Synthesis of bis-2(ethylhexyl)ammonium based ionic liquids for the dissolution of cellulose

by

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Dissertation submitted in partial fulfillment for
the requirements for the degree of
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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Department
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Approved by,

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TRONOH, PERAK

JANUARY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(NOR AMALIA HUSSIN)

ABSTRACT

Over the last decade, Ionic Liquids (ILs) have been used for the dissolution of biomass. This ability of ILs is now sought for their application in the selective dissolution of biomass for the manufacturing of ethanol. However, there are significant knowledge gaps in understanding of the chemistry of the interaction of biomass and ILs. While imidazolium ILs have been used successfully in dissolution of biomass, bis-2(ethylhexyl)ammonium based ILs has not been explored for the biomass dissolution. Hence, this study reports on the synthesis of a novel ILs based on bis-2(ethylhexyl)ammonium cation with different types of anions. This project will consist of two phases. The first phase is the synthesis of the new ionic liquids containing bis-2(ethylhexyl)ammonium with several types of anions such as dimethylsulfate, trimethylphosphate, diethylsulfate and triethylphosphate. The physicochemical properties of the synthesized ionic liquids such as water content, melting point, thermal decomposition and density were determined. The characterization of ionic liquids is performed using nuclear magnetic resonance (^{1}H NMR), fourier transform infra-red (FTIR) spectroscopy and elemental analysis (CHNS). The second phase of this project is the dissolution studies of biomass using the newly synthesized ionic liquids. Cellulose was heated in the synthesized ionic liquids at 100 ºC. The dissolved cellulose will be precipitated by adding organic solvents such as acetone, methanol, etc. and the morphology of the recovered biomass will be studied using scanning electron microscope (SEM), transmission electron microscope (TEM) etc. Then, the ionic liquid will be rcylced.

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ABBREVIATIONS & NOMENCLATURE

(PSmim) HSO_4	1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulphate
$[C_3CNMIm]BF_4$	1-Butyronitrile-3-methylimidazolium tetrafluoroborate
$[C_3CNMIm]N(CN)_2$	1-Butyronitrile-3-methylimidazolium dicyanamide
$[C_3CNMIm]N(CN_2)$’$[C_3CNPy]BF_4$	1-Butyronitrile-3-methylimidazolium dicyanamide N-butyronitrile pyridinium tetrafluoroborate
$[C_3CNMIm]NTf_2$	1-Butyronitrile-3-methylimidazolium bis(trifluoromethylsulfonyl)amide
$[C_3CNPy]N(CN)_2$	N-butyronitrile pyridinium dicyanamide
$[C_4mim]Cl$	1-butyl-3-methylimidazolium chloride
^{13}C-NMR	carbon-13 NMR
^{1}H-NMR	Proton NMR
BSE	Back-scattered electrons
C-12	carbon-12
C-13	carbon-13
$C_4H_{10}O$	Diethyl ether
$CDCl_3$	Deuterated chloroform
C-H	carbon-hydrogen
CH_2	Methylene
CH_3	Methyl group
CH_3CN	Acetonitrile
$CHCl_3$	Chloroform
CHNS	Elemental analysis
CO_2	Carbon dioxide
COOH	Carboxylic acid

DI	Deionized
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectrometer
FTIR	Fourier Transform Infrared
FYP	Final year project
GHG	Greenhouse gases
IC	Ion Chromatography
IL	Ionic liquids
K_2CO_3	Potassium carbonate
MHz	Mega Hertz
MSDS	Material Safety Data Sheet
m_T	weight of dried legume straw
m_0	weight of the used legume straw
NMR	Nuclear magnetic resonance
NTf_2^-	bis(trifluoromethylsulfonyl)amide anion
PILC	PETRONAS Ionic Liquid Centre
ppm	parts per million
RCH_2Cl	dichloromethane
RCH_2OH	Primary alcohol
RTILs	Room temperature ionic liquid
SDBS	Spectral Data Base System for Organic Compounds
SEM	scanning electron microscopy
SO_3H	Sulfonic acid
SSA	Specific surface area
TGA	thermogravimetric analysis
TMS	tetramethylsilane
TSILs	task specific ionic liquids
UTP	Universiti teknologi PETRONAS
VOCs	Volatile Organic Compounds
XRD	X-ray diffraction

CHAPTER 1
INTRODUCTION

1. INTRODUCTION

1.1 Background of Study

Ionic liquids are compounds that are completely composed of ions and are liquid at or close to room temperature. With the continuous efforts of chemists, ionic liquids have not only become increasingly popular as reaction and extraction media in research and development, they have also widely been promoted as green solvents, which are regarded as powerful alternatives to the volatile organic compounds (VOCs) in the field of organic synthesis (Yue, Fang, Liu, & Yi, 2011). Since it was reported that ILs can dissolve cellulose, there has been extensive research to explore if this ability to dissolve cellulose can be used in context of lignocellulosic biomass. Many factors affect the biomass dissolution in ILs e.g. species of biomass, particle size and water content.

In addition, when the dissolving temperature is higher than the glass transition of lignin, the dissolution and fractionation of lignocelluloses can be more efficient (Vancov, Alston, Brown, & McIntosh, 2012). The ILs have attracted increasing interest as media for dissolving cellulose from lignocellulosic biomass in the pretreatment step (Fukaya, Hayashi, Wada, & Ohno, 2008). The dissolved cellulose in ILs can be easily regenerated with the addition of an anti-solvent such as water, ethanol or acetone (Zhu et al., 2006) The use of lignocellulosic based materials in various sectors such as automotive and aerospace instead of petro-materials have received great attentions due to the growing global environmental awareness, and concepts of sustainability and industrial ecology (Hamzeh, Ashori, Mirzaei, Abdulkhani, & Molaei, 2011). So this study will mainly concern on the pretreatment step which is the production of new ionic liquid for biomass dissolution.

1.2 Problem statement

In previous research, many ionic liquids have been used for the dissolution of biomass but those ionic liquids were not cost effective and had problems in environmental aspects in the field of dissolution of biomass. Hence, new types of ionic liquids composed of bis-2-(ethylhexyl)ammonium cation are proposed for the dissolution of biomass. The presence of bis-2(ethylhexyl)amine cation and different types of strong hydrogen bond acceptors anions will enhance the biomass dissolution ability of the ionic liquid. The efficiency of each ionic liquid in the biomass dissolution will be tested in order to determine which ionic liquids will give the most promising results in the dissolution of biomass.

1.3 Objectives

The objectives of this study are;

1) To synthesize three types of bis-2(ethylhexyl)amine based ILs.
2) To fully characterize the synthesized ionic liquids.
3) To determine the physico-chemical properties of the synthesized ionic liquids.
4) To perform the biomass dissolution studies using these ionic liquids.

1.4 Scope of Study

The project will evolve mainly on synthesizing the bis-2(ethylhexyl)ammonium based ILs and experimental works on dissolution of biomass. Three types of ionic liquids will be synthesized and tested whether it could be used in the dissolution of cellulose. The project will be supervised by Dr. Lethesh Kallidanthiyil Chellapan and Assoc. Prof Dr. Mohamed Ibrahim bin Abdul Mutalilib.

1.5 Relevancy and Feasibility of the Project

This project is relevant to the author because environments sustainability is one of the focus areas in the chemical engineering course. Nowadays, ionic liquids become a very useful green solvent in the field of chemical engineering. Hence, the synthesis of ionic liquid for the dissolution of biomass will be a great project as it will give promising results to the field of chemical engineering nowadays in sustaining the environment. In addition, this study is feasible within the scope and time frame set by the coordinator because only three types of ILs will be synthesize in this study. Furthermore, the synthesis and characterization process is not time consuming. Hence, this study is feasible within the specified time.

CHAPTER 2

LITERATURE REVIEW & THEORY

2. LITERATURE REVIEW AND THEORY

It is well known that the widespread use of traditional organic solvents such as benzene, toluene, xylene, methanol and ethanol in many industrial chemical processes is an issue of great environmental concern. These solvents are characterized by volatility and liquid ranges not very wide which at atmospheric pressure are approximately 85ºC to 200ºC. As a consequence, about 20 million tons per year of volatile organic compounds (VOCs) are released into the atmosphere due to industrial processes (Brennecke & Maginn, 2001), contributing to climatic changes, air pollution and human health-related issues (Sheldon, 2001). The growing interest for political, economic, social and environmental reasons towards green technologies is therefore leading to search for possible alternative solvents (Seddon, 1997). In this context, an ideal solvent should be characterized by very low volatility, chemical and physical stability, and high potential for recycling (Boschetti, Montagnaro, Rienzo, & Santoro, 2007). Recently, ionic liquids have already been more and more employed as substitutes for the traditional organic solvents in chemical reactions (Sheldon, 2001). PETRONAS Ionic Liquid Center (PILC) of Universiti Teknologi PETRONAS (UTP) is also proposing a new bis-2(ethylhexyl)ammonium based ionic liquid as a green solvent for the future. As a final year student, Assoc. Prof. Dr. Mohamed Ibrahim bin Abdul Mutalib and Dr. Lethesh had given me the opportunity to learn and synthesize the bis-2(ethylhexyl)amine based ionic liquid for the dissolution of biomass as my Final Year Project (FYP). Therefore, a deep understanding about the ionic liquid and dissolution of biomass need to be study before the experimental works can be started.

2.1 What is an Ionic Liquid?

Ionic liquids are new class of solvents consisting entirely of ions. It is different to the organic solvents, ILs have a very large liquid range, negligible vapour pressure, large electrochemical window and high electrical conductivity. They have potential applications both in academy and in industry. They are liquids ranging from alkali silicates and halides to tetraalkylammonium salts (Bockris & Reddy, 1970). It is a salt containing bulky organic cation and polyatomic inorganic or organic anion with melting point of less than the boiling point of water (Parvulescu & Hardacre, 2007). The various possible combinations of different inorganic anion and organic cation of ionic liquids offer opportunities to produce numerous types of ionic liquids (Suojiang, Ning, Xuezhong, Xingmei, & Z., 2005) and their physicochemical properties can be design according to our requirement. Because of this designer property, the interest in in ionic liquids is increasing exponentially. Figure 2.1 and 2.2 illustrates common cations and anions which form ionic liquids.

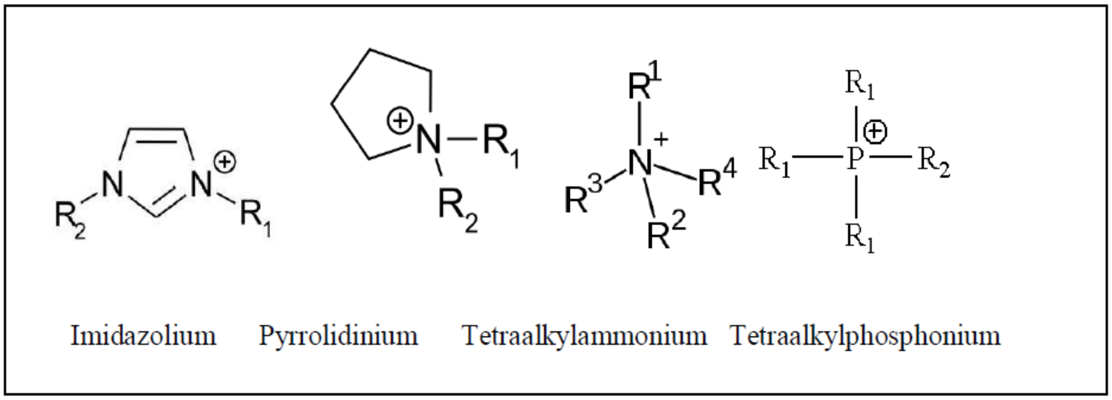


Figure 2.1: Common cation form ionic liquids

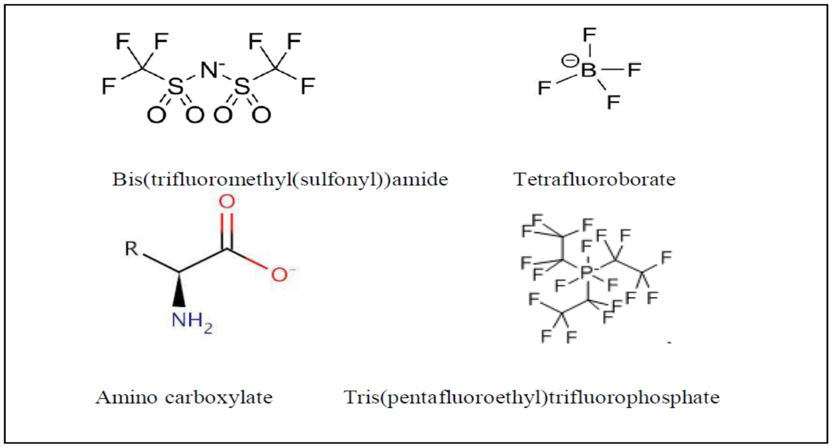


Figure 2.2: Common anion forms ionic liquids

Such examples include cations based on imidazolium, tetraalkylphosphonium, pyrrolidinium, tetraalkylammonium, and anions such as (bis(trifluoromethyl)sulfonylamide and alkylsulfonate with varying alkyl chain length (Hasse et al., 2009). Room temperature ionic liquids (RTILs) possess a unique array of physico-chemical properties that make them suitable in numerous task-specific applications in which conventional solvents are non-applicable or insufficiently effective. Such properties included in Table 2.1 below:

Table 2.1: Properties of modern ionic liquids (Johnson, 2007)

Freezing point	Preferably below 100ºC
Liquidus range	Often > 200ºC
Thermal stability	Usually high
Viscosity	Normally <100 cP, workable
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < 10 $mScm^{-1}$, "Good"
Molar conductivity	< 10 $Scm^2\ mol^{-1}$
Electrochemical window	> 2V, even 4.5 V, except for Bronsted acidic systems
Solvent and/or catalysts	Excellent for many organic reactions
Vapor pressure	Usually negligible

The solubility of different species in ionic liquids depends mainly on polarity and hydrogen bonding ability (Mrit & Peter, 2004). For example, saturated aliphatic compounds are generally only partially soluble in ionic liquids, whereas olefins show somewhat greater solubility, and aldehydes can be completely miscible (Martyn & Kenneith, 2011). Hence, it is important to know which type of ionic liquid that will dissolve the cellulose.

2.1.1 Characteristic of Ionic Liquids

1) Melting point

Ionic liquids are commonly defined as salts with a melting point below 100 °C. The structure of ionic liquids has an impact on their physical properties. Both cation and anion contribute to the melting points of ionic liquids. Large organic cation with less symmetry will lower the melting point because they disturb the efficient packing of ionic in the crystal lattice (McFarlane, Sun, Golding, Meakin, & Forsyth, 2000). The melting point decreases when the size and asymmetry of the cation increases up to a certain point. After that, an increase in the alkyl chain length increases the melting point.

However, the effect of anions on the melting point is more difficult to rationalize. Anions with large delocalization will reduce Coulombic force of attraction between the ions and result in a lower melting point. The presence of hydrogen bonding in the lattice is a major factor in increasing the melting point. Ionic liquids with strongly coordinating anions such as halides have higher melting points than their tetrafluoroborate or hexafluorophosphate analogues because of the formers ability to form hydrogen bonding (Holbrey, 1999).

