Nitrile Functionalised Imidazolium Based Ionic Liquids for Carbon Dioxide Removal

by

Muhammad Fauzi Bin Khamis

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2011

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Nitrile Functionalised Imidazolium Based Ionic Liquids for Carbon Dioxide Removal

by

Muhammad Fauzi bin Khamis

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

AP Dr. Cecilia Devi Wilfred
Project Supervisor

AP DR CECILIA DEVI WILFRED
Senior Lecturer
Chemical Engineering Department
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2011

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.

Muhammad Fauzi bin Khamis

ABSTRACT

The purpose of this project is to provide an overview of the author's Final Year Project. Current technology in separation of carbon dioxide from natural gas such as absorption, adsorption, membrane, refrigeration and cryogenic require relatively large facilities, a large investment, complex mechanical work and the possibility of having a negative impact on the environment *(Litynski, 2011).* Separation with ionic liquids is proposed as a solution to some of the advantages of conventional methods.

A common characteristic of ionic liquids is in viscous liquid phase at room temperature. High viscosity means less carbon dioxide (CO_2) move ability in the respective ionic liquids. A less viscous ionic liquids will have better CO_2 move ability and thus increase the amount of CO_2 absorb.

A study is planned to produce novel ionic liquids that have low viscosity in order to improve CO_2 move ability. This study will synthesize a range of ionic liquids by manipulating cation used. Cations used in this study have different alkyl chain length with nitrile functionality. Then the best **ionic liquids for CO_2 removal** can be analyze and evaluate.

ACKNOWLEDGEMENTS

Firstly, my utmost gratitude to Allah the All-Mighty for his uncountable graces upon me and for the successful completion of this project in due course of time.

I would like to express the inmost appreciation to my supervisor, AP Dr. Cecilia Devi Wilfred, Senior Lecturer of Chemical Engineering Department, UTP. The supervision and continuous support that she gave truly help me throughout completing this project. Her constant guidance, helpful comments and suggestions has helped me not only to complete but also to enhance the expected results of the project. Her kindness, valuable advice, friendly approach and patience will always be appreciated.

Special thanks to PETRONAS Ionic Liquids Centre for their co-operation in this project by providing the equipments and assistance during experimentation. This project would not have been possible without the invaluable help provided.

Lastly, great appreciation to my friends, who were a constant source of support during my work. To all UTP lecturers, students and staff and to all whose their names are not mentioned here but they provided help directly or indirectly.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF GRAPH

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Carbon dioxide (CO_2) is undesired diluents that are present in many natural gas and other gas sources. The removal of CO_2 is a common separation process in natural gas processing and is often required to improve the fuel quality (heating value) of the natural gas. Also, CO_2 in the presence of water can be a corrosive agent to metal pipes. As a consequence, the removal of CO_2 to acceptable specifications is required prior to transport natural gas or in pipelines. In the natural gas processing industry, various technologies have been employed for CO_2 removal including chemical solvents, physical solvents, and membranes. By far, chemical solvents that reversibly react with CO_2 are most commonly used for CO_2 removal. Commonly used chemical solvents comprise of amine solutions. Commercial amine solutions useable for this purpose include monoethanolamine (MEA), N-methyldiethanolamine (MDEA), and diethanolamine (DEA). *(Chinn, Daniel et al., 2009)*

An ionic liquids (ILs) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100°C (212°F) or even at room temperature (room temperature ionic liquids, RTIL's). While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ILs is largely made of ions and short-lived ion pairs. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. It is proving to be increasingly promising as a viable media for not only 'green' synthesis and separations operations, but also for novel applications. Their insignificant vapor pressures, reduces environmental pollution and highly reduces working exposure hazards in comparison with the conventional organic solvents currently being used in the industry. Ionic liquids have unique property set that can provide new options based upon different chemical and physical properties. The properties of ionic liquids can be tailored by varying the cation and anion pairing. One of the common techniques to produce a new ionic liquids is by manipulating the attaching functional groups. The produced ILs will become functionalized ILs.

As for now, two ionic liquids base, which are the methylimidazolium and pyridinium ions have proven to be good starting points for the development of ionic liquids. Even currently, pyridinium ions based ionic liquids are widely used in the industry.

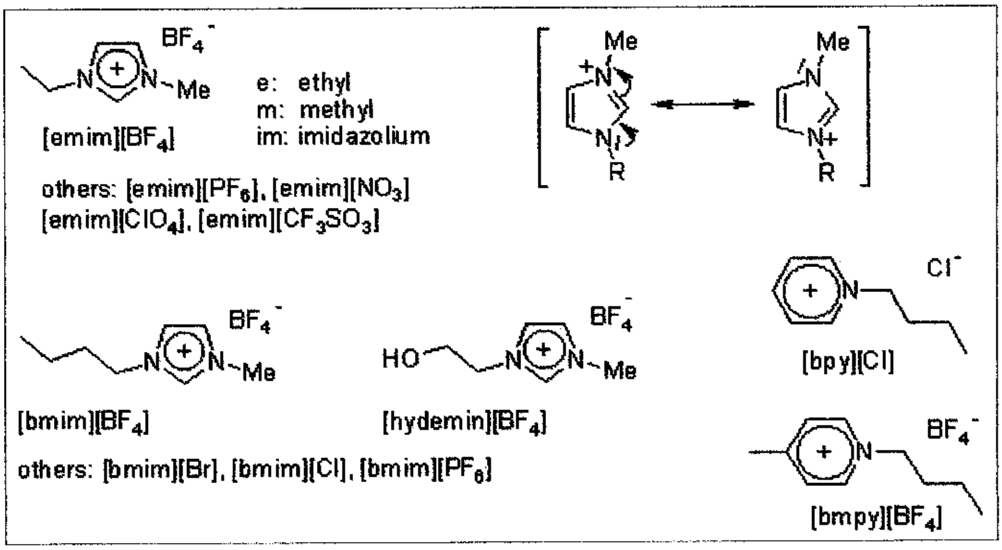


Figure 1: Example of methylimidazolium and pyridinium ions structure

Properties, such as melting point, viscosity, and solubility of starting materials and other solvents, are determined by the substituent on the organic component and by the counter ion. Many ionic liquids have even been developed for specific synthetic problems. For this reason, ionic liquids have been termed "designer solvents". *(P. Wasserscheid et al, 2002).*

ILs have an extremely low vapor pressure, have excellent solvent power for organic and inorganic compounds, are nonflammable, and are easily modified structurally to get desired physical properties. Recently, ILs has attracted much attention due to these unique properties.

Other than that ILs also has large liquidus range and nonflammability, high solvation capacity, negligible vapor pressures, compatibility with strong alkaline solutes, high thermal stability, effective media for Heck and Suzuki reactions, stabilizing effect on palladium catalysts, and low cost. Previous researchers have focused their study on the solubility of alkanes and alkenes, alcohols, carbon monoxide, methane, or oxygen in ILs but few have reported solubility of carbon dioxide in the ILs. *(Pedro J. Coutinho, et al, 2005)*

Imidazolium and phosphonium-based ILs have similar solubility for several gases. Phosphonium-based ionic liquids and the most familiar imidazolium-based ionic liquids have same magnitude of gas solubility. Imidazolium-based ionic liquids and phosphonium-based ionic liquids have similar Henry's law constants for carbon dioxide (CO_2) solubility. The solubility increases as the number of solute carbons increases and when the number of carbon double bonds increases for the hydrocarbon solutes with the same number of carbons for both imidazolium-based room temperature ionic liquids (RTILs) and phosphonium-based RTILs *(Ferguson and Scovazzo, 2007).*

1.2 Problem Statement

Natural gas extracted from plant contains high carbon dioxide. However, the natural gas demands from most industries require clean and pure natural gas. Therefore, separation of carbon dioxide from natural gas is needed to meet this requirement. The technologies available in market for natural gas treating may not be ideally suitable for treating highly contaminated natural gas.

As for now, chemical solvents that reversibly react with CO_2 are most commonly used for CO_2 removal. For example, chemical solvents that comprise of amine solutions such as monoethanolamine (MEA), N-methyldiethanolamine (MDEA), and diethanolamine (DEA). This technique is proven to be an effective CO_2 separation process. The amine solution (amine and water) circulate in a loop between two key steps, which are absorption of CO_2 and regeneration of solvent. Unfortunately, amine treating presents several issues and challenges as stated below *(Chinn, Daniel et al., 2009).*

1. Intensive energy required during the regeneration step to break the chemical bonds between the absorbed CO_2 and solvent.
2. Energy is also required to generate steam within the amine regenerator to strip the CO_2 from the solvent.
3. Corrosivity of the amine. Amines can rapidly corrode low alloy steel such as carbon steel. CO_2 loading capacity is limited by concentration (or dilutes) of the amine solution.
4. Degradation of amine. Amines react with CO_2 (and H_2S, COS, etc) to form various different products that are not reversible in the regeneration step. Amine also degrades thermally.

All the limitations mentioned provide opportunity for new research to find alternative solvent for CO_2 removal process which is ILs. Many researchers have wisely tried to use ILs to enhance carbon dioxide solubility. ILs is a good CO_2 absorber because gas solubility is driven by physical absorption mechanism.

Imidazolium-based ionic liquids with fluorinated anions such as the bis(trifluoromethylsulfonyl)imide, bis(pentafluoroethyl)trifluorophosphate, NTf_2, and pFAP, are the ones with the highest CO_2 solubilities. *(M. Muldoon et al, 2007)*

In the recent past, the amount of experimental and theoretical work on ionic liquids has increased considerably. Current research shows that ionic liquids for CO_2 removal have high viscosity which leads to low CO_2 move ability. A lot of researches were done in manipulating the anion to produce ILs that have low viscosity and high CO_2 solubility. *(Abobakr et al, 2010)*

Very few researches are done on different cation. In order to explore new area of ILs, this research will focus on cation manipulation by manipulating alkyl chain length of functionalized group to synthesize novel ionic liquids that has low viscosity but high CO_2 move ability. This new ionic liquids will use methylimidazolium ions as base.

