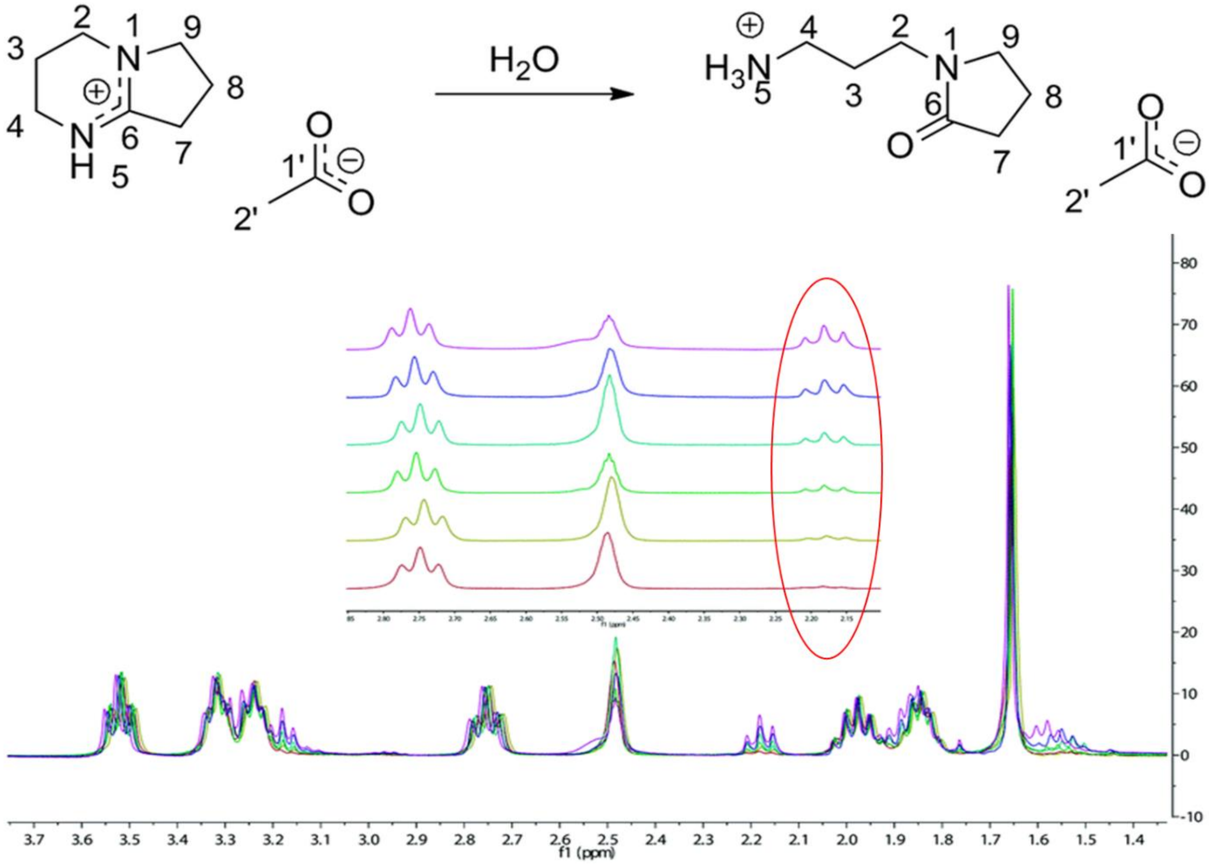


Figure 2.1.5. Top - Hydrolysis of [DBNH][OAc] to [APPH][OAc] and changes in its chemical structure. Bottom – ^{1}H NMR spectra's showing the build-up (circled in red) of the hydrolysis product per cycle. The solvent DMSO-d_6. Image edited for clarity. (Parviainen et al., 2015)

The study performed by Elsayed et al. compares the recyclability of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate ([mTBDH][OAc]) over five cycles of dissolution. Lower hydrolysis of mTBD has been reported compared to DBN (Hyde et al., 2019). 13 wt% cellulose solutions in the ionic liquid were used to produce regenerated cellulose fibres. The ionic liquid itself was recovered by thermal treatment.

The presence of two hydrolysis products of the ionic liquid was found to be present via NMR after the applied processes. These were H-mTBD-1 and H-mTBD-2 which were found to be present at the shift values of 2.24 ppm and 2.78 ppm respectively at 0.5-2.6 wt%. The low concentration indicates that the majority of the ionic liquid was not affected by the Lyocell process or the regeneration process. Figure 2.1.6. shows the molecular structure of the pure [mTBDH][OAc] and the two proposed hydrolysis products with ^{1}H NMR spectra of the pure ionic liquid and regenerated ionic liquid solutions. The signal from H-mTBD-1 was much higher than the H-mTBD-2, which shows that the yield is favoured towards the hydrolysis product H-mTBD-1. (Elsayed et al., 2020)

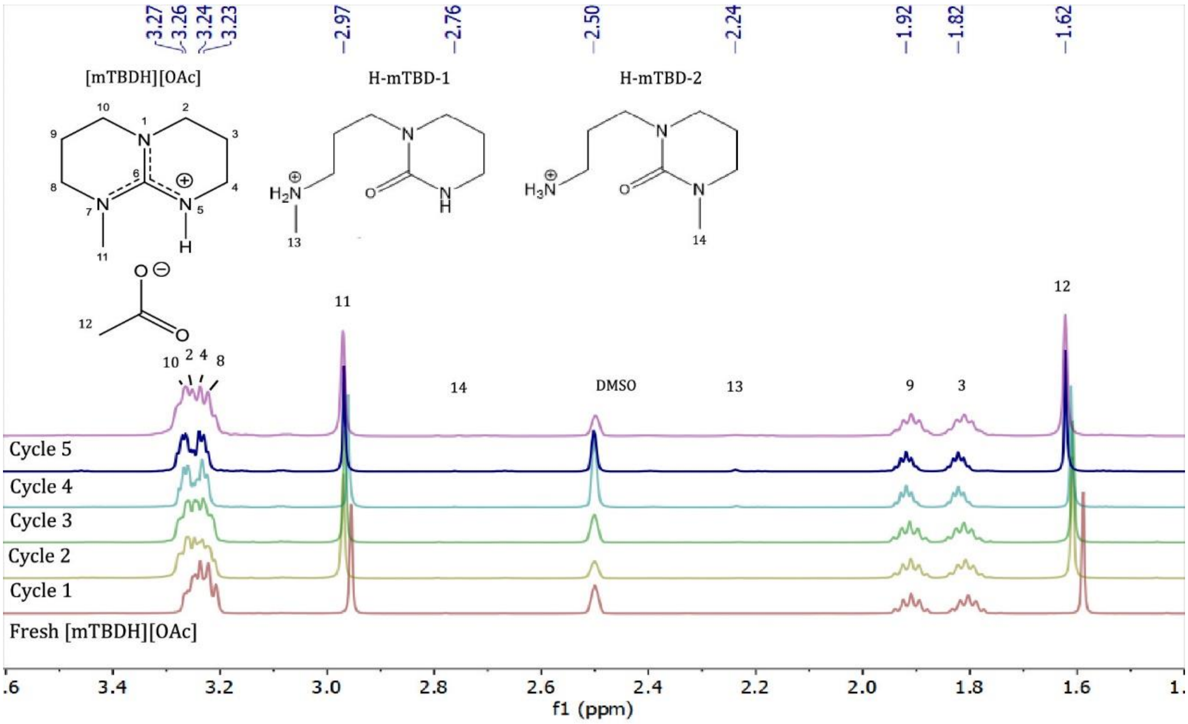


Figure 2.1.6. ^{1}H NMR spectra's for pure [mTBDH][OAc] and recovered [mTBDH][OAc]. Peaks show the acetate, base and hydrolysis products.(Elsayed et al., 2020)

In addition to hydrolysis products, the residual water in the IL after recycling was 2.6 – 3.1 wt %. It is essential to achieve low water content in the IL, as any presence of water in the regenerated ionic liquid will hinder further dissolution of cellulose. It also induces the formation of hydrolysis products. (Elsayed et al., 2020)

2.2 Cellulose in ionic liquids

Ionic liquids have been found to be effective at dissolving cellulose however, it has also been found that ionic liquids are not 100% perfect, and the cellulose can be degraded in the ionic liquid environment, which makes the process of ionic liquid recycling and rejuvenation more difficult. The degradation of cellulose is affected by many factors such as the source of the cellulose, the water content, the ionic liquids used and the treatment conditions (Ohno & Miyafuji, 2014).

Studies done by Swatloski et al. showed that imidazolium-based ionic liquids can dissolve cellulose well, and therefore ionic liquids composed of the imidazolium cation and chloride/acetate anion are used for cellulose research (Swatloski et al., 2002). NMR studies suggest that the cellulose is dissolved well due to the interactions of hydroxyl groups in cellulose with chloride/acetate anions whilst very little interaction occurs with the imidazolium cation (Editor et al., 2010; Remsing et al., 2006; Youngs et al., 2007).

In the study performed by Zhou et al., the depolymerisation of cellulose was evaluated by the reduction of the degree of polymerization (DP). The DP of cellulose decreased from 550 to 430 after dissolving in [Amim]Cl for 8 hours at 100 °C – reducing sugars were produced in the process. The degradation occurs most probably due to the breaking of the hydrogen bonds. It was concluded that the higher the temperature and longer the synthesis time, the bigger the change in DP. In [Amim]Cl it was found that cellulose only degraded slightly if the experiment was performed at 90 °C for 3 hours but when the time and the temperature were increased, the degradation also increased. (Zhou et al., 2020)

The decomposition of cellulose was studied by Ohno and Miyafuji in the ionic liquid 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]). In [C2mim][Cl], it was determined that cellulose decomposes to cellobiose, cellobiosan, glucose, levoglucosan and 5-hydroxymethylfurfural (5-HMF) as shown in figure 2.2.1 by the proposed reaction pathways. (Ohno & Miyafuji, 2014)

In pathway A, cellulose is depolymerised due to a hydrolysis reaction with moisture that is absorbed from air however in pathway B, the cellulose is depolymerised by the reaction of the hydroxy group at the C6 position in the glucose monomer, which occurs randomly in cellulose and as such cellobiosan and cellooligosaccharides are produced. In both pathways, the final product is glucose, which may be further dehydrated to 5-HMF – which produces water as a side product. Hydrolysis and dehydration reactions coexist if the decomposition of cellulose is occurring in the environment with air. The amount of water present is important to control the hydrolysis of cellulose and its degradation products. With less water in the system, it is possible to dissolve cellulose in [C2mim][Cl] without decomposition.(Ohno & Miyafuji, 2014)

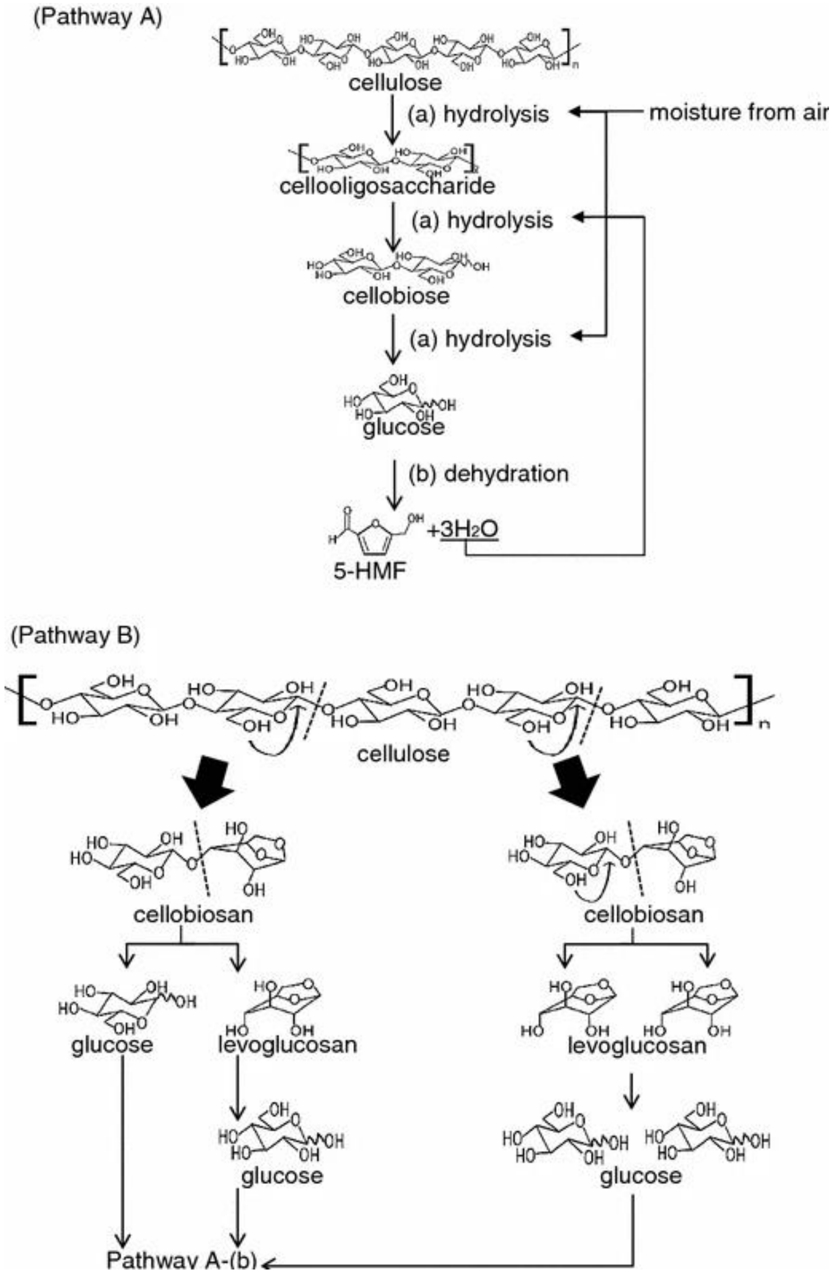


Figure 2.2.1. Proposed pathways for cellulose degradation products. (Ohno & Miyafuji, 2014)

When discussing rejuvenation and recycling of ionic liquids, it is also important to note that biomass usually also contains residual inorganic materials as well, such as salts which originate from the soil and are bound both chemically and physically to wood. In the study by Parvianien et al., the inorganic material builds up in the ionic liquid was also determined. As shown in figure 2.2.2. the inorganic ash content increases in the ionic liquid with each synthesis cycle, meaning that this too needs to be removed when recycling. (Parviainen et al., 2015)

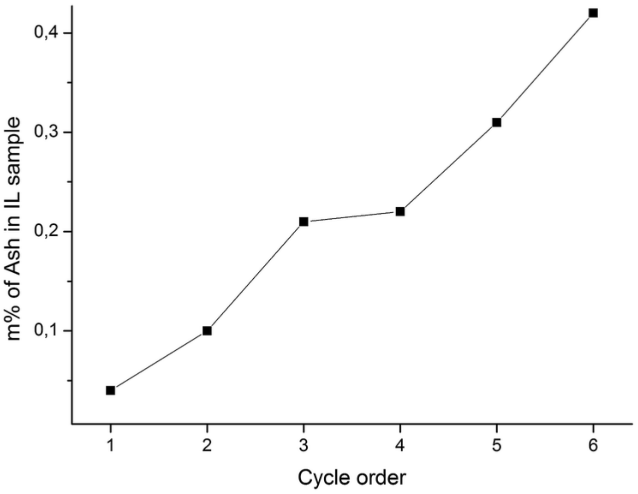


Figure 2.2.2. The build-up of inorganic materials in ionic liquid during recycling. (Parviainen et al., 2015)

In this Master's thesis, the contaminants in the ionic liquid are not studied specifically, however the above must be taken into consideration when choosing techniques for recycling.

2.3 Methods of recovery and recycling

When discussing different types of recycling methods, it is important to remember that ionic liquids are typically divided into two different classes – aprotic and protic ionic liquids. This distinction is important as the structure of the ionic liquid depends on what method of recovery can be used. A general method of recovery involves two steps. The first step involves phase separation, extraction, membrane separation and adsorption. Only one of these methods can be used or a combination of methods. The second step is usually distillation, to remove solvents. The general method of recovery is shown in Figure 2.3.1 and in this section, each separate method will be discussed. (Mai et al., 2014)

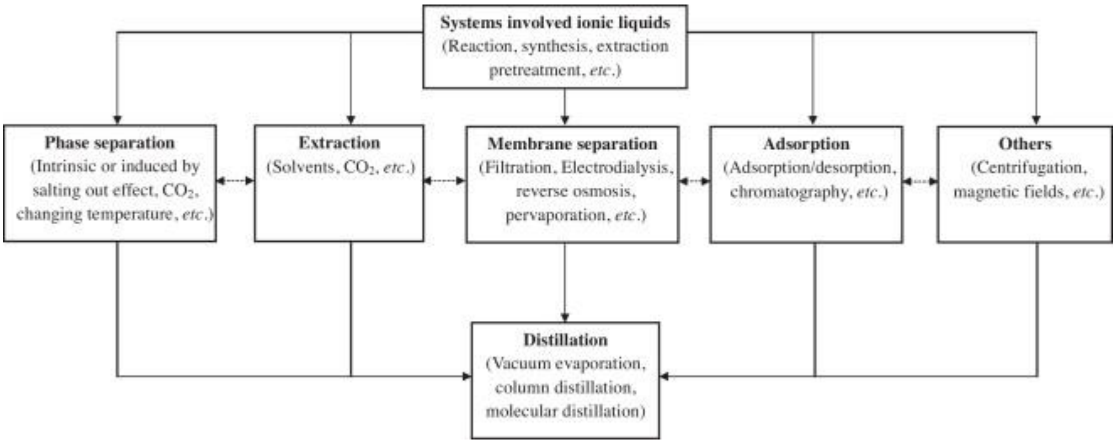
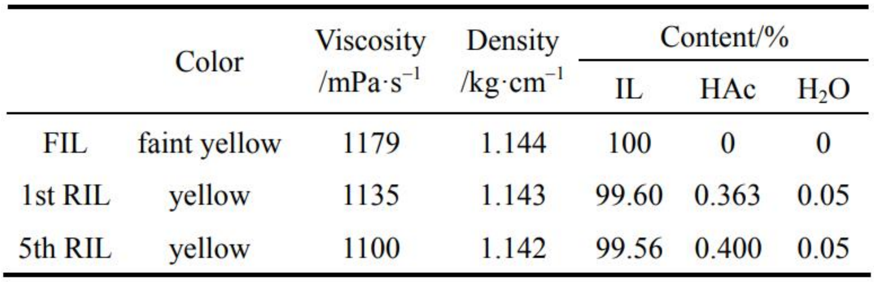


Figure 2.3.1. The general method of ionic liquid recovery. (Mai et al., 2014)

2.3.1 Distillation

Distillation is one of the simplest methods of recovery. Distillation can be used to remove the volatile solvents in the ionic liquid mixture due to the ionic liquids' negligible vapor pressure. Using a vacuum distillation system, it is possible to remove solvents at low temperatures. Typically, distillation is performed as the last step after filtration, extraction etc.(Mai et al., 2014)

1-allyl-3-methylimidazolium chloride ([Amim][Cl]) has been successfully recovered from an aqueous solution by molecular distillation (Apparatus: Pope 2# wiped-film molecular still) in the study performed by Huang et al. [Amim][Cl] was recycled five times and used in cellulose acetylation process. The pure and recycled [Amim][Cl] characteristics were studied and the optimal conditions for molecular distillation were determined. Figure 2.3.2. shows an overview of the properties of the pure and recycled [Amim][Cl]. (Huang et al., 2013)



	Color	Viscosity /$mPa \cdot s^{-1}$	Density /$kg \cdot cm^{-1}$	Content/%		
				IL	HAc	H_2O
FIL	faint yellow	1179	1.144	100	0	0
1st RIL	yellow	1135	1.143	99.60	0.363	0.05
5th RIL	yellow	1100	1.142	99.56	0.400	0.05

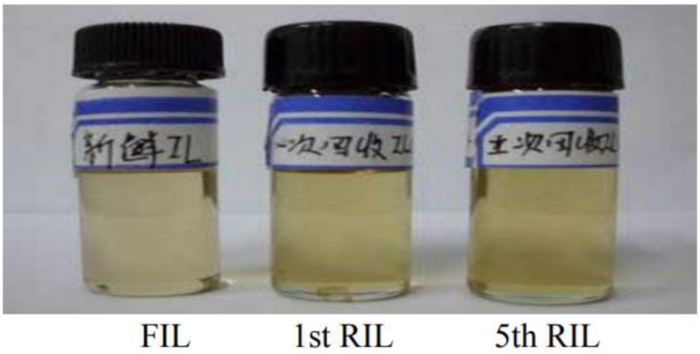


Figure 2.3.2. Properties of [Amim][Cl] used for cellulose acetylation and recycled over 5 cycles. FIL – fresh ionic liquid, 1st RIL – first cycle recycled ionic liquid, 5th RIL – fifth cycle recycled ionic liquid.(Huang et al., 2013)

As can be seen from the figure, the viscosity, density and purity of the ionic liquid after five cycles are quite similar to the pure ionic liquid. However, a colour change was observed, with each cycle [Amim][Cl] turned darker. The purity of [Amim][Cl] was determined by FT-IR and NMR as 99.56% after five cycles. The FT-IR and NMR spectrums are shown in figure 2.3.3. On the FT-IR spectra a new peak at 1715 cm^{-1}

corresponding to C=O of residual acetic acid was observed. The same was observed by NMR, where a peak corresponding to acetic acid residues with methyl protons were observed at δ = 2.0. No other residues were detected, thus [Amim][Cl] shows high recyclability.