2) Density

The density is the most often measured and reported property of ionic liquids, probably because of nearly every application requires knowledge of the density. In general, ionic liquids are denser than water (Wilkes, 2004). The molar mass of the anions has a significant effect on the density of the ionic liquids. The densities of ionic liquids decrease with the increase in the length of the alkyl chains in the cations. The bulkiness of the longer alkyl chain prevent them from efficient close packing leading to a decrease in the density, where as the shorter one packs more affectively.

3) Viscosity

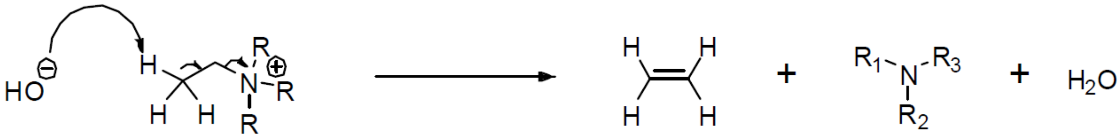
The viscosity of ionic liquids usually is reported as the dynamic viscosity, also called the viscosity coefficient. It affects the diffusion of solutes and practical issues, such as stirring, mixing and pumping operations. Furthermore viscosity also affects other transport properties such as diffusion. Ionic liquids are inherently much more viscous than molecular solvents, and vary over a range of <10 to >1000 cP at room temperature (Wilkes, 2004).

The choice of cations and anions has a strong influence on the viscosity of ionic liquids. Toduka et. al. had studied the effect of alkyl chain length and the nature of the anion on the viscosity of imidazolium based ionic liquids (Tokuda, Hayamizu, Ishii, susan, & Watanabe, 2004). The symmetry of the anion and its ability to form hydrogen bonds will effluence the viscosity of ionic liquids. The fluorinated anions such as $[BF_4]^-$ and $[PF_6]^-$ form viscous ionic liquids because of the formation of complexes with hydrogen bonding donors (Suarez, Einloft, Dullius, Souza, & Dupont, 1998). The viscosity of ionic liquids also depends on the alkyl chain length of the cations. Alkyl groups with modest chain lengths will lower the visocisty. Longer alkyl chains will increase the viscosity because of the increase in the van der Waals forces between the cations, which in turn increase the energy needed for the molecular motions.

4) Thermal stability

Many ionic liquids are reported to be resistant to thermal decomposition and thus suitable for high temperature applications (Anderson & Armstrong, 2005). The thermal stability of ionic liquids is directly linked to the nature of the anions. Ionic liquids containing more nucleophilic and coordinating anions such as halides decompose at lower temperature. Ionic liquids with poor proton abstracting anions such as bis(trifluoromethylsulfonyl)amide are more stable to high-temperature decomposition (Holbrey, 1999).

The decomposition temperature of ionic liquids also depends on the type of cations. Most studies have been performed on imidazolium-bases ionic liquid (Ngo, LeCompte, Hargens, & McEwen, 2000). They are thermally more stable than pyridinium (Tokuda et al., 2004) and tetralakyl ammonium-based ionic liquids (MacFarlane, Forsyth, Golding, & Deacon, 2002). The methyl substitution on the C(2) position of the imidazolium cation increases the thermal stability due to the replacement of the acidic hydrogen (Tokuda et al., 2006). It was also reported that the chain length of the alkyl group on the cation has not much influence on the thermal stability of the ionic liquids. Two important thermal decomposition mechanisms of ionic liquids are Hofmann elimination and reverse Menschutkin reaction. A schematic representation of Hoffmann elimination is given in scheme below.



5) Conductivity

The conductivity of ionic liquids is of vital importance for their applications in electro-chemistry. A large conductivity was expected for ionic liquids because they consist entirely of charge carrier ions. However, the conductivity of ionic liquids was found to be relatively low at room temperature (Tokuda et al., 2006). The conductivity of any solution depends on the number of charge carriers and their mobility. The large constituent ions of the ionic liquid reduce the ion mobility which in turn reduces the conductivity (Ignat'ev, Welz-Biermann, Kucheryna, Bissky, & Willner, 2005).

Although the conductivity of ionic liquids is not much higher than the conventional non-aqueous solvents, ionic liquids do offer the advantage that this property is intrinsic to the pure ionic liuids and thus the addition of any separate salt is avoided. The conductivity of ionic liquids having the same anions with different cations is found to decrease in the order 1-alkyl-3-methylimidazolium > N,N-dialkylpyrrolidium > tetraalkylammonium. This can be explained by the decrease in the planarity of the cation. The flat imidazolium cation has a higher conductivity than the tetrahedral tetraalkylammonium cation. The pyrrolidinium based ionic liquids, adopting an intermediate geometry, have an intermediate conductivity (Ignat'ev et al., 2005). Furthermore, an increase in temperature will lead to an increase in the conductivity of ionic liquids (Vila et al., 2006).

6) Miscibility with water

The water miscibility of ionic liquids primarily depends on the nature of the anion. At room temperature, ionic liquids based on $[PF_6]^{-1}$ and $[Tf_2N]^{-1}$ anions are insoluble in water, Ionic liquids based on anions such as nitrate, acetate, halides etc are fully miscible with water. The water solubility of ionic liquids based on $[BF_4]^-$ and $[CF_3SO_3]^-$ anions depend on the alkyl chain length on the cation.

7) **Flammability of ionic liquids**

Ionic liquids are considered as green solvents because of their nonflammability. This is considered as a safety advantage over volatile organic compounds (VOCs).

8) **Vapour pressure**

Ionic liquids are entirely composed of ions, so they are considered as substances with low or negligible vapour pressure even at high-temperature. Because of this property, ionic liquids cannot escape into the atmosphere, unlike other conventional organic solvents. Therefore, the impact on the environment is minimal. Another advantage is that volatile products can be isolated from ionic liquids by distillation. However it should be noted that, negligibly small vapour pressure is not equal to zero vapour pressure.

2.2 Quaternization Process for Ionic Liquid Synthesis

The formation of the cations may be carried out either via protonation with a free acid or by quaternization of an amine, phosphine or sulfide, most commonly using haloalkane or dialkylsulfates. In this study, quaternization of bis(2-ethylhexyl)amine was performed by using dimethylsulfates, triethylphosphate, diethylsulfate and triethylphosphate. In principle, the quaternization reactions are extremely simple: the amine is mixed with the desired alkylating agent, and the mixture is then stirrer and heated. The reaction temperature and time are very dependent on the alkylating agent employed. The reactivity of the haloalkanes also generally decreases with increasing alkyl chain length. As an illustration, it is generally found to be necessary to heat 1-methylimidazole with chloroalkanes to about 80°C for 2-3 days to ensure complete reaction. The equivalent reaction with bromoalkanes is usually complete within 24 hours, and can be achieved using lower temperatures such as 50-60°C. In the case of bromoalkanes, it is found that care must be taken with large scale reactions, as a storng exothermic reaction can occur as the reaction rates increases. Besides the obvious safety implications, the excess heat generated can result in discoloration of the final product.

A number of different protocols have been reported, but most of the researchers uses a simple round bottom flask/reflux condenser experimental setup for the quaternization reaction. If possible, the reaction should be carried out under nitrogen or some other inert gas in order to exclude water and oxygen during the quaternization. Exclusion of oxygen is particularly important if a colourless halide salt is required.

In general, the most important requirement is that the reaction mixture is kept free of moisture, as the products are often extremely hygroscopic. The reaction may be carried out without the use of a solvent, as the reagents are generally liquids and mutually miscible. A practical advantage of using a solvent in which the product is immiscible is that removal of the majority of the excess solvent and starting material can be achievd simply by decantation. In all case, however, after reaction is complete and the solvent is decanted, it is necessary to remove all excess solvent and starting material by heating the salt under vacuum. Care should be taken at this stage, especially in the case of halide salts, as overheating can result in a reversal of the quaternization reaction. It is not advised to heat the halide salts to temperatures greater than 80°C (Wasserscheid & Welton, 2008).

2.3 What is Biomass?

Recently concerns have been growing worldwide regarding the environmental consequences of heavy dependence on fossil fuels, particularly climate change. The application of renewable energy gives promising results for mitigating emission of greenhouse gases (GHGs) as well as acid rain precursors. As stated by Biomass Energy Centre, biomass is biological material derived from living organisms. In the context of biomass for energy, this is often used to mean plant based material, but biomass can equally apply to both animal and vegetable derived material. It is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals.

Plant biomass includes dead trees and branches, yard clippings and wood chips and also includes plant used for production of fibers, chemicals or fuels. Biomass wastes contain a complex mixture of carbohydrate polymers from the plant cell walls known as cellulose, hemi cellulose and lignin. It is mainly consisted of cellulose, which is the main part of woods constitutes 40-50%, lignin (25-35% in softwood and 16-25% in hardwoods (Rowell, 1984)) and hemicellulose (15-20%) (Browning, 1975). Figure 2.3 shows the percentage of carbohydrate polymers with its molecular structure.

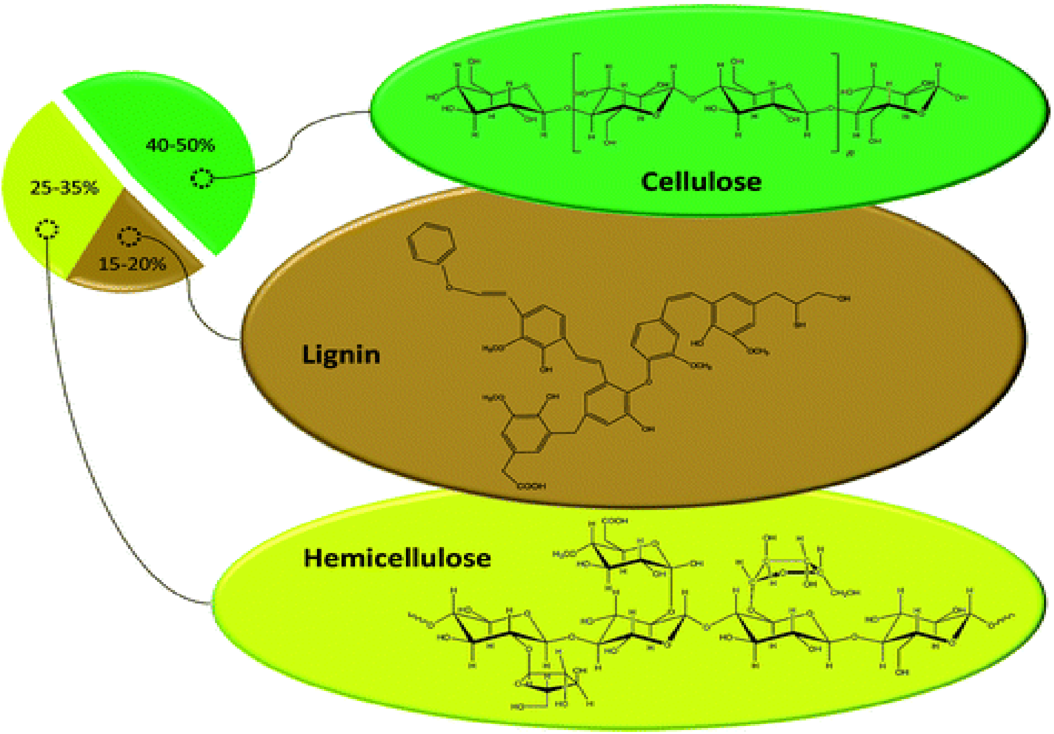


Figure 2.3: Percentage of carbohydrate polymers in plant cell wall

Cellulose, $C_6H_{10}O_5$ is the structural component of the primary cell wall that organized into long, unbranched microfibrils that give support to the cell wall (Crawford, 1981). Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibres have chains length ranging from 800 to 10,000 units. Figure 2.4 shows the arrangement of fibrils, microfibrils and cellulose in plant cell walls. In micro fibrils, the multiple hydroxide groups bonded with each other, holding the chains firmly together and contributing to their high tensile strength. In cell walls, this strength is important as they are meshed into a carbohydrate matrix that helps in keeping the plants rigid and tough.

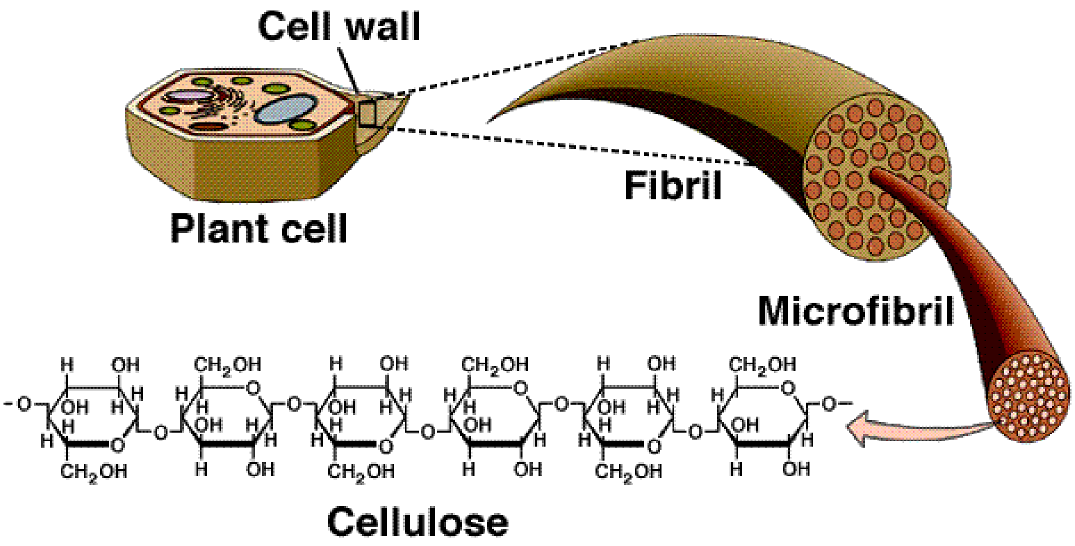


Figure 2.4: Arrangement of fibrils, microfibrils and cellulose in cell walls adopted from (Moore, Clark, & Vodopich, 1998)

A hemicellulose is any of several heteropolymers (matrix polysaccharides) such as arabinoxylans that present in almost all plant cell walls while cellulose is in a form of crystalline, strong and resistant to hydrolysis. Hemicellulose has a random, amorphous structure with little strength and its molecular weight is lower than that of cellulose. They also have a weak undifferentiated structure compared to crystalline cellulose. It is primarily composed of the 5-carbon sugars and xylose (Scurlock & Jonathan, 2004) as can be seen in Figure 2.5.

