ETHER FUNCTIONALIZED IMIDAZOLIUM BASED IONIC LIQUIDS FOR CARBON DIOXIDE REMOVAL

by

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ABSTRACT

The study has been done to produce [C2CN-2-DEEim][DOSS] and [C2CN-Pr-3-Pheim][DOSS] and to prove the effect of ether towards viscosity and CO_2 solubility. The process involves three sections. The first section is alkylation of propanenitrile imidazole, followed by section two by quaternization reaction to produce ether nitrile imidazole. In section three, metathesis reaction is done by mixing the ether nitrile imidazole with Sodium Dioctylsulfosuccinate (DOSS). The characterization of synthesized ionic liquids was conducted, namely Raman Analysis, water content, density, viscosity and thermogravimetry measurement. The thermo-physical and phase behavior properties of the ionic liquids produced obey the theory which is the thermal stability ranges between 250°C to 500°C. It has been found that the ether incorporated in the ionic liquid have an effect towards the viscosity of the ionic liquid and the CO_2 solibility. Aromatic ring in ether hinders the ionic liquid from achieving maximum CO_2 absorbed. The objectives were successfully achieved.

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CHAPTER 1

1. INTRODUCTION

1.1. BACKGROUND STUDY

1.1.1. Ionic Liquid

Ionic liquids (ILs) are organic salts which are liquid below 100°C. ILs are being investigate for a variety of applications including reaction media, separation solvents, non-volatile electrolytes, heat transfer fluids, and gas capture. ILs are liquid over a range of temperature, having high thermal and chemical stability; hence ILs can be used solvents. They have demonstrated success as reaction solvents for a variety of reactions such as olefin dimerization, metathesis, isomerizations, Diels Alder, Friedel-Crafts alkylation and acylations, hydrogenations, and C-C coupling. ILs have negligible vapour pressure which means that fugitive gas emissions are not a problem. This reduces worker exposure, decrease flammability danger, and disallows contamination of the IL into gas phase. Perhaps the most important property of an IL is its ability to be tailored by choice of cation and anion for a particular function. This tune ability can exploit differences in solubility of various gases in ILs, allowing for specific and selective gas absorption. Table 1 shows the properties of general ionic liquid.

Table 1: Properties of General Ionic Liquid

Modern Ionic Liquid	
Freezing point	Preferred below 100°C
Liquidus range	Often >200°C
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 $Scm^2 mol^{-1}$
Vapor pressure	Usually negligible

(Keith E. Johnson, What's an Ionic Liquid, 2007)

1.1.2. Carbon Dioxide

Carbon dioxide (CO_2) is a naturally occurring chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. Carbon dioxide exists in gas form in standard temperature and pressure. Carbon dioxide is colourless and at low concentration, the gas is adourless. 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 a natural gas processing and is often required to improve the fuel quality of the natural gas. Moreover, the presence of water in CO_2 can be a corrosive agent to metal pipes. Therefore, removal of CO_2 prior to transport natural gas in a pipeline is a must to prevent damage to the pipeline. Currently, various type of technology has been implemented in the industry in capturing CO_2, mainly through chemical solvent, physical solvents and membrane.

Chemical solvents that reversibly react with CO_2 are commonly used for CO_2 removal. The amine solution circulates in a loop between two key steps: absorption of CO_2 and regeneration of amine solvent. The CO_2 separation process is effective; however the regeneration of amine solution presents several challenges which include:

(i) **High regeneration energy** – High heating energy is required to break the bonding between the absorbed CO_2 and the amine solvent in the regeneration step. Steam is also required to strip the CO_2 from the solvent.

(ii) **Amine corrosivity** – Amine has been proven to be corrosive and will damage low alloy steel such as carbon steel. Therefore, higher corrosive resistance steel are installed in the CO_2 removal plant, resulting higher cost for setup and maintenance. Amine solution usually will be diluted using water to reduce corrosion, however it will require higher circulation rate to achieve the desired CO_2 removal.

(iii) **CO_2 loading capacity** – The CO_2 loading capacity is driven by the concentration of the amine solution. Although lean in CO_2, the regenerated amine solution still contains CO_2. If the lean amine solution has high concentration of CO_2, the driving force will decrease, reducing the CO_2 removal capacity in the next loop. Therefore, higher circulation rate are required to remove the desired level of CO_2.

(iv) **Degradation of Amine** – Amines react with CO_2 to form various different products that are not reversible in the regeneration step. Amine also has been found to degrade due to high temperature.

Physical absorption using physical solvent is an alternative for removing CO_2. The main advantage of physical absorption in compared to chemical absorption is that it has lower energy requirements. This is due to the fact that physical absorption absorbs CO_2 physically, making it easier to regenerate the physical absorption. Despite this advantage, physical absorption does have its disadvantages including:

(i) **Low CO_2 removal capacity** – Physical solvents has lower CO_2 removal capacity in compared to chemical solvent. Therefore, higher circulation rate and larger column are required to compensate this disadvantage.

(ii) **Hydrocarbon pickup** –Physical absorption tends to absorb valuable hydrocarbon in hydrocarbon treating plant. For processing plant such as natural gas plant, significant amount of hydrocarbon could be lost in the CO_2 removal system.

(iii) **High circulation rate** – The low CO_2 removal capacity will result in higher circulation needed to bring strip the CO_2 to the desired limit. This will result in higher operating cost of the plant.

(iv) **Solvent loss** – Physical solvent can be entrained and lost to the treated gas. Refrigeration or water-washing may be used to minimize losses but this will require additional capital expenses and increased operating cost.

1.2. PROBLEM STATEMENTS

Current technologies for removal of CO_2 from natural gas have several limitations such as:

i) Low carbon dioxide loading capacity

ii) Physically viscous

iii) High regeneration energy

iv) Degradation of solvent

v) Pickup of hydrocarbon

vi) Corrosive solvent

1.3. OBJECTIVE

a) The objective of this research is to **improve the carbon dioxide capturing capability of ionic liquids by reducing the viscosity by incorporating ether functionality to the ionic liquids.**

b) To observe the effect of **aromatic ring** towards CO_2 solubility of ionic liquids.

1.4. SCOPE OF STUDY

- Synthesizing of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] ionic liquids.
- Characterization of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] ionic liquids
    - I) FTIR-ATR, NMR and Elemental Analysis
    - II) Water content
    - III) Thermogravimetry measurements
    - IV) Densities and viscosities measurements
- Testing of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] ionic liquids CO2 loading capacity
- Compare the viscosity of the synthesized ionic liquid with the results obtained from literature.

CHAPTER 2

2. LITERATURE REVIEW

2.1. GENERAL OVERVIEW OF IONIC LIQUIDS

There is various kind of ILs have been synthesis for the past decade. Ionic liquid have received many attention because they offer many excellent properties, such as high chemical stability, less caustic, good solvents for polar and non-polar compound, nonvolatility and good performance in separation and reaction processes. For capturing carbon dioxide to reduce greenhouse gas emission, a great number of experimental data on the solubility of carbon dioxide in ILs at high pressure and above room temperature have been reported, which are important design parameters in establishing equilibrium stage (EQ) and nonequilibrium stage (NEQ) mathematical models to simulate and optimize the absorption and stripping columns. However, compared to the traditional organic solvents, the high viscosity and cost of ILs may become some obstacle for the application in industry.