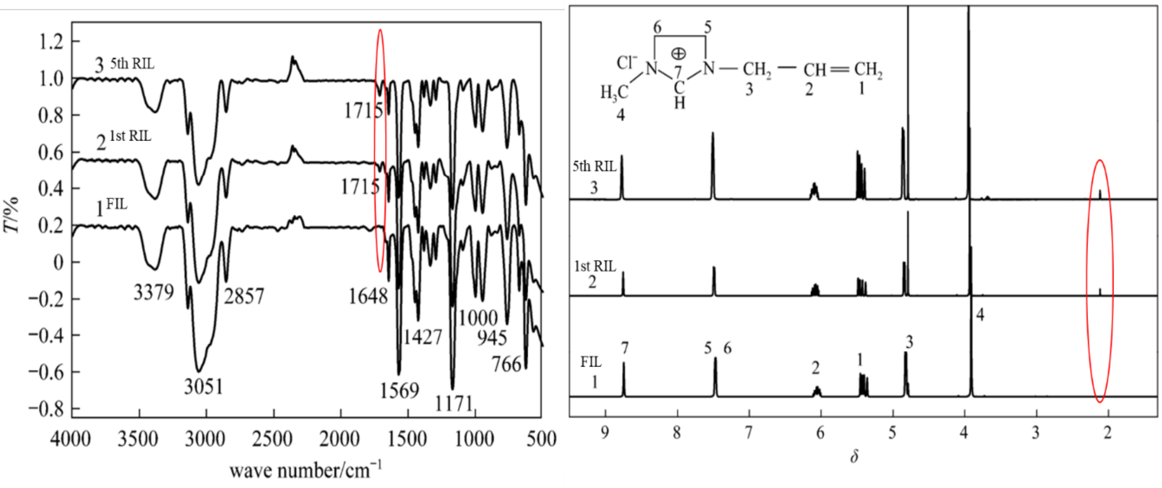


Figure 2.3.3. Left – FT-IR spectra of FIL, 1st RIL and 5th RIL. Right – NMR spectra of FIL, 1st RIL and 5th RIL. FIL – fresh ionic liquid, 1st RIL – first cycle recycled ionic liquid, 5th RIL – fifth cycle recycled ionic liquid. Both images show the acetic acid residues in IL after recycling. Image edited for clarity.(Huang et al., 2013)

Instead of removing solvents in ionic liquid, the direct distillation of aprotic ionic liquids has been studied by Earle et al. Several ionic liquids were distilled at 300 °C and a pressure of 0.1 - 5 mbar in a Kugelrohr apparatus and a sublimation apparatus. The direct distillation of the ionic liquid was successful at low pressures and the distillate and residues were studied by NMR. NMR showed that ionic liquids such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C2mim][NTf2]) can be distilled directly, with no decomposition observed. It was also found that the lower the pressure in the distillation apparatus, the faster the distillation, however the distillation time of 1.0 grams of ionic liquid was four to six hours, making direct distillation an ineffective method for industry, where quantities are larger. (Earle et al., 2006)

1-butyl-3-methylimidazolium chloride ([Bmim]Cl) separation from an aqueous solution by vacuum membrane distillation (VMD) has been studied. The membrane studied was a polyacrylonitrile based hydrophobic membrane where the surface had been modified by CF_4 plasma. The membrane fouling and wetting was studied alongside the recovery of [Bmim]Cl (Wu et al., 2016)

Vacuum membrane distillation (VMD) is a technique that uses a vacuum to remove water vapours from a heated solution across the hydrophobic and porous membrane. The [Bmim]Cl solution of 20% to 60% was heated to 323 K - 353 K and fed into the membrane module. The membrane used had an area of 10.57 cm^2. A cold trap with liquid nitrogen was used to condense the water and the water was drawn out at an absolute pressure of 3.3kPa. The schematic of the VMD setup is shown in figure 2.3.4. (Wu et al., 2016)

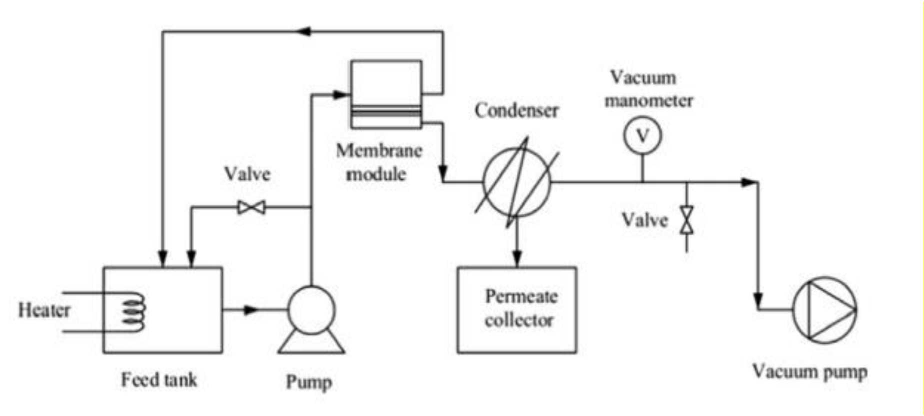


Figure 2.3.4. Vacuum membrane distillation set-up used to distil an aqueous solution of [Bmim]Cl. (Wu et al., 2016)

The technique was found to be successful as the membrane rejection of [Bmim]Cl was almost 100%, however, the rejection rate did decrease to 99.5% at 60 wt% and the temperature of 343 K. From the initial concentration of 20 wt%, after 65 hours of recycling the concentration of the [Bmim]Cl was 53.3 wt% with the recovery of ionic liquid at 99.2%. Unfortunately, using this method leads to the degradation of the membrane and it is necessary to clean the membrane. Otherwise, the ionic liquid will start wetting the top layer of the membrane and after some time, the internal pores will be wetted, and [Bmim]Cl can pass though the membrane. (Wu et al., 2016)

2.3.2 Extraction

A simple method of recovery is by extraction. It requires the use of a solvent that is immiscible with the ionic liquid, to extract products/by-products from the ionic liquid. It has been found that hydrophilic products can be removed from the hydrophobic ionic liquids with water (Huddleston et al., 1998). Diethyl ether and hexane have been proven successful at removing non-volatile and thermally sensitive hydrophobic products from ionic liquid solution (Earle et al., 1999).

The solvent mixture containing acetone, 2-propanol and a small amount of water has been found effective for separating oleophilic solutes, short-chain carbohydrates and lignin fragments from 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) via a two-stage extraction process. The method utilises the strong interaction of water and other hydrogen bond donor solvents with hydrophilic ionic liquids. Dry acetone and [C2mim][OAc] are miscible, whilst adding water to acetone reduces the solubility of acetone in the ionic liquid to 0.05 wt%. In this system, alcohols can be used as a co-solvent, where adding the same amount of alcohol as water in the system returns the ionic liquid back to its single-phase state. The acetone creates a second phase in the system, which allows the removal of non-polar products. The process showed an ionic liquid recovery rate of 89%. (Dibble et al., 2011)

The composition of the recovered ionic liquid studied by Dibble et al. was studied by ^{1}H NMR. After the process, the ionic liquid was darker in colour and contained different contaminants than the ionic liquid before it was used. The ^{1}H NMR spectra of the recovered ionic liquid and ionic liquid prior to use are shown in Figure 2.3.5. The dashed line shows the ionic liquid prior to use and the solid line shows the recovered ionic liquid. The broad peak at 6.25ppm indicates the presence of water – the main contaminant after recovery. The other impurity peaks indicate the possible presence of lignin and carbohydrates in the ionic liquid after treatment. (Dibble et al., 2011)

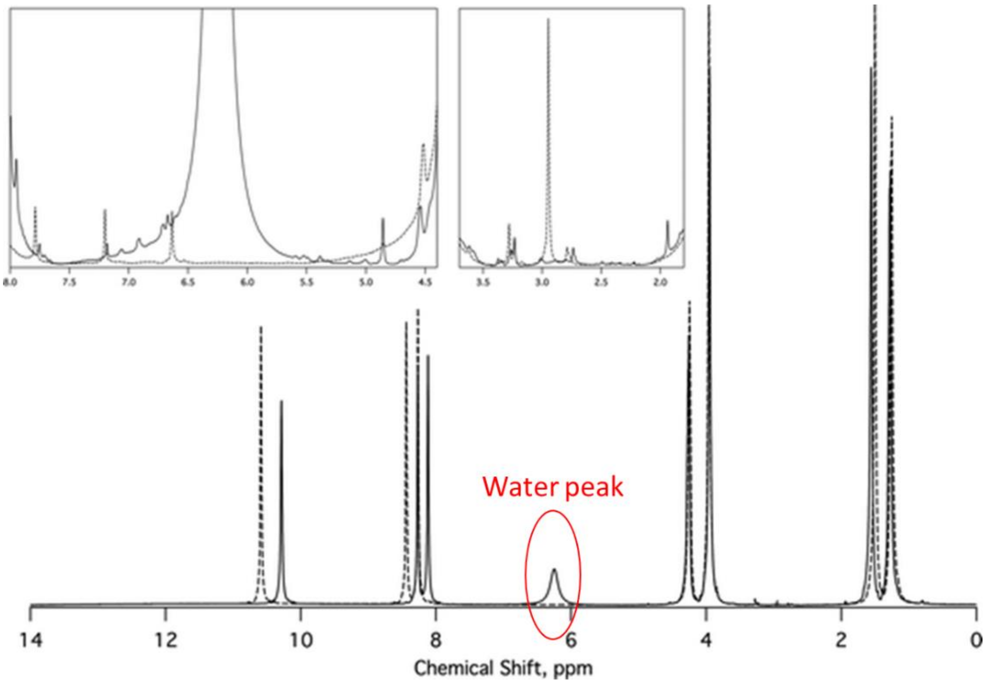


Figure 2.3.5. [C2mim][OAc] prior to treatment (dashed line) and after recovery (solid line). Image edited for clarity. (Dibble et al., 2011)

An alternative solvent considered for extraction is supercritical fluids (SCF). Supercritical CO_2 (scCO_2) is widely used and is also considered a “green” solvent as CO_2 is environmentally common, inexpensive, non-toxic and non-flammable and therefore suits well the areas of green chemistry. Many organic compounds are soluble in ScCO_2 and can therefore be transferred from the ionic liquid phase to the ScCO_2 phase. (Blanchard et al., 2001; Mai et al., 2014)

Binary systems of ionic liquid and CO_2 have been studied. The extraction of solutes from such systems is dependent on the systems phase behaviours. $ScCO_2$ is capable of forming a two-phase system with non-volatile and polar ionic liquids, where CO_2 is soluble in the liquid phase of ionic liquid however the ionic liquid is insoluble in the CO_2 gas phase. This means that when pressure is removed from the system, CO_2 is completely removed. The drawback of this method is that special equipment and knowledge of the ionic liquid - CO_2 phase is required, which means that developing this method can be quite expensive and time-consuming for novel ionic liquids. (Blanchard et al., 2001; Mai et al., 2014)

2.3.3 Induced phase separation

Aqueous solutions of ionic liquid have been found to form an aqueous biphasic system (ABS) when salts are added – this is called salting out. As such, several different salts have been studied to promote induced phase separation of ionic liquid systems. The first effective studies where ABS of aqueous ionic liquid and salts were performed with kosmotropic salts, such as K_3PO_4, where a top ionic liquid-rich layer and a bottom salt-rich layer formed (Gutowski et al., 2003). [Amim][Cl] + salt + water aqueous biphasic systems were studied by Deng et al.

[Amim][Cl] ABS with K_3PO_4, K_2HPO_4 and K_2CO_3 were studied. The method is simple, a known mass fraction of salt was added to a known concentration ionic liquid aqueous solution, mixed and then left for 24 hours to allow the phases to separate. It was found that by increasing the concentration of the salt, the recovery efficiency also improved. Salting out strength goes by the Hofmeister series $K_3PO_4 > K_2HPO_4 > K_2CO_3$. Figure 2.3.6. (left) shows the effect of salt mass percent on recovery efficiency. The highest efficiency of 96.8% was obtained with K_2HPO_4 at 46.48%. (Deng et al., 2009)

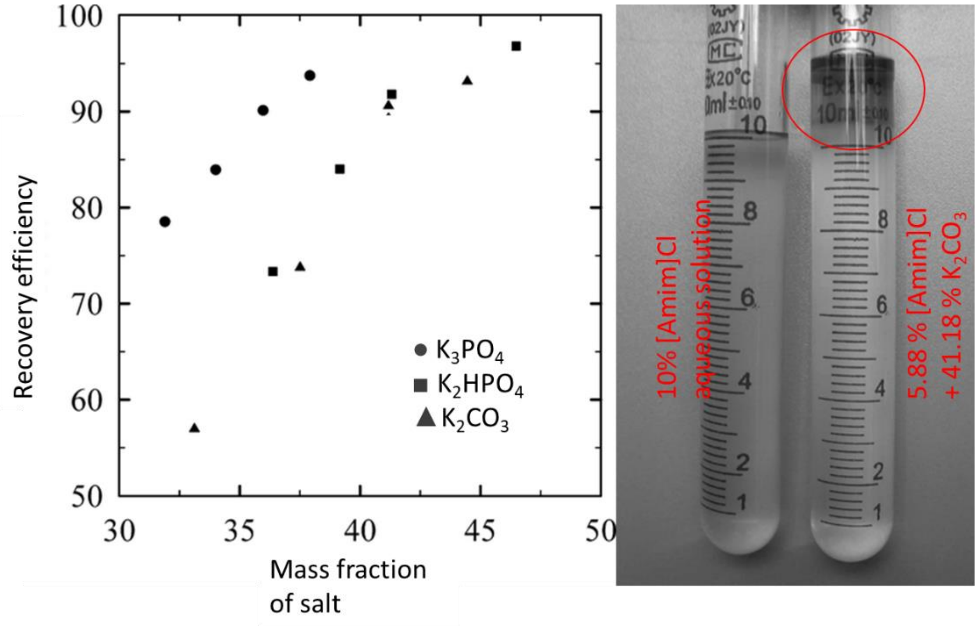


Figure 2.3.6. Left – the effect of mass percentage of salt on recovery efficiency. Right – the ABS of aqueous [Amim][Cl] after the addition of K_2CO_3. Image edited for clarity. (Deng et al., 2009)

The right side of the figure shows the separation, ionic liquid rich phase is on top, and the bottom phase is salt (K_2CO_3) rich. After the separation of the two phases, recovery efficiency of 90.58% was achieved. The recovered [Amim][Cl] was studied by High-performance liquid chromatography (HPLC) and NMR. It showed that the ionic liquid can be reused and recycled in this way, without loss of its properties. (Deng et al., 2009)

Studies with sodium-based salts have also been proven successful. Aqueous 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) was studied with the salts Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4 and NaCl. Again, the recovery efficiency of ionic liquid was affected by the mass fraction of salts. Na_2CO_3 had the extraction efficiency of 98.77% at 16.94 wt%. The strength of salting out was ordered as follows: Na_3PO_4 > Na_2CO_3 > Na_2SO_4 > NaH_2PO_4 > NaCl which again follows the Hofmeister series and Gibbs energy of hydration of ions. Figure 2.3.7.shows again the effect of salt mass fraction on the recovery efficiency as studied by Li et al. (Li et al., 2009).

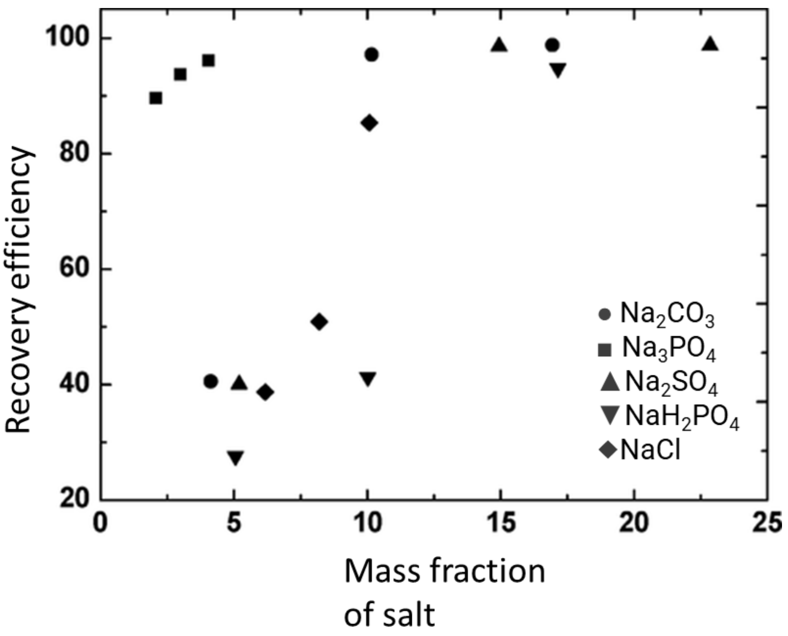


Figure 2.3.7. The effect of mass fraction of salt on the recovery efficiency of [Bmim]BF_4. Image edited for clarity.(Li et al., 2009)

2.3.4 Adsorption

Adsorption is the adhesion of chemical species onto the surface of particles. The adsorption of ionic liquids onto activated carbon (AC), silica (SiO_2), alumina (Al_2O_3), titanium oxide (TiO_2) and clays has been studies, however few studies have been done on adsorption from aqueous solutions of ionic liquid (Mai et al., 2014).