1.3 Objective and Scope of the project

1.3.1 *Main Objective*

The objectives of this study are:

1. To synthesis a range of new ionic liquids that has low viscosity by manipulating alkyl chain length with nitrile functionality (cation manipulation) in order to improve CO_2 absorption for CO_2 removal.
2. To investigate the characterization of chemical and physical properties of the novel ionic liquids.
3. To perform experimental analysis on the study of CO_2 solubility on novel ionic liquids synthesized.

1.3.2 *Scope of Project*

This study will cover the following:

1. Ionic liquids synthesis
    - Producing a range of new ILs solvent that has low viscosity and high CO_2 move ability for CO_2 absorption.
2. Ionic liquids characterization
    - Every new ionic liquids need to go through characterization to determine chemical and physical properties of the ILs solvents.
3. Experimental analysis
    - Conducting actual experiment on ILs synthesised to obtain the CO_2 removal capacity of the new ILs. The new experimental data for the solubility of CO_2 gas in novel ILs synthesized are taken at temperature 298 K and pressures ranging from 5 to 25 bar. Henry's constant of CO_2 in novel ILs synthesized is determined. The solubility of CO_2 gas in novel ILs synthesized is determined based on the mole fraction between the number of moles of CO_2 gas absorbed in novel ILs synthesized and the number of moles novel ILs synthesized used in this experiment.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide

Carbon dioxide (CO_2) is a naturally occurring chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It appears as a gas at standard temperature and pressure. CO_2 is a non-toxic and non-flammable fluid. It has a high chemical stability as it has a very low energy level compared to other carbon compounds.

Natural gas that is transported in pipelines can only contain 2 % of CO_2, yet comes out of the ground with higher levels of the gas, requiring separation process. Thus it is vital to have better technique and solvents that can remove CO_2 more effective and efficiently. *(University of Texas, 2007)*

2.2 Ionic Liquids

Ionic liquids (ILs) is a category of compounds which are made up entirely of ions and are liquid at or below process temperatures. Often salts which are composed entirely of ions are solids with high melting points, for example, above 450 °C. These solids are commonly known as 'molten salts' when heated to above their melting points. Ionic liquids differ from 'molten salts', in that they have low melting points, for example, from −100 °C to 200 °C. They tend to be liquid over a very wide temperature range, with a liquid range of up to about 500 °C or higher. Ionic liquids are generally non-volatile, with effectively no vapor pressure. Many are air and water stable, and can be good solvents for a wide variety of inorganic, organic, and polymeric materials. *(P. Wasserscheid et al, 2002)*

2.2.1 *Room Temperature Ionic Liquids (RTILs)*

Room Temperature Ionic Liquids (RTILs) have unique physico-chemical properties. These properties make them suitable for numerous task-specific applications in which conventional solvents are non-applicable or insufficiently effective. Such properties include:

1. High thermal stability,
2. High electrical conductivity,
3. Large electrochemical window,
4. Low nucleophilicity and capability of providing weekly coordinating or non-coordinating environment,
5. Very good solvents properties for a wide variety of organic, inorganic and organometallic compounds: in some cases, the solubility of certain solutes in RTILs can be several orders of magnitude higher than that in traditional solvents.

Some studies indicated that, although not 100% inert, certain ionic liquids incorporating 1,3-dialkyl imidazolium cations are generally more resistant than traditional solvents under certain harsh process conditions, such as those occurring in oxidation, photolysis and radiation processes.

2.2.2 *Ionic Liquids Properties*

- Density

For the property of density, it depends on the bulkiness of an ionic liquids. If the bulkiness increases, the densities of the comparable ionic liquids are also increase.

- Colour

The colour of less pure ionic liquids generally ranges from yellowish to orange. The colour of ionic liquids is affected by the material used as a start, or also excessive heating during the formation of imidazolium salt. A number of precautions for synthesis of colorless ionic liquids have been described, and a procedure for removal of color from impure ionic liquids using acidic alumina and activated charcoal has also been proposed.

- Thermal Stability

While the thermal decomposition point of neat ionic liquids varies depending on the anion, thermogravimetric analysis (TGA) indicated dynamic thermal stability in excess of 250°C for most imidazolium-based ionic liquids. The TGA data reported are often not fully indicative since it shows only a dynamic property of the ionic liquids where the ionic liquids is heated for short period of time. *(Bonhote et al, 1996)*

- Viscosity

Much more related property which is viscosity of ionic liquids, it depends on the tendency of hydrogen bonding formation and also the strength of the Van der Waals interaction. Viscosity varies from the range of 200 cP to 3000 cP. Viscosity measurement indicates that ionic liquids become less viscous with increase of water content.

- Composition Of Ionic Liquids

The properties of ionic liquids can be tailored by varying the cation and anion pairing. The form of the cation in the ionic liquids absorbent is not thought to be as critical as the anion in the present invention. However cations have been found to be particularly useful in the process of the present invention including 1-butyl-3-methylimidazolium (bmim) and 1-hexyl-3-methylimidazolium (hmim). Ionic liquids useful in the method and process of the present invention are also quite chemically stable. Losses of the ionic liquids through degradation to form byproducts are also minimal. In a preferred embodiment of the process and method of the present invention virtually all of the ionic liquids can be recycled and reused. *(Cesar Cadena at el, 2004)*

To make an ionic liquids, researchers can select from dozens of small anions, such as hexafluorophosphate ($[PF_6]^-$) and tetrafluoroborate ($[BF_4]^-$), and hundreds of thousands of large cations, such as 1-hexyl-3-methylimidazolium or 1-butyl-3-methylimidazolium. Ionic liquids are thus *"designer solvents"*. Chemists are free to pick and choose among the ions to make a liquid that suits a particular need, such as dissolving certain chemicals in a reaction or extracting specific molecules from a solution.

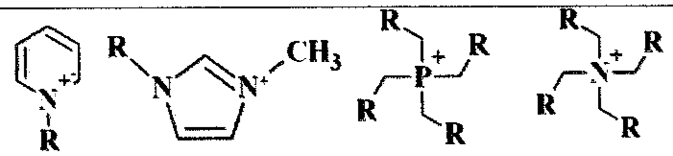
Most commonly used cations:	 **N-alkyl-pyridinium** **1-alkyl-3-methyl imidazolium** **Tetraalkyl-phosphonium** **Tetraalkyl-ammonium**
Some possible anions:	**Water immiscible** → **Water miscible** $[PF_6^-]$ $[BF_4^-]$ $[CH_3CO_2^-]$ $[N(SO_2CF_3)_2^-]$ $[CF_3SO_3^-]$ $[CF_3SO_2^-]$ $[BR_1R_2R_3R_4^-]$ $[NO_3^-]$, $[Cl^-]$
Most common alkyl chains:	**Ethyl, Butyl, Hexyl, Octyl, Decyl**

Figure 2: Example of cation and anion

2.2.3 *Carbon Dioxide Solubility in Imidazolium Based ionic Liquids*

Imidazolium-based ILs are readily prepared, and are now becoming commercially available. A number of investigations have shown that CO_2 is remarkably soluble in imidazolium-based ionic liquids. The major factor controlling CO_2 solubility in this class of ionic liquids is the nature of the anion. The results suggest that the association of CO_2 with the anion is the best indicator of CO_2 solubility in alkylimidazolium-based ILs. Changes in the imidazolium cation involving alkyl groups are expected to have relatively little influence on CO_2 solubility. Both the simulations and the experiments indicate that the molar density of ionic liquids increases significantly with the addition of 10 mol % CO_2, because there is almost no volume expansion when the CO_2 is added. This is in contrast to conventional solvents that show a very small molar density increase because the solvent expands when CO_2 is added. Consistent with this finding, the cation-anion radial distribution functions change very little upon addition of CO_2 into the system. That is, the underlying fluid structure of the IL is relatively unperturbed by the addition of CO_2, due to the strong Coulombic interactions responsible for the organization of the liquid. *(Cesar Cadena at el, 2004)*

2.2.4 *Ionic Liquids Synthesis*

To synthesis ILs is relatively easy, but a lot of substantial investments in determination of physical and chemical properties need to be done in order to determine its usefulness as a solvent. The synthesis of ionic liquids can generally be split into two sections:

- Quaternization reaction: Formation of the desired cation
- Anion exchange: Two types of anion exchange which are metathesis and acid-base neutralization reaction.

In some cases only the first step is required, as with the formation of ethylammonium nitrate. In many cases the desired cation is commercially available at reasonable cost, most commonly as a halide salt, thus requiring only the anion exchange reaction without quaternization step. *(P. Wasserscheid et al, 2002)*

2.2.4.1 Quaternization

As mentioned in the previous section, in ionic liquids synthesis there are two steps which are quaternization reaction and anion exchange reaction. However, some ionic liquids need to go through another step, alkylation. It is an intermediate step before can proceed with quaternization reaction.

R = butyl, hexyl, octyl, decyl
X = Br, Cl

Figure 3: General quaternization reaction diagram

2.2.4.2 *Metathesis*

When not possible to form desired anion directly, anion exchange step is necessary. From quaternization process, the ILs will undergo anion exchange where X^- exchanges with another anion. For example, anion dioctylsulfosuccinate (DOSS) will exchange with X^- and a new ionic liquids is formed. Different type of ionic liquids can be obtained by varying the R group and anion X-.