"Ideal" solvent requirements may include low toxicity, low cost, high solute selectivity, inertness to materials, non-flammability, high-capacity of solutes, low carrier selectivity, and moderate interfacial tension. Ionic Liquid can meet some of these requirements now, but it remains necessary to address issues of cost, availability, toxicity and recycling

2.2. CURRENT STUDY ON IONIC LIQUIDS

2.2.1. Imidazolium based ionic liquid for CO_2 removal

Currently, Pyridinium-based ionic liquids have been research extensively for carbon dioxide removal. However, study on imidazolium-based ionic liquids has been minimal and the properties are yet to be explored. Abobakr K. Ziyada cited the potential of imidazolium based ionic liquid in removing CO_2. Imidazolium based ionic liquid has been proven to be versatile, more adaptable and attractive. The advantage of imidazolium based functionalized ionic liquid over most other functionalities ionic liquid is that their properties can be tuned and controlled to a greater extent, resulting in increased number of applications (Abobakr K. Ziyada, 2011). Imidazolium based ionic liquid can be modified to better suit or pinpoint an application. Report by Jessica also shows that imidazolium based ionic liquid has high gas solubility in compared to pyrinidium, alkylammonium and alkylphosphonium based ionic liquid. (Jessica et al, 2009)

2.2.1. Dioctylsulfosuccinate anion has high potential to remove CO_2

Currently, anion such as $[PF_6]$, [bFAP], $[Tf_2N]$ were widely being studied and the CO_2 solubility in ionic liquid using these anion was reported by Jessica. The ionic liquids reported by Jessica have CO_2 removal capacity of roughly 50% in mol. Abobkr K. Ziyada, a researcher in UniversitiTeknologi PETRONAS and his colleagues studied other anion which is applicable for removal of CO_2. Anion such as DDS, SBA, BS, TFMS and DOSS were incorporated to $[C_2CNC_nim]$ cation. The result shows that DOSS has the highest CO_2 solubilty and is higher than other anion reported by Jessica (Abobakr K. Ziyada, 2011).

2.2.2. High viscosity of ionic liquids using DOSS anion.

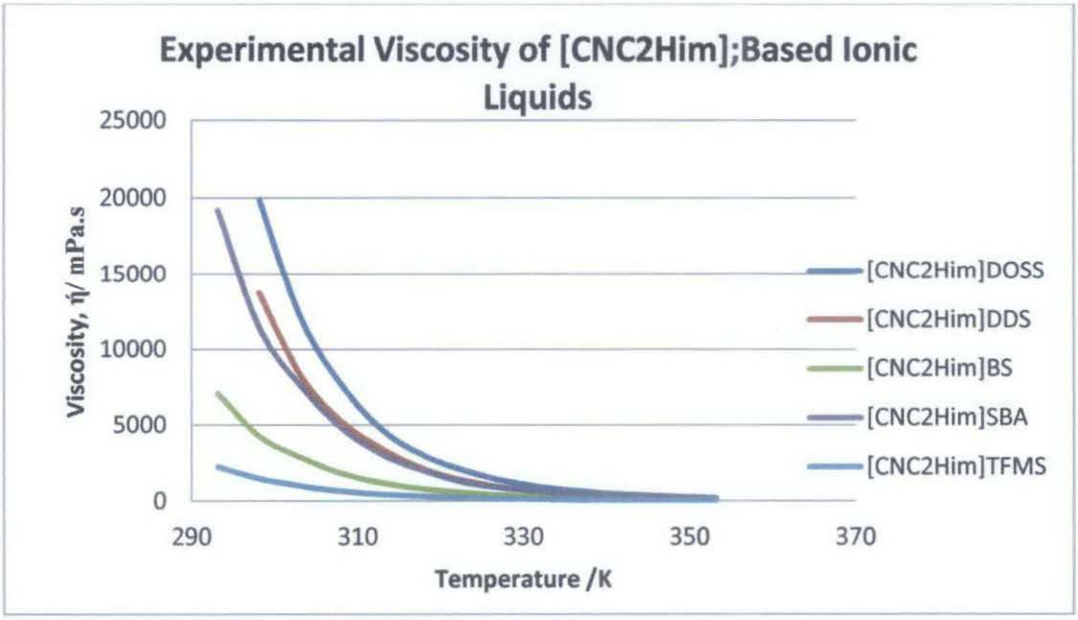


Figure 1: Experimental Viscosity of [CNC2Him]; based ionic Liquids

Figure 1 show the viscosity of [C_2CNHim] incorporated with anion which was studied by Abobakr K. Ziyada. Despite having the highest potential of removing CO_2, DOSS has been found to be highly viscous, compared to other anion being studied. In application, high viscosity of ionic liquid will requires higher energy to pump the solvent into the CO_2 removal column. Therefore, it is preferable in the industry to use low viscosity solvent in the CO_2 removal plant.

2.2.3. Effect of anion and cation in an ionic liquids

Jessica has also cited the effect of cation and anion in ionic liquids toward gas solubility. The anion has been found to have higher effects on gas solubility in compared to the cation. The cation can be used to fine tune the properties of ionic liquids. In this case, DOSS has been proven to be very suitable for the removal of carbon dioxide. To counter the effect of viscosity, the cation needs to be slightly modified and introduce a new functionalized ionic liquid. Ether has been theoretically proven to decrease the viscosity of an ionic liquid, thus increasing the carbon dioxide capturing capability (Mark J Muldoon et al, 2007).

2.2.4. Incorporating ether functionalized to an ionic liquid

Report shows that by inserting an ether functional group into the alkyl chain, the CO_2-philicity of an ionic liquid will increase (Mark J Muldoon et al, 2007). The addition of ether groups is believed to improve CO_2 philicity by increasing the flexibility of alkyl chains, leading to increased free volume. The ether oxygen has also been shown to interact with the carbon of CO_2. Yannick H Heinz also reported the same observation in his work. The oxygen atom of an ether functional group has two lone pairs of electrons, which induce a negative charge on the atom, makin ethers very powerful organic solvents. The negatively charged oxygen atom attracts the positively charged carbon atom from the CO_2 molecule or the slighty positively charged hydrogen atom from H_2S. (Yannick H Heinz et al, 2009)

2.3. CHARACTERISTIC OF IONIC LIQUIDS

Ionic liquid materials can provide new options based upon different chemical and physical properties. Since there are many known and potential cations and anions, the potential number of ionic liquids is enormous.

2.3.1. Melting Point

Due to its low symmetry, the intermolecular interaction is weak for the cation, making the melting point lower. A good distribution of charge also contributes to lower melting point of an ionic liquid.

2.3.2. Colour

Ionic liquids has been found to be colourless according to reports. Typically for less pure ionic liquids, the colour ranges between yellowish to orange. The material used as a start and excessive heating during formation of imidazolium saltmay also effects the colour of the ionic liquids.

2.3.3. Vapour Pressure and Thermal Stability

One of the unique characteristic of ionic liquids is having a low vapour pressure. For thermal stability, it is mainly depends on the anion of the ionic liquid. Generally, the thermal stability of ionic liquids is limited by the strength of their heteroatom-carbon and their heteroatom-hydrogen bonds.

2.3.4. Density

As the bulkiness of an ionic liquid increase, the densities of the comparable ionic liquids are also increase.

2.3.5. Viscosity

The viscosity of ionic liquids depends on the tendency to form hydrogen bonding and also the strength of the Van der Waals interaction. By increasing the water content also decreases the viscosity of the ionic liquids. Viscosity measurement will indicates that ionic liquid will become less viscous with increase of water content.