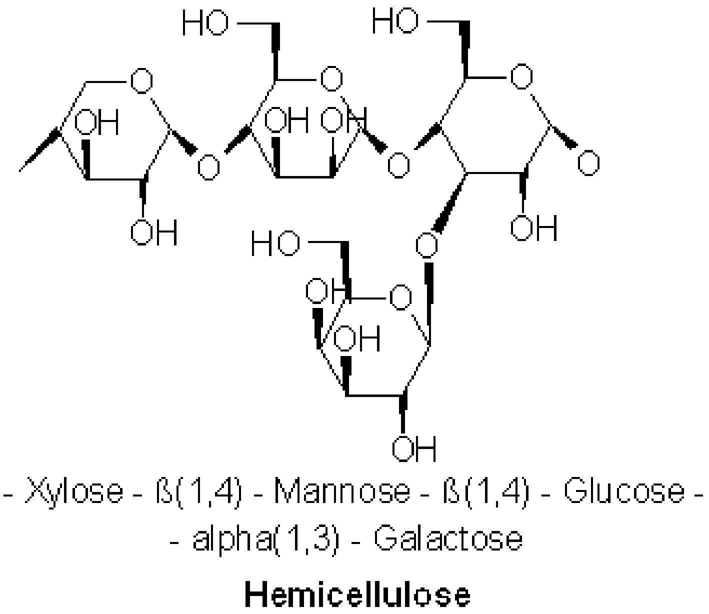


Figure 2.5: Structure of hemicelluloses

Lignin as an irregular polymer forms a network in which cellulose and hemicellulose fibre are embedded and also provides structural integrity in plants (Huber *et al.,* 2006). Due to complex structure of lignocellulose, it is resistant to most chemicals and hydrolysis, which definitely form a barrier for its utilization (Lynd *et al.*, 2002; Zhu *et al.*, 2006). It remains as residual compound after the sugars in the biomass have been converted to ethanol. Figure 2.6 shows the arrangement of cellulose, lignin and hemicellulose in a plant cell wall that involve in ethanol synthesize.

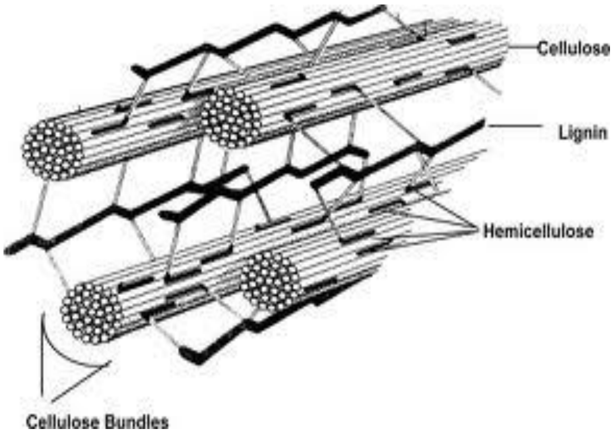


Figure 2.6: Typical plant cell wall arrangement

There are few differences between biomass and fossil fuels. The most vital difference is one time of scale. Biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. According to Bhattacharya et. al, sustainable biomass production and its use for energy generation does not lead to net buildup of CO_2 levels in the atmosphere because CO_2 released during its combustion is sequestrated during new growths. Furthermore, use of biomass can lead to net CO_2 emission reduction if substituted for fossil fuels; the potentials of such substitution and GHG emission reduction in any country would depend on its sustainable biomass production potential (Bhattacharya, Salam, Pham, & Ravindranath, 2003). Hence, it maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels. It is different from fossil fuels as fuels offer high energy density but making use of energy involves burning the fuel, with the oxidation of the carbon to carbon dioxide and the hydrogen to water (vapour). Unless they are captured and stored, these combustion products are usually released to the atmosphere, returning carbon sequestered millions of years ago and thus contributing to increased atmospheric concentrations. Therefore, biomass is a great option in sustainable the environment. Hall and House also has discussed that biomass appears to be the most important as compared to other renewable energy sources in terms of technical and economy feasibility during the next few decades (Hall & House, 1994).

2.4 Dissolution of Biomass

Practically, dissolution of biomass in common solvents is difficult due to the three dimensional network structures of lignin which binds the plant cells together providing mechanical strength to structure. Recently, there are various types of solvents have been used for processing of cellulose. For example in paper making, wood is treated with alkaline solution (Elton, 2006). However, the conventional solvents used for cellulose had problems with volatility as it generates toxic gas and difficulty in recovery for recycle use (Fukaya, Sugimoto, & Ohno, 2006). To avoid that problem, there have been many reports regarding the use of ionic liquids as the green solvent for the dissolution of biomass due to their several advantageous properties. Muhammad et. al has reported their works on dissolution of biomass using three different types of ionic liquids which are 3-(1-methylimidazolium-3-yl) propane-1-sulfonate, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ((PSmim) HSO_4) and 2-hydroxyethanaminium acetate ionic liquid (Muhammad, Man, Khalil, & Elsheikh, 2010).

Ionic liquids for the dissolution of biomass tend to be highly hygroscopic (Brandt (A et al., 2012), which can bring water/moisture into the pretreatment process. Water can also be introduced by moist biomass. Hence, the effect of water on cellulose dissolution is investigated. According to Mazza et. al, increasing water content progressively reduced cellulose solubility. Adding a small amount of water to cellulose solution in [C_1mim]DMP formed cellulose aggregates (Mazza M, Catana D-A, Vaca-Garcia C, & C, 2009). This is consistent with the finding by Swatloski et. al (2002), that cellulose solubility decreased significantlu in some ionic liquids when a small amount of water was present. They argued that this probably was a result of competitive hydrogen bonding (Luo, Cai, & Gu, 2013).

According to their studies, the dissolution of bamboo biomass was done by using 5 wt% solutions of dried biomass. The results showed that only 3-(1-methylimidazolium-3-yl) propane-1-sulfonate ionic liquid has the ability to dissolve biomass completely while in case of (PSmim) HSO_4 ionic liquid, partial dissolution was observed. Other ionic liquid was found ineffective in the dissolution of bamboo biomass.

Apart from that, there is a research study by Wei *et. al*, which employed an IL-water mixture to treat lignocellulosic biomass and its shows a promising results . This is due to the adding of water decreases the viscosity and process cost (Wei, Li, Ma, & Hou, 2012). The materials used in this study are dried IL, 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) and agriculture residue legume straw as the biomass material. The experiments starts with the biomass were sieved and classified and then dried at 105ºC for 2 hours and then pretreated by benzene-alcohol in a Soxhlet extractor before the test (Wei et al., 2012). Based on experimental method by Wei *et. al.,* 1 g legume straw was added into 20 g [C_4mim]Cl-water mixture. The experiments are conducted under ambient pressure (0.1 MPa) in a 50 mL glass vial with a magnetic stir bar. A condenser with an ice-water mixture was connected with the top of the glass vial for condensing the vaporized steam. For a high pressure experiments, it was carried out in a 50 mL sealed Teflon-lined autoclave. A dried N_2 was injected into the reactor from a gas cylinder with aim to obtain a specific system pressure, which could be monitored by a pressure gauge. The reactor was immersed in oil bath under constant stirring (~500 rpm) and maintained the desired temperatures are maintained within ±2ºC for the necessary time. After heating is stopped, the mixture was filtered and separated into the insoluble residue and liquid and then the residue is washed using hot deionized water (60ºC) with vacuum filtration for six times. Then, it was dried at 105ºC for 12 hours and weighed (m_T) (Wei et al., 2012).

2.5 Characterization of Ionic Liquids

According to Fukaya et. al, the chemical structure for a series of ionic liquids prepared was confirmed by ^{1}H-NMR and ^{13}C-NMR and the purity of ionic liquids was estimated (Yukinobu Fukaya, Yoshiki Iizuka, Kenta Sekikawa, & Ohno, 2007). The measurements of ^{1}H-NMR and ^{13}C-NMR spectra were carried out on a JEOL ECX-400. Figure 2.7 shows the equipment of JEOL ECX-400 NMR.

Figure 2.7: JEOL ECX-400 NMR Spectroscopy

2.5.1 Proton (^{1}H) NMR

In ^{1}H-NMR, hydrogen atoms act as little magnets and a hydrogen nucleus can also be aligned with an external magnetic field or opposed to it. The alignment where it is opposed to the field is less stable (at higher energy). It is possible to make it flip from the more stable alignment to the less stable by supplying exactly the right amount of energy as can be seen in Figure 2.8.

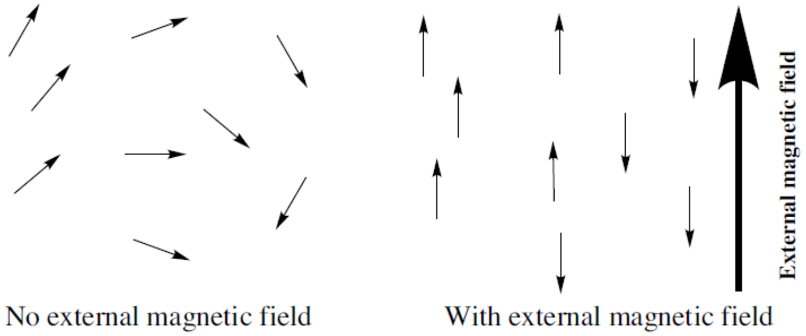


Figure 2.8: Comparison of no external magnetic field and with external magnetic field.

The energy needed to make this flip depends on the strength of the external magnetic field used, but is usually in the range of energies found in radio waves – at frequency of about 60-100 MHz (Kumar Bhaskar & Das, 2007). For real protons, they have other rings around them – especially electrons. Hydrogen atoms' environment is very important as the effect of electrons is to cut down the size of the external magnetic field felt by the hydrogen nucleus. The basic schematic NMR spectrum can be seen in Figure 2.9 below:

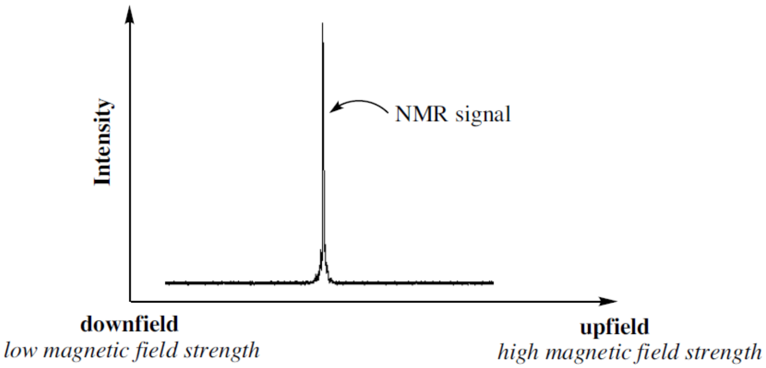


Figure 2.9: Schematic NMR spectrum

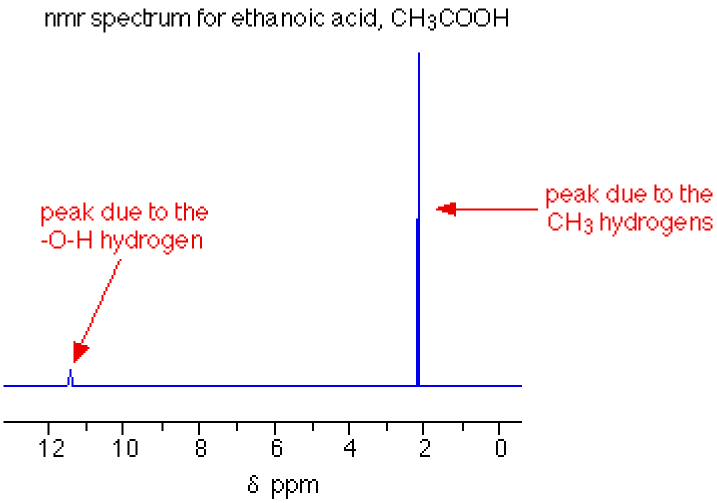


Figure 2.10: Simple NMR spectrum of ethanoic acid adopted from ("Urea and the beginnings of organic chemistry ")

Based on Figure 2.10 which is the NMR spectrum produced from graphs taken from the Spectral Data Base System for Organic Compounds (SDBS) at the National Institute of Materials and Chemical Research in Japan, there are two peaks because there are two different environments for the hydrogens – in the CH_3 group and attached to the oxygen in the COOH group. They are in different places in the spectrum because they need slightly different external magnetic fields to bring them in to resonance at a particular radio frequency. The size of the two peaks gives important information about the numbers of hydrogen atoms in each environment. However, the height of the peaks does not matter but the ratio of the areas under the peaks is important. Based on peaks in Figure 7, the ratio of 3 (for larger peaks) to 1 (for the smaller peak).It shows a ratio of 3:1 in the number of hydrogen atoms in the two environments which is an ethanoic acid, CH_3COOH. Tetramethylsilane (TMS) is really a needed standard for comparison in NMR spectroscopy. The molecular structure of TMS can be seen in Figure 2.11.

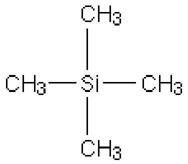


Figure 2.11: Tetramethylsilane, TMS

Zero-point which is at the right-hand end of the scale is where to find a peak due to the hydrogen atoms in TMS. Everything else is compared with TMS. Some NMR spectra show the peak due to TMS (at zero) and others leave it out. Essentially, when analyzing a spectrum which has a peak at zero, it can be ignored because the peak is the TMS peak. TMS is chosen because as standard because;

1) It has 12 hydrogen atoms all of which are in exactly the same environment. They are joined to exactly the same things in exactly the same way which will produce only single peak, but a strong peak because it contains a lot of hydrogen.
2) The electrons in the C-H bonds are closer to the hydrogen atoms in this compound than in almost any other compound. It means that these hydrogen nuclei are the most shielded from the external magnetic field, and therefore the magnetic field must be increase to the greatest amount to bring the hydrogen back into resonance.

The TMS will produce a peak on the spectrum at the extreme right-hand side hence almost any other peaks will produced to the left of the spectrum .As can be seen in Figure 10, the peak at chemical shift 2.0 is downfield of TMS. It means that the hydrogen atoms which caused that peak need a magnetic field two millionths less than the field needed by TMS to produce resonance. The downfield is more towards to the left of chemical shift. The types of group lies on each peak can be determined by using the chemical shift. Figure 2.12 shows the chemical shift of proton NMR which is measured in parts per million-ppm.