AC is used commonly to remove organic material from wastewater. Anthony et al studied the removal of 1-n-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]) from aqueous solu7tion by activated carbo, which proved to be successful. The disadvantage of the method is that large quantities of ionic liquid are required. It was found that 50 times more activated carbon is required to remove [bmim][PF6] from an aqueous solution than toluene, which was removed from a water solution by Chatzopoulus et al. It was determined that AC could be used to purify waste solutions, but they cannot be used alone for recovery. (Anthony et al., 2001; Chatzopoulos & Varma, 1995)

Both Palomar et al. and Lemus et al. have studied the recovery of imidazolium based ionic liquids from aqueous solutions by activated carbon adsorption. When using activated carbon, it is necessary to also consider regeneration of the AC, acetone was uses as a regenerating agent, which was later removed by atmospheric distillation, resulting in the recovered ionic liquid. 1-octyl-3-methylimidazolium hexafluorophosphate ($OmimPF_6$) was recovered by AC adsorption and studied by ^1H-

NMR. It was found that after recovery via AC adsorption, the same peaks were observed for both pure and regenerated ionic liquid, as shown in figure 2.3.8. (Lemus et al., 2012; Palomar et al., 2009)

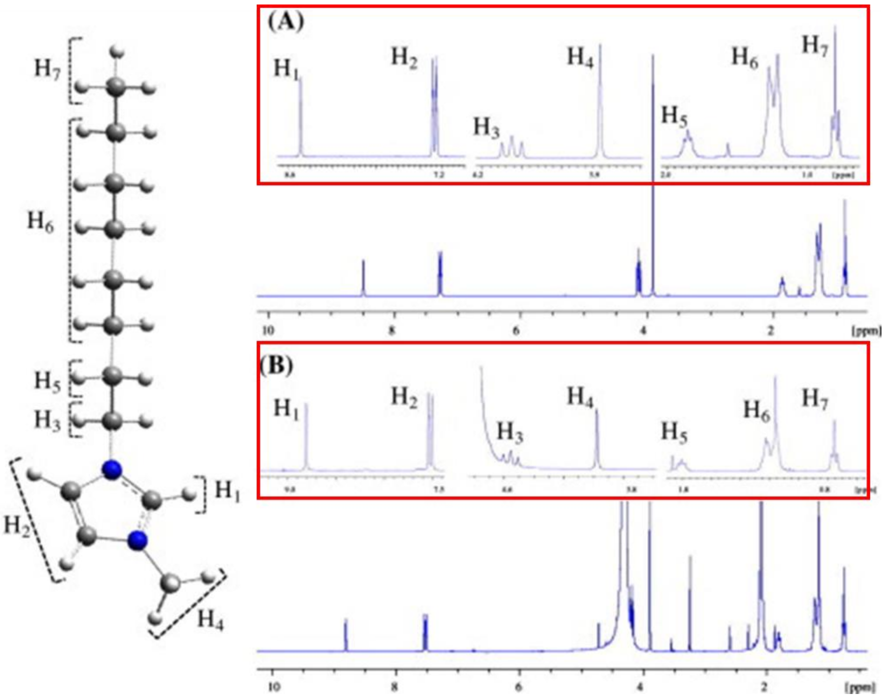


Figure 2.3.8. NMR spectra of (A) pure $OmimPF_6$ and (B) $OmimPF_6$ regenerated by AC. (Lemus et al., 2012)

In addition to successful recovery of the ionic liquid, it was found that modification of the AC surface increased the adsorption. ACs with polar groups on the surface were found to be more efficient at removing hydrophilic ionic liquids from aqueous waste solutions. Whilst adsorption itself is quite a robust method, the major drawback of it is that it requires adsorption/desorption data for efficient application. (Lemus et al., 2012; Mai et al., 2014)

2.3.5 Membrane based methods

Membrane based methods such as nanofiltration, electrodialysis, reverse osmosis and pervaporation could potentially also be used for ionic liquid recovery. Membrane methods are commercially readily available and well know. The method uses less energy compared to others and less solvents, which makes it more applicable to industry. Membrane separation methods could be most effective at removing low volatile materials (providing an advantage over distillation), where the membrane is selective towards the ionic liquid but doesn’t allow other molecules to pass through it. However, to use membranes effectively, then it is most likely necessary to use a combination of the different membrane methods available. (Mai et al., 2014)

Pervaporation is a method of separation based on the preferential partitioning of solute through a membrane based on its chemical potential gradient. If a chemical potential gradient is present, any compound can be separated if is partitions between bulk solvent and membrane. 1-butyl3-methylimidazolium hexafluorophosphate [Bmim][PF_6] was separated from water, ethyl hexanoate, chloro butane and naphthalene via poly(octylmethylsiloxane)(POMS), polyether block amide (PEBA) and poly(vinyl alcohol)(PVA) membranes. The recovery of 99.2% was obtained for all solutes by pervaporation as shown in figure 2.3.9. (Schäfer et al., 2001)

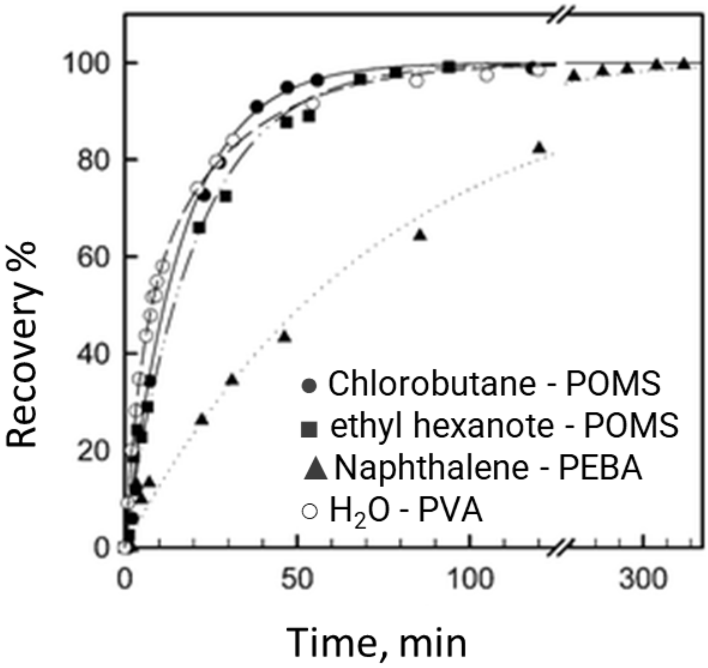


Figure 2.3.9. Recovery of solutes vs the time taken to reach maximal recovery. (Schäfer et al., 2001)

The separation of naphthalene is significant, as it is a low volatility substance, with a boiling point of 118 °C but by using pervaporation, it was possible to remove the solute at 50 °C. Due to the process requiring much less energy (compared to distillation), it is a greener solution of separation. From the figure it can be seen that recovery rate is low, however this is due to the fact that a membrane of small area was used in the laboratory tests, when applying this method to industry, much larger membranes can be produced, which will speed up the process. (Schäfer et al., 2001)

2.3.6 Other methods

The separation of ionic liquids from contaminants have also been studied by physical forces such as centrifugation and magnetic forces. In the study performed by Birdwell et al. hydrophobic ionic liquids were separated centrifugal separator. It was found that dispersions of immiscible liquids were separated quite well, with the best separations occurring when interfacial tensions were low, viscosities low and the density differences large. (Birdwell et al., 2007)

1-butyl-3-methylimidazolium tetrachloroferrate ($[Bmim]FeCl_4$) is a magnetic ionic liquid, this means that the ionic liquid has a response to the magnetic field and thus has the potential for separation techniques using the magnetic field. It has been found that $[Bmim]FeCl_4$ can se separated efficiently from water in a two-phase mixture, however the same cannot be said for a homogenous mixture of the ionic liquid and water. In a mixture, the magnetic susceptibility of the ionic liquid is too weak and interfered by the water molecules. However, it is believed that ionic liquids with a higher magnetic susceptibility in water could be synthesised by modification of cation and anion structure and possibly in the future it will be possible to remove magnetic ionic liquids from a homogenous mixture. (Lee et al., 2007)

As these two methods of separation by centrifugation and magnetic field are currently only applied to very specific ionic liquid systems, then they will not be discussed further in the context of this master’s thesis. The methods studied in this thesis were chosen on the basis of their simplicity and therefore their ease of use in industrial application. Methods requiring more complex equipment and knowledge were therefore not chosen and also methods not applicable to [mTBNH][OAc] due to its structure were not chosen.

3. EXPERIMENTAL PART

3.1 Materials and methods

Cellulose (ɑ- cellulose) used in this work is knife milled fine art inkjet paper provided by Hahnemühle (Ref no:10643123). [mTBNH][OAc] is produced by the Liuotin group in Finland with Aalto University. 95% purity [C2mim][Cl] is provided by Sigma Aldrich. All solvents (ethanol, acetone, DMSO, ethyl acetate, DMF, toluene, chloroform, THF and hexane) are produced by Sigma Aldrich and are laboratory grade.

3.1.1 Liquid-Liquid extraction

The solubility of vinyl laurate and [mTBNH][OAc] was tested in several solvents (water, ethanol, acetone, DMSO, ethyl acetate, DMF, toluene, chloroform, THF and hexane). 2 ml of each solvent was added to a vial. 2-3 drops of ionic liquid/vinyl laurate were added to each solvent and the solubilities were noted. The vials were shaken to ensure mixing.

As a result, hexane was used for liquid-liquid extraction. [mTBNH][OAc] was distilled in rotary evaporator to remove acetone and alcohols. The solution was washed with hexane by liquid-liquid extraction to remove unreacted vinyl laurate. Hexane was added to the solution in excess and solution stirred with magnetic stirrer for 10 minutes. After stirring, solution was left to settle for another 10 minutes. Top layer of hexane was removed. The liquid-liquid extraction with hexane was repeated. To remove excess moisture and hexane in the sample, the solution was dried under a vacuum at 90 °C. The above-described procedure is named cleaning procedure CP-1. Analysis of the procedure was done by Fourier-transform infrared spectroscopy (FT-IR) and rheology.

3.1.2 Activated carbon washing

Activated carbon was used to attempt removal of organics from [mTBNH][OAc] which had been used for synthesis procedures. Activated carbon tablets were crushed by mortar and pestle, added to the ionic liquid, stirred for 30 minutes, and then filtered with filter paper and glass slit sieve filter.

Activated carbon was studied further by combining the cleaning procedure CP-1 with carbon washing. Solution of [C2mim][Cl] used in synthesis process was cleaned. The cleaning procedure CP-1 was performed and carbon washing as described above was performed as well. Carbon was removed from the solution by filtering. Solutions were studied by FT-IR and rheology. The same procedure was repeated for [mTBNH][OAc].

3.1.3 Thin film distillation

Thin film distillation apparatus was used to remove solvents such as acetone, methanol, ethanol, water and DMSO from [mTBNH][OAc] solutions after they had been used for synthesis processes. The thin film distillatory consist of 2 chillers, 2 heaters, vacuum pump, loading vessel, thin film evaporation cylinder with condenser (cold finger), collection vessel and rotational mixer. The apparatus is shown in figure 3.1.1.

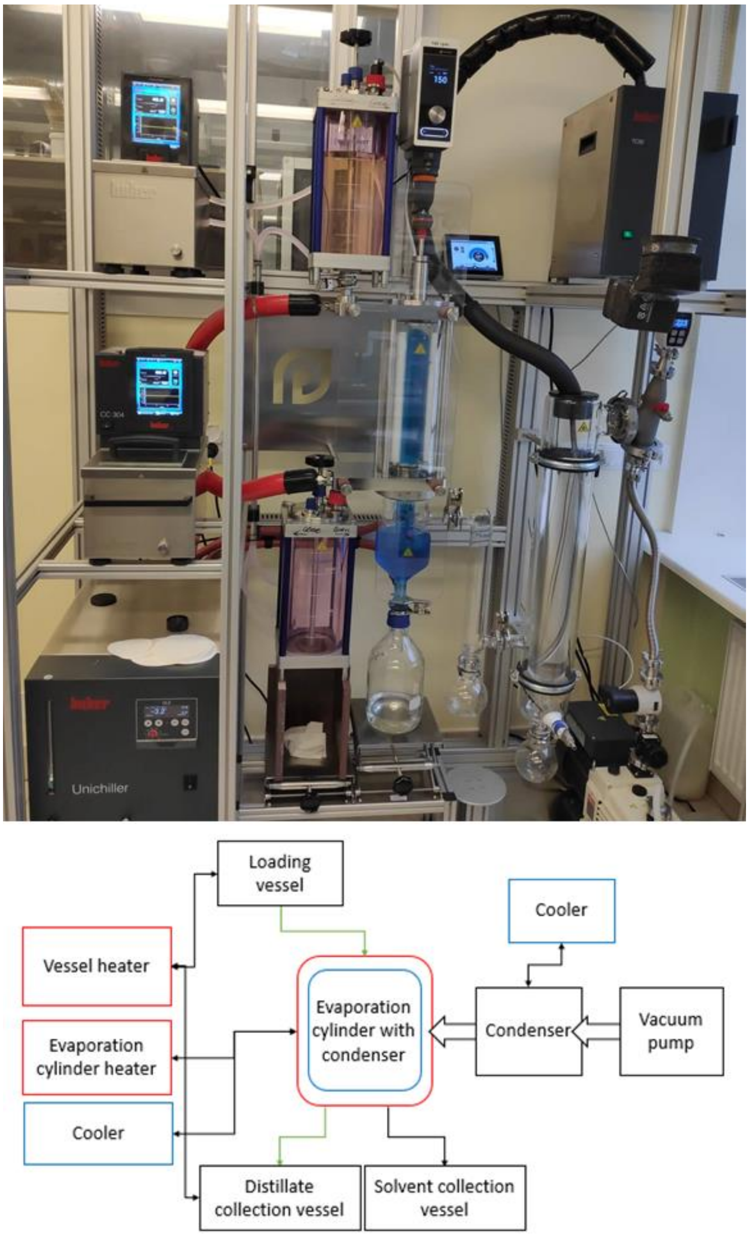


Figure 3.1.1. Thin film distillatory apparatus used to remove solvents from the ionic liquid. Green arrows show movement of ionic liquid. Scheme and photograph by author.

The optimal conditions to remove the solvents were determined by vapour-pressure graphs. The conditions used for removing solvents used in synthesis are shown in Table

3.1.1. Cooling T°C indicates the temperature of the cold finger, evaporation T°C indicates the temperature of the distillation, vessel T°C indicates the temperature of the feeding and collector vessels. Pressure indicates the pressure within the whole distillation set-up and rotations per minute shows the speed at which the distilled liquid was spread over the distillation chambers walls.

The first step of distillation involves the removal of volatile solvents, such as ethanol and acetone. The second step is performed to remove the DMSO. Hence, the removal of volatile substances is further called the first cycle of distillation and the removal of DMSO is referred to as the second cycle.

Table 3.1.1. Optimal conditions found to remove solvents from the [mTBNH][OAc] solution used for synthesis. Cooling T°C - temperature of the cold finger, evaporation T°C - temperature of distillation. vessel T°C - temperature of the feeding/collector vessels, pressure - within whole distillation set-up, rpm - speed at which the distilled liquid was spread over the distillation chambers walls.

Solvent	**Pressure (mbar)**	**Cooling T°C**	**Evaporation T°C**	**Vessel T°C**	**Rotations per minute (rpm)**
Acetone/methanol	300	-3 °C	50 °C	30 °C	150
DMSO	1	-15 °C	80 °C	40 °C	150
Water	50	-1.5 °C	50 °C	30 °C	150
Ethanol	250	-3 °C	80 °C	Room T°C	150

3.1.4 Rheology

Rheology measurements of cellulose solutions were made with Physica MCR 501 machine. The measuring head used was CP25-2 with diameter of 24.966 mm, angle 2 ° and truncation 51 µm. The temperature set for testing was 21 °C. Frequency sweep and flow curve measurements were taken. The sample was added to the measuring platform by spatula. Care must be taken to avoid bubbles forming. After each sample, the measuring platform was cleaned with distilled water and ethanol.

Rheology measurements were made for samples shown in Table 3.1.2. Cellulose was weighted to small, capped bottles. Ionic liquid was added to each bottle. All bottles were covered with parafilm to reduce air and moisture exposure of the sample. The solutions were put to stir on a magnetic stirring plate. After 1 hour of stirring, heating was added (100 °C) for 30 minutes. The solutions were stirred for 24 hours.

Table 3.1.2. Samples prepared and analysed by rheology.

Ionic liquid treatment	Cellulose concentrations of samples prepared, %
Pure [mTBNH][OAc]	3, 2.5, 2, 1.5, 1, 0
[mTBNH][OAc] cleaned by CP-1	3, 2.5, 2
[mTBNH][OAc] cleaned by CP-1 and washed with activated carbon	3, 2.5, 2, 1.5, 1, 0
Thin film distillatory distilled [mTBNH][OAc] and washed with hexane	3, 2.5, 2, 1.5, 1, 0
Thin film distillatory distilled [mTBNH][OAc] – removed solvents and DMSO	0
[mTBNH][OAc] twice used for synthesis, twice distilled – removed solvents and DMSO	0

3.1.5 Salting out

In literature, the salting out method has been used in the separation of aqueous ionic liquid solutions (refer to 2.3.3). An attempt at salting out was made with 10%, 20% and 45% K_2CO_3 and 5%, 10% and 22% Na_2CO_3 solutions in aqueous ionic liquid.

Aqueous IL solution of [C2mim][Cl] waste was made in ratio 1:1. [C2mim][Cl] was used as a large quantity of it was readily available and it is less expensive than the ionic liquid [mTBNH][OAc]. Solutions of Na_2CO_3 and K_2CO_3 solutions were made with distilled water. Salt solution was added to the aqueous ionic liquid solution and stirred for 5 minutes at room temperature. Solution was then divided into 3 parts. 1st part was placed in freezer to see the effect of temperature on solutions. 2nd part was heated to 60 °C and stirred for 1 hour. Final part was taken to centrifuge for 5 minutes at 2000 rpm. The solutions were all left at room temperature for 24 hours.

3.1.6 Column filtration

One step distilled ionic liquid [mTBNH][OAc] was used for column chromatographic fractionation. Thin-layer chromatography was performed to determine solubility of waste mixture in certain solvents and solvent systems. To perform column filtration, it is necessary to choose the correct solvent. Some possible solvents were tested – pure ethyl acetate, 10:1 ratio of ethyl acetate and acetone, pure chloroform and 10:1 ratio of chloroform to methanol. A small drop of the recycled IL was placed on the thin film chromatography paper (Pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV). The paper was then placed in beaker that contained the solvent. After solvent had reached the end of the paper strip, the paper was analysed under UV light. Highlighter was used to make visible the spots that appeared under the UV.

Eluents of chloroform-methanol and ethyl acetate-acetone in 10:1 ratio were tested in a column (150 ml) filled with SiO_2 powder (200g). Waste liquid of 2g was fractionated.

The eluent was poured in the column to wet the stationary phase, 2g of waste solution dissolved in 50 ml of eluent was added to the column. The column was pressurized to accelerate the fractionation. Separated fractions were collected and concentrated by rotary evaporator. The separates fractions were studied by NMR.

3.1.7 Quality study

After the second cycle of distillation (all volatile solvents and DMSO removed), NMR study was performed on [mTBNH][OAc] to assess the quality. Chloroform-d and DMSO-d6 were used as solvents, at a concentration of 60 mg/ml. The first step was to perform the attribution of chemical shifts, this involved the attribution of ^{1}H NMR spectra prediction for 5-methyl and 7-methyl isomers in chloroform. To quantify the result of NMR, integrals under the peaks were measured and calculations made.

3.1.8 Study of ionic liquid hydrolysis

To study the effect of water on the ionic liquid at elevated temperatures, 4.5% aqueous solution of the ionic liquid was made. The solution was separated into 4 beakers, each beaker was heated for 2 hours to 60 °C, 70 °C, 80 °C, 90 °C respectively. Beakers were covered with parafilm. After heating, the solutions were placed in vacuum oven to remove the water. ^{1}H NMR spectra was obtained for each solution. In addition, pH was measured by pH meter of the pure IL, pure IL with water, IL after heating and IL after removal of water.

After studying by NMR, fractional distillation of the ionic liquid was carried out to separate remaining water, hydrolysed ionic liquid, ionic liquid and any of its degradation products. Fractional distillation was set up. To increase surface area in the round bottomed flask, broken glass was added to the flask. The set-up of distillation can be seen in Figure 3.1.2.

Figure 3.1.2. Fractional distillation apparatus.

During distillation, the temperature of oil, ionic liquid and vapours were closely monitored. Distillation was done in several stages. The boiling temperatures and the pressure were changed. Four fractions of ionic liquid were collected 1st fraction was at ionic liquid at 90 °C and 40 mbar pressure in the system. The 2nd fraction was collected with the ionic liquid at 110 °C, 3rd fraction at 120 °C and 4th fraction at 130 °C. FT-IR and NMR analysis off all four fractions was performed.

For the remaining IL which did not evaporate, simple distillation without fractionating column was also performed. The simple distillation fraction was also collected and analysed by FT-IR and proton NMR.

3.1.9 Fourier-transform infrared spectroscopy

Fourier-transform infrared spectroscopy (FT-IR) was used to analyse samples. The machine used for FT-IR was INTERSPEC 200-X FTIR Spectrometer with an ATR unit attachment.

4. RESULTS AND DISCUSSION

This section of the thesis will present and discuss the results of the practical work.

4.1 Solubility test

The solubility of vinyl laurate and [mTBNH][OAc] was studied in several solvents as described in section 3.1.1. The obtained solubility table is shown in table 4.1.1. Vinyl laurate solubility was tested alongside [mTBNH][OAc] as it is used in the synthesis process and most likely residues (unreacted vinyl laurate etc.) of it are present in the ionic liquid after synthesis.

Table 4.1.1. The dissolving capabilities of ionic liquid [mTBNH][OAc] (IL) and vinyl laurate (VL) in different organic solvents is shown. “++” means that the IL/VL dissolve very well, “+” means that IL/VL dissolves well, “-“ that IL/VL doesn’t dissolve well and “--" means that the IL/VL did not dissolve at all.