3.2. IONIC LIQUIDS SYNTHESIS

The procedures of preparing the ether functionalized ionic liquids can be divided into three (3) sections:

- **SECTION A: Alkylation Reaction – Preparation of propanenitrile imidazole**
- **SECTION B: Quaternization Reaction – Preparation of [C_2CN-2-DEEim][Br] and [C_2CN-Pr-3-Pheim][Br]**
- **SECTION C: Metathesis Reaction – Preparation of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS]**

3.2.1. SECTION A: Alkylation Reaction

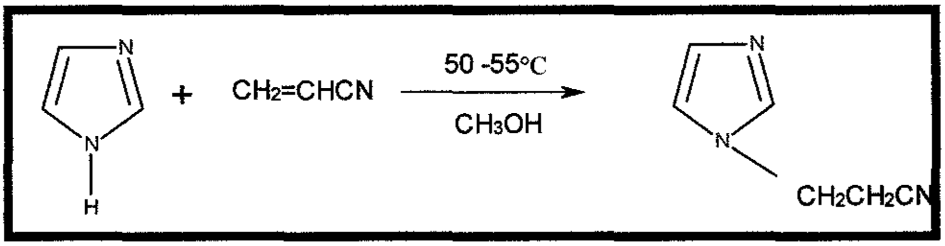


Figure 2: Synthesis of Propanenitrile imidazole

Alkylation is the transfer of an alkyl group from one molecule to another. Acrylonitrile was introduced to an imidazole molecule to form propanenitrile imidazole. The procedures of preparing propanenitrile imidazole are as shown in table 2.

Table 2: Procedure of Preparing Propanenitrile Imidazole

Equipment Setup	Procedure
 Figure 3: Reflux Apparatus Setup	1. 250ml round-bottomed flask is flushed with dry nitrogen 2. The flask was charged with imidazole (17.278, 0.254mol) in methanol (43ml, 1.0 mol) and mixed with acrylonitrile (20ml, 0.304mol). 3. The solution was heated under reflux and under nitrogen atmosphere at 50-55°C for 10 hours and then cooled to room temperature.
 Figure 4: Rotary Evaporator Setup	4. The volatile materials were removed from the mixture under vacuo at 70°C. The viscous liquid left was propanenitrile imidazole.
 Figure 5: Vacuum Oven	5. The produced propanentrile imidazole was left to dry in a vacuum oven at 70°C for 48 hours.

3.2.2. SECTION B: Quaternization Reaction

Quaternization reaction is any reaction in which a tertiary amine is converted to a quaternary ammonium compound. 2-bromoethyl ethyl ether and 3-phenoxypropyl bromide were used to synthesize [C_2CN-2-DEEim][Br] and [C_2CN-Pr-3-Pheim][Br] respectively. Table 3 and Table 4 shows the chemical structure of ether used and the quarternization reaction of respective ethers.

Table 3: Chemical structure and Process Reaction of 2-bromoethyl ethyl ether

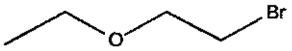
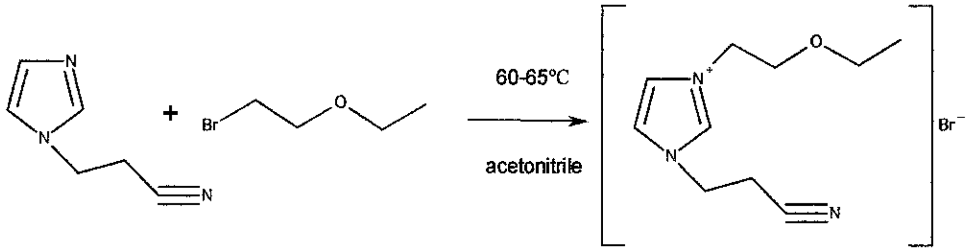
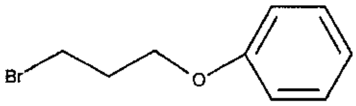
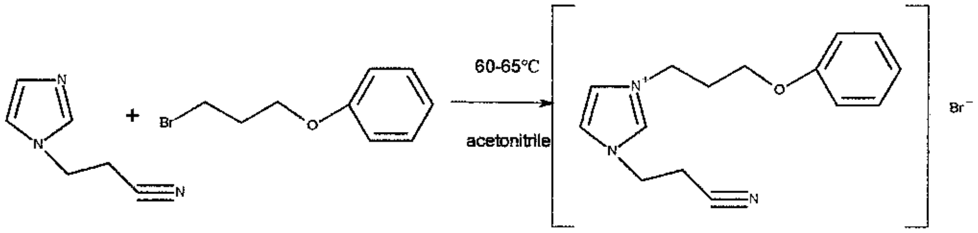
Description	**2-bromoethyl ethyl ether**
Chemical Structure	
Process Reaction	

Table 4: Chemical structure and Process Reaction of 2-bromoethyl ethyl ether

Description	**3-phenoxylpropy bromide**
Chemical Structure	
Process Reaction	

The procedure of preparing [C_2CN-2-DEEim][Br] and [C_2CN-Pr-3-Pheim][Br] are as shown in table 5.

Table 5: Procedure of quaternization process

Equipment Setup	**[C_2CN-2-DEEim][Br]**	**[C_2CN-Pr-3-Pheim][Br]**
 **Figure 3: Reflux Apparatus Setup**	1. 250ml round-bottomed flask is flushed with dry nitrogen	
	2. The flask was charged with propanenitrile imidazole (15.00g, 0.124mol) in acetonitrile (50ml, 0.95mol) and mixed with **2-bromoethyl ethyl ether** (15.36ml, 0.136 mol).	2. The flask was charged with propanenitrile imidazole (10.483g, 0.087mol) in acetonitrile (50ml, 0.95mol) and mixed with **3-phenoxypropyl bromide** (15.00ml, 0.095 mol).
	3. The solution was heated under reflux and under nitrogen atmosphere at 60-65°C for 48 hours and then cooled to room temperature. The compound is then washed with ethyl acetate for three times	
 **Figure 4: Rotary Evaporator**	4. The volatile materials were removed from the mixture under vacuo at 80°C. The viscous liquid left was the intermediate ether nitrile imidazolium.	

 **Figure 5: Vacuum Oven**	5. The produced intermediate ether nitrile imidazolium was left to dry in a vacuum oven at 70°C for 48 hours.

3.2.3. SECTION C: Metathesis Reaction

Metathesis reaction or anion exchange is a molecular process involving the exchange of bonds between the two reacting chemical species, which results in the creation of products with similar or identical bonding affiliations.[C_2CN-2-DEEim][Br] and [C_2CN-Pr-3-Pheim][Br] will undergo metathesis reaction with dioctysulfosuccinate sodium, DOSS to form [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] respectively. The byproduct of this reaction is Sodium Bromide, NaBr. Table 7 and table 8 shows the metathesis reaction of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] respectively.