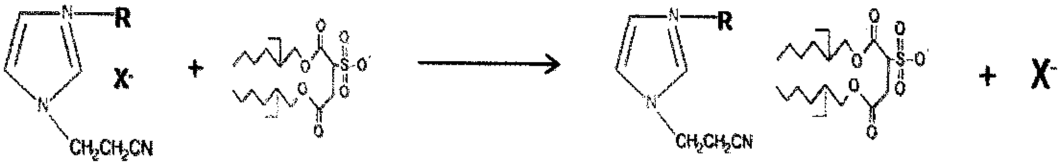


Figure 4: General metathesis reaction diagram

2.2.5 *Alkyl Chain Length of Functionalised Group*

The structural, chemical and physical properties of ILs could be modified by altering the combination of cations and anions; furthermore, the functional groups and alkyl chain length have a prominent influence on the properties. Thus manipulation of alkyl chain length in the functionalized group will effect on the viscosity and solubility of CO_2. (*Abobakr K. Ziyada et al., 2011)*

For the cations, there were two factors that influenced the CO_2 solubility. The biggest effect was seen in increasing alkyl chain length on the cation. For a given cation, the CO_2 solubility increased with increasing chain length, and these results are consistent with those reported elsewhere. It was thought that this may be due to entropic reasons, as the density of ILs decreases with increasing alkyl chain length; therefore, there may be more free volume within the longer chain ILs. *(Mark J. Muldoon et al., 2007)*

The physical properties such as density and viscosity are essential for the design of process equipment. The lower density of these ILs might be due to the presence of a long alkyl chain compared to the other nitrile-functionalized ILs. The relation is that longer alkyl chain length results in lower density and thus higher CO_2 solubility. However, from research done by others suggested that addition of functional group or increasing the alkyl chain length has been found to give higher viscosity values.

Higher viscosity will results in lower CO_2 solubility because CO_2 have more difficulties to absorb into viscous solvent. These statements contradicted with each other, thus further research need to be done. Even, there are not yet any researches on manipulation of functional group with longer alkyl chain length done. *(Abobakr K. Ziyada et al., 2011)*

The hypothesis is that longer chain of functional group will produce ionic liquids with low viscosity, thus higher CO_2 move ability. This is because longer chain will create more space and volume between the carbon atoms in the chain. But this will also depend on the orientation of the ionic liquids whether it crosses or parallel to each other. If the orientation crosses each other, it will tangle and resulting in viscous ionic liquids. If the orientation is parallel, the ionic liquids fit into each other in the space created by the carbon atoms thus the product will be less viscous. To confirm this hypothesis, experiments need to be carried out.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

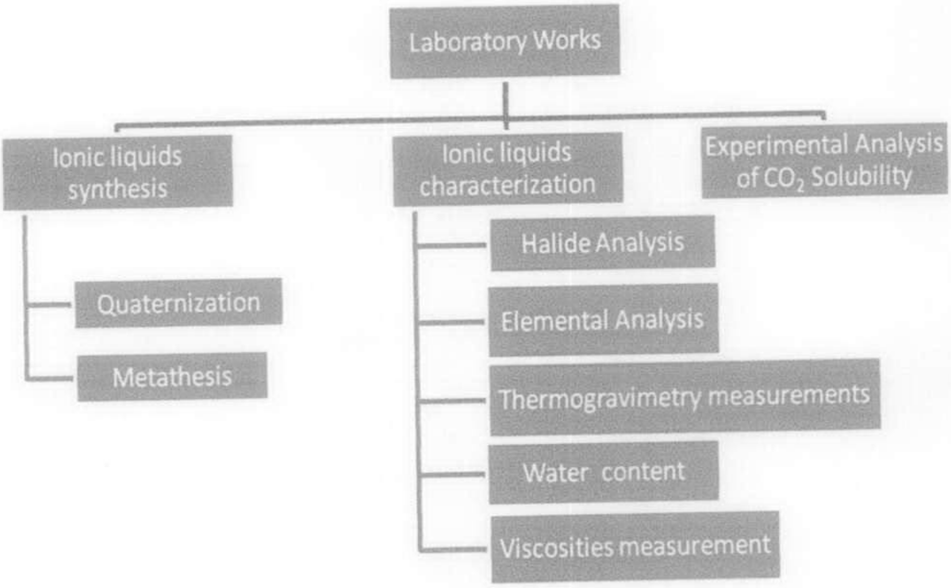


Figure 5: Activities breakdown

Project activities are mostly more to laboratory works. The activities are further breakdown into 3 major activities that will be carried out throughout this project.

3.2 Ionic Liquids Synthesis

The novel ILs are synthesized using the general procedures for synthesis of 1-propionitrile-3-alkylimidazolium bromide. These procedures have been based on basic procedures outlined in the **Thermophysical Properties of 1-Propyronitrile-3-alkylimidazolium Bromide Ionic Liquids at Temperatures from (293.15 to 353.15) K (Abobakr et al., 2010).**

The procedures can be further divided into 2 sections:

1. Quaternization
    a. Synthesis of 1-methyl-3-propionitrile imidazole chloride
    b. Synthesis of 1-methyl-3-butyronitrile imidazole chloride
2. Metathesis
    a. Synthesis of [C_2CNMim][DOSS]
    b. Synthesis of [C_3CNMim][DOSS]

3.2.1 Theoretical Calculation

Before the experiment was carried out, theoretical calculations need to be done to estimate how much of the reactant needed and also how much the product we desired. This part is crucial to make sure enough yield of ILs to proceed with ionic liquids characterization and testing for CO_2 removal. The expected yield is to be more than 20g of ILs. Basic equations to calculate mole, volume, mass and density are used with the assumption of equimolar reaction of 1 to 1 mole. The calculation tables are as in Appendix A section.

3.2.2 Quaternization

3.2.2.1 Synthesis of 1-methyl-3-propionitrile imidazole chloride

First step of the ionic liquids synthesis, to form the cation, is the quartenization. After quaternization, we obtain nitrile functionalized ILs.

1. Add 3-chloropropionitrile (6.0 ml, 0.07mol) to the 1-methyl imidazole.
2. Cool the resulting compound to room temperature.
3. Wash the resulting compound with ethyl acetate for three times.
4. Remove the remaining solvent at 80 °C in *vacuo*.
5. Dry in vacuum oven for 72 hours to give 1-methyl-3-propionitrile imidazole chloride.

Then the process proceeds with metathesis.

3.2.2.2 Synthesis of 1-methyl-4-butyronitrinile imidazole chloride

First step of the ionic liquids synthesis, to form the cation, is the quartenization. After quaternization, we obtain nitrile functionalized ILs.

1. Add 4-chlorobutyronitrile (6.0 ml, 0.06mol) to the 1-methyl imidazole.
2. Cool the resulting compound to room temperature.
3. Wash the resulting compound with ethyl acetate for three times.
4. Remove the remaining solvent at 80 °C in *vacuo*.
5. Dry in vacuum oven for 72 hours to give 1-methyl-3-butyronitrile imidazole chloride.

Then the process proceeds with metathesis.

3.2.3 Metathesis

3.2.3.1 Synthesis of [C_2CNMim][DOSS]

The final step in ionic liquids synthesis is metathesis:

1. Mix 1-methyl-3-propionitrile imidazole chloride (0.07 mol) and sodium dioctylsulfosuccinate (0.07 mol) in 50 mL of acetone.
2. Stir the mixture at room temperature for 48 hours.
3. Separate the solid precipitate and remove solvent under vacuum
4. Cool the resulting pale yellow viscous compound to room temperature.
5. Wash with dichloromethane.
6. Remove remaining solvent under vacuum at 80 °C for 48 hours to get [C_2CNMim][DOSS].

3.2.3.2 Synthesis of [C_2CNMim][DOSS]

The final step in ionic liquids synthesis is metathesis:

1. Mix 1-methyl-3-butyronitrile imidazole chloride (0.04 mol) and sodium dioctylsulfosuccinate (0.04 mol) in 50 mL of acetone.
2. Stir the mixture at room temperature for 48 hours.
3. Separate the solid precipitate and remove solvent under vacuum
4. Cool the resulting pale yellow viscous compound to room temperature.
5. Wash with dichloromethane.
6. Remove remaining solvent under vacuum at 80 °C for 48 hours to get [C_3CNMim][DOSS].

After metathesis process, the product will be characterized and tested for CO_2 removal.

3.3 Ionic Liquids Characterization

The methods for characterizing and properties measurement are based on the journal by *Abobakr K. Ziyada et. al (2011).*

3.3.1 *Elemental Analysis*

The Raman scattering technique is a vibrational molecular spectroscopy which derives from an inelastic light scattering process. With Raman spectroscopy, a laser photon is scattered by a sample molecule and loses (or gains) energy during the process. The amount of energy lost is seen as a change in energy (wavelength) of the irradiating photon. This energy loss is characteristic for a particular bond in the molecule. Raman can produce a precise spectral fingerprint, unique to a molecule or indeed and individual molecular structure. In this respect it is similar to the more commonly found FT-IR spectroscopy. The machine used is Thermo Scientific DXR RAMAN spectroscopy.