Solvent	Ionic liquid	Vinyl laurate	Comments
EtOH	++	++	IL dissolved completely, instantly
			VL dissolved well
Ac	++	++	IL went to bottom, after mixing, completely dissolved
DMSO	++	+	IL went to bottom, after mixing, completely dissolved
			VL made droplets when dissolved
EtOAc	++	++	IL went to bottom, after mixing, completely dissolved
DMF	++	++	IL went to bottom, after mixing, completely dissolved
Toluene	+	Cloudy	After mixing, solution was not clear with IL and VL
Chloroform	+	++	IL floats at top, after mixing it dissolves
THF	+	++	IL layer at the bottom, after mixing it dissolves
Water	+	-	Did not dissolve well, however after mixing fully dissolved
Hexane	--	+	IL sticks to bottom, does not dissolve at all

The above table shows that using liquid-liquid extraction with [mTBNH][OAc] might prove to be difficult. This is due to the fact that [mTBNH][OAc] dissolves well in most common solvents. The only solvent immiscible with [mTBNH][OAc] is hexane, whilst vinyl laurate did dissolve in hexane. Out of the studied solvents, hexane has the lowest dielectric constant (ε) at 1.88, making it the most nonpolar solvent on the list. Interestingly however, toluene has ε of 2.38, which is quite similar to hexane, however [mTBNH][OAc] still manages to dissolve in it, albeit not as well, a dispersion of [mTBNH][OAc] was observed that did not separate over time.

From this, it could be assumed that [mTBNH][OAc] is immiscible with solvents that have ε below 2. Cyclohexane has a ε of 2.02, benzene 2.27, pentane 1.84 and heptane 1.92 – it would be interesting to see solubility of [mTBNH][OAc] in these solvents as well due to the dielectric constants of these solvents being in the same range. However, as pentane is volatile at room temperature, it poses another problem in its use in liquid-liquid extraction systems and as benzene is carcinogenic, it would not be a good solvent to use as well.

In the context of this work, only single solvents were tested as a possible solvent to be used in liquid-liquid extraction, however it could be possible that a solvent mixture, as studied by Dibble et al., could also be effective in liquid-liquid extraction.

4.2 Liquid-liquid extraction

Rheology measurements were performed on samples as mentioned in table 3.1.2. As a result of solubility tests, hexane was used for liquid-liquid extraction and rheology measurements made. The shear rate vs viscosity of pure [mTBNH][OAc] and [mTBNH][OAc] washed with hexane is shown in figure 4.2.1.

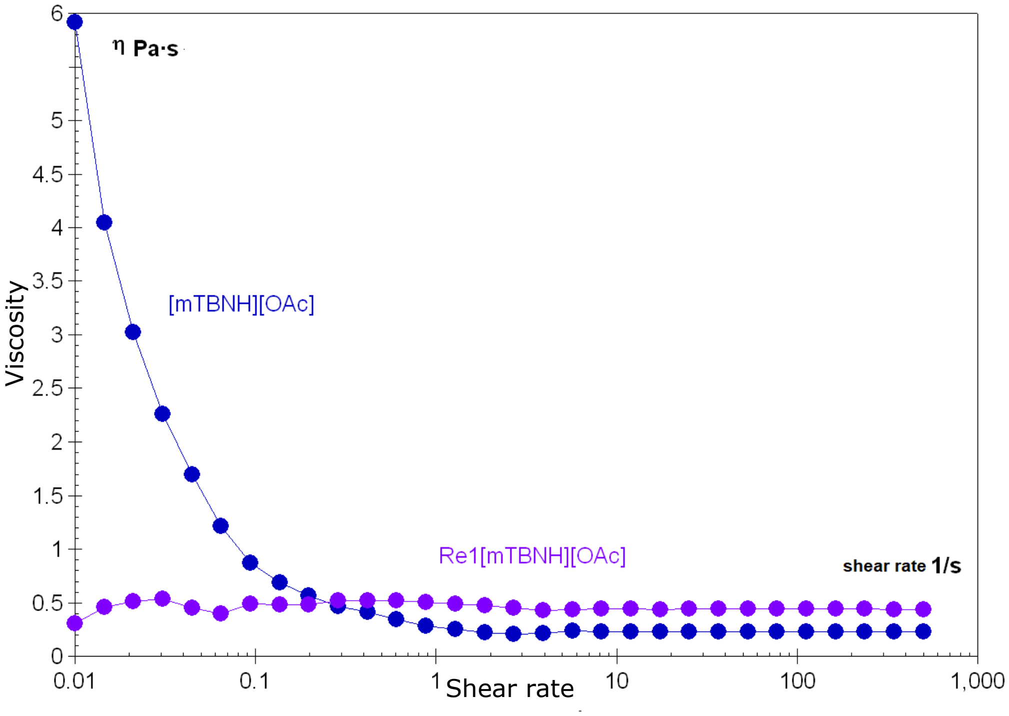


Figure 4.2.1. The viscosity vs the shear rate of pure [mTBNH][OAc] (blue) and recycled (washed with hexane) [mTBNH][OAc] (purple) (Re1[mTBNH][OAc] on graph) prepared by cleaning procedure CP-1 (described under 3.1.1.).

From the figure, liquid-liquid extraction by hexane has changed the flow behaviour of [mTBNH][OAc]. The pure ionic liquid exhibits viscosity growth when the shear rate is decreased below 1 1/s. This is most likely due to the electrostatic interaction within the IL and the structure of the ionic liquid. However, the recycled ionic liquid has no dependency on the shear rate within the studied range. This shows that the ionic liquid must still be contaminated with a substance that is changing the internal structure of the IL. Additionally, the recycled ionic liquid exhibits higher viscosity than the pure ionic liquid, which indicates that the contaminant has a higher molecular weight than [mTBNH][OAc].

Cellulose solutions in pure and hexane washed ionic liquid were made and studied by rheology. The figure 4.2.2. shows the flow behaviour of [mTBNH][OAc] without cellulose and with cellulose (both pure and hexane washed IL).

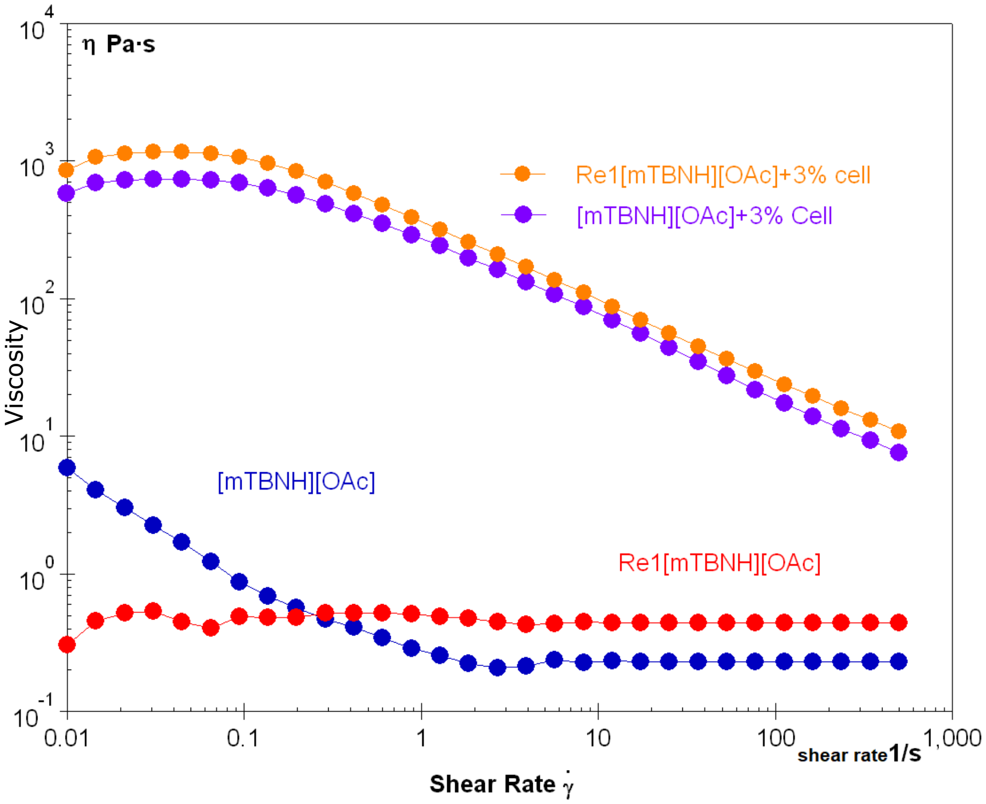


Figure 4.2.2. The graph compares the shear rate vs the viscosity of pure [mTBNH][OAc] (blue) and recycled [mTBNH][OAc] (red) (Re1[mTBNH][OAc] on graph) with cellulose solution at 3% concentration prepared from the pure IL (purple) and from the recycled IL (orange).

The solvation of α- cellulose in [mTBNH][OAc] (both pure and recycled) has changed the flow behaviour of the ionic liquid completely. This indicates that the solution is dominated by the cellulose macromolecules. The flow curves are very identical for pure IL and recycled IL solutions of cellulose, but the viscosity of the recycled IL solutions is higher than the viscosity of pure ionic liquid solution, indicating again that molecules of a high molecular weight are contaminating the ionic liquid solution. It is significant that liquid-liquid extraction however does not impact the dissolution properties of ionic liquid, at least up to 3% concentration.

The damping factor and complex viscosity of the solutions were also compared, as can be seen in figure 4.2.3. The oscillation rheometric viscosity curves for both pure [mTBNH][OAc] and recycled [mTBNH][OAc] are similar, but the damping factor behaves slightly different. When the angular frequency is decreased, the damping factor of recycled [mTBNH][OAc] solution is lower than the damping factor of pure IL solution. As both solutions contain the same concentration of cellulose and should have a similar elastic response, it can be concluded that the recycled IL contains a low molecular weight contaminant that increases the dissipative response of the solution. The residues have a molecular weight that is lower than cellulose but higher than the IL. Most probably, these residues are products of cellulose degradation and similar cellulose degradation process could have occurred as discussed in 2.2.

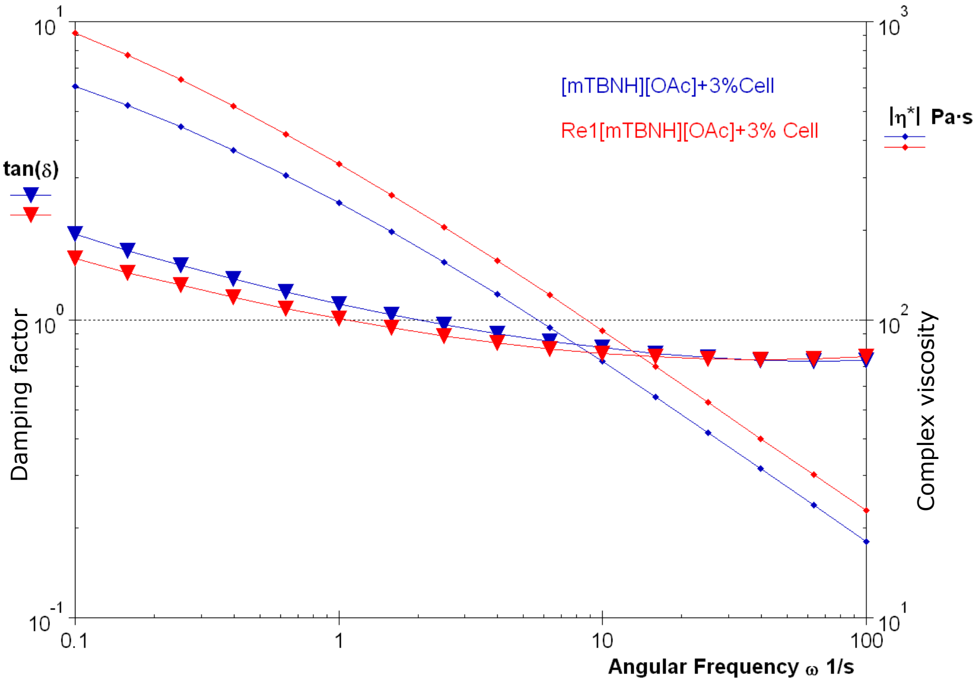


Figure 4.2.3. Comparison of damping factor and complex viscosity vs the angular frequency of 3% cellulose concentration in pure [mTBNH][OAc] (blue) and recycled [mTBNH][OAc] (red).

FT-IR spectra of both pure and hexane washed [mTBNH][OAc] were also taken. The FT-IR measurements show that [mTBNH][OAc] is not affected much by the hexane liquid-liquid extraction. Figure 4.2.4 shows the obtained FT-IR spectra and it is seen that peaks mostly overlap, comparing the spectra identity gives the correlation coefficient of 0.9889, indicating that after hexane liquid-liquid extraction [mTBNH][OAc] contained very low amount of contaminants.

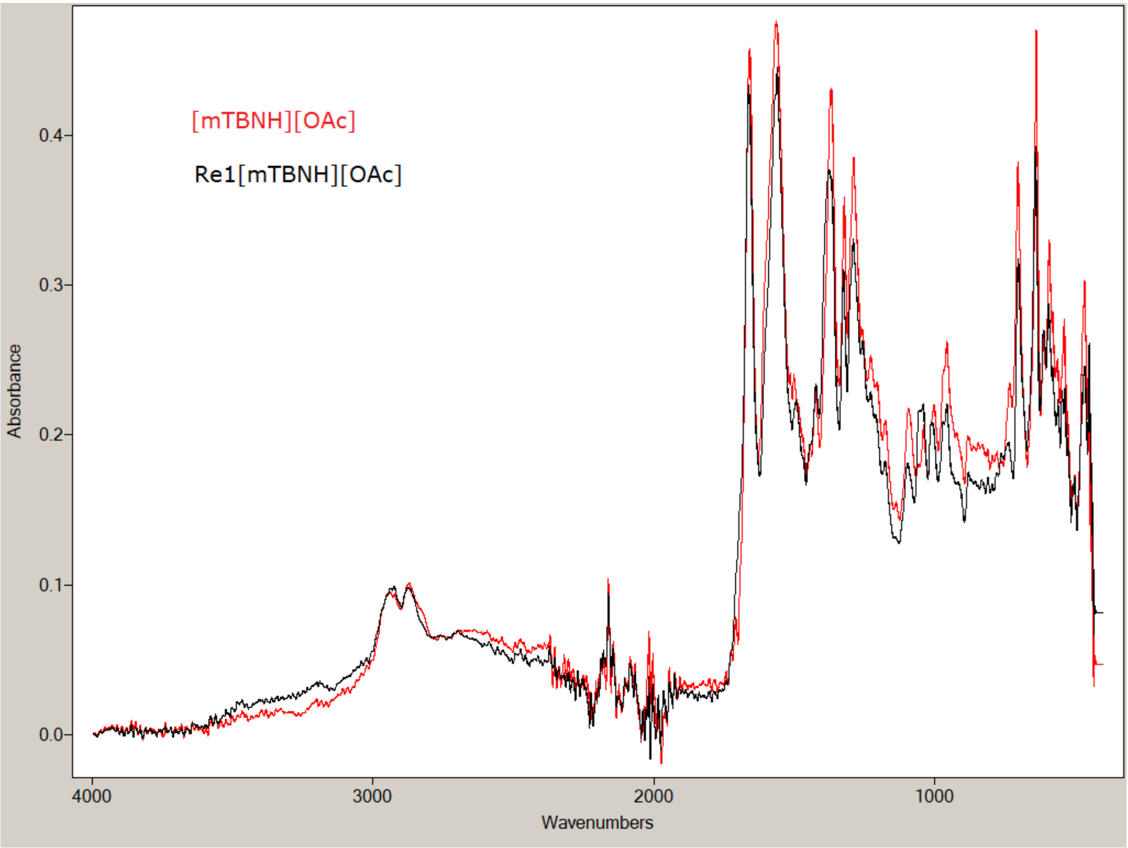


Figure 4.2.4. Spectra of pure [mTBNH][OAc](red) and [mTBNH][OAc] cleaned with CP-1 (black).

However, it is worth mentioning here that FT-IR is not the best indicator of [mTBNH][OAc] purity. Figure 4.2.5. shows spectra of cellulose, pure [mTBNH][OAc] and [mTBNH][OAc] 3% concentration cellulose solution. Spectra of pure [mTBNH][OAc] and cellulose containing [mTBNH][OAc] overlap, the presence of cellulose in the solution does not affect the FT-IR spectra. This is seen well with the broad peak at 3500 cm^{-1} for cellulose (circled in red), which does not show up in the ionic liquid spectra at all. This peak corresponds to OH groups in cellulose, and as it does not show in the IL + cellulose solutions spectra, it can be concluded that ionic liquid overlaps the absorption spectrum of cellulose.

As such, due to the fact that [mTBNH][OAc] adsorption is strong, it is very likely that any contaminants present in the solution are not distinguishable by FT-IR.

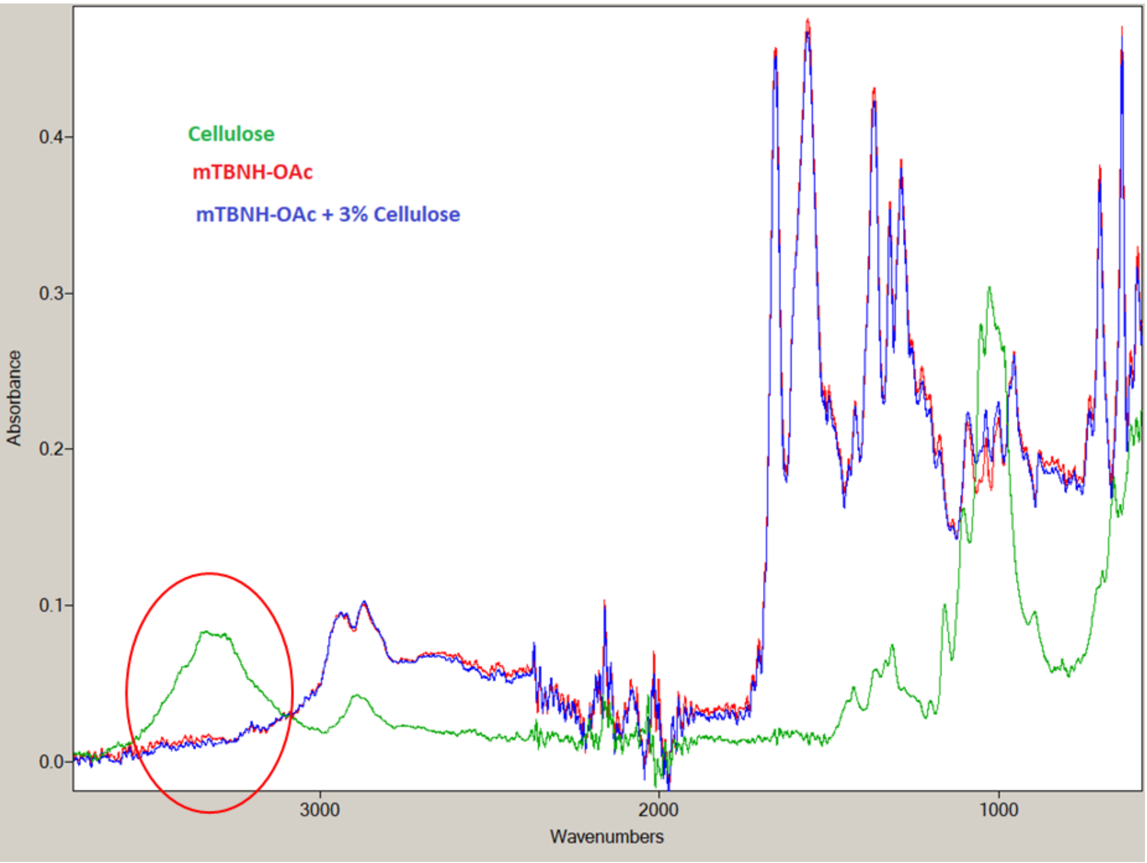


Figure 4.2.5. FT-IR spectra for cellulose (green), pure [mTBNH][OAc] (red) and 3% cellulose [mTBNH][OAc] solution (blue). Red circle indicates distinct peak for cellulose.