Table 6: Metathesis Reaction of [C2CN-2-DEEim][DOSS]

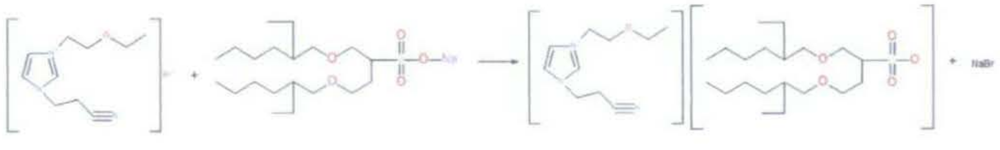
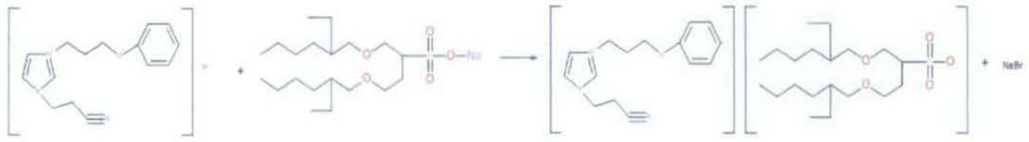
Description	**Synthesis of [C_2CN-2-DEEim][DOSS]**
Metathesis Reaction	

Table 7: Metathesis Reaction of [C2CN-Pr-3-Pheim][DOSS]

Description	**Synthesis of [C_2CN-Pr-3-Pheim][DOSS]**
Metathesis Reaction	

The procedure of preparing [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] are as shown in Table 9.

Table 8: Procedure of Metathesis Reaction

Equipment Setup	**[C_2CN-2-DEEim][DOSS]**	**[C_2CN-Pr-3-Pheim][DOSS]**
 **Figure 6: Metathesis reaction**	1. 20.00g, 0.1238 mol of **[C_2CN-DEEim][Br]** wasmixed with **Sodium DOSS** 32.431g, 0.1238 mol in 50 ml of acetone in a 250 ml round bottomed flask. The mixture was stirred at room temperature for 48 hours.	1. 20.00g, 0.059484 mol of **[C_2CN-DEEim][Br]** wasmixed with **Sodium DOSS** 26.444g, 0.059484 mol in 50 ml of acetone in a 250 ml round bottomed flask. The mixture was stirred at room temperature for 48 hours.

 **Figure 4: Rotary Evaporator**	2. The solid precipitate was separated and the solvent removed in vacuo. The resulting pale yellowish viscous compound was washed with ethyl acetate and diethyl ether.
 **Figure 5: Vacuum Oven**	3. The compound was then dried in a vacuum oven for 48 hours.

3.3. CHARACTERIZATION AND PROPERTIES MEASUREMENT

The new ionic liquid must be characterized and the property of ionic liquid is studied. The four measurements that are studied are namely RAMAN analysis, water content, thermogravimetrymeasurement, and density and viscosities measurement.

3.3.1. FTIR-ATR, NMR and Elemental Analysis

Shimadzu FTIR-8400S spectrometer with 4cm^{-1} resolution with a wave number range of 350 to 7800 cm^{-1} will be used. H NMR spectra is taken in $CDCl_3$ solvent and recorded on a BrukerAvance 300 spectrometer and CHNS-932 (LECO instruments) elemental analyzer is used to characterize the ether functionalized ionic liquid.

3.3.2. Water Content

The water content of the synthesized ionic liquid is determined using coulometric Karl Fischer titrator, DL 39 (Mettler Toledo) with Hydranalcoulomat AG reagent (Riedel-de Haen). The measurement is made in triplicate and the average values are recorded.

3.3.3. Thermogravimetry Measurements

Perkin-Elmer, Pyris V-3.81 is used to measure the decomposition temperature of the synthesized ionic liquid. The sample is placed in aluminium pans under nitrogen atmosphere at a heating rate of 10°C.min^{-1}. The measured start temperature (T_s) and decomposition temperature (T_d) are recorded.

3.3.4. Density and Viscosity Measurements

The density and viscosity measurements of the synthesized ionic liquid is carried out at a temperature range 293.25 K to 353.15 K using a Stabinger viscometer (Anton-Paar model SVM3000). The temperature is control to within ±0.01°C. The repeatability of measurements were 0.35%, and $\pm 5 \times 10^{-4}$ g.cm^{-3} for viscosity and density respectively.

3.4. CO_2 ABSORPTION TEST

Solubility test will be conducted to measure the capturing capability of an ionic liquid. In brief, the sorption chamber is flooded with carbon dioxide from a gas cylinder and its pressure is manipulated. The mol of CO_2 absorbed by the ionic liquid can be calculated using ideal gas law, $PV=ZnRT$. The mol fraction vs time and mol fraction vs pressure was prepared and will be discussed in the result and discussion section. The procedures of CO2 absorption test and setup are as shown below.