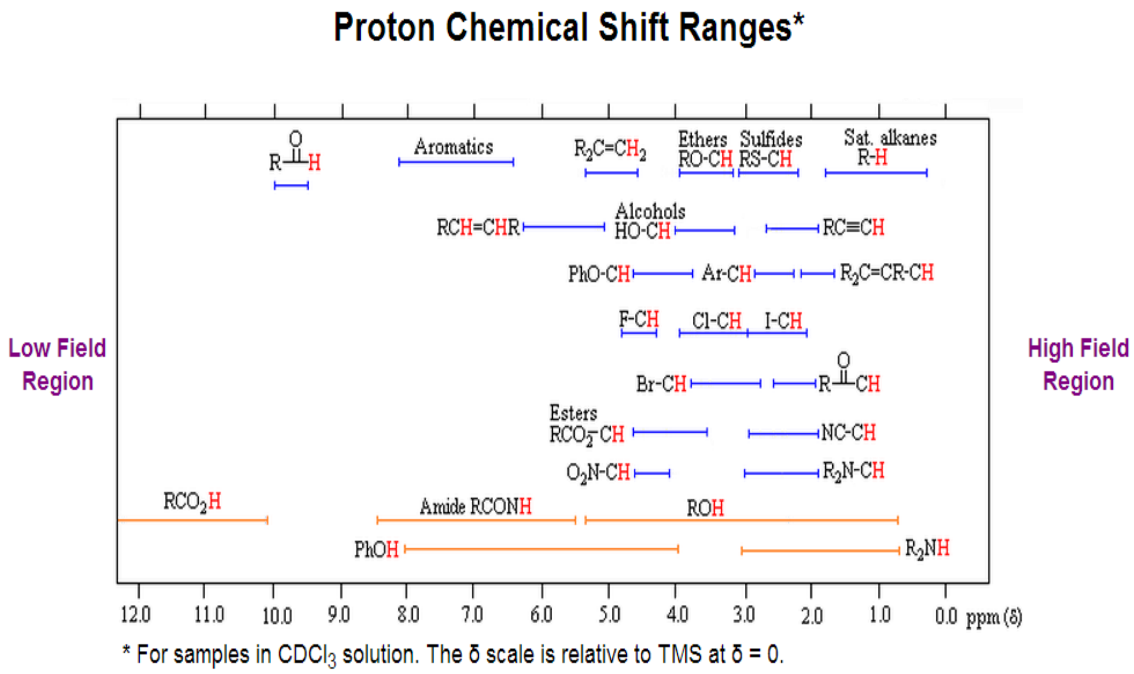


Figure 2.12: Proton chemical shift ranges adopted from Organic Chemistry, Michigan State University

For the solvents used for ^{1}H NMR, tetrachloromethane, CCl_4 is suitable because it does not contain any hydrogen atom hence it will not produce any confusing peaks in the spectrum. A deuterium solvent such as $CDCl_3$ also can be used as solvents instead of $CHCl_3$ because deuterium atoms have sufficiently different magnetic properties from ordinary hydrogen that it will not produce peaks in the area of the spectrum needed (Kumar Bhaskar & Das, 2007).

2.5.2 Carbon-13 (^{13}C) NMR

In carbon-13 NMR spectroscopy, carbon-13 also acts as little magnets. About 1% of all carbon atoms are the C-13 isotope which other than that (apart from tiny amounts of the radioactive C-14) is C-12. C-13 NMR relies on the magnetic properties of the C-13 nuclei. Carbon-13 nuclei fall into a class known as "spin ½" nuclei. The effect of this spin is a C-13 nucleus can behave as a little magnet but C-12 nuclei do not have this property. It can be aligned with an external magnetic field or opposed to it. Again, the alignment where it is opposed to the field is less stable (at a higher energy). It is possible to make it flip from the more stable alignment to the less stable by supplying exactly the right amount of energy (see Figure 2.13).

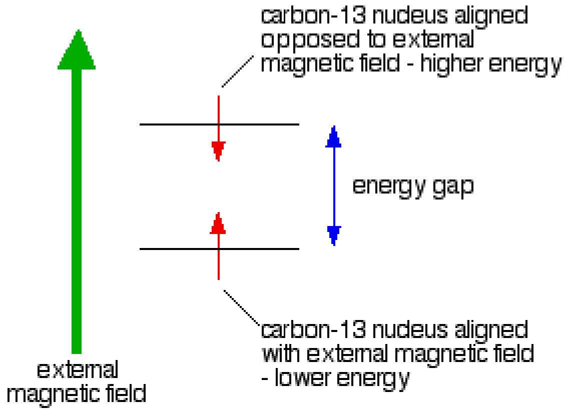


Figure 2.13: Effect of carbon-13 nucleus by external magnetic field adopted from (Chemguide)

The energy needed to make this flip depends on the strength of the external magnetic field used, but it is usually in the range of energies found in radio waves which is at frequencies of about 25-100 MHz. The features of a carbon-13 NMR spectrum can be seen in Figure 2.14. It is a simple example of a carbon-13 NMR spectrum obtained from SDBS at the National Institute of Materials and Chemical Research in Japan.

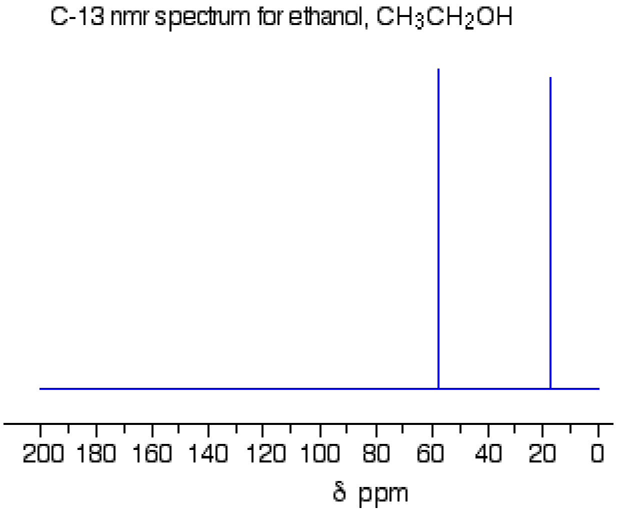


Figure 2.14: Simple example of carbon-13 NMR spectrum for ethanol

Based on Figure 14, there are two peaks because of two different environments for the carbons. The carbon in the CH_2 group is attached to 3 hydrogens and a carbon. The carbon in the CH_2 group is attached to 2 hydrogen, a carbon and an oxygen. The two lines are different in places in the NMR spectrum because they need different external magnetic fields to bring them into resonance at a particular radio frequency. In addition, the carbon-13 NMR is suitable for a more complicated compound such as 1-methylpropanoate (also known as isopropyl propanoate or isopropyl propionate). Figure 2.15 shows the carbon-13 NMR spectrum for the compound.

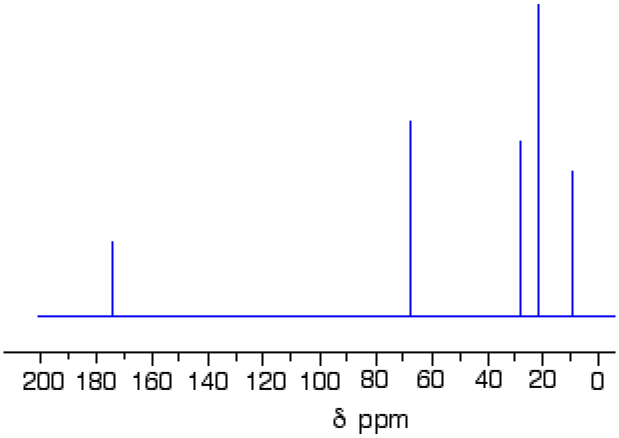


Figure 2.15: Carbon-13 NMR spectrum of 1-methylpropanoate

As can be seen in Figure 2.15, there are five lies in the spectrum which means that there must be 5 different environments for the carbon atoms in the compound.

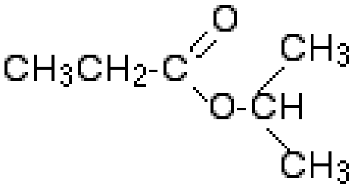


Figure 2.16: Structural formula of 1-methylpropanoate

Based on Figure 2.16, the number of carbon atoms contained in the 1-methylpropanoate is six. However, the lines in the spectrum are only five lines. This is because; two of the carbons are in exactly the same environment. The CH_3 groups on the right hand side of the molecule (see Figure 13) are attached to exactly the same things. However, the CH_3 group on the left is not in the same environment although the group is the same. It is the same with CH_3 on the right which the carbon is attached to 3 hydrogen and another carbon but the similarity is not exact. The carbon in the left-hand CH_3 group is attached to a carbon atom which in turn is attached to a carbon with two oxygens on it and so on down the molecule. It is not exactly the same environment as the carbons in the right-hand CH_3 group as they attached to a carbon which is attached to single oxygen and so on down the molecule. It can be concluded that each line in a carbon-13 NMR spectrum recognizes a carbon atom in one particular environment in the compound. If two or more carbon atoms in a compound have exactly the same environment, they will be represented by a single line (www.chemguide.co.uk). In addition, the peak at about 60 (larger chemical shift) is due to the CH_2 group because it has a more electronegative atom attached. The types of group lies on each peak can be determined by using carbon-13 chemical shift ranges as shown in Figure 2.17 while Table 2.2 shows the typical chemical shifts in carbon-13 NMR spectra.

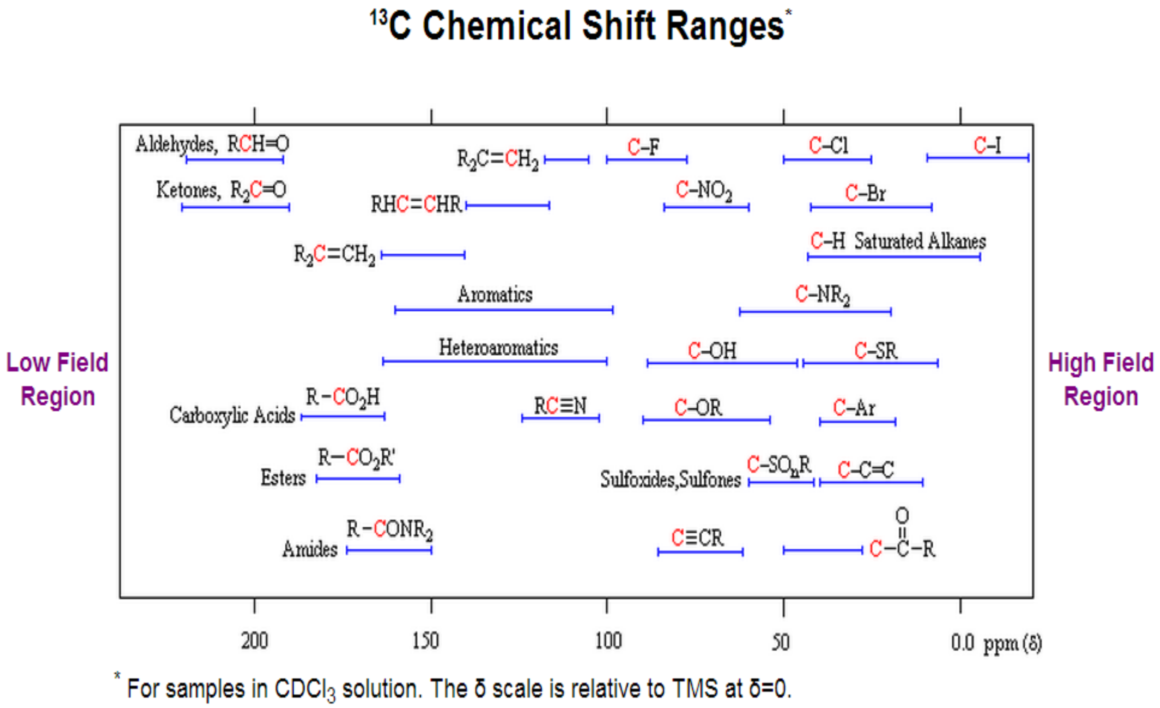


Figure 2.17: Carbon-13 chemical shift ranges

Table 2.2: Typical chemical shifts in C-13 NMR spectra

Carbon environment	Chemical shift (ppm)
C=O (in ketones)	205-220
C=O (in aldehydes)	190-200
C=O (in acids and esters)	170-185
C in aromatic rings	125-150
C=C (in alkanes)	115-140
RCH_2OH	50-65
RCH_2Cl	40-45
RCH_2NH_2	37-45
R_3CH	25-35
CH_3CO^-	20-30
R_2CH_2	16-25
RCH_3	10-15

2.5.3 FTIR and CHNS

Apart from proton and carbon-13 NMR, the characterization of ionic liquids can be done by Fourier Transform Infrared (FTIR) spectroscopy and Elemental Analysis (CHNS). According to Thermo Nicolate Corporation, FTIR can identify unknown materials, determine the quality or consistency of a sample, and it could determine the amount of components in a mixture (Thermo Nicolet, 2001). Figure 2.18 shows the picture of FTIR spectroscopy used in laboratory.

Figure 2.18: FTIR spectroscopy

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. According to Fadeeva et.al., major elements of an organic substance namely carbon, hydrogen and nitrogen are commonly determined using commercially available CHN and CHNS analyzers. Figure 2.19 shows the picture of CHNS analyzers. Currently, both old types of analyzers (Carlo Erba, models 1106 and 1108; Hawlett-Packard, model 185; Perkin Elmer, model 240;etc) and new types (Euro EA 3000; Perkin Elmer 2400, series II; CE 440; Vario EL III; etc.) are used in the practice of organic elemental analysis (V.P. Fadeeva, V.D Tikhova, & Nikulicheva, 2008).

Figure 2.19: CHNS Analyzers

2.6 Determination of physico-chemical properties of synthesized ionic liquids

According to Yukinobu Fukaya et. al., the physico-chemical properties of ionic liquids synthesized are determined by using specific equipments. The amount of water was confirmed by Karl Fischer coulometric titration (Yukinobu Fukaya et al., 2007). The differential scanning calorimetry (DSC) measurement that is used to determine the melting point of synthesized ionic liquids were carried out using DSC at a scanning rate for both heating and cooling of 1ºCmim^{-1} in the temperature range -100ºC to 100ºC. The thermogravimetric analysis (TGA) used for determination of thermal decomposition temperature. Viscosity and density measurement was carried out with Brookfield viscometer.

2.7 Morphological study of pretreated biomass

Mark Davis *et. al*. had used solid-state carbon-13 NMR spectroscopy to study the changes in the cellulose morphology that occur during the enzymatic hydrolysis. The NMR studies have observed increases in the crystallinity of the cellulose and an increase in cellulose as the enzymatic digestion processes (Mark Devis, John Baker, Tauna Rignall, & Himmel). Other than that, researchers from the Oak Ridge National Laboratory of the United States Department of Energy (US-DOE) and the Georgia Institute of Technology (United States) has reported the use of small-angle neutron scattering to probe the structural impact of acid pretreatment on the lignocellulosic structure of switchgrass. This technique is reported to provide new insights into morphological changes of pretreated biomass, in the search for cost-effective pretreatment processes for cellulose-ethanol production ("Probing morphological changes in pretreated lignocellulosic biomass by small-angle neutron scattering ", 2010). Other than that, Ayla Sant Ana da Silva et. al. has discussed the characterization of pretreated materials are by examining the surface morphology at the nanoscopic scale, measuring the specific surface area (SSA), and analyzing the degree of crystallinity (da Silva, Teixeira, Endo, Bon, & Lee, 2013). Figure 2.20 shows the example of surface morphology of sugarcane bagasse.