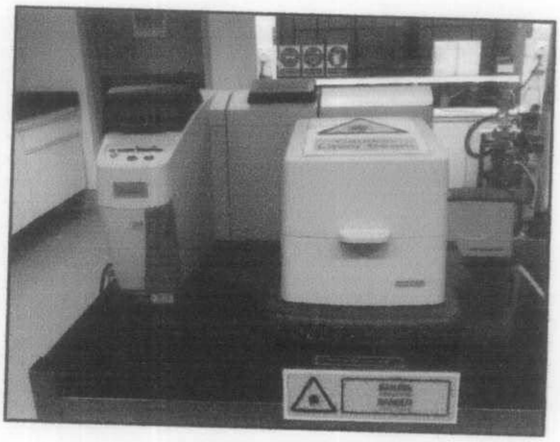


Figure 6: Thermo Scientific DXR RAMAN spectroscopy

3.3.2 *Water Content*

For determining water content of the ionic liquids, a coulometric Karl Fisher titrator (DL 39 Mettler Toledo) with CombiCoulomat fritless Karl Fischer reagent (Merck) is used. The measurement for each ionic liquids will be made in triplicate, and average values will be reported.

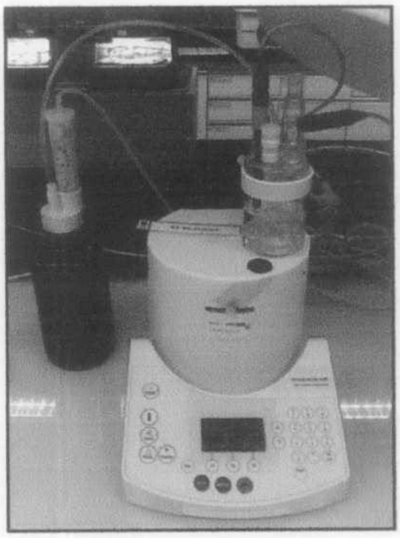


Figure 7: Karl Fisher titrator (DL 39 Mettler Toledo)

3.3.3 *Viscosity Measurements*

The density and viscosity of all ionic liquids will be measured in temperature of 298 K at atmospheric pressure using Brookfield CAP +2000. The dynamic viscosity is the ratio between the applied shear stress and the rate of shear. It is a measure of the resistance to flow of the liquid.

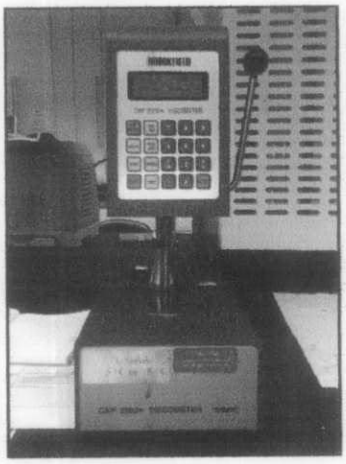


Figure 8: Brookfield CAP +2000

3.3.4 *Halide Content*

Ion chromatography is a process that allows the separation of ions and polar molecules based on their charge. It can be used for almost any kind of charged molecule including large proteins, small nucleotides and amino acids.The machine to be used is Metrohm 850 Ion chromatography system. Sample need to be diluted 10000 times before injected into the machine to measure concentration of chlorine.

Figure 9: Metrohm 850 Ion chromatography system

3.3.5 *Thermogravimetry Measurements*

The start and onset temperatures of the present synthesized ionic liquids will be determined by using Perkin-Elmer, Pyris V-3.81. The samples will be placed in aluminum pans under nitrogen atmosphere at a heating rate of 10°C.min^{-1}.

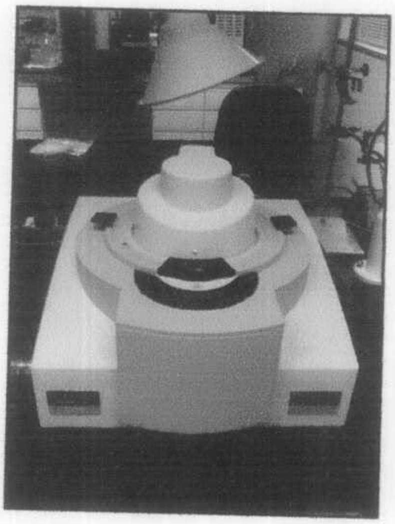


Figure 10: Perkin-Elmer, Pyris V-3.81

3.4 Experimental Analysis for Carbon Dioxide Solubility

The equipment to measure CO_2 removal is CO_2 solubility cell. The pressure of CO_2 will be set at 5, 15, and 25 bar. The temperature was set at 298 K. The pressure of CO_2 was measured in 5 minutes interval. Then the graph CO_2 Weight Percent (%) versus Time, t (min) was plotted to compare the capability of each sample to absorb CO_2. All data for this CO_2 solubility experiment as attached in Appendix B.

Figure 11: CO_2 solubility cell

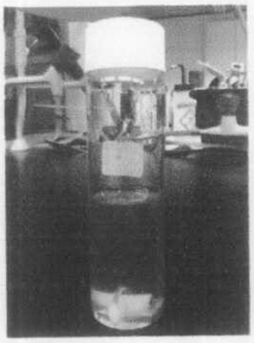
CHAPTER 4

RESULTS & DISCUSSION

4.1 Synthesis of Ionic Liquids

After quaternization process and metathesis process these are the final product:

Table 1: Product after metathesis

Cation	Sample	Colour	Physical State	Yield (g)
3-chloropropionitrile	 [C_2CNMim][DOSS]	Slightly Orange	Viscous	35.652
4-chlorobutyronitrile	 [C3CNMim][DOSS]	Yellowish	Viscous	20.75

4.2 Reaction Scheme

4.2.1 *Synthesis Of [C_2CNMIM][DOSS]*

Based on the reactant used, during quaternization process where 1-methyl imidazole added to 3-chloropropionitrile to get 1-methyl-3-propionitrile imidazole chloride the reaction is as follows:

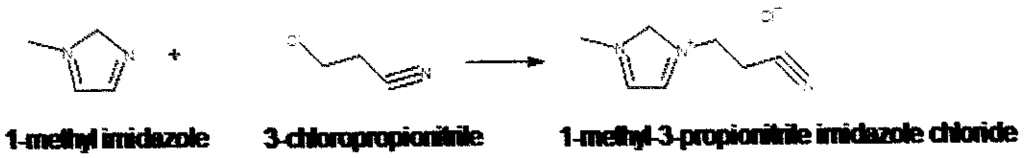


Figure 12: Quaternization of 1-methyl imidazole with 3-chloropropionitrile

Proceed next to metathesis process, assuming equimolar reaction, the final product is [C_2CNMim][DOSS] as diagram below:

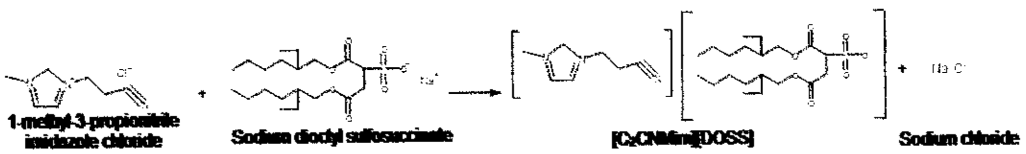


Figure 13: Metathesis of [C_2CNMim][DOSS]

4.2.2 *Synthesis Of [C_3CNMIM][DOSS]*

Based on the reactant used, during quaternization process where 1-methyl imidazole added to 4-chlorobutyronitrile to get 1-methyl-3-butyronitrile imidazole chloride the reaction is as follows:

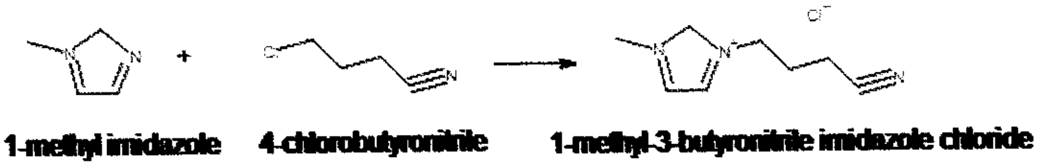


Figure 14: Quaternization of 1-methyl imidazole with 4-chlorobutyronitrile

Proceed next to metathesis process, assuming equimolar reaction, the final product is [C_3CNMim][DOSS] as diagram below:

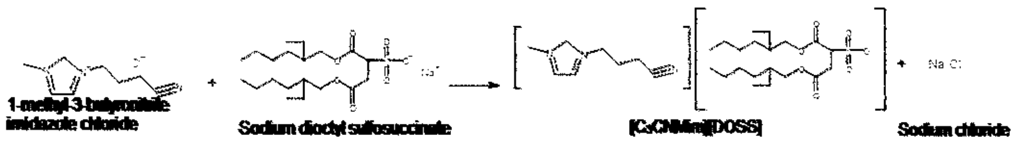
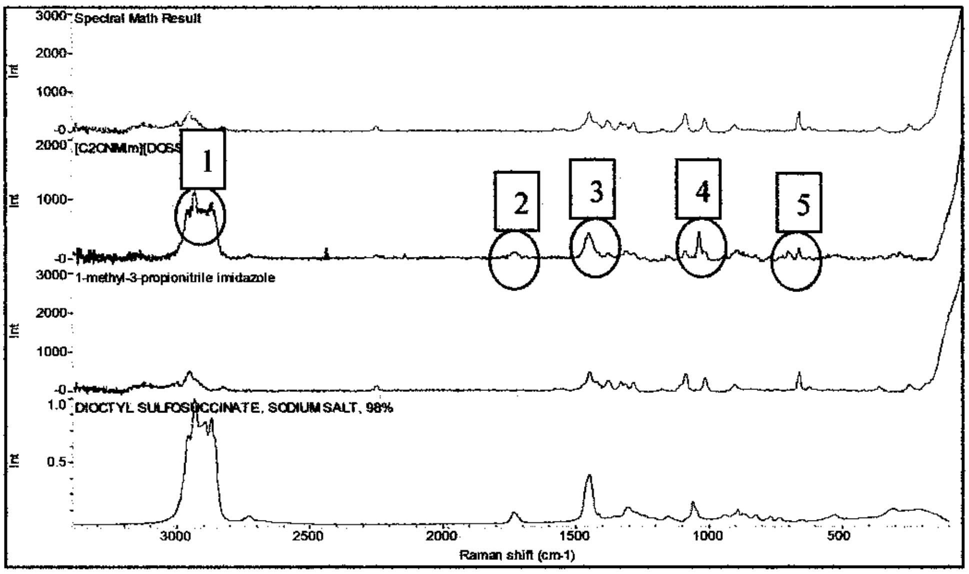