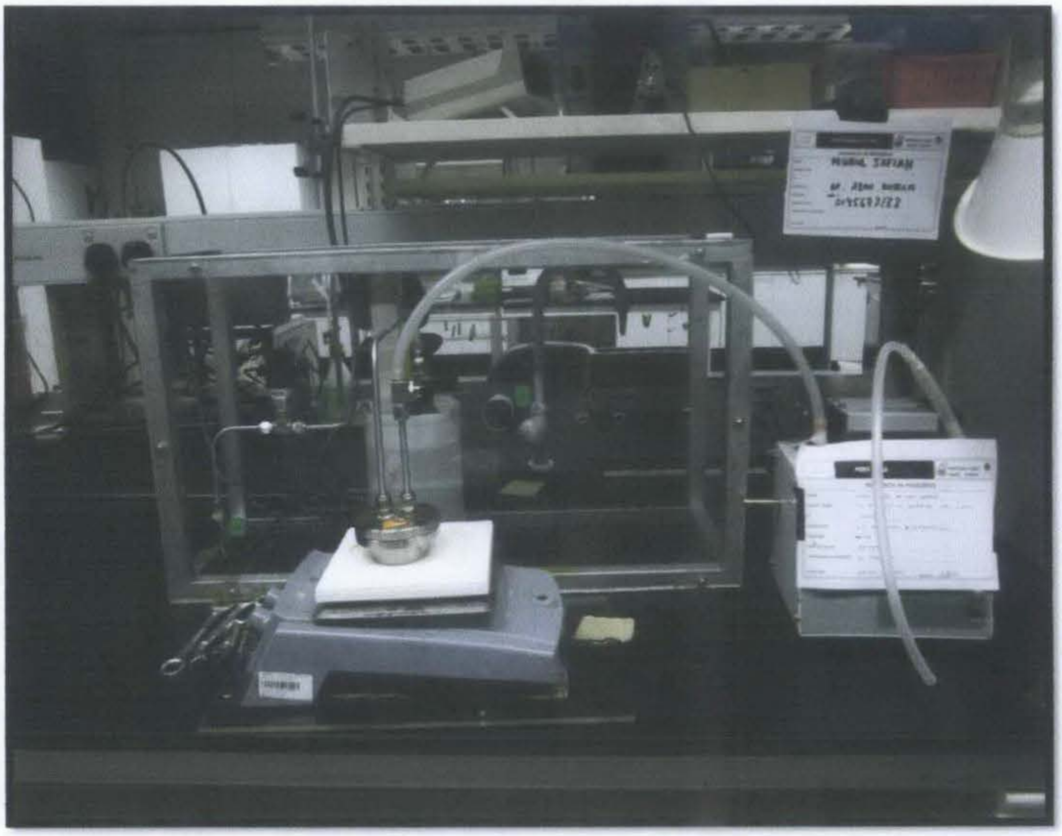


Figure 7: CO2 Solubility Testing Setup

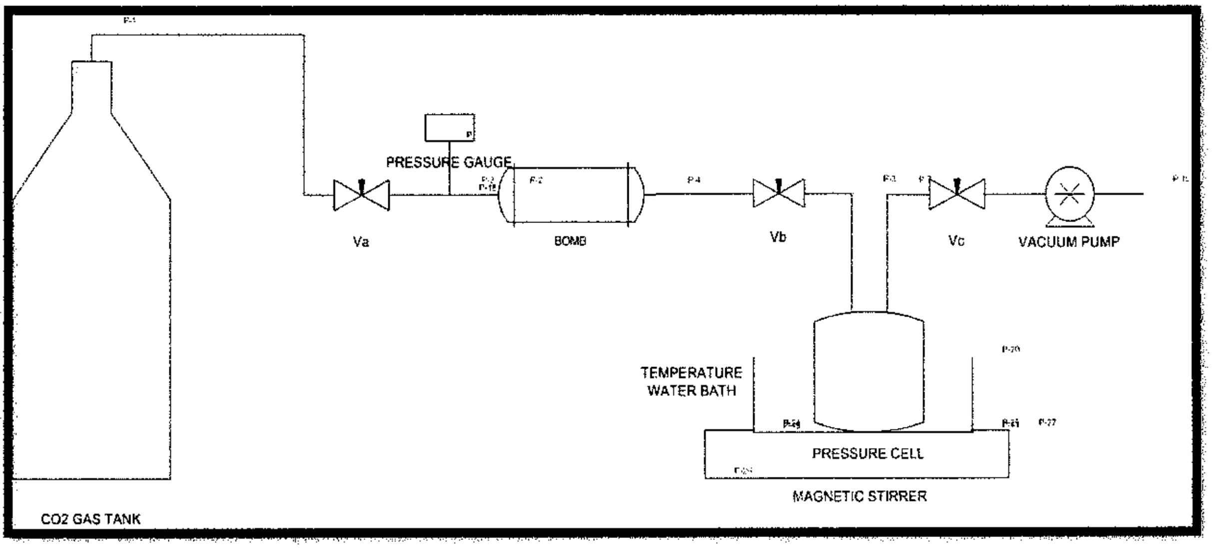


Figure 8: Schematic diagram of CO2 solubility test setup

Procedure:

1. Make sure Va, Vb and Vc are close tightly.
2. Open the regulator valve on the CO_2 gas tank.
3. Open Va until the desire pressure are achieved. Release pressure by opening Vb.
4. Insert ionic liquid inside the pressure cell.
5. Make sure Va and Vb are close. Open Vc and on the vacuum pump for 5 minutes.
6. Close Vc and open Vb slowly. The pressure was collected in 5 minutes interval for 2 hours.

3.4.1. Calculation for Mole Fraction of CO_2 in Ionic Liquid

The amount of CO_2 gas is determined by the Ideal Gas Law. It is a good approximation to the behavior of many gases under many conditions. The ideal gas law is a good approximation since the compressibility factor is assumed to be close to unity. The ideal gas law is as shown below

$$PV=ZnRT$$

Where

P is the absolute pressure of the gas (Pa)

Absolute Pressure = Gauge Pressure + Atmospheric Pressure

V is the volume of the gas (m^3)

Z is the compressibility factor, which depends on the temperature and pressure (dimensionless)

nis the amount of substance of the CO_2 gas (mol)

R is the gas constant (8.314 $JK^{-1}mol^{-1}$)

T is the absolute temperature (K)

The volume of CO_2 introduced into the system,

$$P_1V_1 = P_{initial}V_{initial}$$

The number of moles of CO_2 introduced into the system $n_1$is calculated using ideal gas law.

$$n_1 = P_1V_1/RT$$

Number of moles of CO_2 gas that is absorbed into the ionic liquids, $n_{absorbed}$is calculated using the following equation.

$$P_1V_1/Z_1n_1 = P_2V_2/Z_2n_2$$

$$n_{absorbed} = n_2 - n_1$$

Mole fraction of CO_2absorbed, x_{CO2} is calculated using the following equation.

$$x_{CO2} = (n_{absorbed} / n_{absorbed} + n_{IL})$$

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. CHARACTERIZATION OF IONIC LIQUIDS

4.1.1. Water Content

Table 9: Water content of [C2CN-2-DEEim][DOSS] and [C2CN-Pr-3-Pheim][DOSS]

	Water Content, ppm	
	[C_2CN-2-DEEim][DOSS]	**[C_2CN-Pr-3-Pheim][DOSS]**
First reading	532.527	554.445
Second Reading	487.684	593.561
Third Reading	485.672	579.889
Mean	**501.961**	**575.965**

Discussion:

The water content of[C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] was obtained. The water content of [C_2CN-2-DEEim][DOSS] is slightly lower than [C_2CN-Pr-3-Pheim][DOSS]. The presence of aromatic ring in [C_2CN-Pr-3-Pheim][DOSS] might affect the water content of the ionic liquid. However, no such literature has cited the effect of aromatic ring towards water content of an ionic liquid. The water content of the synthesized ionic liquids is found to be in the region of common ionic liquids, which is between 100 ppm to 1000 ppm.

4.1.2. ThermogravimetryAnalysis

Thermogravimetry analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Figure 15 and figure 16 shows the effect of temperature towards the weight of ionic liquid for [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] respectively.

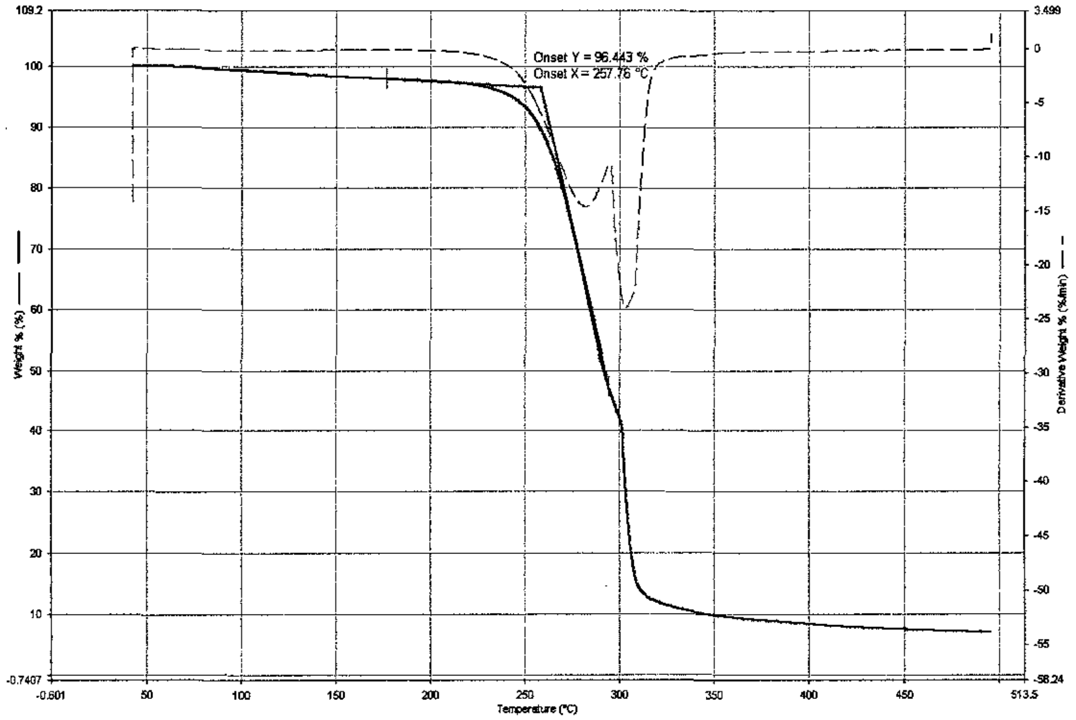


Figure 9: Thermogravimetry Measurement of [C2CN-2-DEEim][DOSS]