4.3 Thin film distillation

Distillation by the thin film distillatory was simple for volatile solvents such as acetone and methanol. The distillation of DMSO however is much more complicated. DMSO is a low volatile solvent, therefore very low pressure was required to remove DMSO from ionic liquid without having to use a high temperature. Temperatures above 80 °C should not be used as it is known [mTBNH][OAc] will degrade at higher temperatures.

The removal of DMSO also increases the viscosity of [mTBNH][OAc], which makes the removal of recycled IL more difficult from the distillatory, as the removal of DMSO is difficult, it poses the question whether it needs to be removed at all, as DMSO is used as a co-solvent in the cellulose valorisation processes. Therefore, to reduce the amount of energy used in ionic liquid recovery, it might be more efficient to not remove DMSO, however the removal of it was still studied.

As the removal of volatile solvents is performed first, this is called the 1st step of distillation and DMSO removed second, this is called the 2nd step of distillation. The obtained ionic liquid after distillation of solvents was a very dark brown colour as shown in figure 4.3.1. The pH of the recovered ionic liquid from water was 8, from acetone the PH was 7, the pure IL however has pH of 12.

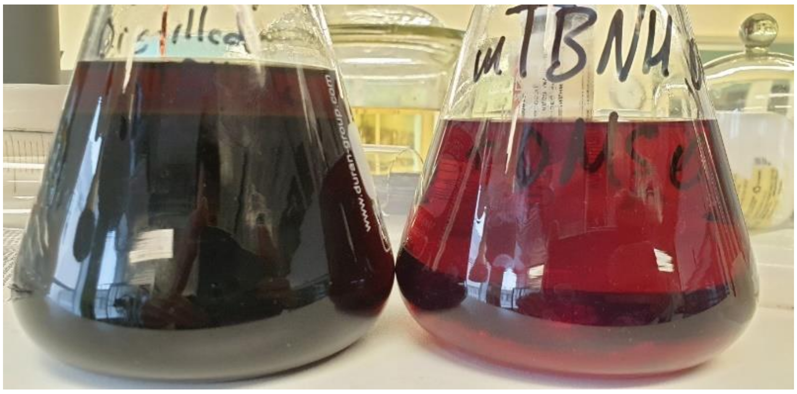


Figure 4.3.1. [mTBNH][OAc] after 1st step of distillation from acetone (left) and water (right).

The yield of the 1st step and 2nd step of distillation was calculated and is shown in table 4.3.1. The table shows the yield from waste solutions which were primarily water and primarily acetone. The yield after the 1st step is the same in both cases, approximately 36 g of [mTBNH][OAc] is recovered from 1 litre of waste solution. However, the same cannot be said for DMSO. The yield from acetone waste solution is almost 2 times higher at 243.67 g per one litre of waste solution. This indicates that the water waste solution contained more DMSO.

Table 4.3.1. The yield of [mTBNH][OAc] recycled by thin film distillation. The table shows the yield from primarily water waste solutions and acetone waste solutions. 1st step of distillation shows the removal of water/acetone, the second step shows the removal of DMSO.

		Water waste solution	Acetone waste solution
1st step of distillation	Load (L)	12	4
	Output (g)	433	144.7
	Yield (g/L)	**36.1**	**36.2**
2nd step of distillation	Load (L)	0.450	0.245
	Output (g)	57.4	59.7
	Yield (g/L)	**127.5**	**243.67**
% of IL in original solution		**0.228%**	**1.49%**

One major drawback of the current distillatory is the absence of a feeding pump. Several problems occurred due to the fact that the flow of waste solution to distillation chamber is not continuous nor controllable. Therefore, it is also inefficient to determine the rate of recovery. Nevertheless, in these conditions, the removal of 1 litre of acetone took 1 hour, 1 litre of water took 2 hours and 245 ml of DMSO containing ionic liquid waste took 3 hours, approximately 12 hours would be needed to remove DMSO from 1 litre of the same waste solution.

The ionic liquid recycled by thin film distillation was also studied by rheometry. Figure 4.3.2. shows the flow behaviour of pure [mTBNH][OAc], [mTBNH][OAc] 3% cellulose solution, [mTBNH][OAc] cleaned by hexane washing, [mTBNH][OAc] cleaned by thin film distillation and [mTBNH][OAc] washed by activated carbon (discussed further in 4.4.1). [mTBNH][OAc] cleaned by thin film distillation has a similar flow behaviour to pure [mTBNH][OAc], however in 3% cellulose solution it has a lower viscosity, this is due to the fact that DMSO was not removed from the solution (i.e., only 1st step of distillation was done).

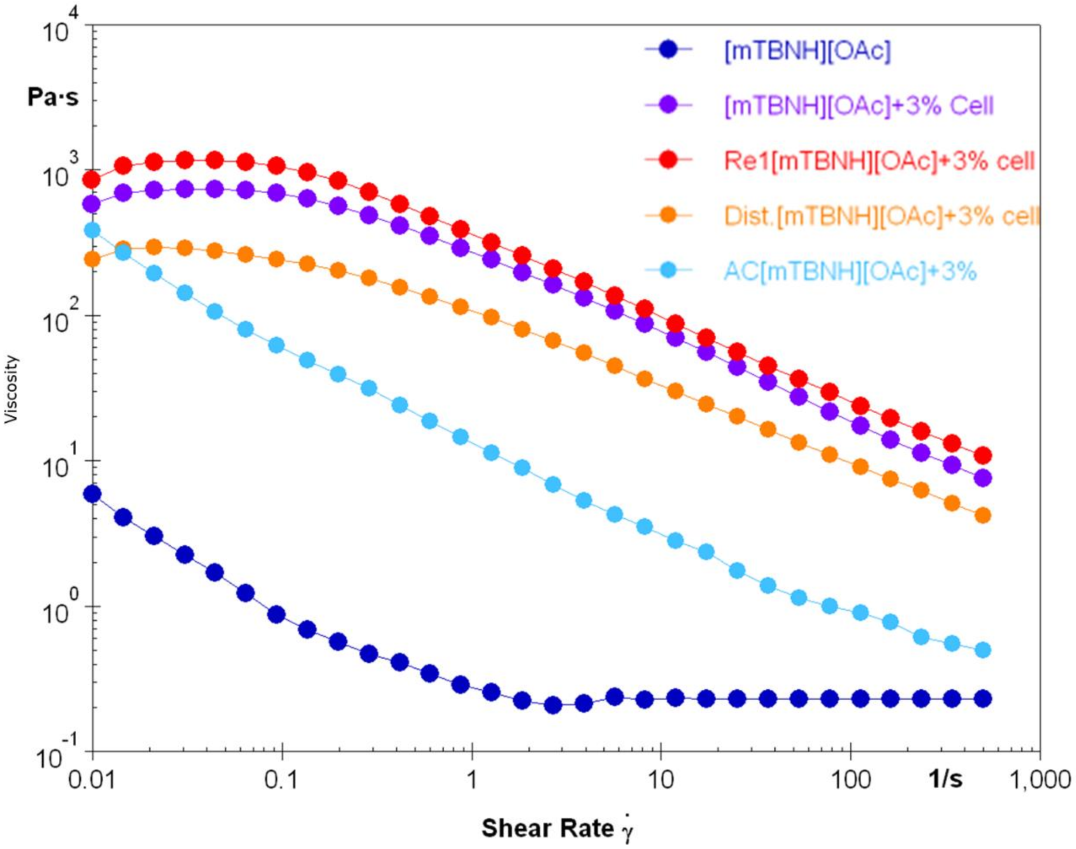


Figure 4.3.2. The flow behaviour of pure [mTBNH][OAc] (dark blue), 3% cellulose solution of pure [mTBNH][OAc] (purple), 3% cellulose solution of hexane extracted [mTBNH][OAc] (red), 3% cellulose solution of thin film distilled [mTBNH][OAc] (orange) and 3% cellulose solution of activated carbon washed [mTBNH][OAc] (light blue).

Figure 4.3.3. compares pure [mTBNH][OAc], [mTBNH][OAc] used for synthesis once and distilled once and [mTBNH][OAc] which has been used twice for synthesis and also been distilled twice. All solvents including DMSO have been removed from [mTBNH][OAc]. The figure shows that the ionic liquid, which has been used for synthesis

once and distilled once, has a very similar flow behaviour as pure [mTBNH][OAc]. This is good because it means thin film distillation is working well and the ionic liquid is not being changed in the process. However, it can be seen that after a second round of synthesis and solvent removal, the flow behaviour has changed at shear rates below 10 1/s. As the viscosity has increased, it can be assumed that a substantial build-up of cellulose degradation products are present in the ionic liquid after two rounds of synthesis.

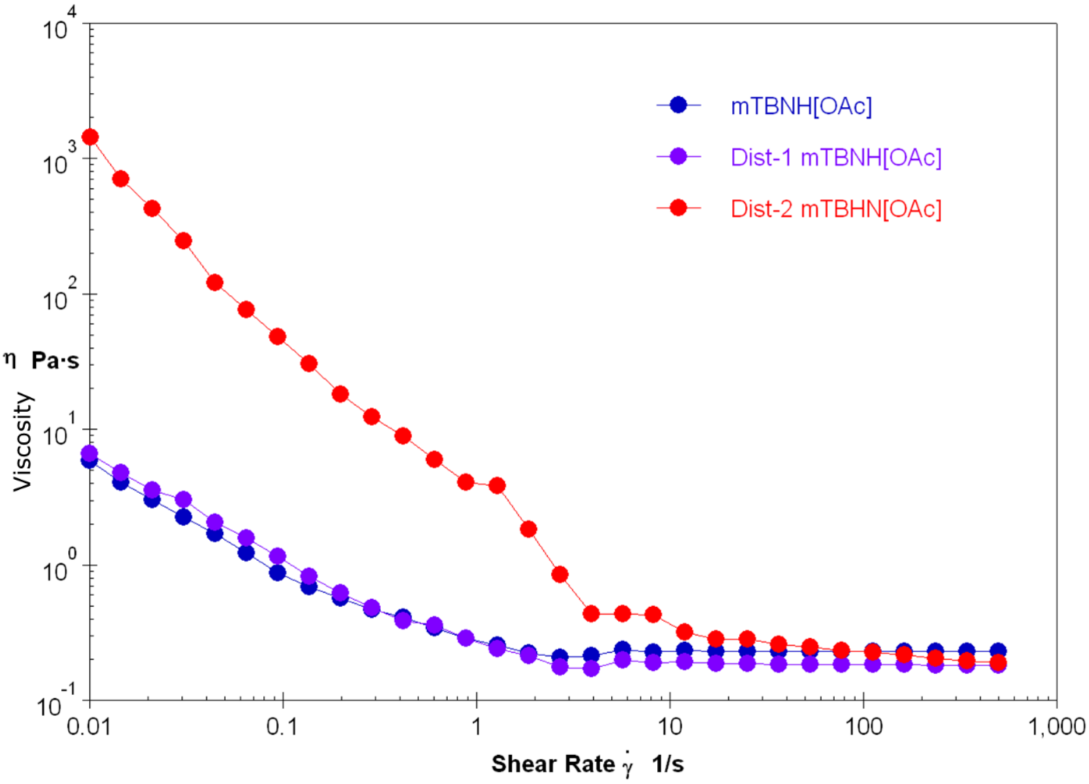


Figure 4.3.3. Flow behaviour of pure [mTBNH][OAc] (blue), [mTBNH][OAc] used for synthesis once and thin film distilled once (purple), [mTBNH][OAc] used for synthesis twice and thin film distilled twice (red).

4.4 Quality of recycled IL

To quantitively study the recycled ionic liquids purity by proton NMR, the predicted spectra’s for 5- and 7- methyl isomers of [mTBNH][OAc] needed to be generated. The predicted spectra’s are provided in appendix 1. The producer of [mTBNH][OAc] states that isomers are present in 50:50 ratio, however the NMR spectra for pure [mTBNH][OAc] shows that the ionic liquid is composed mainly of the 7-methyl isomer. The spectra for pure [mTBNH][OAc] is also provided in appendix 1.

Figure 4.4.1. shows the NMR spectra for both pure [mTBNH][OAc] and thin film distilled [mTBNH][OAc]. The recycled [mTBNH][OAc] spectra show a shar peak at 2.6 ppm –

this corresponds to the protons of DMSO, indicating that after removal of all solvents (including DMSO) by the thin film distillatory, some DMSO still remains in the ionic liquid.

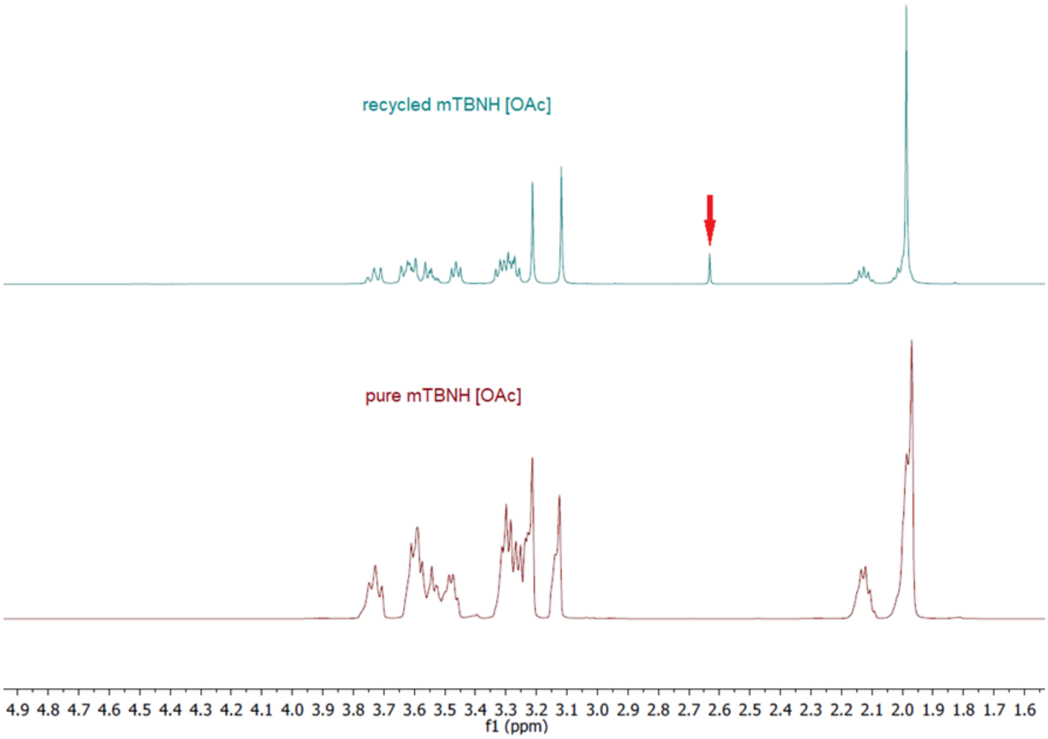


Figure 4.4.1. Recycled (thin film distilled) and pure [mTBNH][OAc] ^{1}H NMR spectra in Chloroform-d, red arrow indicates the presence of DMSO.

Initially looking at the spectra, it doesn't seem like there are any other contaminants present, however upon closer study of the recycled ionic liquids spectra, it can be seen that this is not the case. Figure 4.4.2. shows recycled [mTBNH][OAc] spectrum in range 4.0 ppm to 0.0 ppm. At 1.25 ppm and 0.88 ppm we can see some additional peaks not present in pure [mTBNH][OAc]. As the peaks are small, then the concentration of the substance causing the peaks in the solution is also small.

A similar study conducted by Wen et al. was done for IL [Amim][Cl], where it was found that these peaks correspond to 20 protons of CH_2 group in the laurate chain and three protons of the CH_3 group at the end of the laurate chain (Wen et al., 2017). Vinyl laurate is used in cellulose synthesis, which is how it is present in the solution. These peaks could therefore be attributed to the lauroyl chain, which means that there is a high chance of cellulose-based by products that are present in the recycled solution, however no signals corresponding to the cellulose backbone (in the range of 3.0 - 5.5 ppm (Wen et al., 2017)) are present, indicating that cellulose itself is not present.

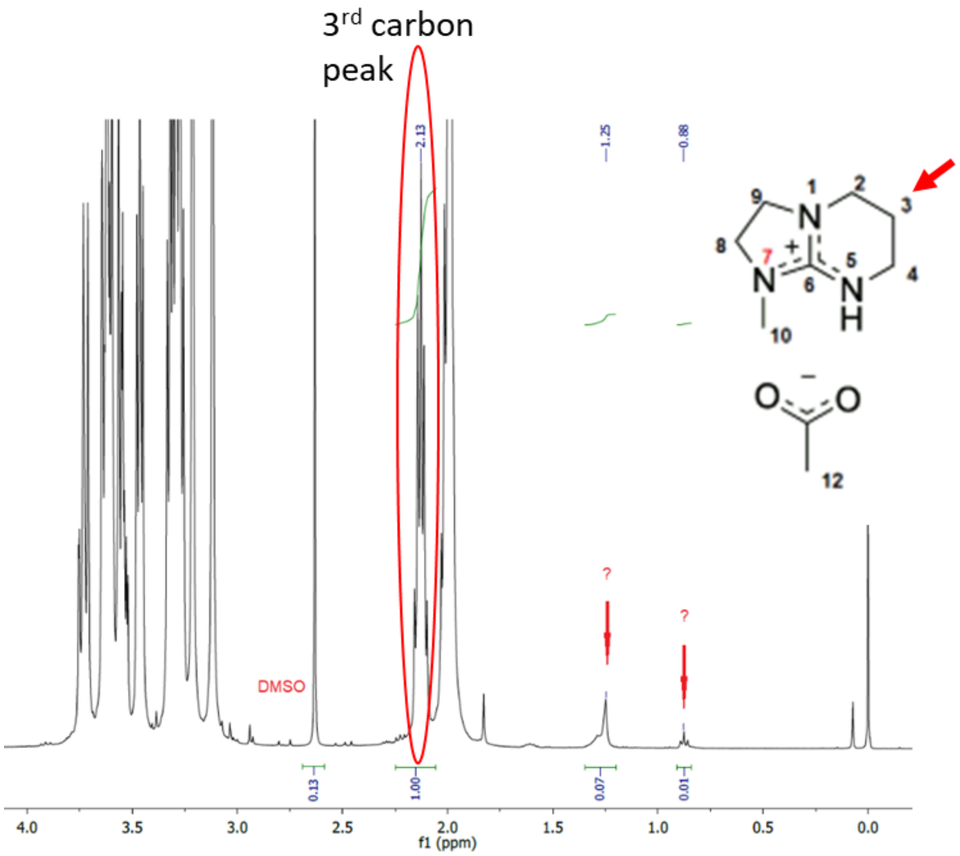


Figure 4.4.2. Recycled [mTBNH][OAc] ^{1}H NMR spectra in chloroform-d in range 4.0 - 0.0 ppm.

To evaluate the results quantitively, the integrals under specific peaks were measured. The peak at 2.13 ppm (figure 4.4.2.) corresponds to the 3rd carbon in [mTBNH][OAc] protons. In this position, protons undergo minor influence of neighbouring atoms as the CH_2 group is bonded only to other carbon atoms and as such the integral of the peak is set to 1 and the signal of the 2 protons at the C3 position of the IL is used as a reference. The 6 protons corresponding to DMSO peak at 2.6 ppm has an integral of 0.13. The two peaks at 1.25 ppm and 0.88 ppm (unknown substance but assumed to be related to lauroyl chains) have an integral of 0.07 and 0.01 respectively. The ratio of protons from different substances can be calculated through integrals in the following way.

$$\frac{IL\ mol}{DMSO\ mol}=\frac{Integral\ {}^{2.13}/_{2}}{Integral\ {}^{2.6}/_{6}}=\frac{0.5}{0.0217}=23.04$$

$$\frac{IL\ mol}{Laurate\ mol}=\frac{Integral\ {}^{2.13}/_{2}}{Integral\ {}^{0.88}/_{3}}=\frac{0.5}{0.0033}=151.52$$

The total composition of recycled IL in moles is 95.2% of IL, 4.1% of DMSO and 0.6% of laurate chains. As the chemical structure of the laurate chains present is unclear, then the ratios by weight can only be calculated approximately using the molecular weights of 199 g/mol for [mTBNH][OAc], 78g/mol of DMSO and 155g/mol of laurate. Thus, the total composition of the solutions by weight are 97.8% IL, 1.7% DMSO and 0.5% laurate residues.