Figure 15: Metathesis of [C_3CNMim][DOSS]

4.3 RAMAN Analysis

4.3.1 *[C_2CNMIM][DOSS]*

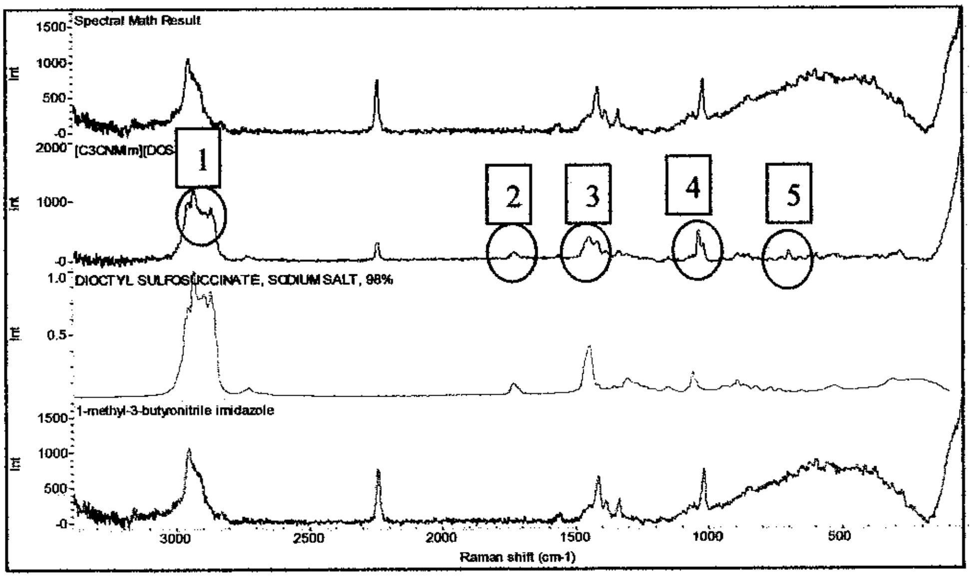


Graph 1: RAMAN analysis of [C_2CNMIM][DOSS]

Top graph in the above graph is synthetic spectral math taken by combining library data of 1-methyl-3propionitrile and NaDOSS. The resulting ionic liquids theretically should be almost the same as the synthetic graph.

Peak number 1 is functional group of (=(C-H)) that show double bond in the ionic liquids. Second peak is (C=O) functional group that indicate DOSS. Third peak is (C=C) that show carbon bond in the ionic liquids. Fourth peak is (CH3) and fifth peak is aliphatic chain vibration that indicates imidazolium in the ionic liquids. It show that the ionic liquids above is [C_2CNMIM][DOSS].

4.3.2 *[C_3CNMIM][DOSS]*



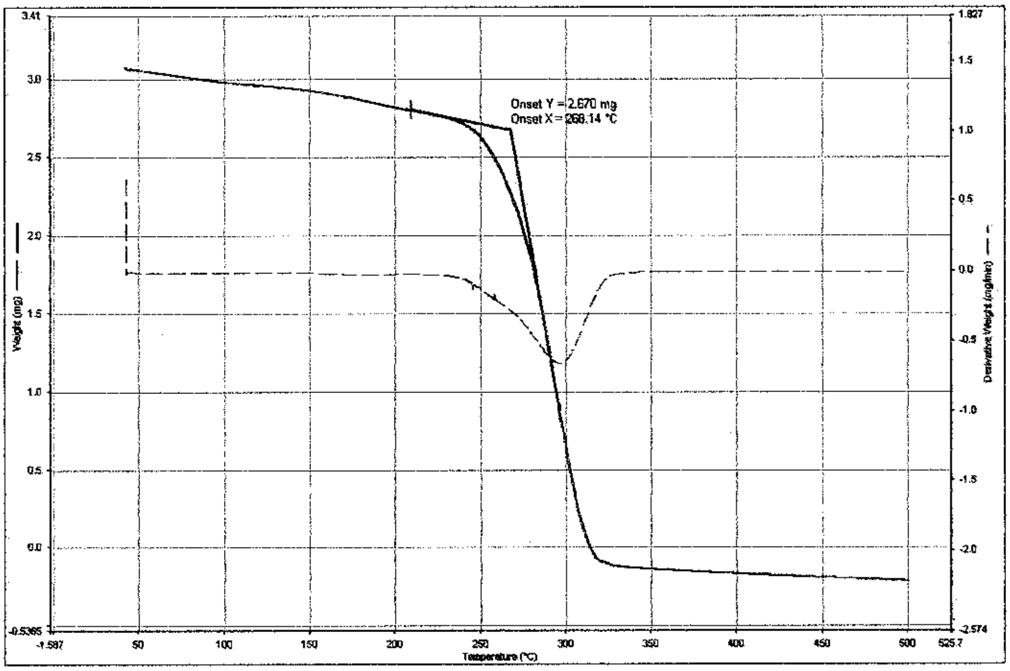
Graph 2: RAMAN analysis of [C_3CNMIM][DOSS]

Basically both graphs will look the same as the components in both ionic liquids are the same. The only difference is the length of the carbon chain. So if we get the same shape of graph we can conclude that the resulting product is [C_3CNMIM][DOSS].

4.4 Thermogravimetry Analysis

4.4.1 *[C_2CNMIM][DOSS]*

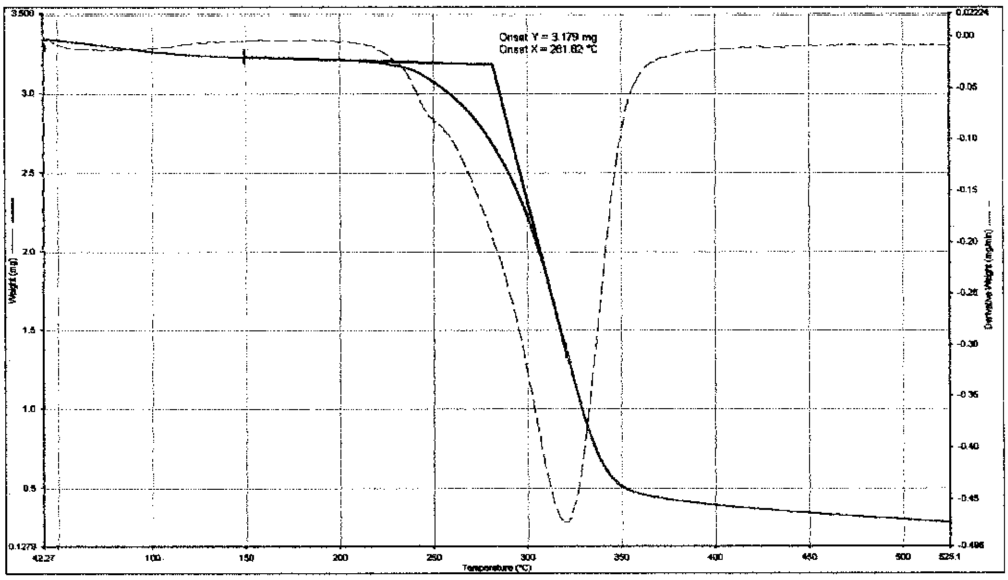
The graph below shows that the [C_2CNMim][DOSS] pure and free from any starting material. This ILs is thermally stable up to 268.14 ^{0}C and start to decomposing with complete decomposition occurring above 330 ^{0}C. This high thermal stability ILs is suitable for the removal of CO_2 from natural gas.



Graph 3: TGA result for [C_2CNMim][DOSS]

4.4.2 *[C_3CNMIM][DOSS]*

The graph below shows that the [C_3CNMim][DOSS] pure and free from any starting material. This ILs is thermally stable up to 281.82 ^{0}C and start to decomposing with complete decomposition occurring above 360 ^{0}C. This high thermal stability ILs is suitable for the removal of CO_2 from natural gas.



Graph 4: TGA result for [C_3CNMim][DOSS]

Theoretically thermal stability of commercial ILs are between 200 – 500 ^{0}C. The thermal stability mainly depends on the alkyl chain of the cation and the type of anion. Since the anions used for both ILs are the same, the only factor that will affect the thermal stability is cation used. *(Yunus et al,2010)*

Both ILs decompose at 261 ^{0}C and 281^{0}C. The difference of temperature is not big because the structure of both ILs almost the same. The difference is alkyl chain length. From result above [C_3CNMim][DOSS] is more thermally stable compared to [C_2CNMim][DOSS]. Longer alkyl chain of functionalized group gives more thermally stable ionic liquids.

4.5 Water Content

Theoretically, for any novel ionic liquid the allowable water content is 500ppm. Using coulometric Karl Fisher titrator, the average of 3 readings for each ILs is as in table below:

Table 2: Water content of ILs

No	Sample	Water (ppm)	Water (%)
1	[C_2CNMim][DOSS]	458.9	0.045
2	[C_3CNMim][DOSS]	665.7	0.067

From the data, we can see that [C_3CNMim][DOSS] water content is slightly higher than allowed. This is because the sample exposed to the atmosphere where it absorb moisture from air. The ILs should be put in vacuum line longer and kept inside special box to ensure no moisture contaminate ILs.