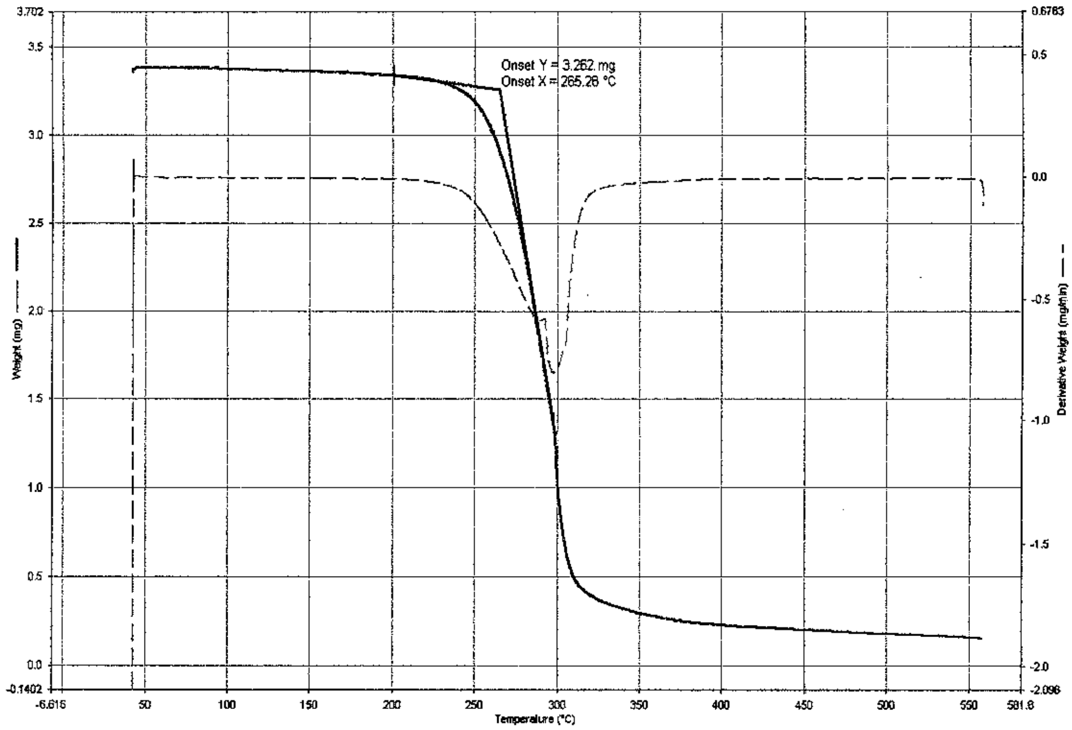


Figure 10: Thermogravimetry Measurement of [C2CN-Pr-3-Pheim][DOSS]

Table 10: Thermogravimetry Measurement of [C2CN-2-DEEim][DOSS] and [C2CN-Pr-3-Pheim][DOSS]

Thermogravimetry Measurement, °C	
[C_2CN-2-DEEim][DOSS]	[C_2CN-Pr-3-Pheim][DOSS]
257.76	265.28

Discussion:

The thermogravimetry measurement of [C_2CN-2-DEEim][DOSS]and [C_2CN-Pr-3-Pheim][DOSS]was obtained. It can be seen clearly the derivative changes in thermogravimety analysis for both ionic liquids are having two minimum values, illustrated by the red-dashed line. This shows that the bonding between cation and anion of the ionic liquid is weak. The bond between the cation and anion was broken and the cation and anion decompose at different rate. However, both ionic liquid can be conclude to be having moderate thermal stability in compared to common ionic liquid, having decompose temperature of up to 500°C.

4.1.4. Viscosity Measurement

Table 12: Viscosity of [C2CN-2-DEEim][DOSS] and [C2CN-Pr-3-Pheim][DOSS]

Viscosity, cp at 298.15K		
[C_2CN-2-DEEim][DOSS]	**[C_2CN-Pr-3-Pheim][DOSS]**	**[C_2CNHim][DOSS]**
14535.0	34803.0	19896.3

Discussion

The viscosity of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] was obtained. The viscosity for both synthesized ionic liquid was compared to [C_2CNHim][DOSS] obtained from literature. The viscosity of [C_2CN-2-DEEim][DOSS] has been found to be slightly lower than viscosity of [C_2CNHim][DOSS]. According to ZhaofuFei [6], the viscosity of ionic liquid will decrease with increase of ether chain in the ionic liquid. However, the viscosity [C_2CN-Pr-3-Pheim][DOSS] is very high compared to [C_2CNHim][DOSS]. Preliminary conclusion can be made that the presence of aromatic ring in ionic liquid will increase its viscosity; however no literature has cited the effect of aromatic ring towards viscosity in an ionic liquid.

4.1.5. RAMAN Analysis

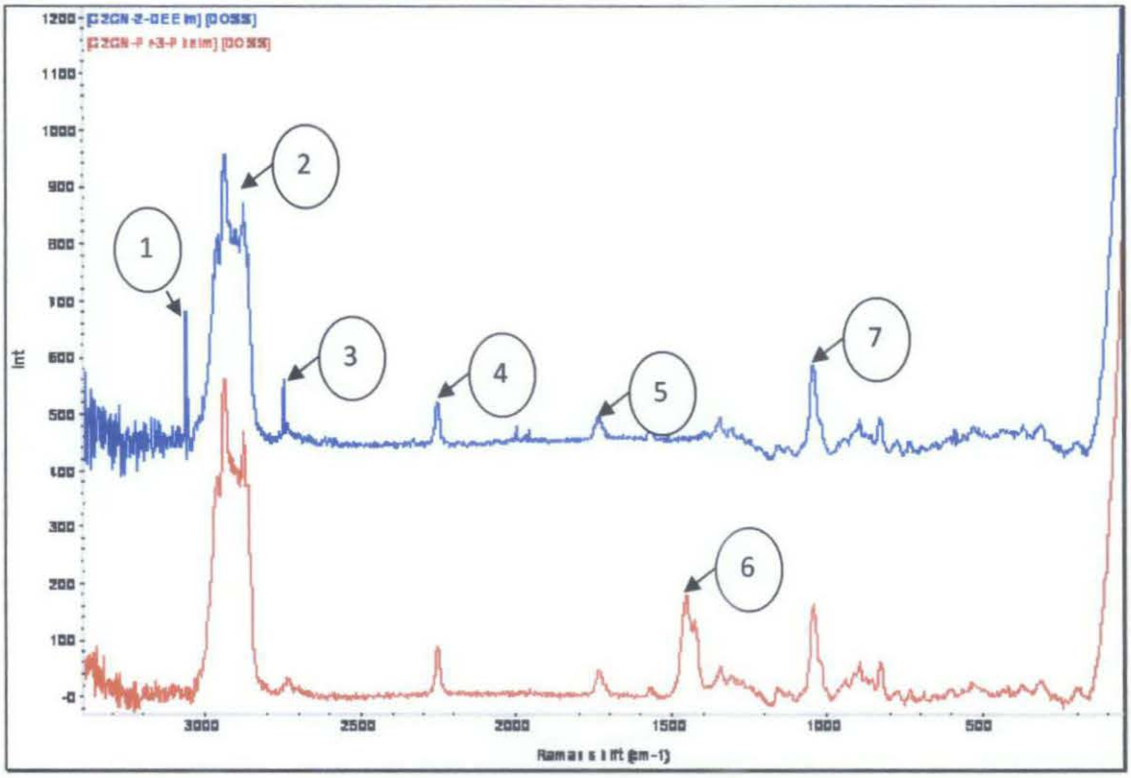


Figure 11: Raman Analysis of synthesized ionic liquids

Discussion:

The graph shows that the Raman analysis of [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS]. At position 1 shows the presence of anhydrous in [C_2CN-2-DEEim][DOSS]. This shows that the ionic liquid absorbs moisture. Position 2 shows the existence of DOSS both ionic liquid. Position 3 shows that a CH_3 chain exist in both ionic liquid. The CH_3 bond are from the DOSS anion. Position 4 shows that nitrile functional group exist in both ionic liquids. The nitrile was introduced to the ionic liquid during alkylation process of acrylonitrile with imidazole. Position 5 shows the existence of (C=O) in the ionic liquids. The (C=O) exist in the anion of the ionic liquid. Position 6 shows the aromatic ring of the ionic liquid. It can be seen that only [C_2CN-Pr-3-Pheim][DOSS] has the aromatic peak whereas [C2CN-2-DEEim][DOSS] does not has any aromatic in it. Lastly, position 7 show the existence of (C – O – C) in both ionic liquids. This proves that ether does exist in the ionic liquid.

4.2. CO_2 SOLUBILITY OF IONIC LIQUID

4.2.1. CO_2 solubility in [C_2CN-2-DEEim][DOSS]

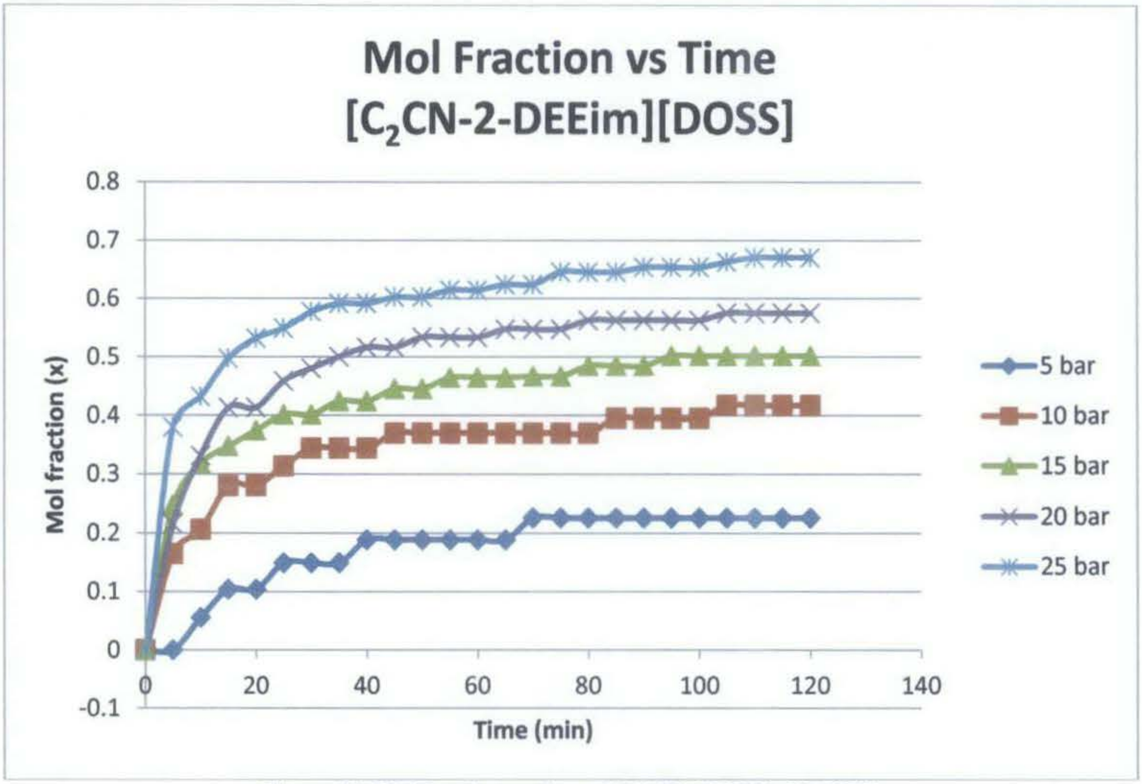


Figure 12: Mol fraction vs time of [C2CN-2-DEEim][DOSS]

Discussion

The mol fraction of CO_2 absorbed vs time in minute was plotted. The effect of pressure towards CO_2 solubility in [C_2CN-2-DEEim][DOSS] can clearly be seen. As the pressure increase, the mol fraction absorbed will increase. Since [C_2CN-2-DEEim][DOSS] is a physical solvent, [C_2CN-2-DEEim][DOSS] tends to prefer to absorb CO_2 in high pressure. From the results obtained, the time taken for [C_2CN-2-DEEim][DOSS] to achieve equilibrium is roughly 100 minutes. When the [C_2CN-2-DEEim][DOSS] was removed from the pressure cell to atmospheric pressure, the ionic liquids started to release air bubble, suspected to be CO_2. Therefore, [C_2CN-2-DEEim][DOSS] easily releases CO_2 at low pressure.

4.2.2. CO_2 solubility in [C_2CN-Pr-3-Pheim][DOSS]

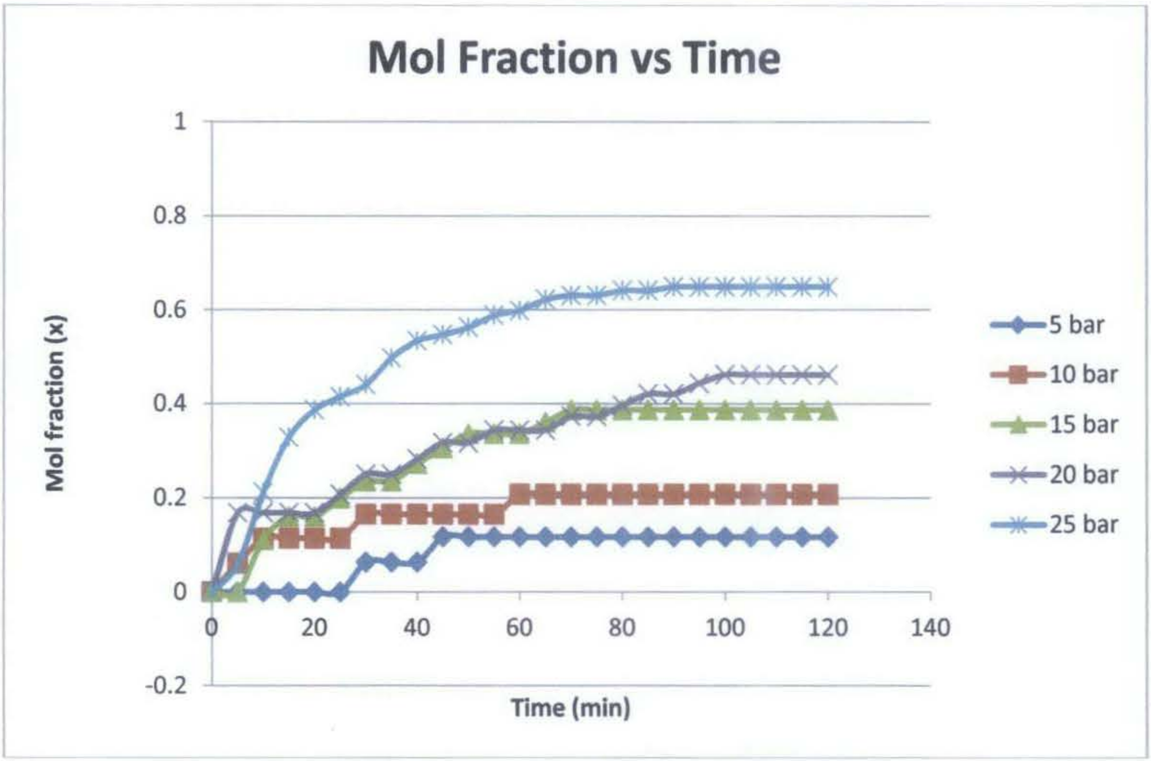


Figure 13: Mol fraction vs time of [C2CN-Pr-3-Pheim][DOSS]