The presence of laurate residues is also well supported by the fact that during thin film distillation, it was noticed some residues collected in the system. These residues were collected and studied by FT-IR. It was found that the spectra is quite similar to that of cellulose laurate. The FT-IR spectra is provided in appendix 2.

4.5 Methods found to be inefficient

4.5.1 Activated carbon

Similar rheology analysis was performed for solutions which were washed by activated carbon and liquid-liquid extraction by hexane was performed. Figure 4.5.1. compares cellulose solutions of pure [mTBNH][OAc] and [mTBNH][OAc] which has been recycled by hexane liquid-liquid extraction, thin film distillation and activated carbon washing. The figure clearly shows that washing by activated carbon decreases the solubility of cellulose in [mTBNH][OAc], the flow behaviour has changed drastically compared to pure [mTBNH][OAc] cellulose solution. The same drastic change in flow behaviour is also shown in figure 4.3.2.

This was also observed visually, after treatment with activated carbon, the cellulose did not dissolve in the [mTBNH][OAc] as effectively anymore and solutions remained cloudy, indicating the loss of solvation properties. Therefore, the activated carbon was not studied further as a possible recycling method.

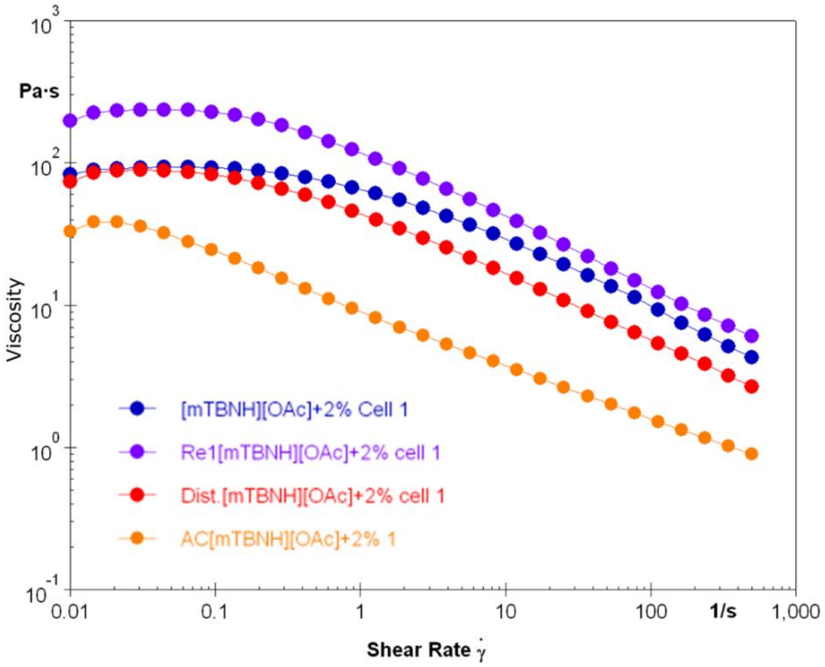


Figure 4.5.1. The flow behaviour 2% cellulose solution of pure [mTBNH][OAc] (blue), 2% cellulose solution of hexane extracted [mTBNH][OAc] (purple), 2% cellulose solution of thin film distilled [mTBNH][OAc] (red) and 2% cellulose solution of activated carbon washed [mTBNH][OAc] (orange).

4.5.2 Salting-out

The induced phase separation by salts which was studied by literature, was also tested for [C2mim][Cl]. The test was performed for [C2mim][Cl] waste as it was readily available in the laboratory and is a cheaper ionic liquid compared to [mTBNH][OAc]. The salting out was performed with the salts Na_2CO_3 and K_2CO_3 using the concentrations that were successful in the articles by Deng et al. and Li et al. as discussed under the literature review. Figure 4.5.2 shows the solutions after following the same procedure as in literature.

No phase separation was observed for [C2mim][Cl] at any of the salt concentrations studied. Phase separation also did not occur upon heating nor cooling of the solutions, but heating did cause the solution to become cloudy. As such, the method was not studied further and deemed unsuccessful, however in literature many other salts have been studied as well for salting-out. There lies a possibility that other salts may be effective, however as Na_2CO_3 and K_2CO_3 were the only readily available salts at this time, other salts could not be tested. The possibility that a higher concentration of the same salts would be effective has been out ruled as well, as the solutions tested had reached the saturation point.

Figure 4.5.2. Induced phase salting out solutions. Left shows the solution after centrifugation and allowing 24 hours for separation. Right shows the same solutions after 24 hours in freezer.

4.5.3 Column filtration

The correct solvent needed to be chosen for column filtration. Figure 4.5.3. shows the chromatography strips after testing solvents. It is seen that separation occurred best with ethyl acetate:acetone in the ratio 10:1 and chloroform:methanol in 10:1 ratio as solvent, and as such these solvents were used for column filtration.

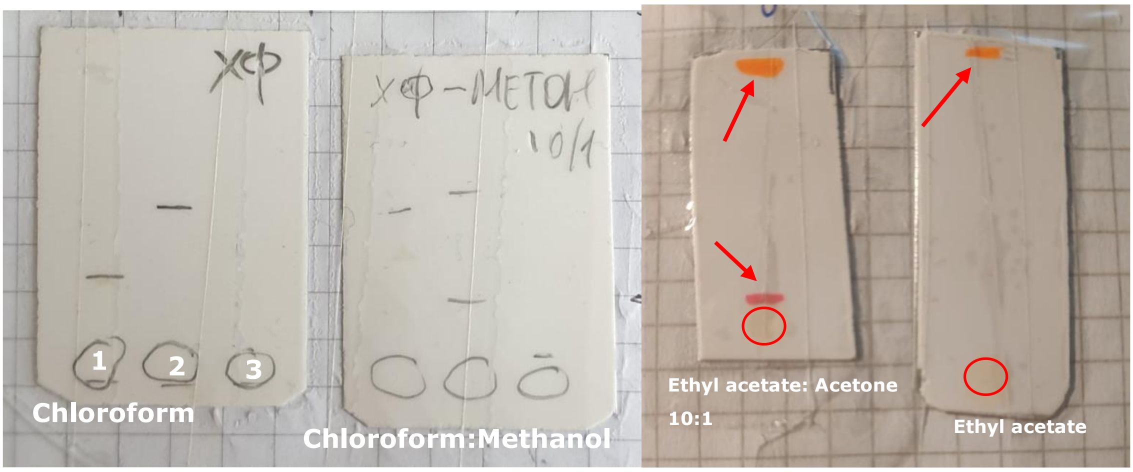


Figure 4.5.3. The thin film chromatography strips after looking under the UV light. The left circle on the left images is pure [mTBNH][OAc], middle circle 2 step distilled [mTBNH][OAc] and the right circle 1 step distilled. The right image had only 2 step distilled [mTBNH][OAc].

From column filtration, 3 separate fractions of liquid were obtained. It was observed that during column filtration, 2 fronts in the separation column occurred, these were collected separately. The third fraction was a solid fraction that remained on the top of the column. The fractions were studied by ^{1}H NMR after removal of eluent by rotary evaporator. Figure 4.5.4. shows the collected fractions.

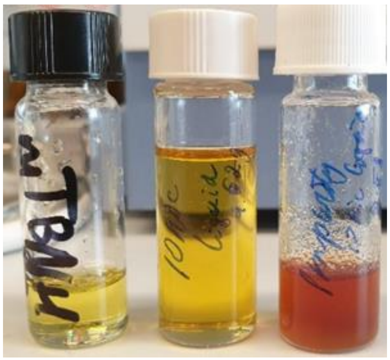


Figure 4.5.4. Three separate fractions of ionic liquid. The right vial is solid fraction, left (fraction 1) and middle (fraction 2) are separate fronts of solution.

The NMR spectra for the fraction 1 and fraction 2 are shown in figure 4.5.5. Spectra show low fractionation efficiency of the column, as could be seen peaks corresponding to aliphatic chains (near 1 ppm), DMSO (at 2.5 ppm) present in both fractions, yellow fraction mostly consist of DMSO and aliphatic moieties, brown fraction consists mostly of IL, DMSO, and traces of aliphatic substances.

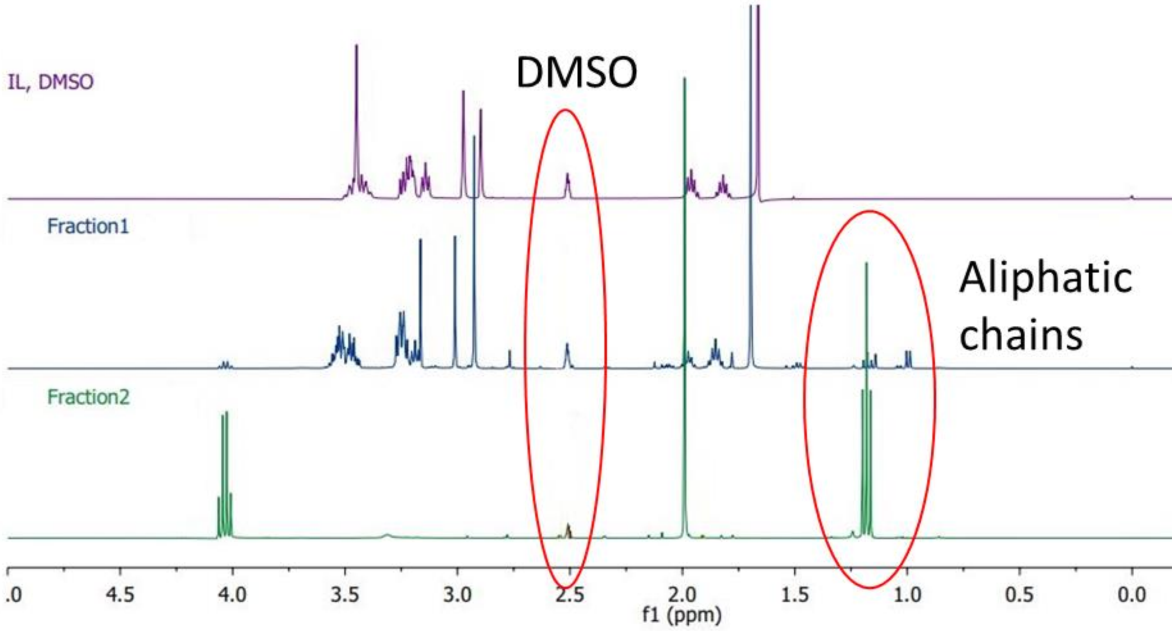


Figure 4.5.5. NMR spectra of pure [mTBNH][OAc] in DMSO and the separated fractions of [mTBNH][OAc] after column filtration. Fraction 1 – brown fraction, fraction 2 – yellow fraction.

To conclude, it was determined that column filtration is not an efficient method for fractionating IL from its waste due to low productivity, 500ml of eluent was needed to fractionate 2g of the IL solution. Additionally, it is time consuming as fractionating rate was 0.5g/hour. Therefore, column chromatography will not be efficient to regenerate reasonable amounts of IL from 1-2 litres of waste solutions which has been produced in one synthesis cycle. Lastly, the NMR shows that aliphatic chains are still present in the ionic liquid after column filtration, showing no improvement in ionic liquid purity.

4.6 Ionic liquid hydrolysis and fractional distillation

As it is known from literature, that the ionic liquid [mTBDH][OAc] shows slight hydrolysis in the presence of water, the same was studied for [mTBNH][OAc]. Hydrolysis of the ionic liquid is important to study because any presence of water in the ionic liquid will inhibit cellulose solvation and will affect the purity of the ionic liquid upon recovery, as hydrolysis products are difficult to remove. The description of samples prepared is shown under 3.1.8.

The NMR spectra was studied again in the same method as described under 4.4. The integrals of peaks were taken with the peak at C3 location of [mTBNH][OAc] taken as 1 as the reference point. It was found that with increasing temperature, the integral under the peaks corresponding to carbons in the ionic liquid decreased thus indicating that the slight hydrolysis of the ionic liquid occurs with increasing temperature. The highest change in peak intensity was detected for C2 and C10 positions (these locations can be seen in appendix 1). The C10 carbon is however outside of the main ring, therefore hydrolysis at this carbon could be more likely to occur due to weaker interactions. Table 4.6.1. shows the peak intensities of each carbon in the ionic liquid and the change in peak area. The NMR spectra where data was taken from are provided in appendix 3.

Table 4.6.1. Peak intensities in ppm at each carbon location in the ionic liquid with the area of each peak taken when the peak at 2.13 ppm corresponding to C3 is equal to 1.

2 h at T, °C		Peak integral at carbon locations, ppm							
		C3 (reference)	C3	C4	C9	C2	C8	C8	C10
		2.13	2	3.07	3.16	3.3	3.6	3.7	1.89
Integral under the peak	60	1	0.69	0.98	1.53	3.45	0.7	2.73	2.59
	70	1	0.69	0.97	1.52	3.14	0.71	2.65	2.56
	80	1	0.69	0.93	1.48	3.38	0.74	2.6	2.52
	90	1	0.7	0.94	1.5	3.38	0.73	2.63	2.52
			Delta	**0.04**	**0.03**	**0.07**	**-0.03**	**0.1**	**0.07**

From the table it can be seen slight hydrolysis of the ionic liquid, confirming that at low concentrations of water, hydrolysis does occur similar to [mTBDH][OAc] studied by Elsayed et al. This is an issue when we want to clean the IL, hydrolysis products are more difficult to remove and through thin film distillation it will not be possible to remove all the water in the solution.

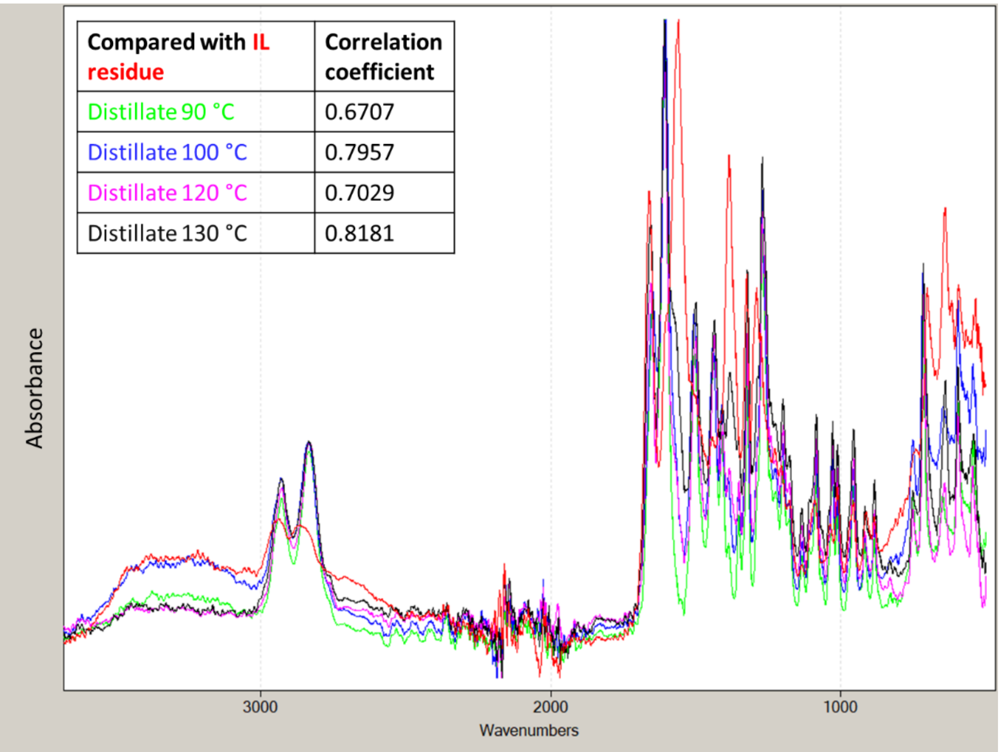
In addition to the area under peaks, the pH of the solution was also studied. The results are shown in table 4.6.2. however, the pH did not change much with the presence of water, it did increase slightly, however overall solution remains highly alkaline.

Table 4.6.2. pH of pure [mTBNH][OAc], [mTBNH][OAc] and water at 4.5%, [mTBNH][OAc] and water after heating, [mTBNH][OAc] after heating with water removed.

Temperature (T, °C)	Pure IL pH	IL & H_2O pH	IL & H_2O & T °C pH	IL & T °C - H_2O pH
60	11.9	12.23	12.15	12.24
70			12.07	12.36
80			12.08	12.36
90			12.05	12.24

After studying hydrolysis, fractional distillation was performed to attempt removal of water, IL hydrolysis products and IL fractions. Four different fractions were collected at different temperatures. The final fraction was collected from simple distillation. Distillation of the ionic liquid was time consuming and the collected fraction quantities were very small – direct distillation of the ionic liquid is therefore quite difficult and requires further analysis and development for a more efficient procedure. FT-IR and NMR were performed to analyse the fractions.

Figure 4.6.1. shows the FT-IR spectra for all collected fractions from fractional distillation and IL residue from simple distillation, the figure also shows the correlation coefficients of the distillate spectra's compared with the simple distillation IL residue. Overall, the spectra of all distillates resemble pure [mTBNH][OAc] (presented in figure 4.2.4.). It can be seen that the first fraction collected at 90°C has the lowest correlation coefficient, this possibly indicates that the first fraction could contain hydrolysis products of the ionic liquid. The distillate collected at 130°C has the highest correlation coefficient, which indicates that this collected fraction is structurally more similar to simple distillation IL residues.



Compared with IL residue	**Correlation coefficient**
Distillate 90 °C	0.6707
Distillate 100 °C	0.7957
Distillate 120 °C	0.7029
Distillate 130 °C	0.8181

Figure 4.6.1. FT-IR spectra of ionic liquid fractions, collected via fractional distillation and correlation co-efficient of each fraction with the IL fraction collected in simple distillation.

Proton NMR was also performed on the samples. Table 4.6.3. shows integrals of the peaks for some carbon locations of the ionic liquid. No distinct correlation can be made from the data, however the peak integrals for C3 and C2 are highest in the 120°C distillate whilst C8 and C10 distillate are highest in the 90°C. Data in the table is taken from NMR spectra presented in appendix 3.

Table 4.6.3. Integrals of ^{1}H NMR peaks for distillate fractions at C3, C2, C8 and C10 positions.

Carbon location	C3	C2	C8	C10
ppm	2	3.3	3.6	1.89
Samples	**Integral under peak**			
Distillate 90°C	3.7	2.57	3.81	2.52
Distillate 110°C	1.67	1.11	1.69	1.11
Distillate 120°C	4.09	9.87	3.36	2.11
Distillate 130°C	1.91	4.21	1.96	1.25
Simple distillation IL residues	0.58	1.65	0.58	1.48

Another noticeable difference in the spectra is that instead of one sharp peak for certain carbon locations, many smaller peaks can be seen in the same location, an example of this is shown in figure 4.6.2. The NMR spectra for pure [mTBNH][OAc] shows the C3 and C10 peaks as sharp singular peaks, whilst the distillate obtained at 90°C shows pattern splitting, indicating that nearby carbon atoms have different sets of hydrogen atoms bonded – this was not observed as intensively in prior NMR spectra. Another thing observed from distillate NMR spectra is peaks were wider than previously. The NMR spectra are presented in the appendix 3.