4.6 Halide Content

As the cation used in this experiment have chlorine, halide content must be measured to ensure that concentration of chloride ion inside the ionic liquids do not exceed 500ppm. Using **Metrohm 850 Ion chromatography** system, the result as follows:

Table 3: Halide content for ILs

No	Sample	Halide (ppm)	Halide (%)
1	[C_2CNMim][DOSS]	12385.297	1.2%
2	[C_3CNMim][DOSS]	15660.581	1.6%

The concentrations of chloride ion in the ILs are too high. The reason is because not proper technique during washing the resulting ILs. Repeat washing the ILs with dichloromethane (DCM) to remove excessive chloride ion. Unfortunately, after washing, the machine broke down and data after washing are not available.

4.7 Viscosity

The dynamic viscosities of the ionic liquids were measured and the result in the table below:

Table 4: Viscosity of ILs

No	Sample	Viscocity (cP)
1	[C_2CNMim][DOSS]	10598.4
2	[C_3CNMim][DOSS]	9640.0

From research, the commercial ionic liquids that have been produced worldwide have the viscosity range between 200 to 3000 cP *(Lee Ferguson)*. Both of the final products are viscous and out of commercial viscosity range. However [C_3CNMim][DOSS] that has longer alkyl chain on the functionalized group has lower viscosity compared to [C_2CNMim][DOSS]. The difference is not too significant since the alkyl chain length difference is only 1 carbon chain. Bigger difference in alkyl chain might shows more significant difference.

4.8 CO_2 Solubility

Using CO_2 solubility cell, ionic liquids was placed in the cell where CO_2 pressure was applied. The pressure can be manipulated to give data on CO_2 solubility at different pressure. Theoretically higher pressure will give higher CO_2 solubility.

Using ideal gas law, **PV=ZnRT**

Where,

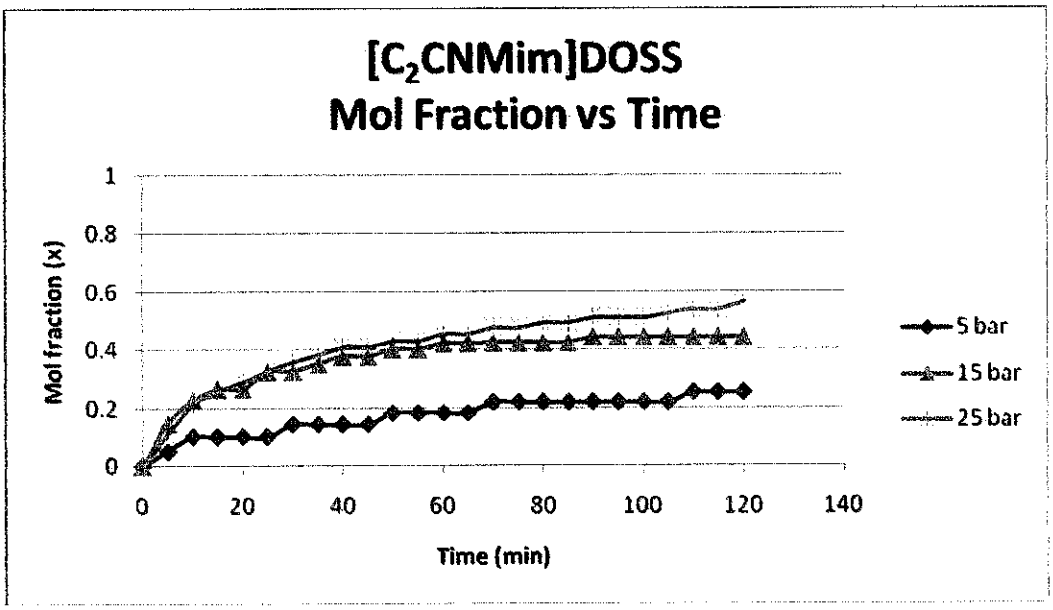
P = pressure
V= volume
Z=compressibility factor
N=mole of CO_2
R=gas constant
T=temperature

CO_2 capacity of novel ionic liquids can be calculated.

Data and calculation are shown in the appendix B.

4.8.1 *[C_2CNMim][DOSS]*

From data gathered and calculation made, graph of mol fraction CO_2 absorb versus time can be plotted as below.

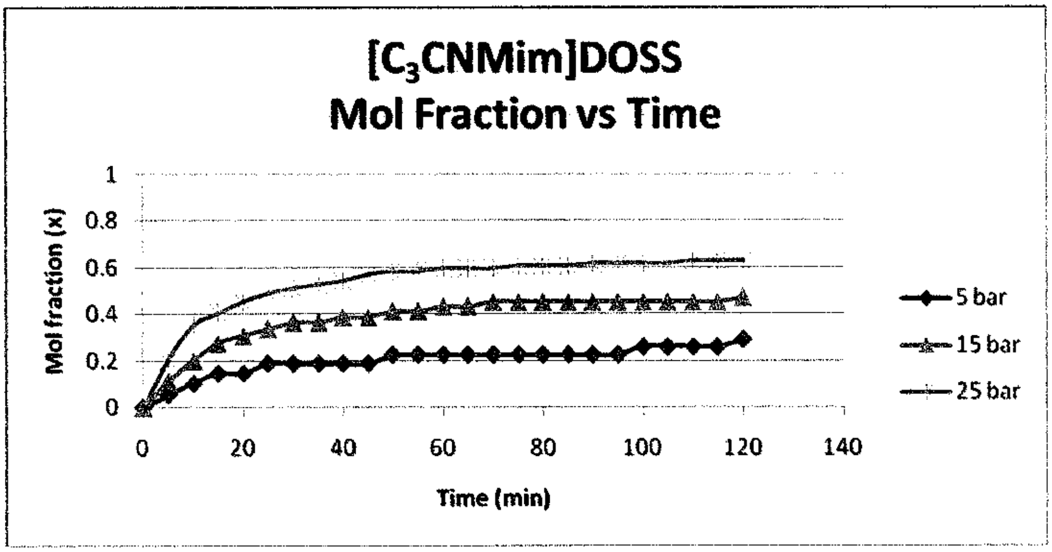


Graph 5: Mol fraction CO2 vs Time for [C_2CNMim][DOSS]

From graph above, we can see that higher pressure of CO_2 applied will give better CO_2 solubility. The data taken every 5 minutes interval until the reading are constant. At the end, at 5 bar 25% CO_2 absorb, 15 bar 44% CO_2 absorb and at 25 bar 56% CO_2 absorb.

4.8.2 *[C_3CNMim][DOSS]*

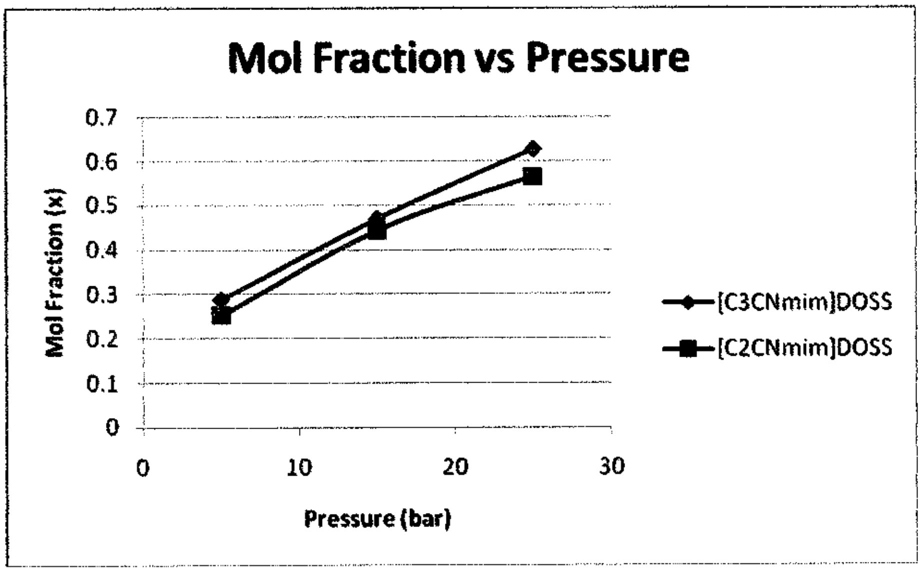
From data gathered and calculation made, graph of mol fraction CO_2 absorb versus time can be plotted as below



Graph 6: Mol fraction CO_2 vs Time for [C_3CNMim][DOSS]

From graph above, we can see that higher pressure of CO_2 applied will give better CO_2 solubility. The data taken every 5 minutes interval until the reading are constant. At the end, at 5 bar 29% CO_2 absorb, 15 bar 47% CO_2 absorb and at 25 bar 63% CO_2 absorb.

4.8.3 *[C_2CNMim][DOSS] Vs [C_3CNMim][DOSS]*



Graph 7: Comparison between [C_2CNMim][DOSS] vs [C_3CNMim][DOSS]

After data are collected, a graph of mol fraction of CO_2 absorb versus Pressure was plotted to see the difference of CO_2 solubility between the two ILs. From graph above, we can see that [C_3CNMim][DOSS] has better CO_2 solubility compared to [C_2CNMim][DOSS]. However the difference is quite small. This is because of the difference in alkyl chain length is small, which is only 1 carbon chain. If the alkyl chain longer, it might shows higher CO_2 solubility.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

Trough out this semester the research done, the primary objective of this experiment is achieved in order to synthesize novel ionic liquids for CO_2 removal. However the viscosity is still quite high. Through the experiment, data shows that the alkyl chain length of functionalized group affect the viscosity and CO_2 solubility capacity. From the experiment above, it is proven that [C_3CNMim][DOSS] has lower viscosity and higher CO_2 capacity compared to [C_2CNMim][DOSS].