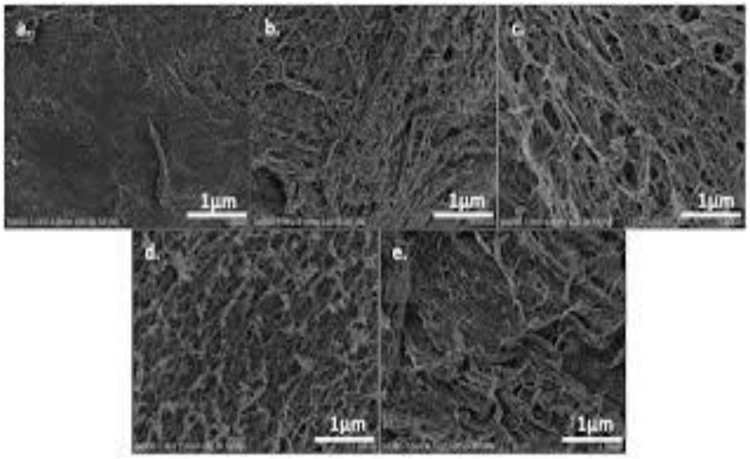


Figure 2.20: Surface morphology of pretreated bagasse adopted from (da Silva et al., 2013)

The morphology of pretreated biomass is studied by using scanning electron microscopy, (SEM). SEM uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample (Goldstein, 2003). Figure 2.21 shows the typical SEM instrument in laboratory.

Figure 2.21: A typical SEM instrument adopted from http://serc.carleton.edu

The SEM is routinely used to generate high resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions such as;

1) Acquiring elemental maps or spot chemical analyses using EDS
2) Discrimination of phases based on mean atomic number (commonly related to relative density) using BSE.

It is also widely used in to identify phases based on qualitative chemical analysis or crystalline structure. Precise measurement of very sall features and objects down to 50 nm in size is also accomplished using the SEM (Zhang, Sun, He, Lu, & Zhang, 2005).

CHAPTER 3

RESEARCH METHODOLOGY

3. RESEARCH METHODOLOGY

3.1 Synthesis of bis-2(ethylhexyl)ammonium Based ILs

3.1.1 Materials and Tools

The list of materials and its price that will be used for the synthesis of bis(2-ethylhexyl)amine functionalized ionic liquids is summarized in Table 3.1 below:

Table 3.1: Materials used in synthesis of bis-2(ethylhexyl)amine based ILs

Chemical	Molecular weight (g/mol)	Price
Bis(2-ethylhexyl)amine	241.46	RM 240.49 per 250 mL
Dimethyl sulfate	126.13	RM 166.20 per 100 mL
Trimethyl phosphate	140.07	RM 160 per 50 g
Triethyl phosphate	182.15	RM 238.50 per 100 mL
Diethyl sulfate	154.18	RM 188 per 100 g
Acetonitrile, CH_3CN	41.05	RM 88.00 per 2.5L
Potassium carbonate, K_2CO_3	138.21	RM 47.00 per kg
Diethyl ether, $C_4H_{10}O$	74.12	RM 80.00 per 2.5L
n-Hexane	86.18	RM 274.85 per 100 mL

The materials are requisited from Petronas Ionic Liquid Centre (PILC) and being supervised by Dr. Lethesh Kallidanthiyil. All chemicals were used as received, without any additional purification step. The Material Safety Data Sheet (MSDS) for each chemical are attached in Appendix 1. The tools and apparatus used in this experiment are;

1) Round bottom flasks
2) Measuring cylinder
3) Measuring pipette
4) Rotary evaporator
5) Oil bath
6) Heating plates / hot plates
7) Magnetic stir bar
8) Filter paper
9) Filter funnel

The equipment that will employ in the process of synthesis and characterization of ionic liquid is included in Table 3.2.

Table 3.2: Equipment used for synthesis of bis-2(ethylhexyl)amine based ILs

Function	Equipment
Melting point, °C	Differential Scanning Calorimetry (DSC)
Water content	Karl-Fischer titration method
Density, kg/m^3	Anton Paar Viscometer
Viscosity	Anton Paar Viscometer
Thermal decomposition temperature	Thermal Gravimetric Analysis (TGA)
Characterization	Nuclear Magnetic Resonance (NMR) spectroscopy, Fourier Transform Infrared (FTIR) Spectroscopy, Elemental Analysis (CHNS)

3.1.2 Experimental procedures

Bis-2(ethylhexyl)ammonium based ionic liquids can be prepared by the quaternization of bis-2(ethylhexyl)amine with two equivalents of different alkylating agents in acetonitrile in the presence of potassium carbonate. The desired anions are dimethyl sulfate, trimethyl phosphate, diethyl sulfate and triethyl phosphate. The molar ratio of bis-2(ethylhexyl)amine and alkylating agents is 1:2 (Wasserscheid & Welton, 2008) and four equivalents of potassium carbonate was used. Table 3.3, 3.4 & 3.5 shows the calculation for each reactant needed in the synthesis of that particular ILs.

Table 3.3: Amount of reactant needed in the synthesis of bis-2(ethylhexyl)amine dimethylsulfate

Component	Molecular weight (g/mol)	Equivalent	Mass (g)	Mole	Density (kg/L)	Volume (mL)
Bis(2-ethylhexyl)amine	241.46	1	2.0	0.00828	0.8	2.5
Dimethyl sulfate	126.13	2	2.1	0.01656	1.33	1.6
Potassium carbonate	138.02	4	4.6	0.03312	-	-
Acetonitrile	41.05	-	-	-	786	25

Table 3.4: Amount of reactant needed in the synthesis of bis-2(ethylhexyl)amine trimethyl phosphate

Component	Molecular weight (g/mol)	Equivalent	Mass (g)	Mole	Density (kg/L)	Volume (mL)
Bis(2-ethylhexyl)amine	241.46	1	2.0	0.00828	0.8	2.5
Trimethyl phosphate	140.08	2	2.3	0.01656	1.197	1.9
Potassium carbonate	138.02	4	4.6	0.03312	-	-
Acetonitrile	41.05	-	-	-	786	25

Table 3.5: Amount of reactant needed in the synthesis of bis-2(ethylhexyl)amine diethyl sulfate

Component	Molecular weight (g/mol)	Equivalent	Mass (g)	Mole	Density (kg/L)	Volume (mL)
Bis(2-ethylhexyl)amine	241.46	1	2.0	0.00828	0.8	2.5
Diethyl sulfate	154.18	2	2.6	0.01656	1.177	2.2
Potassium carbonate	138.02	4	4.6	0.03312	-	-
Acetonitrile	41.05	-	-	-	786	25

The process synthesis started by measuring the amount of reactant needed in the synthesis. To a suspension of potassium carbonate, in acetonitrile, bis-2(ethylhexyl)amine was added followed by alkylating agents. The reaction mixture was then stirred at 800 rpm and heated in oil bath at 80°C under reflux for 48 hours to ensure complete reaction. Figure 3.1 shows the stirring and heating process of ILs syntheys.

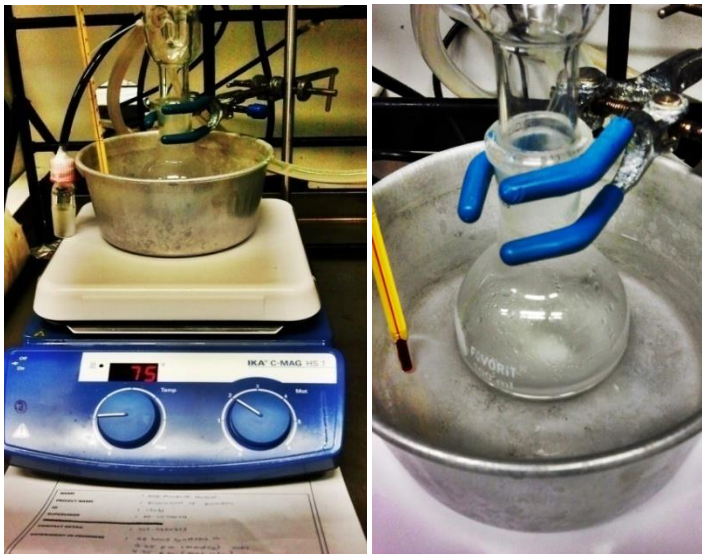


Figure 3.1: Synthesis of ILs

After 48 hours, potassium carbonate was removed by filtration and washed with n-hexane to ensure any solvents are completely removed from the ionic liquids. Figure 3.2 shows the filtering step.

Figure 3.2: Filteration of potassium carbonate from synthesized ILs

The solvent is then removed under rotary evaporator for 2-3 hours under temperature of 60°C and pressure of 350 hPa. Figure 3.3 shows the process of evaporating solvents by using the rotary evaporator.

Figure 3.3: Removing any solvents left in synthesized ILs by using rotary evaporator for 2-3 hours

After that, the liquids are dried for 72 hours by using vacuum line under temperature of 60°C and stirred at 315 rpm. This step was done in order to ensure the complete removal of solvents and water content from the ILs. It is essential to obtain a very dry ionic liquid because it may affect the process of dissolution of biomass.. If the ILs were still containing high amount of water or any other solvents, the biomass dissolution may not give a good result. Figure 3.4 shows the process of drying the ILs by vacuum line.

Figure 3.4: Drying the synthesized ILs by using vacuum line for at least 72 hours

The characterization of synthesized ionic liquids was performed using ^{1}H NMR spectroscopy (Bruker Avance 400 spectrometer, operating at 400 MHz for ^{1}H), FTIR spectroscopy and CHNS elemental analysis. The water content of ionic liquids was determined by a coulometric Karl Fischer titrator. The viscosity and density of the ILs will be measured by Anton Paar Viscometer. The melting point will be measured using DSC and thermal decomposition temperature will measured using Thermal Gravimetric Analysis (TGA).

It is observed that **2-Ethyl-N-(2-ethylhexyl)-N,N-dimenthylhexan-1-aminium methyl sulfate** was obtained as a yellowish viscous liquid. From characterization using the NMR and FTIR, the IL produced as expected and hence could be used for dissolution of biomass. Therefore, it could be synthesized at a larger scale. Calculation for each reactant required to synthesis the ILs at the larger scale is tabulated in Table 3.6 below:

Table 3.6: Amount of reactant needed in the synthesis of bis-2(ethylhexyl)amine dimethylsulfate

Component	Molecular weight (g/mol)	Equivalent	Mass (g)	Mole	Density (kg/L)	Volume (mL)
Bis(2-ethylhexyl)amine	241.46	1	10.00	0.0414	0.8	12.5
Trimethyl phosphate	126.13	2	10.45	0.0828	1.33	7.86
Potassium chloride	138.02	4	23.0	0.1656	-	-
Acetonitrile	41.05	-	-	-	786	55

However, the synthesis of bis-2(ethylhexyl)amine with trimethyl phosphate in acetonitrile shows a very unusual liquid. Hence, the process of synthesizing the IL was changed to a solvent free ionic liquid. The bis-2(ethylhexyl)amine was quaternized by the reaction with one equivalents of trimethyl phosphate. The reaction was carried out in solvent free condition without acetonitrile and the potassium carbonate. The reaction mixture is left under reflux for 48 hours with a stirring speed of 850 rpm. After 48 hours, the liquid is washed with n-hexane to ensure the removal of unreacted starting materials and the ILs further dried in vacuum line for 72 hours.

3.2 Dissolution of biomass using bis-2(ethylhexyl)amine based ILs

3.2.1 Materials

The materials used for dissolution of cellulose are micro crystalline cellulose and synthesized bis-2(ethylhexyl)ammonium based ionic liquids.

3.2.2 Experimental Procedures

The following experimental procedure will adopt for the biomass dissolution studies. Macro crystalline cellulose will be select for the dissolution studies. Suspensions of biomass (1,2,3,4,5 wt. %) in dried ionic liquids will prepare under dry nitrogen gas atmosphere. The mixtures will heat from 25 ^{0}C to 100 ^{0}C in 5 ^{0}C increments under nitrogen gas in a temperature controlled oil bath, and will stir for 30 (or 60) min at each temperature. The lowest temperature to give a clear solution will record as the dissolution temperature. The dissolved biomass can be precipitated from the ionic liquids by adding water/acetone mixture and can be recovered by filtration. The morphology of the pretreated biomass will study using scanning electron microscope (SEM). The alteration in the crystal structure of the pretreated biomass will be studied using XRD. Figure 3.5 shows the summary of the experimental procedures adopted in the synthesis of ILs and dissolution of biomass in this study.