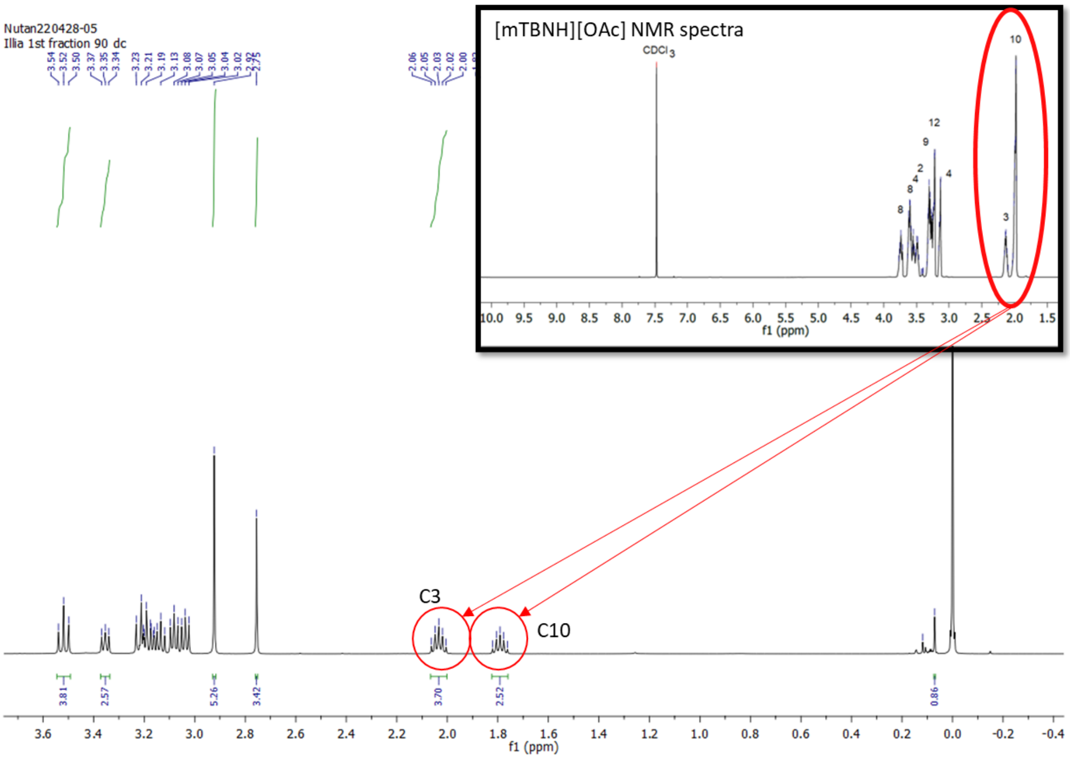


Figure 4.6.2. ¹H NMR spectra for distillate collected at 90°C compared with pure [mTBNH][OAc] spectra. In this spectrum, splitting pattern is observed at C3 and C10 locations.

Overall, both FT-IR and NMR show that during fractional distillation, different fractions of [mTBNH][OAc] can be collected at high temperatures and low pressures, therefore there is a potential for ionic liquid recycling by direct distillation.

CONCLUSION

[mTBNH][OAc] is ionic liquid with strong potential for cellulose dissolution and modification. However, to make its use economical recycling and rejuvenation of the ionic liquid need to be developed. It was found that after esterification of cellulose in IL, the ionic liquid waste contains lauroyl residues. Unfortunately, residues cannot be effectively removed from the waste by liquid-liquid extraction, activated carbon washing, salting-out nor column filtration. This is a problem as contaminants in the ionic liquid could affect the re-use of the ionic liquid. The salting-out method should be studied further as there are several salts studied in literature which were not studied in the context of this master's thesis.

Thin film distillation was found to be efficient at removing both high-volatile and low-volatile solvents from the waste solution. This is good as these solvents can be used again in processes where purity is not of utmost importance. It was also found via rheology that after one cycle of synthesis and distillation, the IL has similar rheological properties as pure [mTBNH][OAc], indicating that after the 1st round of synthesis there is potential that contaminants do not need to be removed. After the 1st synthesis round and solvents distillation, IL with purity of 97.8% was obtained.

However, the removal of contaminants is difficult and most likely needs to be performed after a few rounds of synthesis and thin-film distillation, to avoid the accumulation of contaminants in the IL. Most likely the best method for IL regeneration will be removal of solvents via thin-film distillation and consequent direct fractional distillation of the ionic liquid. Fractional distillation could allow to remove hydrolysis products as well from the IL solution.

SUMMARY IN ENGLISH

Ionic liquids (salts that are liquid below 100°C) are green solvents with great potential in the field of cellulose valorisation. However, to make the use of ionic liquids economically beneficial in industrial processes, it is necessary to recycle and reuse ionic liquids. This master's thesis focuses on the ionic liquid 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-enium acetate ([mTBNH][OAc]) which has been used in cellulose synthesis processes. The aim of the work is to develop a recycling method and ionic liquid quality analysis method, that could be used to evaluate ionic liquid recycled in different ways.

Literature overview of ionic liquid recycling methods is presented and discussed. Methods which were considered to be "simple" and easily applicable to the industrial scale were tried and tested on [mTBNH][OAc] waste solution. The removal of solvents (both high-volatile and low-volatile) was done by thin film distillation. The attempt to remove other contaminants was made by liquid-liquid extraction, activated carbon washing, induced phase separation and column filtration.

None of these methods were found to be effective at removing contaminants from the ionic liquid whilst retaining the ionic liquids properties. Thin film distillation was however found to be an effective method for the removal of high-volatile and low-volatile solvents such as acetone, ethanol, water and DMSO.

Recycling methods studied were evaluated by FT-IR, rheology and proton NMR. The latter was also used to evaluate the ionic liquids purity after recycling. [mTBNH][OAc] with 97.8% purity was successfully obtained, however it was found that the ionic liquid still contained lauroyl residues – the removal of these residues needs to be further studied, the proposed solution would be to perform fractional distillation of the ionic liquid itself. The beginning of this was started in the work, however it needs to be studied and developed further.

KOKKUVÕTE EESTI KEELES

Ioonsed vedelikud (soolad, mis on vedelad temperatuuril alla 100 °C) on rohelised lahustid, millel on suur potentsiaal tselluloosi väärindamisel. Ioonsete vedelike suurimaks probleemiks on nende hind, mille tõttu ei ole nende kasutamine tööstuses majanduslikult kasulik. Selle muutmiseks tuleb ioonseid vedelikke ringlusse võtta ja taaskasutada. Käesolev magistritöö keskendub ioonsele vedelikule 5-metüül-1,5,7-triasabitsüklo[4.3.0]non-6-eeniumatsetaadile ([mTBNH][OAc]), mida on kasutatud tselluloosi sünteesiprotsessides. Töö eesmärgiks on välja töötada taaskasutusmeetod ja taastatud kõnealuse ioonse vedeliku kvaliteedi analüüsi meetodid, mille abil saaks hinnata erineval viisil puhastatud ioonseid vedelikke.

Esitatakse ja käsitletakse kirjanduse ülevaadet ioonsete vedelike taaskasutamise meetoditest. Meetodeid, mida peeti "lihtsateks" ja kergesti rakendatavateks tööstuslikus mastaabis, katsetati [mTBNH][OAc] jäätmelahustega. Lahustid (nii lenduvad kui ka mittelenduvad) eemaldati õhukese kile destilleerimis meetodil. Teisi saasteaineid püüti eemaldada vedelik-vedelik ekstraheerimise, aktiivsöega pesemise, indutseeritud faaside eraldamise ja kolonnfiltreerimisega.

Ükski eelnimetatud meetoditest ei osutunud tõhusaks saasteainete eemaldamise meetodiks ioonsest vedelikust, säilitades samal ajal ioonse vedeliku spetsiifilisi omadusi. Siiski leiti, et õhukese kile destillatsioon on tõhus meetod lenduvate ja mittelenduvate lahustite, näiteks atsetoon, etanool, vesi ja DMSO eemaldamiseks.

Uuritud meetodeid hinnati FT-IR-i (Fourier'-teisendusega infrapunaspektroskoopia), reoloogia ja prooton NMR-i (tuumamagnetresonants) abil. Viimast kasutati ka ioonsete vedelike puhtuse hindamiseks peale taaskasutamise meetodi rakendamist. Edukalt saadi 97,8% puhtusega [mTBNH][OAc], kuid leiti, et ioonne vedelik sisaldas siiski lauroüüli jääke. Jääkide eemaldamist tuleb veel uurida, pakutud lahendus oleks ioonse vedeliku fraktsioneeriva destillatsiooni teostamine. Selle uurimist on töös alustatud, kuid vajab edasist arendamist.

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APPENDICES

Appendix 1: NMR spectra of pure [mTBNH][OAc]

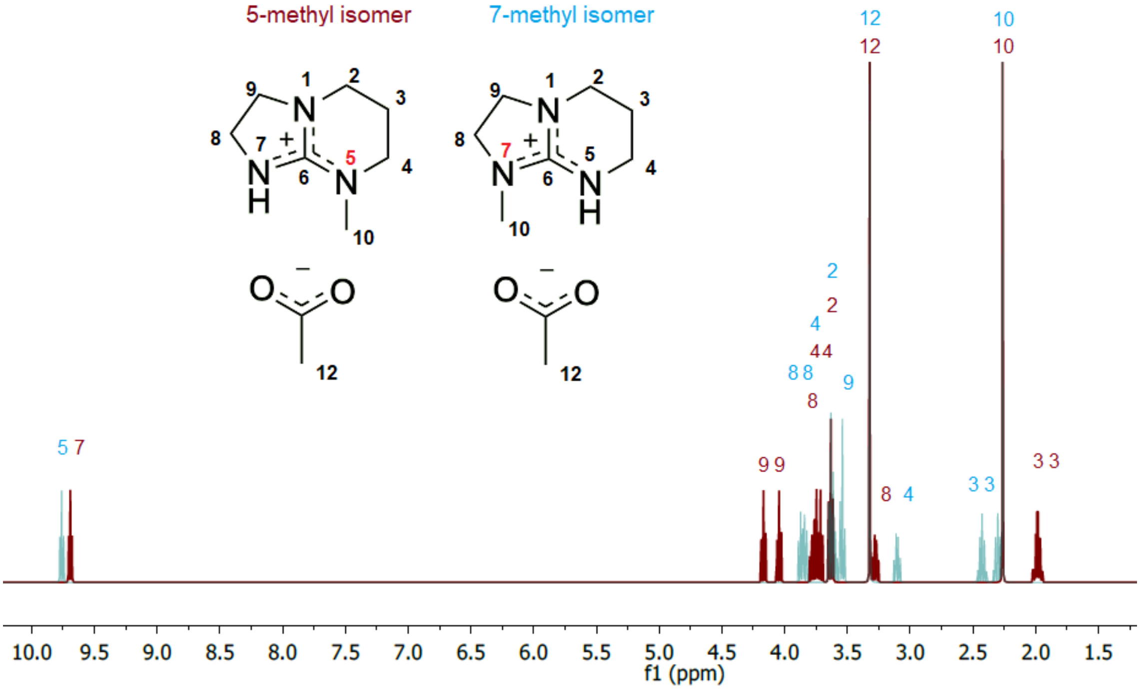

Figure A1.1. Predicted ^{1}H NMR spectra for 5- and 7- methyl isomers overlapped.

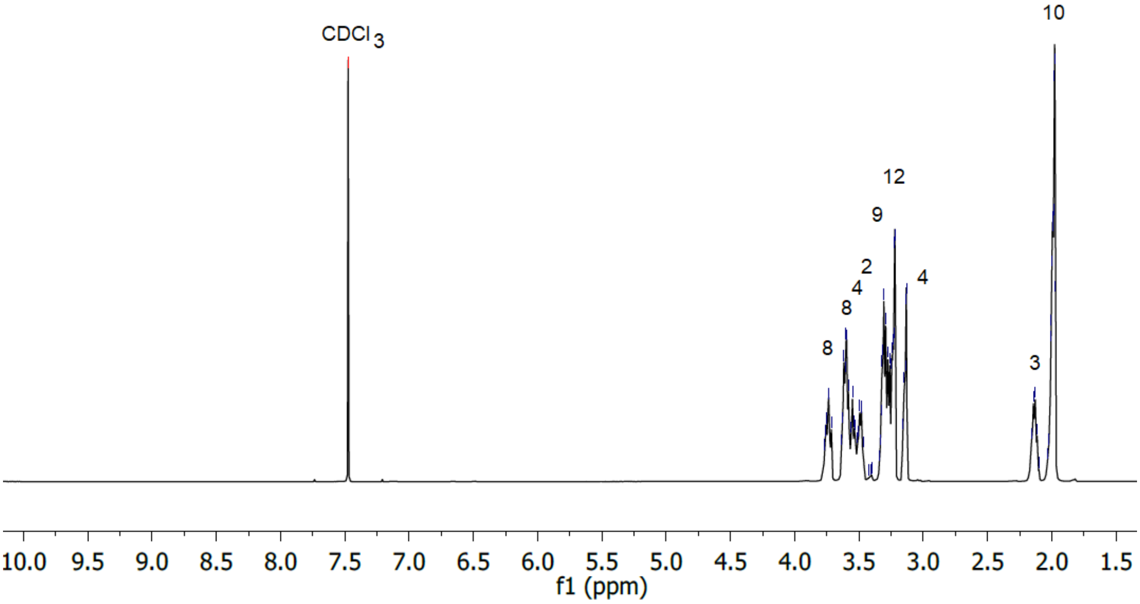

Figure A1.2. [mTBNH][OAc] ^{1}H NMR spectra in Chloroform-d.

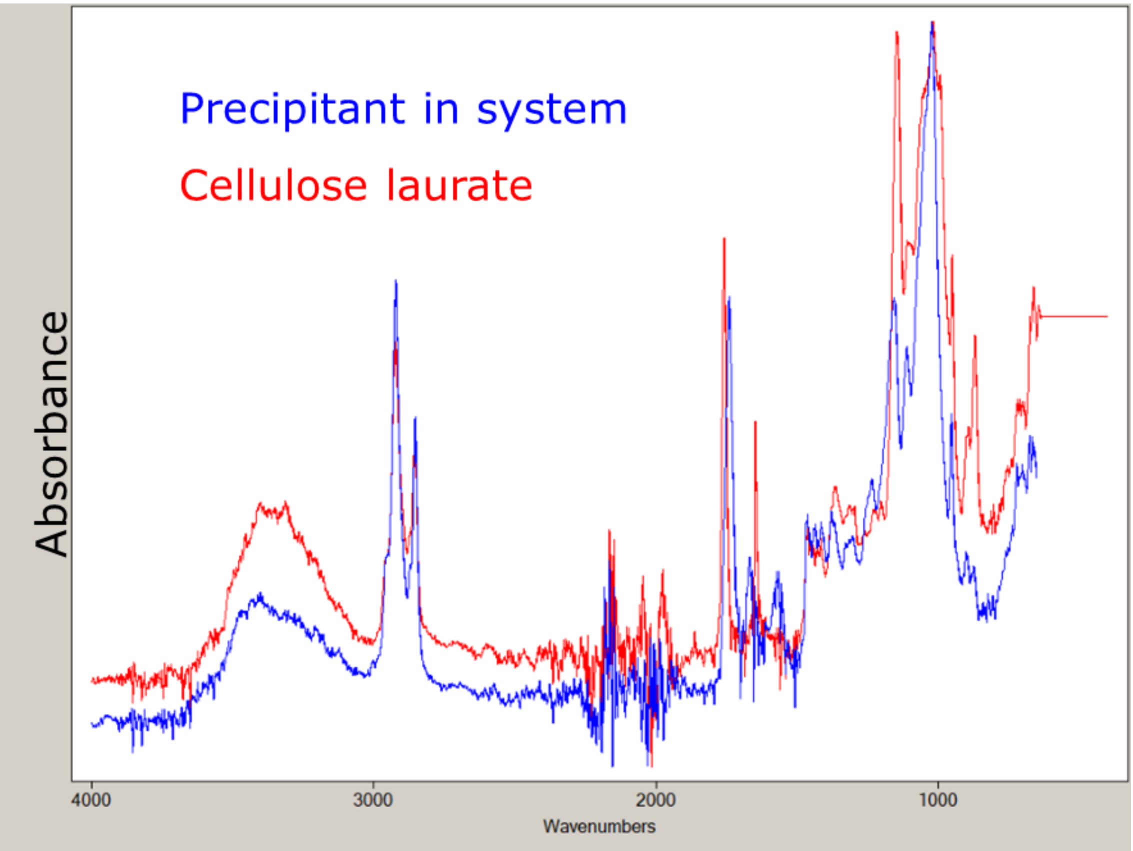

Figure A2.1. FT-IR spectra of precipitant collected during thin film distillation (blue) compared with FT-IR of cellulose laurate (red).

Appendix 3. NMR of hydrolysis and fractional distillation

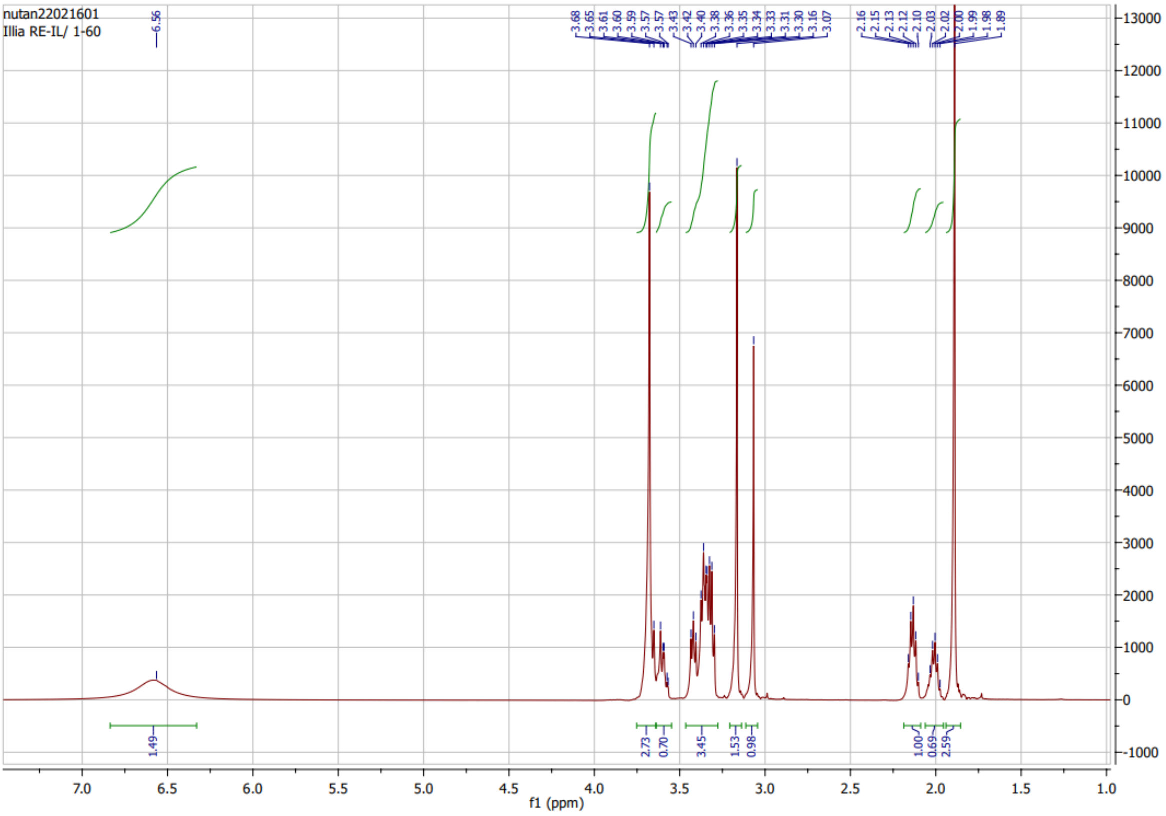

Figure A3.1. NMR spectra of 4.5% aqueous ionic liquid solution heated to 60 °C for 2 hours.