In conclusion, ionic liquids is a very good alternative for CO_2 removal solvent and further research can improve the viscosity and CO_2 capacity of the ionic liquids.

5.2 Recommendations

From the experiments done, some recommendations can be done to improve the data gathered. Preventive maintenance should be carried out frequently since the equipments are highly sensitive and easy to break. This is essential to make sure experiment progress not hindered by faulty equipments. In term of CO_2 solubility experiment, Magnetic Suspension Bar (MSB) should be used to measure CO_2 solubility in ILs rather than CO_2 solubility cell. MSB can give better and more accurate result. All ILs produced must be kept in dry atmosphere since the ILs produced absorb water. Before starting ILs synthesis, practice to synthesize any ILs from any journal. Follow all the steps in the journal to familiarize with lab works. For further research, longer alkyl chain length should be used to see significant effect of alkyl chain length of functionalized group towards viscosity and CO_2 solubility.

REFERENCES

Abobakr K. Ziyada, 2010, *Densities, Viscosities, and Refractive Indices of 1-Hexyl-3-propanenitrile Imidazolium Ionic Liquids Incorporated with Sulfonate-Based Anions*, Ph.D. Thesis, Universiti Teknologi PETRONAS, Perak.

Anthony J., Anderson J., Maginn E. and Brennecke J., 2005. "Anion effects on gas solubility in ionic liquids," *The Journal of Physical Chemistry* 109:6366–6374.

Anthony J., Anderson J., Maginn E. and Brennecke J., 2002. "Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate," *The Journal of Physical Chemistry* 106:7315–7320.

Bonhote, P., Dias, A.P., Papageorgiou, N., Kalyanasundram, K., Gratzal, M. 1996, *Inorganic Chemistry*, Mc Graw Hill.

Cadena C., Anthony J.L., Shah J.K., Morrow T.I., Brennecke J., and Maginn E.J.. 2004. *Why Is CO2 So Soluble in Imidazolium-Based Ionic Liquids?*, Thesis, University of Notre Dame.

Carvalho P.J., Álvarez V.H., Machado J.J.B., Pauly J., Daridon J., Marrucho I.M., Aznar M. and Coutinho J.A.P., 2009. "High pressure phase behavior of carbon dioxide in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids," *The Journal of Supercritical Fluids* 48 : 99–107.

Carvalho P.J., Álvarez V.H., Marrucho I.M, Aznar M., Coutinho J.A.P., "High carbon dioxide solubilities in trihexyltetradecylphosphonium based ionic liquids," *The Journal of Supercritical Fluids.* 58: 198–207

Chinn, Daniel, 16 June 2005, *CO2 Removal from Gas Using Ionic Liquid Absorbents*, United States Patent Application Publication (US2005/0129598 A1)

Domanska and K. Paduszynski, 2008. "Phase equilibria study in binary systems (tetra-n-butylphosphonium tosylate ionic liquid + 1-alcohol, or benzene, or n-alkylbenzene)," *The Journal of Physical Chemistry* 112: 11054–11059.

Hutchings J.W., Fuller K.L., Heitz M.P. and Hoffmann M.M., 2005. "Surprisingly high solubility of the ionic liquid trihexyltetradecylphosphonium chloride in dense carbon dioxide," *Green Chemistry* 7:475–478.

Ionic Liquids Department, University of Torino, November 2004 <http://lem.ch.unito.it/didattica/infochimica/Liquidi%20Ionici/index.html>

Muldoon M., Aki S., Anderson J., Dixon J. and Brennecke J., 2007. "Improving carbon dioxide solubility in ionic liquids," *The Journal of Physical Chemistry* 111: 9001–9009

Shiflett M.B. and Yokozeki A., 2009. "Phase behavior of carbon dioxide in ionic liquids: [emim][acetate], [emim][trifluoroacetate], and [emim][acetate] + [emim][trifluoroacetate] mixtures," *The Journal of Chemical Engineering Data* 54 : 108–114.

Peter Wasserscheid, Thomas Welton, 2002. *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Rogers R.D. and Seddon K.R., 2003. "Ionic liquids—solvents of the future?" *Science* 302: 792–793.

Yunus, N. M. Mutalib, M.I.A. Man, Z. Bustam, M.A. Murugesan, T. 2010. "Thermophysical properties of 1-alkylpyridium bis-(trifluoromethylsulfony)imide ionic liquids," *Journal of Chemical Thermodynamic*, 40: 491-495

APPENDIX A

THEORETICAL CALCULATION

Quaternization Process

For calculation purposes, reactants are set at 6.0 cm3. Through equimolar concept, the mass and volume of 1-methyl imidazole can be obtained. For quaternization process, 1-methyl imidazole is excessive.

Table 5: Theoretical calculation for 1-methyl-3-propionitrile imidazole chloride

Quarternization	Mole	Volume (cm3)	Density (g/cm3)	Mass (g)
Reactant				
1-methyl imidazole ($C4H6N2$)	0.0767	6.1117	1.0300	6.2951
3-chloropropionitrile ($C3H4ClN$)	0.0767	6.0000	1.1440	6.8640
Product				
1-methyl-3-propionitrile imidazole chloride ($C7H10N3Cl$)	0.0767			[redacted]

Table 6: Theoretical calculation for 1-methyl-4-butyronitrile imidazole chloride

Quarternization	Mole	Volume (cm3)	Density (g/cm3)	Mass (g)
Reactant				
1-Methyl Imidazole ($C4H6N2$)	0.0634	5.0573	1.0300	5.2090
4-chlorobutyronitrile ($C4H6ClN$)	0.0634	6.0000	1.0950	6.5700
Product				
1-methyl-3-butyronitrile imidazole chloride ($C8H12N3Cl$)	0.0634			[redacted]

From the calculation made above, the expected product mass is 13.15g for 1-methyl-3-propionitrile imidazole chloride and 11.77g for 1-methyl-4-butyronitrile imidazole chloride. However the actual product will be less than calculated.

Methatesis Process

After quaternization process completed, the products are weighted to get the actual yield mass. The actual mass of Product 1 is 11.77g and 7.57g for Product 2. From the mass, we can further calculate mass of sodium dioctylsulfosuccinate needed for methatesis process.

Table 7: Theoretical calculation to produce [C_2CNMim][DOSS]

Methathesis	Mole	Mass (g)
Reactant		
1-methyl-3-propionitrile imidazole chloride (C7H10N3Cl)	0.0686	[redacted]
Na[DOSS] (C20H37NaO7S)	0.0686	30.5122
Product		
[C_2CNMim][DOSS] (C27H47N3O7S)	0.0686	[redacted]

Table 8: Theoretical calculation to produce [C_3CNMim][DOSS]

Methathesis	Mole	Mass (g)
Reactant		
1-methyl-3-butyronitrile imidazole chloride (C8H12N3Cl)	0.0408	[redacted]
Na[DOSS] (C20H37NaO7S)	0.0408	18.1499
Product		
[C_3CNMim][DOSS] (C28H49N3O7S)	0.0408	[redacted]

The calculations above show that the expected mass of the final product is 38.25g for [C_2CNMim][DOSS] and 23.33g for [C_3CNMim][DOSS].

APPENDIX B

CARBON DIOXIDE SOLUBILITY

[C_2CNMim][DOSS]

Table 9: CO_2 solubility in [C_2CNMim][DOSS] at 5 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	3.8	0.9808	0.042199059	-	0
5	3.79	0.9808	0.042088009	0.00011105	0.0525239513
10	3.78	0.9809	0.041972679	0.00022638	0.1015335158
15	3.78	0.9809	0.041972679	0.00022638	0.1015335158
20	3.78	0.9809	0.041972679	0.00022638	0.1015335158
25	3.78	0.9809	0.041972679	0.00022638	0.1015335158
30	3.77	0.9809	0.04186164	0.00033742	0.1441562436
35	3.77	0.9809	0.04186164	0.00033742	0.1441562436
40	3.77	0.9809	0.04186164	0.00033742	0.1441562436
45	3.77	0.9809	0.04186164	0.00033742	0.1441562436
50	3.76	0.981	0.041746346	0.00045271	0.1843340619
55	3.76	0.981	0.041746346	0.00045271	0.1843340619
60	3.76	0.981	0.041746346	0.00045271	0.1843340619
65	3.76	0.981	0.041746346	0.00045271	0.1843340619
70	3.75	0.981	0.041635318	0.00056374	0.2196135789
75	3.75	0.981	0.041635318	0.00056374	0.2196135789
80	3.75	0.981	0.041635318	0.00056374	0.2196135789
85	3.75	0.981	0.041635318	0.00056374	0.2196135789
90	3.75	0.981	0.041635318	0.00056374	0.2196135789
95	3.75	0.981	0.041635318	0.00056374	0.2196135789
100	3.75	0.981	0.041635318	0.00056374	0.2196135789
105	3.75	0.981	0.041635318	0.00056374	0.2196135789
110	3.74	0.9811	0.041520058	0.000679	0.2531481327
115	3.74	0.9811	0.041520058	0.000679	0.2531481327
120	3.74	0.9811	0.041520058	0.000679	0.2531481327