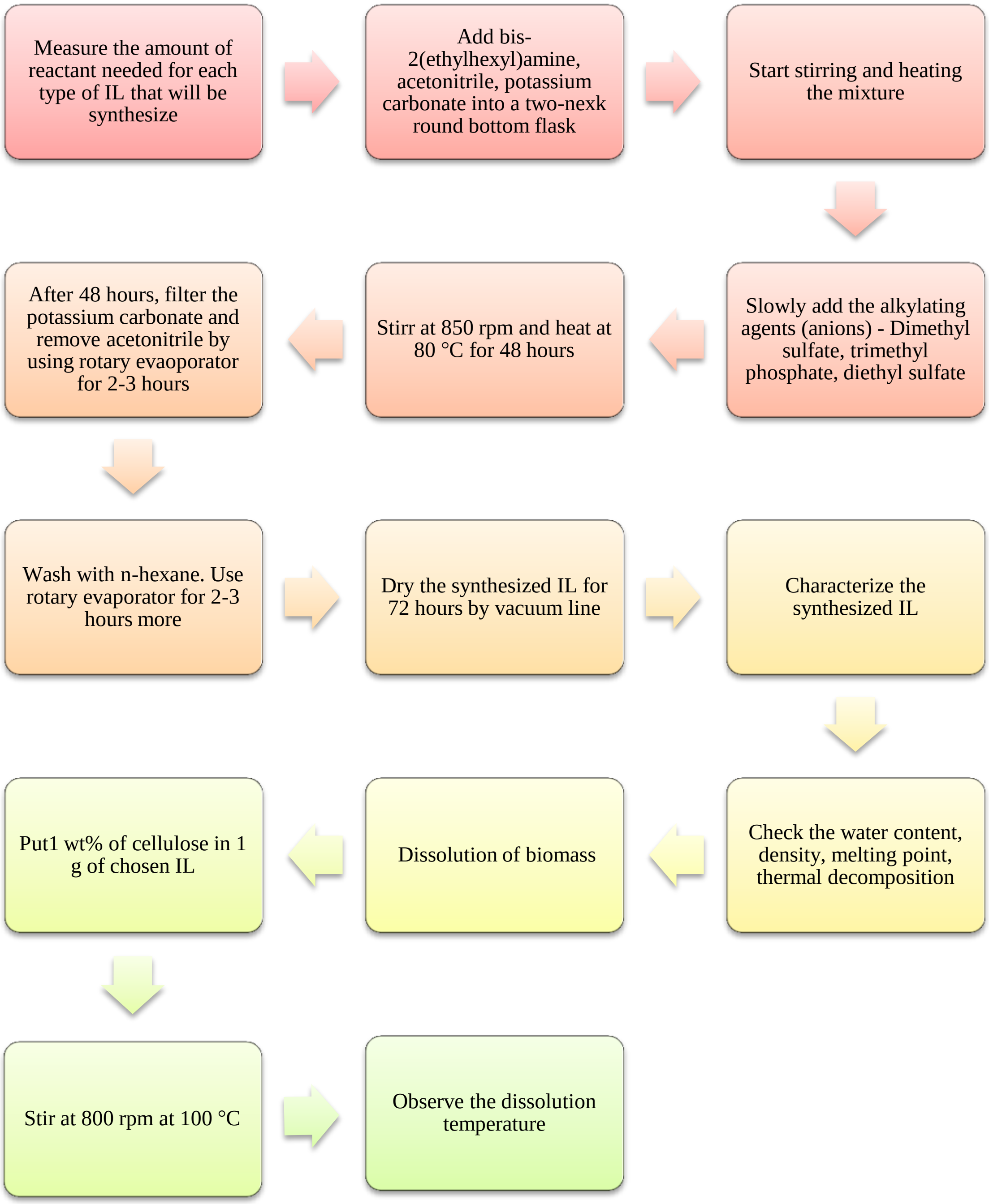
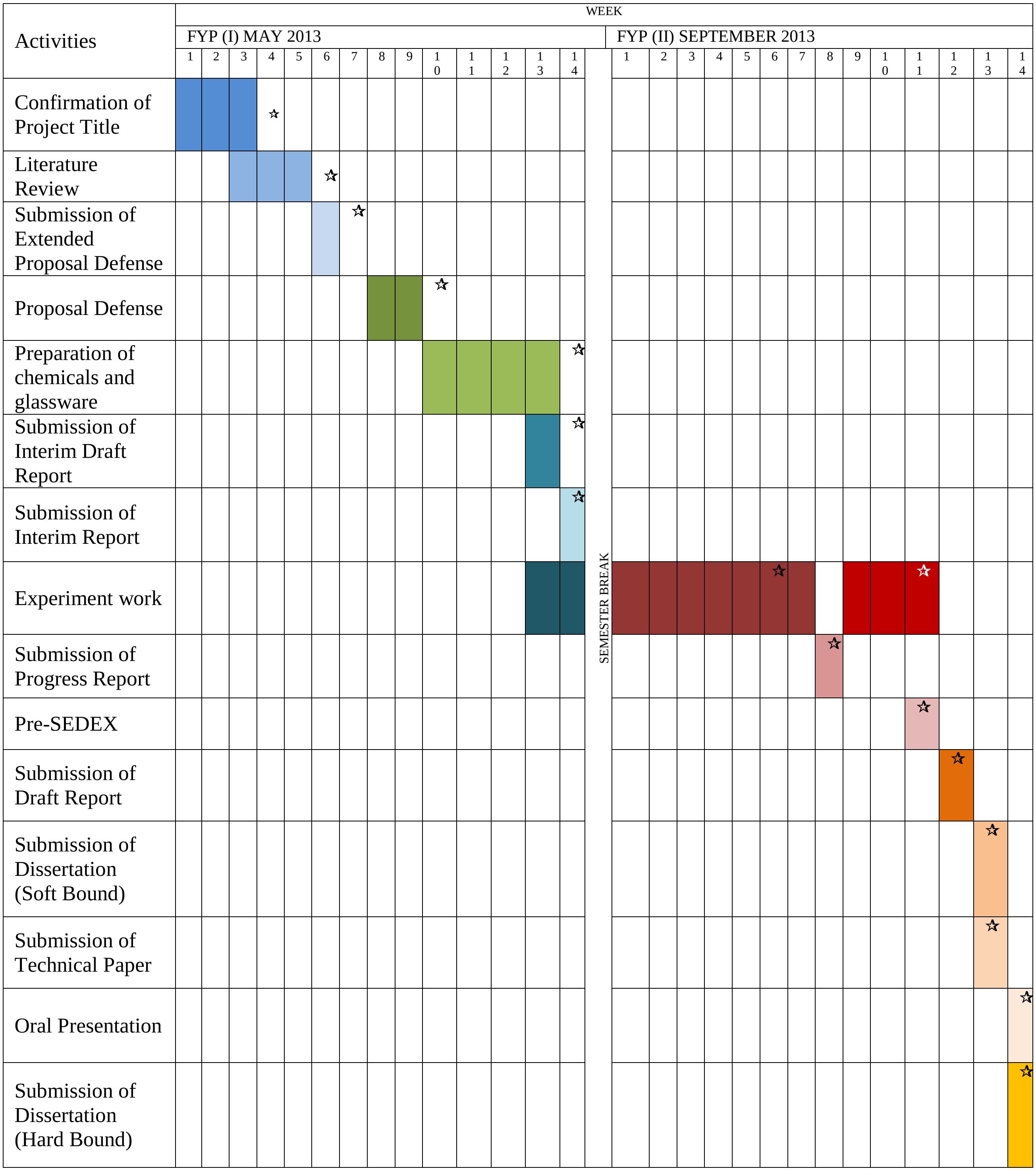


Figure 3.5: Summary of experimental procedures

3.3 Gantt Chart and Key Milestones



Activities	WEEK																												
	FYP (I) MAY 2013															FYP (II) SEPTEMBER 2013													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Confirmation of Project Title	■	■	■	☆											SEMESTER BREAK														
Literature Review			■	■	■	☆																							
Submission of Extended Proposal Defense						■	☆																						
Proposal Defense								■	■	☆																			
Preparation of chemicals and glassware										■	■	■	■	☆															
Submission of Interim Draft Report													■	☆															
Submission of Interim Report														■☆															
Experiment work													■	■		■	■	■	■	■	■☆	■		■	■	■☆			
Submission of Progress Report																							■☆						
Pre-SEDEX																										■☆			
Submission of Draft Report																											■☆		
Submission of Dissertation (Soft Bound)																												■☆	
Submission of Technical Paper																												■☆	
Oral Presentation																													■☆
Submission of Dissertation (Hard Bound)																													■☆

☆Indicates the task is done

CHAPTER 4

RESULTS & DISCUSSION

4. RESULTS AND DISCUSSION

4.1 Variety of the Synthesized IL

The chemical structures of the cation and anions used in this study are listed in Figure 4.1 and 4.2. Precisely, only one cation is used which is 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium. Dimethyl sulfate, triemethyl phosphate, diethyl sulfate, triethyl phosphate is chosen as the alkylating agents for the anions.

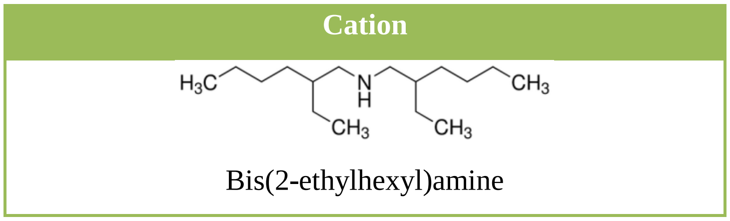


Figure 4.1: Cation of synthesized ILs

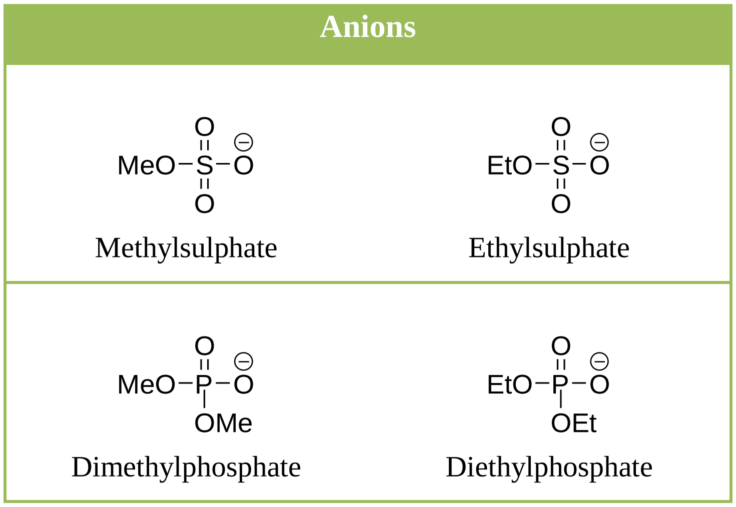


Figure 4.2: Anions of synthesized ILs

As for now, three types of ionic liquids had been synthesized which is bis-2(ethylhexyl)ammonium with dimethyl sulfate, diethyl sulfate and trimethyl phosphate. Table 4.1 shows the observation for each ionic liquid after the synthesis.

Table 4.1: Observation for each ionic liquid after synthesis

Ionic liquid	Observation
2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate 	- IL produced is pale-yellow viscous liquid. - Have light odor.
2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium dimethyl phosphate (solvent-free) 	- Brownish viscous liquid. - Stronger odor than 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate
2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulfate 	- IL produced is orange-brown liquid. - The most viscous liquid compared to others. - After evaporating the solvents contained in the liquid with rotary evaporator, the liquid solidified but after few hours, it turns to viscous liquid again. 

Based on the characterization, only bis-2(ethylhexyl)ammonium with dimethyl sulfate have been synthesized according to the Figure 4.3.

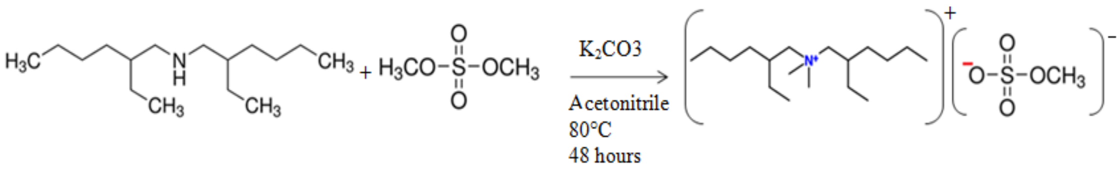


Figure 4.3: Reaction of bis-2(ethylhexyl)amine cation and dimethyl sulfate anion

Initially, the inexpensive secondary amine bis-2(ethylhexyl)ammonium was quaternized by the reaction with two equivalents of dimethyl sulfate. The reaction was carried out in acetonitrile in the presence of potassium carbonate. Acetonitrile is used as the solvents to ensure the purity of the ionic liquid (Donata, Marida, & Migen, 2004). After 48 hours of heating under reflux, complete conversion of the starting amine was achieved. Potassium salts were removed by filtration and solvent removed under vaccum. 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate was obtained as a pale yellow liquid in a very good yield. Figure 4.4 shows the first attempt of IL synthesis while Figure 4.5 shows the second attempt to synthesize the 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methylsulphate ionic liquid.

Figure 4.4: First attempt of 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate

Figure 4.5: Second attempt of 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate ionic liquid

It is observed that the second 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methylsulphate ionic liquid have higher purity compared to the first attempt IL. This is due to the steps taken while synthesizing the IL. However, there is no difference in the molecular structure of the IL formed. Only the colour of the IL was affected. The product was characterized by ^{1}H NMR (Bruker Avance 400 MHz) and FTIR analysis. Figure 4.6 shows the ^{1}H NMR spectrum for the IL.

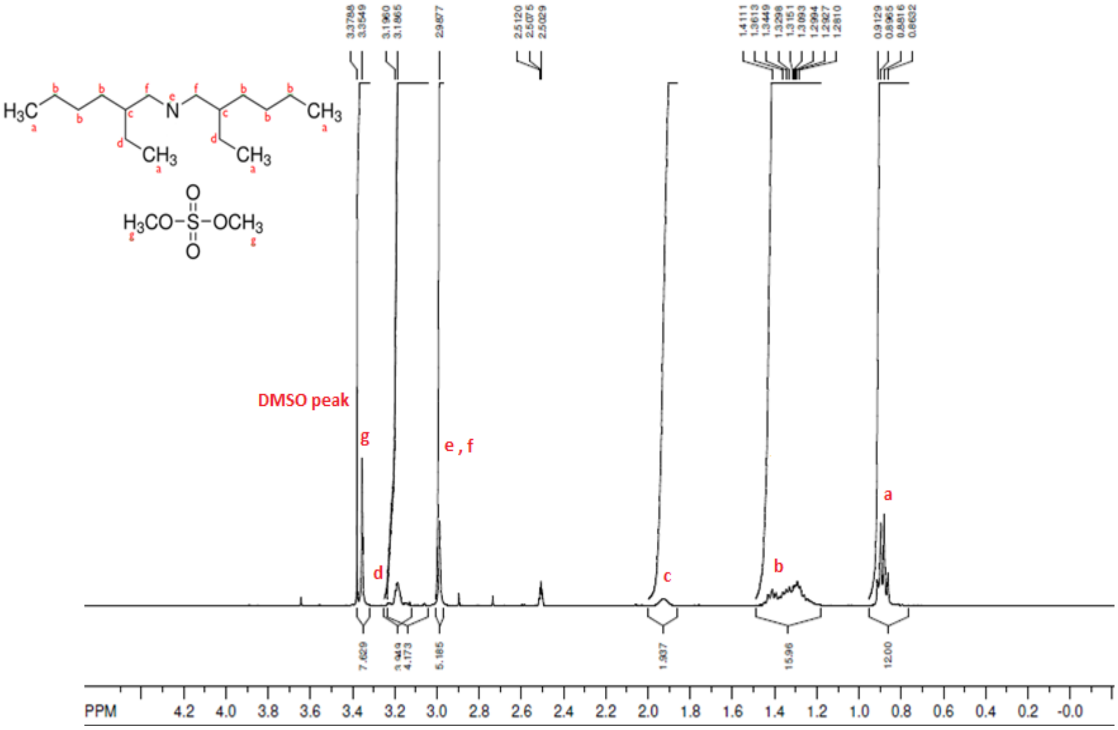


Figure 4.6:^{1}H NMR spectrum for bis-2(ethylhexyl)amine sulfate IL

Based on Figure 4.6, there are 7 peaks that was correspond to the 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate IL. Peaks (a), (b), (c), (d) and (e) refers to the cation and f refers to the sulphate peak. The peak (g) is referred to the solvent peak. Table 4.2 shows the summary of the peaks in the spectrum.

Table 4.2: Summary of number of protons at each peak for bis-2(ethylhexyl)amine sulfate IL

Peak (s)	Molecular structure	Number of protons	Chemical shift (ppm)	Integrated value
a	R-CH$_3$	12	0.9	12.00
b	R-CH$_2$-R	16	1.2-1.4	15.96
c	R$_3$-CH	2	1.9	1.937
d	R-CH$_2$-R	4	3.2	3.049
e	N-CH$_3$	4	3.0	5.185
f,g	Sulphate anion	3	3.4	3.000

The other characterization of bis-2(ethylhexyl)amine sulfate is by FTIR. Figure 4.7 shows the spectrum.