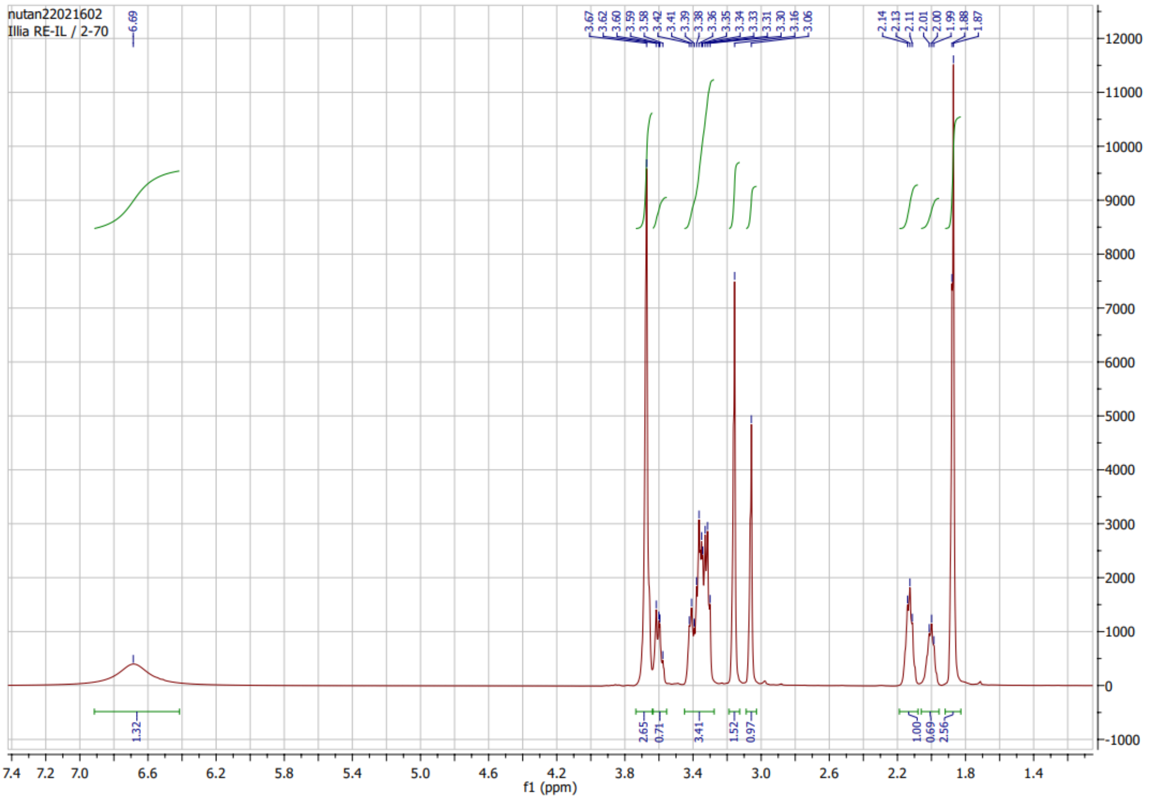

Figure A3.2. NMR spectra of 4.5% aqueous ionic liquid solution heated to 70 °C for 2 hours.

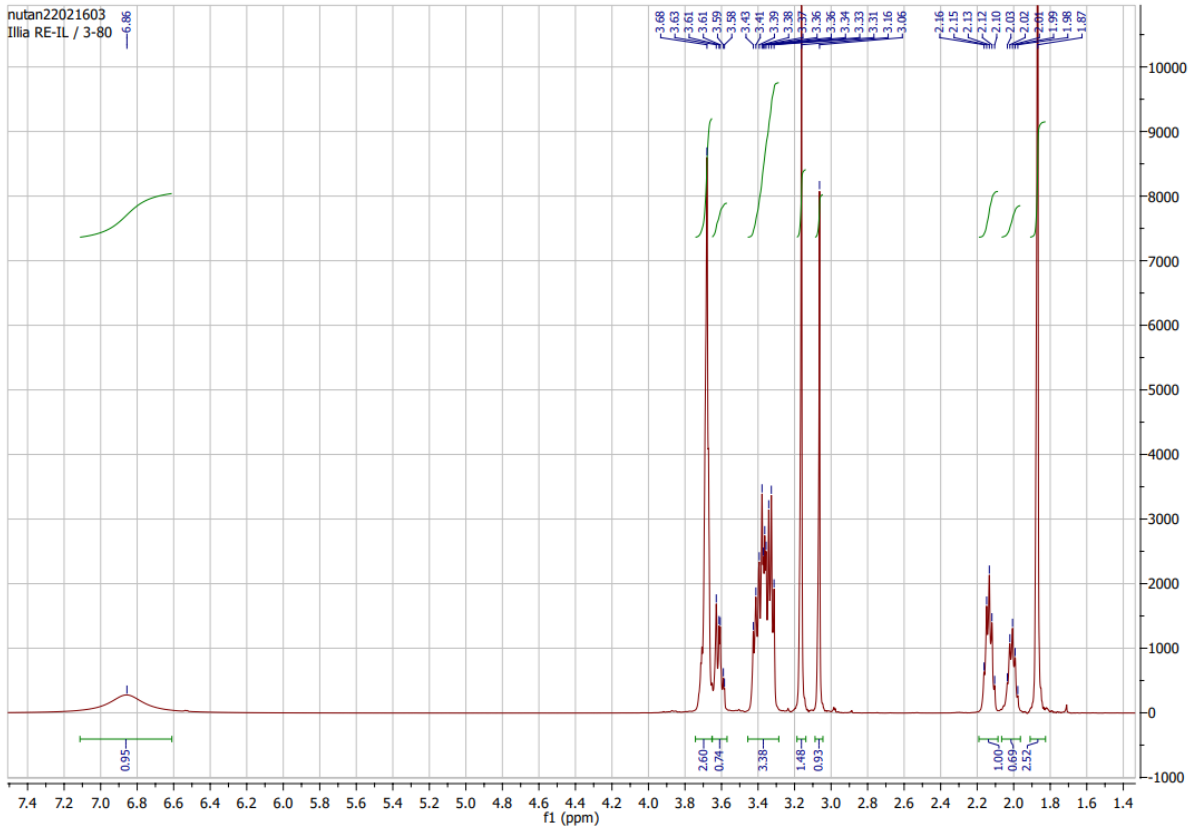

Figure A3.3. NMR spectra of 4.5% aqueous ionic liquid solution heated to 80 °C for 2 hours.

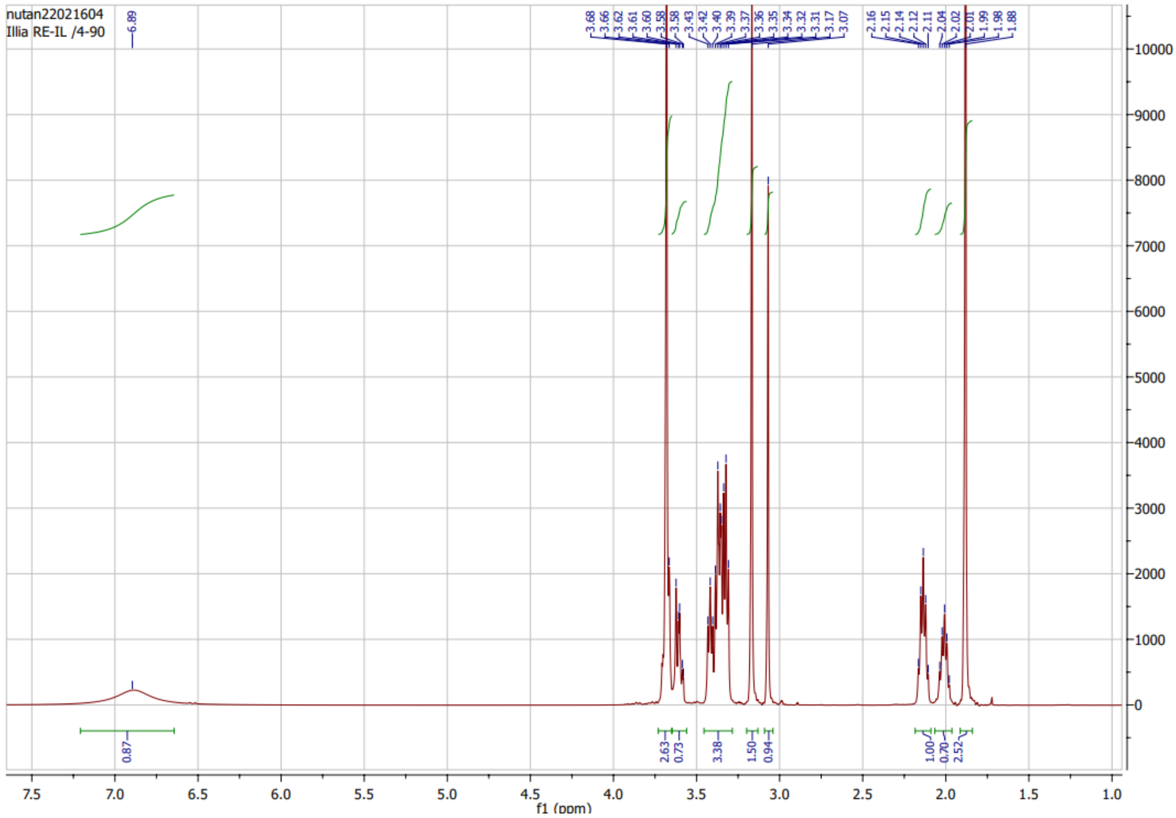

Figure A3.4. NMR spectra of 4.5% aqueous ionic liquid solution heated to 90 °C for 2 hours.

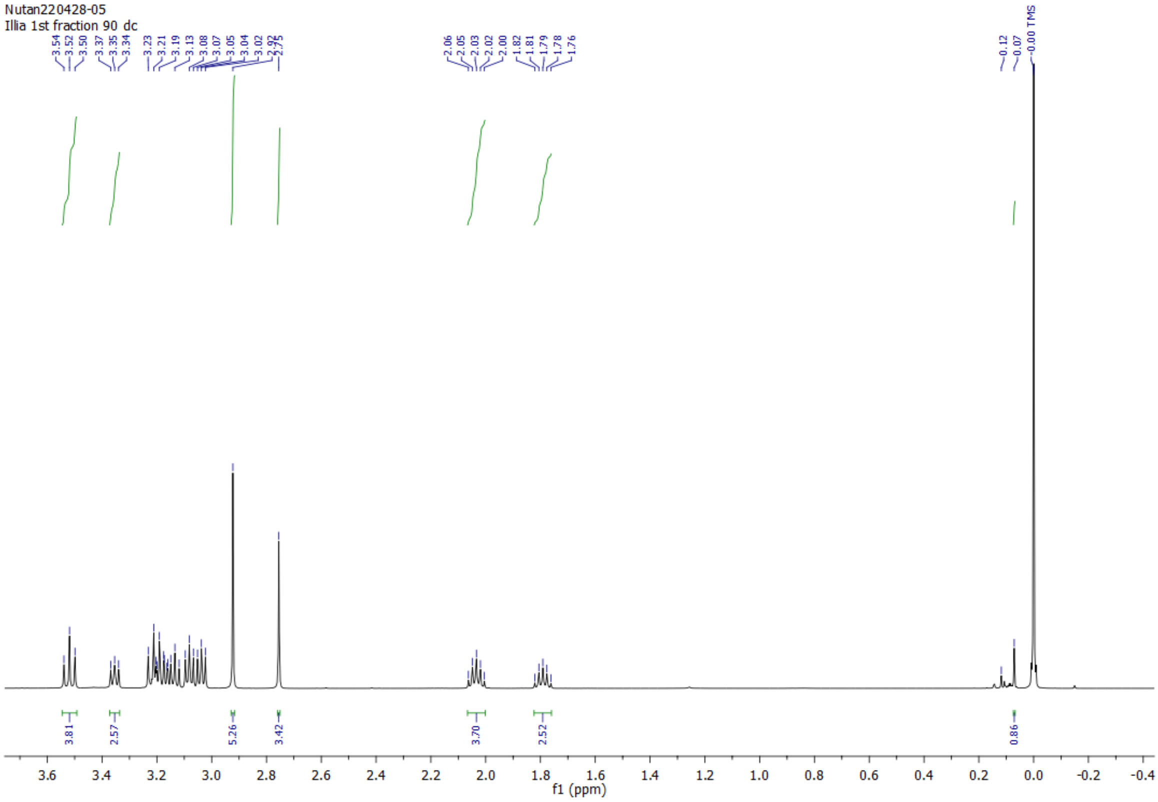

Figure A3.5. NMR spectra for distillate collected at 90 °C from IL fractional distillation.

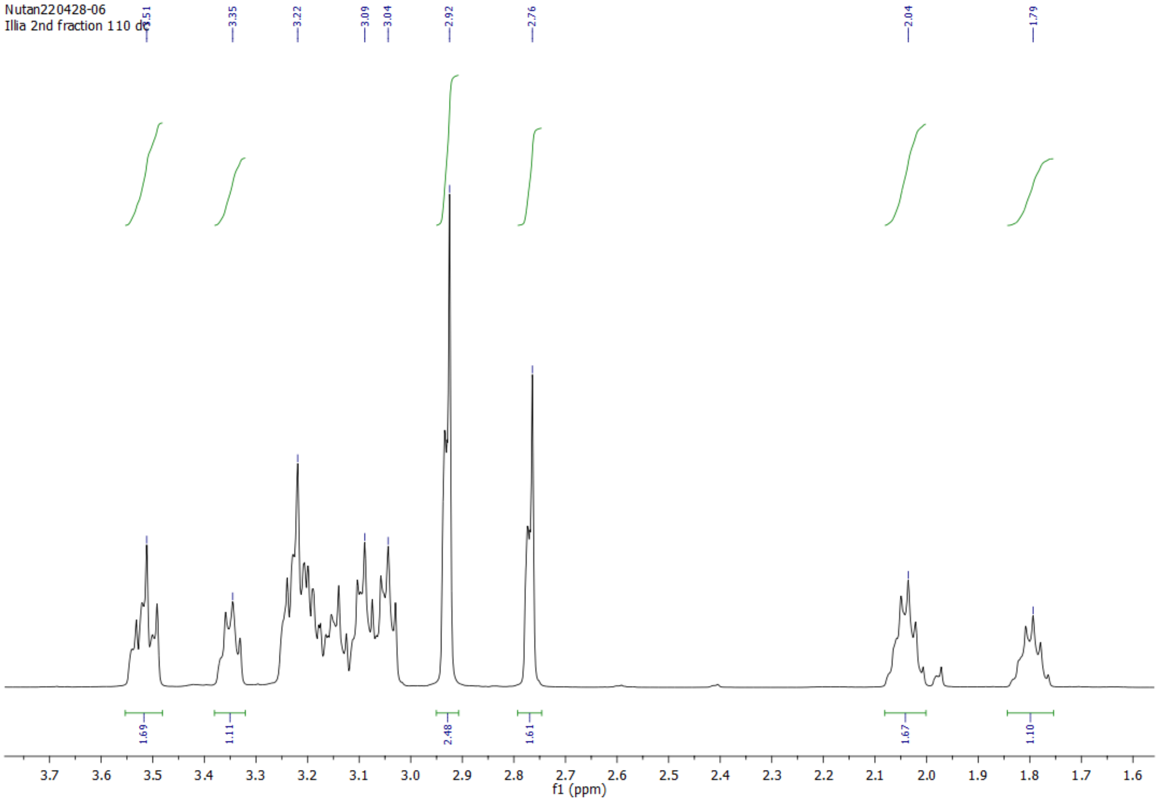

Figure A3.6. NMR spectra for distillate collected at 110 °C from IL fractional distillation.

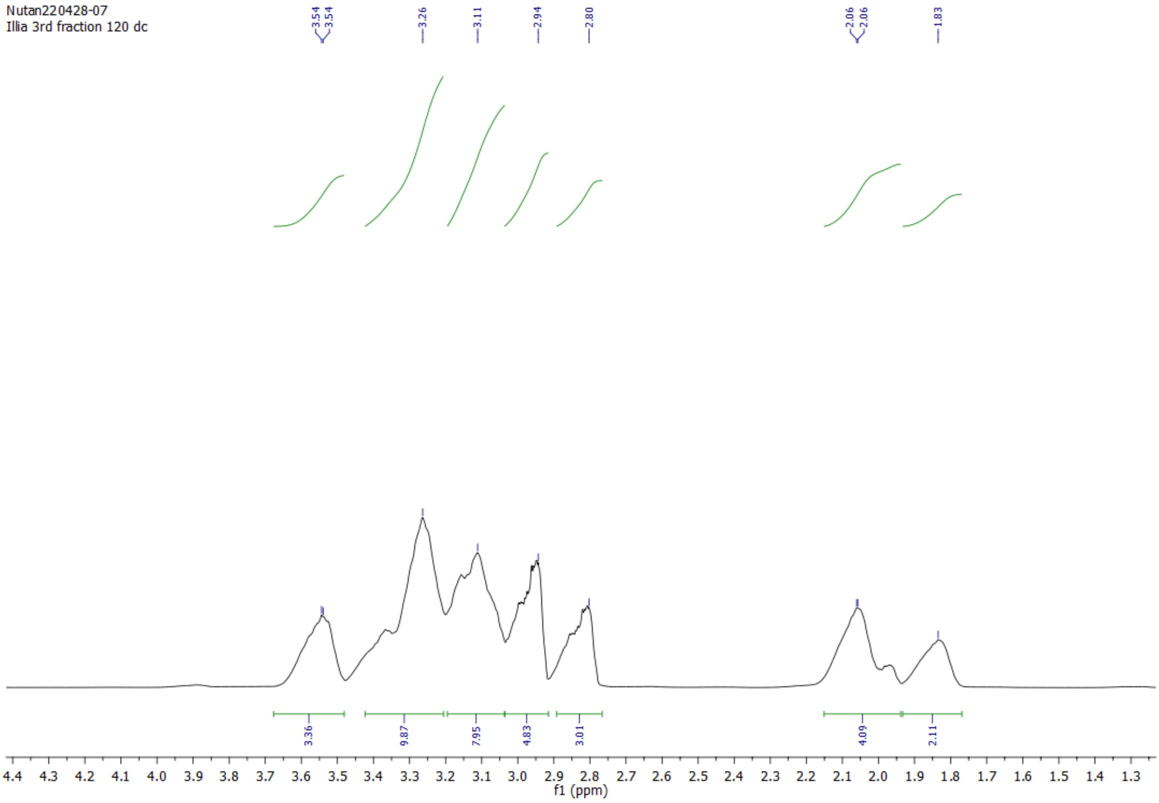

Figure A3.7. NMR spectra for distillate collected at 110 °C from IL fractional distillation.

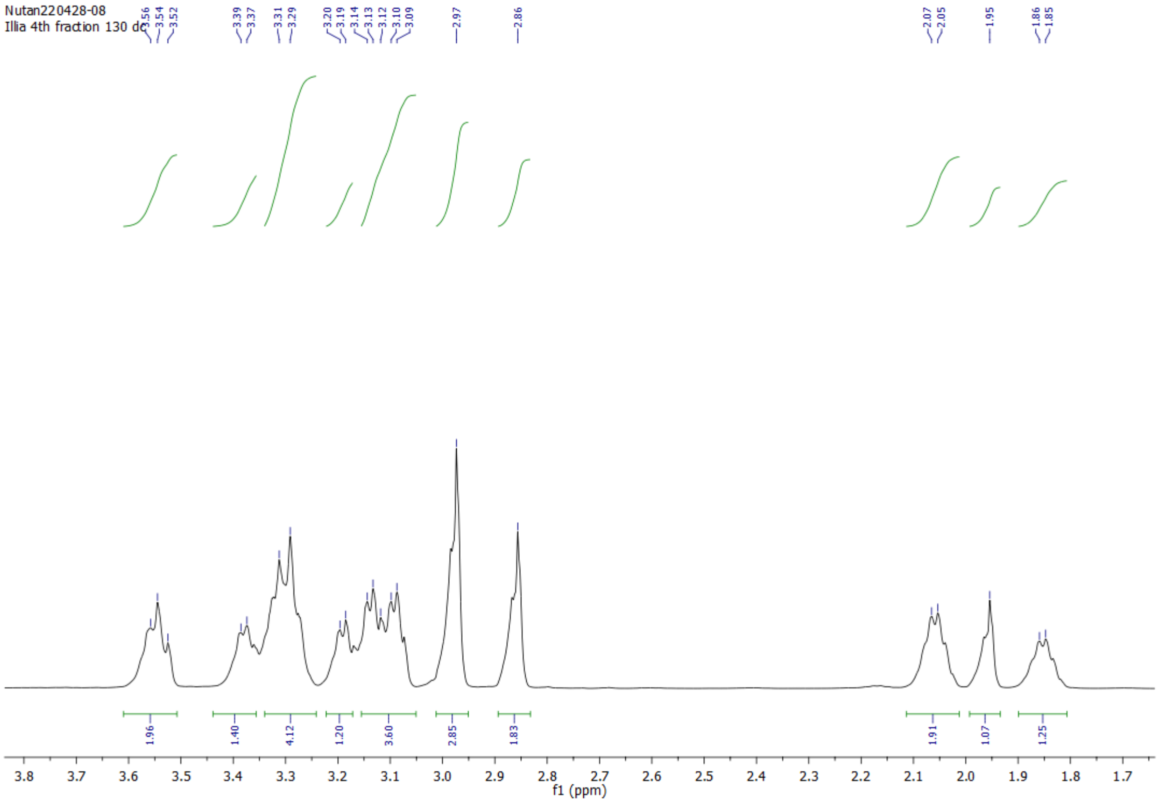

Figure A3.8. NMR spectra for distillate collected at 110 °C from IL fractional distillation.