Table 10: CO_2 solubility in $[C_2CNMim][DOSS]$ at 15 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	11.91	0.9381	0.138280918	-	0
5	11.88	0.9381	0.137932603	0.000348315	0.1481444791
10	11.86	0.9382	0.137685716	0.000595202	0.2290938028
15	11.85	0.9383	0.137554962	0.000725956	0.2660324888
20	11.85	0.9383	0.137554962	0.000725956	0.2660324888
25	11.83	0.9384	0.137308168	0.00097275	0.3269068440
30	11.83	0.9384	0.137308168	0.00097275	0.3269068440
35	11.82	0.9384	0.1371921	0.001088817	0.3521760494
40	11.81	0.9385	0.137061427	0.001219491	0.3784467168
45	11.81	0.9385	0.137061427	0.001219491	0.3784467168
50	11.8	0.9386	0.136930781	0.001350137	0.4026647944
55	11.8	0.9386	0.136930781	0.001350137	0.4026647944
60	11.79	0.9386	0.136814738	0.00146618	0.4226462429
65	11.79	0.9386	0.136814738	0.00146618	0.4226462429
70	11.79	0.9387	0.136800163	0.001480755	0.4250617983
75	11.79	0.9387	0.136800163	0.001480755	0.4250617983
80	11.79	0.9387	0.136800163	0.001480755	0.4250617983
85	11.79	0.9387	0.136800163	0.001480755	0.4250617983
90	11.78	0.9387	0.136684132	0.001596785	0.4435942703
95	11.78	0.9387	0.136684132	0.001596785	0.4435942703
100	11.78	0.9387	0.136684132	0.001596785	0.4435942703
105	11.78	0.9387	0.136684132	0.001596785	0.4435942703
110	11.78	0.9387	0.136684132	0.001596785	0.4435942703
115	11.78	0.9387	0.136684132	0.001596785	0.4435942703
120	11.78	0.9387	0.136684132	0.001596785	0.4435942703

Table 11: CO_2 solubility in [C_2CNMim][DOSS] at 25 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	20.19	0.8913	0.246724365	-	0
5	20.17	0.8913	0.246479963	0.000244403	0.1091911931
10	20.15	0.8915	0.246180319	0.000544046	0.2143649263
15	20.14	0.8916	0.246030548	0.000693817	0.2581439699
20	20.13	0.8916	0.245908388	0.000815977	0.2903963971
25	20.12	0.8917	0.245758664	0.000965701	0.3262947375
30	20.11	0.8918	0.245608974	0.001115391	0.3587289093
35	20.1	0.8918	0.245486841	0.001237524	0.3829659904
40	20.09	0.8919	0.245337198	0.001387167	0.4102754066
45	20.09	0.8919	0.245337198	0.001387167	0.4102754066
50	20.08	0.8919	0.245215079	0.001509286	0.4308328875
55	20.08	0.8919	0.245215079	0.001509286	0.4308328875
60	20.07	0.892	0.245065483	0.001658882	0.4541425499
65	20.07	0.892	0.245065483	0.001658882	0.4541425499
70	20.06	0.8921	0.244915921	0.001808445	0.4756134550
75	20.06	0.8921	0.244915921	0.001808445	0.4756134550
80	20.05	0.8921	0.244793829	0.001930536	0.4919274656
85	20.05	0.8921	0.244793829	0.001930536	0.4919274656
90	20.04	0.8922	0.244644314	0.002080051	0.5105738795
95	20.04	0.8922	0.244644314	0.002080051	0.5105738795
100	20.04	0.8922	0.244644314	0.002080051	0.5105738795
105	20.03	0.8922	0.244522236	0.002202129	0.5248131060
110	20.02	0.8922	0.244400158	0.002324207	0.5382472123
115	20.02	0.8922	0.244400158	0.002324207	0.5382472123
120	20	0.8922	0.244156002	0.002568363	0.5629585875

[C$_3$CNMim][DOSS]

Table 12: CO_2 solubility in [C$_3$CNMim][DOSS] at 5 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	3.82	0.9807	0.042425485	-	0
5	3.81	0.9807	0.042314423	0.00011106	0.0539430041
10	3.8	0.9808	0.042199059	0.00022643	0.1041406596
15	3.79	0.9808	0.042088009	0.00033748	0.1476737249
20	3.79	0.9808	0.042088009	0.00033748	0.1476737249
25	3.78	0.9809	0.041972679	0.00045281	0.1886209776
30	3.78	0.9809	0.041972679	0.00045281	0.1886209776
35	3.78	0.9809	0.041972679	0.00045281	0.1886209776
40	3.78	0.9809	0.041972679	0.00045281	0.1886209776
45	3.78	0.9809	0.041972679	0.00045281	0.1886209776
50	3.77	0.9809	0.04186164	0.00056384	0.2244916503
55	3.77	0.9809	0.04186164	0.00056384	0.2244916503
60	3.77	0.9809	0.04186164	0.00056384	0.2244916503
65	3.77	0.9809	0.04186164	0.00056384	0.2244916503
70	3.77	0.9809	0.04186164	0.00056384	0.2244916503
75	3.77	0.9809	0.04186164	0.00056384	0.2244916503
80	3.77	0.9809	0.04186164	0.00056384	0.2244916503
85	3.77	0.9809	0.04186164	0.00056384	0.2244916503
90	3.77	0.9809	0.04186164	0.00056384	0.2244916503
95	3.77	0.9809	0.04186164	0.00056384	0.2244916503
100	3.76	0.981	0.041746346	0.00067914	0.2585281640
105	3.76	0.981	0.041746346	0.00067914	0.2585281640
110	3.76	0.981	0.041746346	0.00067914	0.2585281640
115	3.76	0.981	0.041746346	0.00067914	0.2585281640
120	3.75	0.981	0.041635318	0.00079017	0.2885955872

Table 13: CO_2 solubility in [C_3CNMim][DOSS] at 15 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	11.85	0.9383	0.137554962	-	0
5	11.83	0.9384	0.137308168	0.000246794	0.1125269232
10	11.81	0.9385	0.137061427	0.000493535	0.2022735019
15	11.79	0.9386	0.136814738	0.000740224	0.2755214856
20	11.78	0.9387	0.136684132	0.00087083	0.3091079393
25	11.77	0.9387	0.136568102	0.00098686	0.3364374318
30	11.76	0.9388	0.136437536	0.001117426	0.3647152007
35	11.76	0.9388	0.136437536	0.001117426	0.3647152007
40	11.75	0.9388	0.136321518	0.001233444	0.3878938658
45	11.75	0.9388	0.136321518	0.001233444	0.3878938658
50	11.74	0.9389	0.136190993	0.001363969	0.4120286842
55	11.74	0.9389	0.136190993	0.001363969	0.4120286842
60	11.73	0.9389	0.136074987	0.001479975	0.4319354537
65	11.73	0.9389	0.136074987	0.001479975	0.4319354537
70	11.72	0.939	0.135944502	0.00161046	0.4527751337
75	11.72	0.939	0.135944502	0.00161046	0.4527751337
80	11.72	0.939	0.135944502	0.00161046	0.4527751337
85	11.72	0.939	0.135944502	0.00161046	0.4527751337
90	11.72	0.939	0.135944502	0.00161046	0.4527751337
95	11.72	0.939	0.135944502	0.00161046	0.4527751337
100	11.72	0.939	0.135944502	0.00161046	0.4527751337
105	11.72	0.939	0.135944502	0.00161046	0.4527751337
110	11.72	0.939	0.135944502	0.00161046	0.4527751337
115	11.72	0.939	0.135944502	0.00161046	0.4527751337
120	11.71	0.939	0.135828508	0.001726454	0.4700571948

Table 14: CO_2 solubility in $[C_3CNMim][DOSS]$ at 25 bar

Time (min)	Pressure (bar)	Z	Mol CO_2 (n)	Mol absorb (n)	Fraction absorbed (x)
0	20.43	0.8899	0.249993774	-	0
5	20.39	0.8901	0.24950431	0.000489464	0.2012438330
10	20.35	0.8904	0.248930946	0.001062828	0.3536208554
15	20.33	0.8905	0.24865837	0.001335404	0.4073671445
20	20.31	0.8906	0.248385855	0.001607919	0.4528521553
25	20.29	0.8907	0.248113401	0.001880373	0.4918446941
30	20.28	0.8908	0.247963279	0.002030496	0.5110446263
35	20.27	0.8908	0.247841009	0.002152766	0.5256422505
40	20.26	0.8909	0.247690934	0.002302841	0.5424101689
45	20.24	0.891	0.247418649	0.002575125	0.5699883911
50	20.23	0.8911	0.247268655	0.002725119	0.5838061597
55	20.23	0.8911	0.247268655	0.002725119	0.5838061597
60	20.22	0.8911	0.247146427	0.002847348	0.5944262024
65	20.22	0.8911	0.247146427	0.002847348	0.5944262024
70	20.22	0.8911	0.247146427	0.002847348	0.5944262024
75	20.21	0.8912	0.24699648	0.002997295	0.6067367712
80	20.21	0.8912	0.24699648	0.002997295	0.6067367712
85	20.21	0.8912	0.24699648	0.002997295	0.6067367712
90	20.2	0.8912	0.246874265	0.00311951	0.6162311179
95	20.2	0.8912	0.246874265	0.00311951	0.6162311179
100	20.2	0.8912	0.246874265	0.00311951	0.6162311179
105	20.2	0.8912	0.246874265	0.00311951	0.6162311179
110	20.19	0.8913	0.246724365	0.003269409	0.6272681910
115	20.19	0.8913	0.246724365	0.003269409	0.6272681910
120	20.19	0.8913	0.246724365	0.003269409	0.6272681910