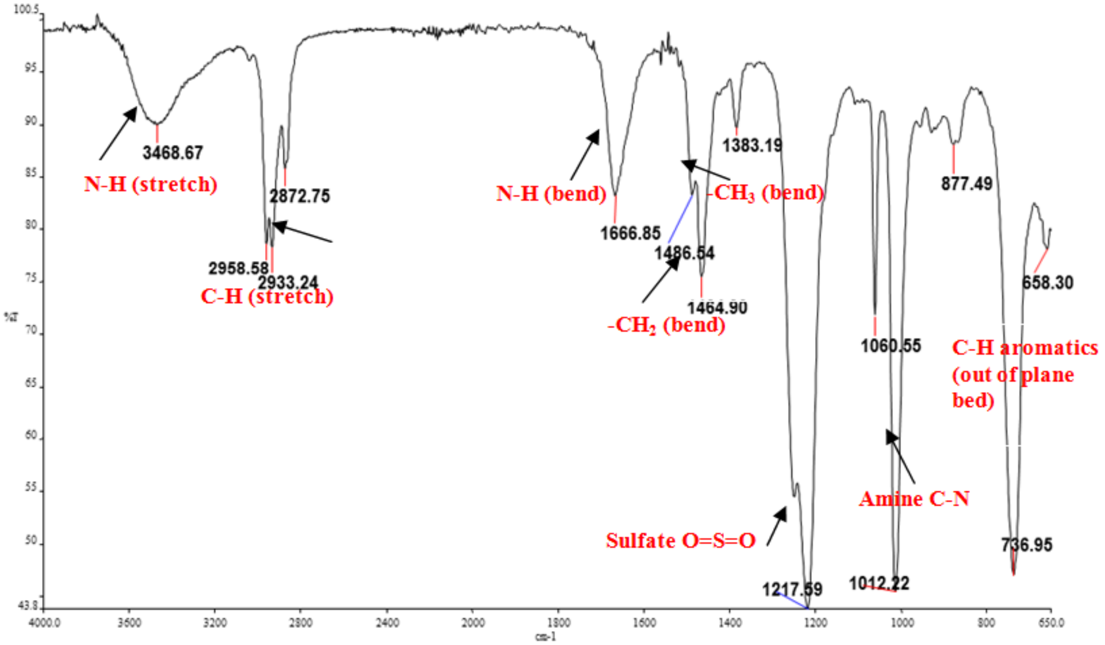


Figure 4.7: FTIR spectrum for bis-2(ethylhexyl)amine sulfate

An infrared spectrometer determines the positions and relative sizes of all the absorptions, or peaks, in the infrared region and plots them. This plot of absorption intensity versus wavenumber/wavelength is referred to as the infrared spectrum of the compound as can be seen in Figure 31. The spectrum exhibits at least 3 strongly absorbing peaks at 1217.59 cm^{-1}, 1012.22 cm^{-1}, and 736.95 cm^{-1} for the sulfates (S=O), amine (C-N) and C-H aromatics (out of plane bed) respectively. The summary of each peak are tabulated in Table 4.3:

Table 4.3: Summary of each peak from the FTIR spectrum for the bis-2(ethylhexyl)amine sulfate IL.

Peak	Wavelength (cm^{-1})	Remarks
N-H_2 (stretch)	3468.67	Represents stretch in primary amide. Bending occurs around 3350 and 3180 cm^{-1}. Peak shifting results in a higher wavelength value.
C-H (stretch)	2933.24	*sp*^{3}C-H absorption always occur at frequencies less than 3000 cm^{-1}
N-H (bend)	1666.85	Bending occurs at this wavelength for primary amide (-NH_2) and secondary amide (-NH).
-CH_3 (bend)	1486.54	Methyl groups have a characteristic absorption
-CH_2 (bend)	1464.90	Methylene groups have a characteristic bending absorption
Sulfate O=S=O	1217.59	Strong absorption to the sulfate group is quite in tense. In addition to the characteristic position of absorption, the shape and intensity of this peak are also unique to O=S=O bond.
Amine, C-N (stretch)	1012.22	C-N stretch occurs in the range 1350-1000 cm^{-1}
C-H aromatics	736.95	This C-H bond is out of plane bed which the frequency ranges from 900-690 cm^{-1}

Based on the absorption of each component from the spectrum, it is clearly seen that bis-2(ethylhexyl)amine sulfate is successfully synthesized according to the scheme. Although FTIR might not gives quantification result, but it still gives proves that the IL is completely reacted according to our expected scheme of reaction. Other than the bis-2(ethylhexyl)amine sulfate ionic liquid, there are also attempts to introduce alkyl groups other than methyl group such as trimethyl phosphate and diethyl sulfate. Bis-2(ethylhexyl)amine is expected to react with trimethyl sulfate via reaction scheme in Figure 4.8.

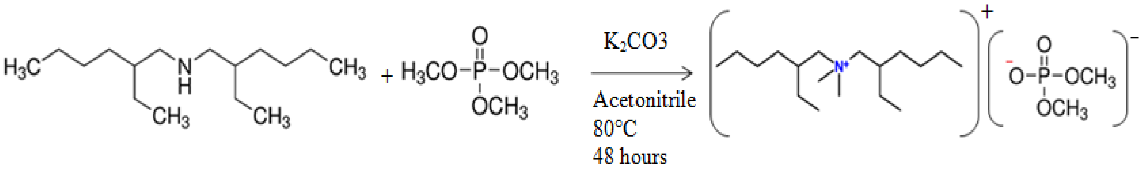


Figure 4.8: Reaction of bis-2(ethylhexyl)amine cation with trimethyl phosphate anion

The first synthesis attempt is the quarternization of bis-2(ethykhexyl)amine with trimethyl phosphate in acetonitrile at 80°C. However, the reaction was not successful. It may be due to the less reactivity of trimethylphosphate compared to the dimethylsulphate. Hence, it is decided to change the method to solvent-free condition in a higher temperature.

Initially, the inexpensive secondary amine bis-2(ethylhexyl)amine was treated with one equivalent of trimethyl phosphate. The reaction was carried out in solvent free condition. After 48 hours of heating under reflux which is at 100°C, a viscous brownish liquid was obtained in low yield. After drying the liquid in vacuum for 72 hours, the product was characterized by ^{1}H NMR (Bruker Avance 400 MHz) and FTIR analysis. Figure 4.9 shows the ^{1}H NMR spectrum for the IL.

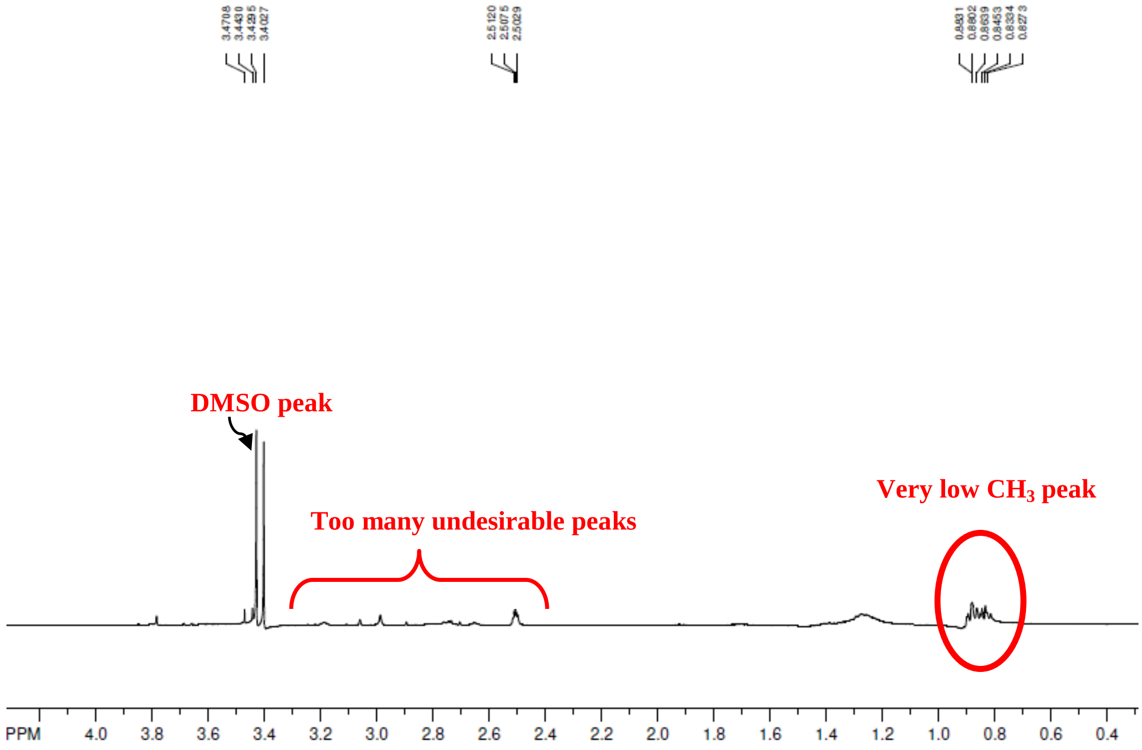


Figure 4.9: ^{1}H NM\R spectrum of bis-2(ethylhexyl)amine with trimethyl phosphate

As can be seen from Figure 4.9, the 1H NMR spectrum is not corresponds to the expected product. Majority of the peaks were not corresponds to any proton in the compound of bis-2(ethylhexyl)amine and trimethylphosphate. The FTIR spectrum in Figure 4.10 also shows a similar trend which is not favorable to the reaction scheme of bis-2(ethylhexyl)amine and trimethyl phosphate.

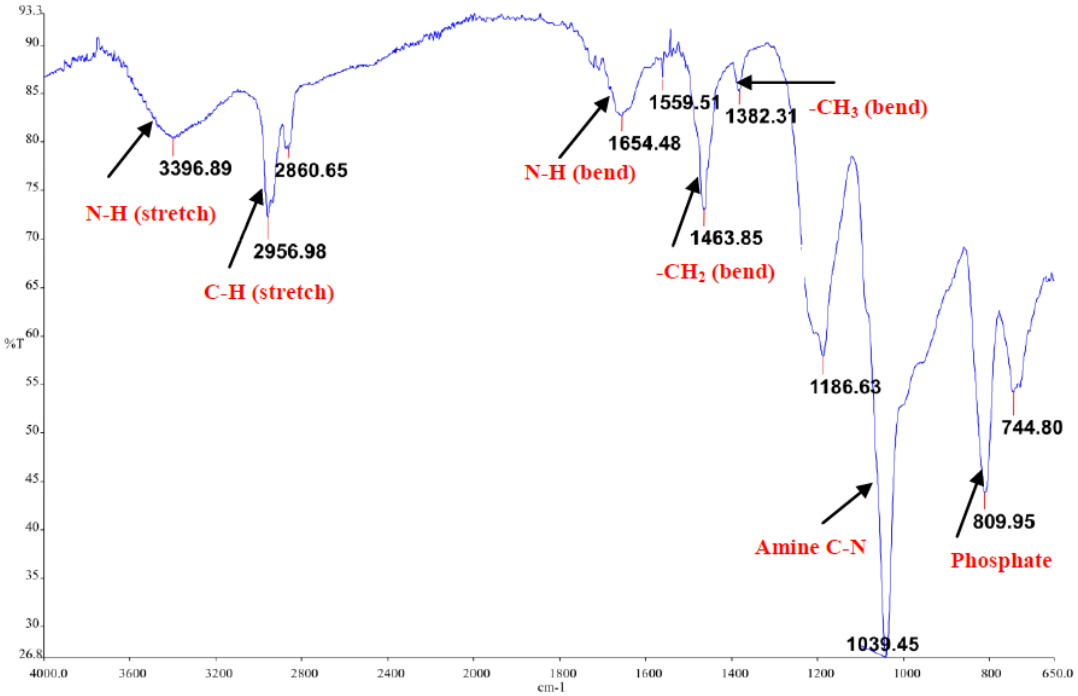


Figure 4.10: FTIR spectrum for bis-2(ethylhexyl)amine trimethyl phosphate

From the FTIR (Figure 4.10) and ^{1}H NMR spectrum (Figure 4.9), it can be concluded that the quarternization of bis-2(ethylhexyl)amine and trimethylphosphate is not possible at the given set of conditions. This may be because of lower temperature. Apart from dimethyl sulfate and trimethyl phosphate as the alkylating agent in the synthesis of ILs, diethyl sulfate was also used for the quaternization reaction. Figure 4.11 shows the reaction scheme expected for the bis-2(ethylhexyl)amine with diethyl sulfate.

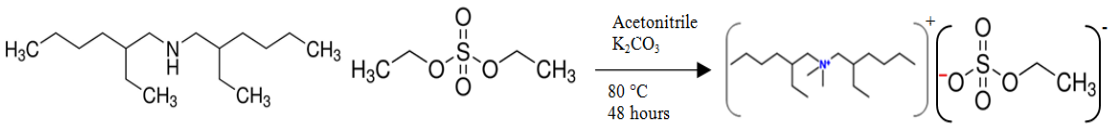


Figure 4.11:Reaction of bis-2(ethylhexyl)amine cation with diethyl sulfate anion

However, the reaction of bis-2(ethylhexyl)amine and diethyl sulfate produced a very unusual liquid. The liquid was orange colour and it was solidified after evaporating with rotary evaporator. Figure 4.12 shows the liquid formed after the synthesis.

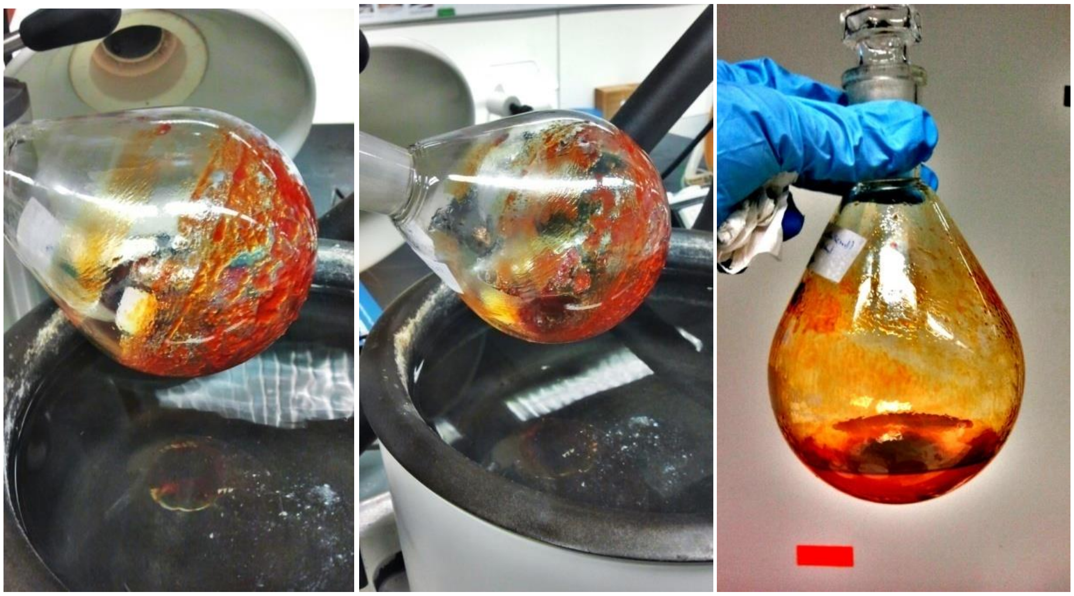


Figure 4.12: Bis-2(ethylhexyl)amine diethyl sulfate

This attempt was also not successful, because of the steric hindrance due to presence of ethyl group in the 2-position of the bis-2(ethylhexyl)amine.

4.2 Dissolution of Cellulose

The only IL synthesized for the time being is 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate. Water content was checked prior to dissolution of cellulose because high water content in the ILs will adversely affect the dissolution of cellulose. The water content was checked by using Karl Fischer titration method and the result shows 3000 ppm. Cellulose was used instead of original biomass due to the unavailability of dried biomass for the time being. Furthermore, the structure of cellulose is far simpler than the original biomass such as bamboo biomass. So the dissolution would be easier by cellulose.

The dissolution of biomass is started by weighing of 1 wt% of cellulose in 1 g of ionic liquid. Prior to the dissolution reaction, the cellulose was dried in the vacuum oven to remove any moisture. High water content in the dissolution reaction will affect the solubility of cellulose in the ionic liquid. The sample container containing the IL and cellulose is then put in oil bath at 100°C and stirred at 850 rpm for 3 hours. However, after 3 hours, the cellulose was not dissolved. Figure 4.13 shows the undissolved cellulose in the IL after 3 hours.

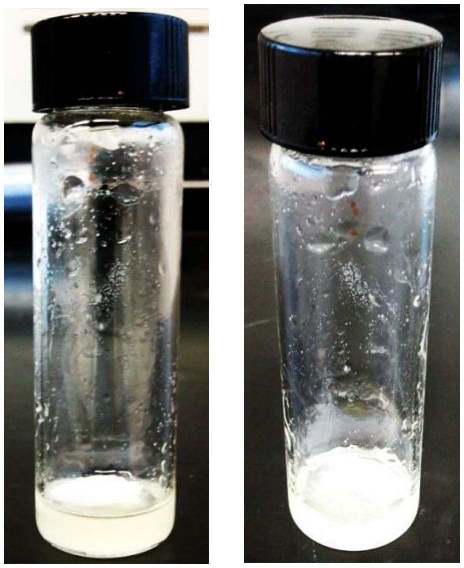


Figure 4.13: Cellulose does not dissolve after 3 hours

According to the literature reviewed, the cellulose could be dissolve in 2 hours time. Since the cellulose still did not dissolve in the IL after 3 hours, it could be assumed that the water content of the IL was still high. The water content must be reduced to lower than 1000 ppm to enhance the dissolution process. However, the reaction was proceeded to see when the cellulose will starts to dissolve. The process was continued for 48 hours more at similar condition (100 °C and 850 rpm). Unfortunately, the cellulose still not dissolved. Then, the process was continued until 7 days. After 7 days, the color of IL starts to change to brownish and the cellulose starts to dissolve. Figure 4.14 shows the IL contains only some amount of cellulose left undissolved.

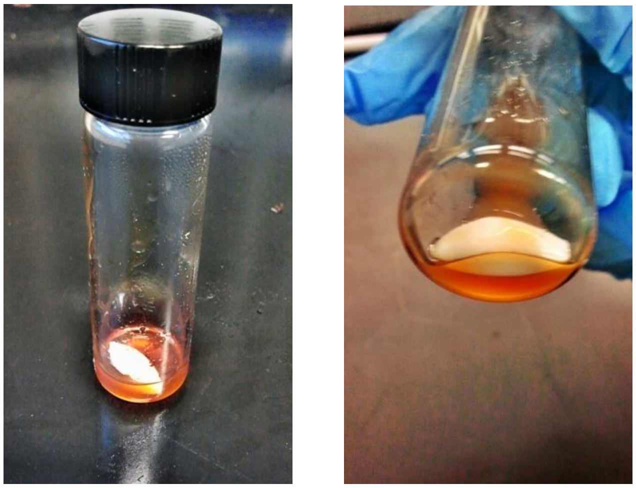


Figure 4.14: Cellulose starts to dissolve after 7 days

After 2 weeks' time, the cellulose was completely dissolved. Figure 4.15 shows the ionic liquid with no more cellulose left undissolved.

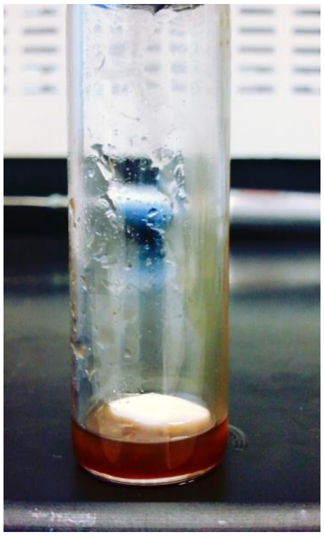


Figure 4.15: Cellulose completely dissolved after 14 days

The solubility of cellulose was depends on the effectiveness of ionic liquid to effectively break the extensive network of intra- and intermolecular hydrogen bonds in cellulose, thus allowing cellulose dissolution in the ionic liquid. If the ionic liquid contains high amount of water, competitive hydrogen bonding of water with cellulose was likely to blame for the impairment. This effect also means that water can be used to precipitate cellulose from ionic liquids.

The choose of anions really affected the biomass dissolution. Good hydrogen bond acceptors are the main key point in effective biomass dissolution. The cellulose solubility increased nearly linearly with the anion's hydrogen-bonding accepting ability. In this case, methyl sulfate anion in the ionic liquid used likely to be a good hydrogen bond acceptor. Not only the anion properties, the pretreatment temperature also had a major impact on cellulose solubility in the ionic liquid. Hence, a higher temperature must be employed in the pretreatment process such as at 120 °C – 160 °C for 3-12 hours. In addition, ionic liquids containing anions that are high basicity seems to be very effective in the biomass dissolution. The dimethyl sulfate anion had a higher basicity as compared to trimethyl phosphate anion. It is expected the bis-2(ethylhexyl)amine sulfate would be a good ionic liquid for biomass dissolution

CHAPTER 5

RECOMMENDATIONS & FUTURE WORK

5. RECOMMENDATIONS AND FUTURE WORKS

Based on experimental works that had been done for the past few weeks, there are few recommendations needed for future work.

5.1 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate IL

For 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate ionic liquid, there are few recommendations to ensure the IL produced is pure and effective for the dissolution of biomass.

1) Ensure that dimethyl sulfate was added slowly after bis-2(ethylhexyl)amine, acetonitrile and potassium carbonate are added. This step could affect the colour and purity of the IL formed.
2) Wash the synthesized IL with n-hexane for few times and put under rotary evaporator for minimum of 2-3 hours. This step is to ensure the ionic liquid is pure from any unreacted starting materials and water.
3) Dry the ionic liquid until the water content is below than 50 ppm to ensure the effectiveness in biomass dissolution.

5.2 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium dimethylphosphate Ionic Liquid

For 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium dimethylphosphate ionic liquid, it is suggested to;

1) Optimize the temperature during the synthesis. Use higher temperature such as 100°C, 120°C and so on because the longer chain in trimethyl phosphate may need a higher temperature to break down the bond.
2) Optimize the duration of the synthesis. A longer time (72 hours or more) could be favorable for this type of ionic liquid.
3) Solvent-free ionic liquid.

5.3 Reaction Process in Synthesizing the Ionic Liquids

In order to extend the variety of these ionic liquids studied, it is suggested to synthesis the ionic liquids based on studies conducted by Wasserschied et. al. They have developed a very elegant way to obtain long-chain alkyl sulfates that were previously either not accessible or difficult to synthesize. The two step synthesis is based on a quaternization step with dialkyl sulfate as alkylating agent (like the one we have studied now), followed by a transesterification reaction of the alkyl sulfate anion. The scheme of the reactions can be seen in Figure 5.1 below.

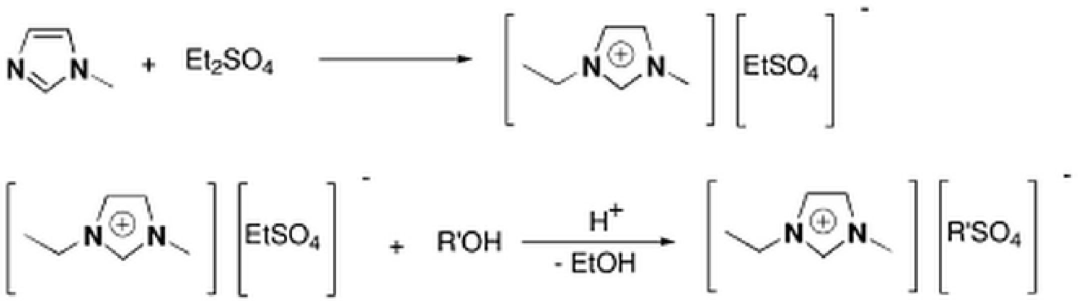


Figure 5.1: Two step synthesis of [EMIM][R'SO4] ionic liquid by a quaternization/transesterification sequence

In the first step amine is alkylated, e.g. with diethylsulfate. This is followed by transesterification step where a long chain alcohol and an acidic catalyst such as methanesulfonic acid are added to the intermediate obtained after quaternization. In order to shift the equilibrium of this reaction to the products, ethanol liberated in the transformation must be efficiently removed by applying mild vacuum. Figure 5.2 shows some of the alcohols converted in this manner.

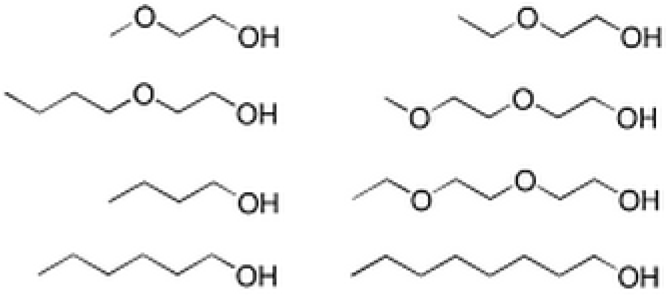


Figure 5.2: Alcohols applied in the transesterification of [EMIM]

According to Wasserschied, all the modified alkyl sulfate ionic liquids obtained with these alcohols show attractively low viscosities and their melting points were all below 0°C. Thus, this synthesis sequence created a new class halogen-free ionic liquid with attractive physicochemical properties. No organic solvent is needed in the whole reaction sequence. Moreover, the reaction sequence is very atom-efficient with ethanol being the only by-product. Last but not least, these ionic liquids does not contain any halide impurities, as the whole synthesis is halogen-free which makes these products highly suitable for a wide variety of technical applications (Wasserscheid & Welton, 2008).

However, our studies are still in the first phase which is to synthesis the new novel of bis(2-ethylhexyl)amine based ionic liquids. Since only two types of ILs had been synthesized, the next task is to synthesis two more types of ILs which is bis(2-ethylhexyl)amine diethyl sulfate and bis(2-ethylhexyl)amine triethyl phosphate. After the characterization of ILs could be done, we will move into the second phase of the experiments which is dissolution of cellulose. In this phase, the morphology of the soluble cellulose will be studies and hence, the efficiency of dissolution of cellulose using the synthesized ILs will determine the best ILs for application. For the time being, dissolution of biomass could be proceed with the synthesized ILs bis(2-ethylhexyl)amine dimethyl sulfate and bis(2-ethylhexyl)amine trimethyl phosphate.

5.4 Dissolution of Biomass

Recommendations for the biomass dissolution are listed as below;

1) Use a higher temperature such as 120 °C and above at 1000 rpm. Observe the dissolution in 2-3 hours interval.
2) Optimize the amount of ionic liquid in 1 wt% of cellulose. For example, 1 wt% of cellulose in 2,3,4 and 5 grams of ionic liquid.
3) Ensure the IL used is very dry with the amount of water content less than 50 ppm.

5.5 Future Works

For continuity of project purposes, there are few work in progress and future works to be done;

1) In progress – Synthesize the 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methylsulfate at larger scale. Previous synthesized bis-2(ethylhexyl)amine sulfate IL was not enough for biomass dissolution. After that, determine the physico-chemical properties of the IL such as water content, density, thermal decomposition temperature, melting point and viscosity.
2) Synthesize a solvent-free 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium dimethylphosphate at different temperature (100°C -120°C) for more than 72 hours.
3) Synthesis other type of ionic liquid. Try for other types of alkylating agents such as triethyl phosphate.
4) For dissolution of biomass, continue working on 2,3,4,5 wt% cellulose in 1 gram of IL. If the cellulose does not dissolve, add 1 more gram ionic liquid and leave for reaction for 48 hours.
5) After dissolution, biomass recovery process must be done and recycle the ionic liquid. Study the morphology of the treated cellulose by using SEM and XRD.

CHAPTER 6

CONCLUSION

The main targets of this study are to synthesize and characterization of the novel bis-2(ethylhexyl)ammonium based ionic liquids. Three types of anions had been promoted with bis-2(ethylhexyl)amine cation which is methyl sulfate, dimethyl phosphate and methyl sulfate. 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate shows a promising result as an ionic liquid but bis-2(ethylhexyl)amine with trimethyl phosphate and bis-2(ethylhexyl)amine diethyl sulfate is not working as expected reaction scheme. The characterization from ^{1}H NMR and FTIR proves the 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate is an ionic liquid while the other two liquids were not ionic liquids.

Moreover, this study is aimed to explore the potential of synthesized ionic liquids for the dissolution of cellulose. 2-Ethyl-N-(2-ethylhexyl)-N,N-dimethylhexan-1-aminium methyl sulphate was the only ionic liquid used for cellulose dissolution. Experimental works had shown that cellulose was completely dissolved after 14 days of reaction. This long period taken to dissolve is probably because of high water content in the synthesized IL. Therefore, the ionic liquid need to be dried more before continues to cellulose dissolution.

There are some recommendations for future works for ILs synthesis. Firstly, temperature optimization for synthesis of solvent-free bis-2(ethylhexyl)amine with trimethyl phosphate. Secondly, the ionic liquid synthesized must be dried until the water content is less than 50 ppm prior to cellulose dissolution. Thirdly, determine the physic-chemical properties for the synthesized IL such as density, viscosity, thermal decomposition temperature and melting point. Last but not least, new methods in synthesizing the IL is proposed for future work which is to add transesterifications steps after quaternization reactions. This synthesis sequence created a new class halogen-free ionic liquid with attractive physicochemical properties. Therefore, all objectives had been successfully achieved although parts of them are still in progress for future work.

APPENDICES

Appendix 1: MSDS of bis-2(ethylhexyl)amine

Appendix 2: MSDS of dimethyl sulfate

Appendix 3: MSDS of trimethyl phosphate

Appendix 4: MSDS of diethyl sulfate

Appendix 4: MSDS of n-hexane

Appendix 5: MSDS of acetonitrile

Appendix 6: MSDS of potassium carbonate

Appendix 7: Proton NMR spectrum for bis-2(ethylhexyl)amine sulfate – DMS 1

Appendix 8: Proton NMR spectrum for bis-2(ethylhexyl)amine trimethyl phosphate – TMP 1

Appendix 9: FTIR spectrum for bis-2(ethylhexyl)amine sulfate – DMS 1

Appendix 10: FTIR spectrum for bis-2(ethylhexyl)amine trimethyl phosphate – TMP 1

Appendix 11: Differences of FTIR spectrum between DMS 1 and TMP 1

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