Discussion

The mol fraction of CO_2 absorbed vs time in minute was plotted. Similar to [C_2CN-2-DEEim][DOSS], the CO_2 solubility in [C_2CN-Pr-3-Pheim][DOSS] increases with increase in pressure. The time taken for the [C_2CN-Pr-3-Pheim][DOSS]to achieve equilibrium is roughly 100 minutes. [C_2CN-Pr-3-Pheim][DOSS]are much more effective with increase in pressure, a typical properties of physical solvent. Similar to [C_2CN-2-DEEim][DOSS], [C_2CN-Pr-3-Pheim][DOSS]releases air bubbles of CO_2 when removed from the pressure cell. However, the ionic liquid starts foaming while releasing air bubbles of CO_2. Preliminary conclusion can be made that the ionic liquid is highly viscous, making the CO_2 bubble much harder to escape from the ionic liquid. This hypothesis can be justified from the viscosity measurement of both ionic liquids obtained in the characterization section.

4.2.3. CO_2 solubility in ionic synthesized ionic liquids as a function of pressure

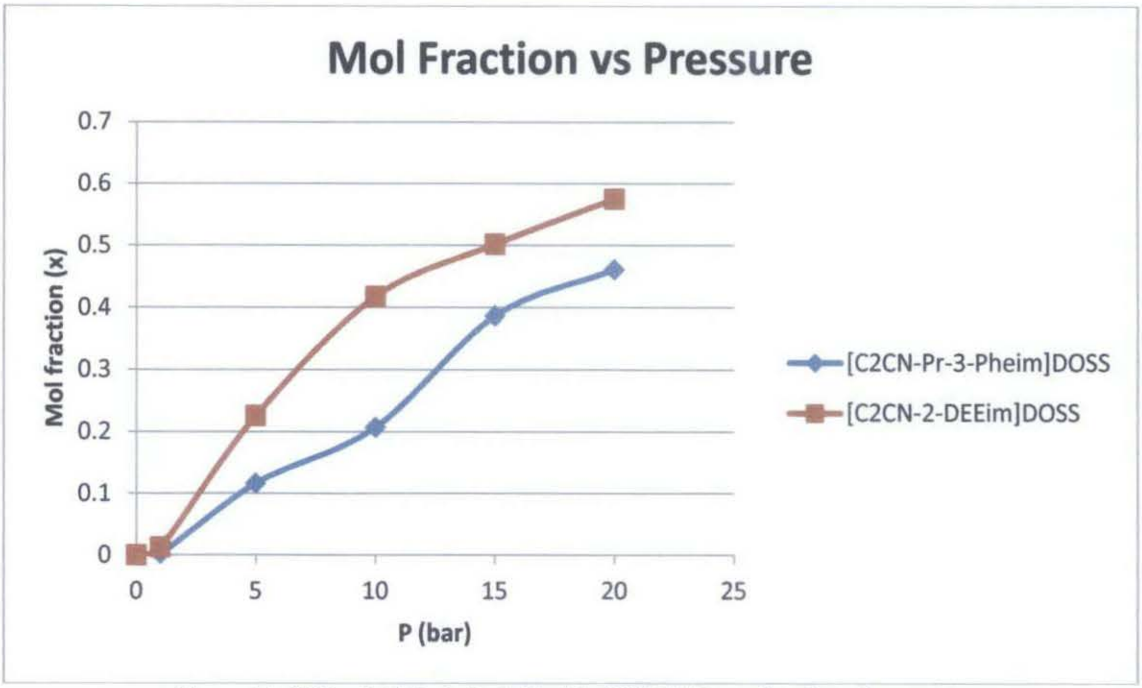


Figure 14: CO2 solubility in ionic liquid at 298.15 K as a function of pressure

Discussion:

The CO_2 solubility in [C_2CN-Pr-3-Pheim][DOSS], [C_2CN-2-DEEim][DOSS] and [C_2CNDim] at 298.15 K as a function of pressure was plotted. The CO_2 solubility in [C_2CN-2-DEEim][DOSS] and [C_2CN-Pr-3-Pheim][DOSS] was compared. With the same DOSS anion, the solubility of CO_2 in [C_2CN-2-DEEim][DOSS] was found to be higher in compared to [C_2CN-Pr-3-Pheim][DOSS] at each reading. The explanation for this observation is [C_2CN-Pr-3-Pheim][DOSS]has been found to be more viscous than[C_2CN-2-DEEim][DOSS], making it harder for CO_2 to penetrate the ionic liquid. The aromatic ring in [C_2CN-Pr-3-Pheim][DOSS] hinders the CO_2 from being in contact with the imidazolium alkyl chain. However, there is currently no literature which cited the effect of aromatic ring towards CO_2 gas solubility.

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APPENDICES

Calculation for preparation of [C_2CN-2-DEEim][DOSS]

ALKYLATION

Imidazole			Acrylonitrile			Propanenitrile imidazole		
MW	68.077	g/mole	MW	53.06	g/mole	MW	121.137	g/mole
Density	1.03	g/cm3	Density	0.806	g/cm3	mole	0.254	mole
Mole	0.254	mole	Mole	0.304	mole	mass	30.74542	g
Mass	17.278	g	Vol	20	ml@cm3			

QUARTENIZATION

Propanenitrile imidazolium			2-bromo ethyl ether			ether nitrile imidazolium		
MW	121.137	g/mole	MW	153.02	g/mole	MW	274.157	g/mole
Density	-	g/cm3	Density	1.357	g/cm3	mole	0.124	mole
Mole	0.124	mole	Mole	0.136	mole	mass	33.94797	g
Mass	15.000	g	Vol	15.35944	ml@cm3			

METATHESIS

Ether nitrile imidazolium			Sodium DOSS			END PRODUCT		
MW	274.157	g/mole	MW	444.56	g/mole	MW	615.8232	g/mole
mole	0.072951	mole	mole	0.072951	mole	mole	0.072951	mole
mass	20	g	mass	32.43105	g	mass	44.92486	g

Calculation for preparation of [C_2CN-Pr-3-Pheim][DOSS]

ALKYLATION

Imidazole			Acrylonitrile			Propanenitrile imidazole		
MW	68.077	g/mole	MW	53.06	g/mole	MW	121.137	g/mole
Density	1.03	g/cm3	Density	0.806	g/cm3	mole	0.254	mole
Mole	0.254	mole	Mole	0.304	mole	mass	30.74542	g
Mass	17.278	g	Vol	20	ml@cm3			

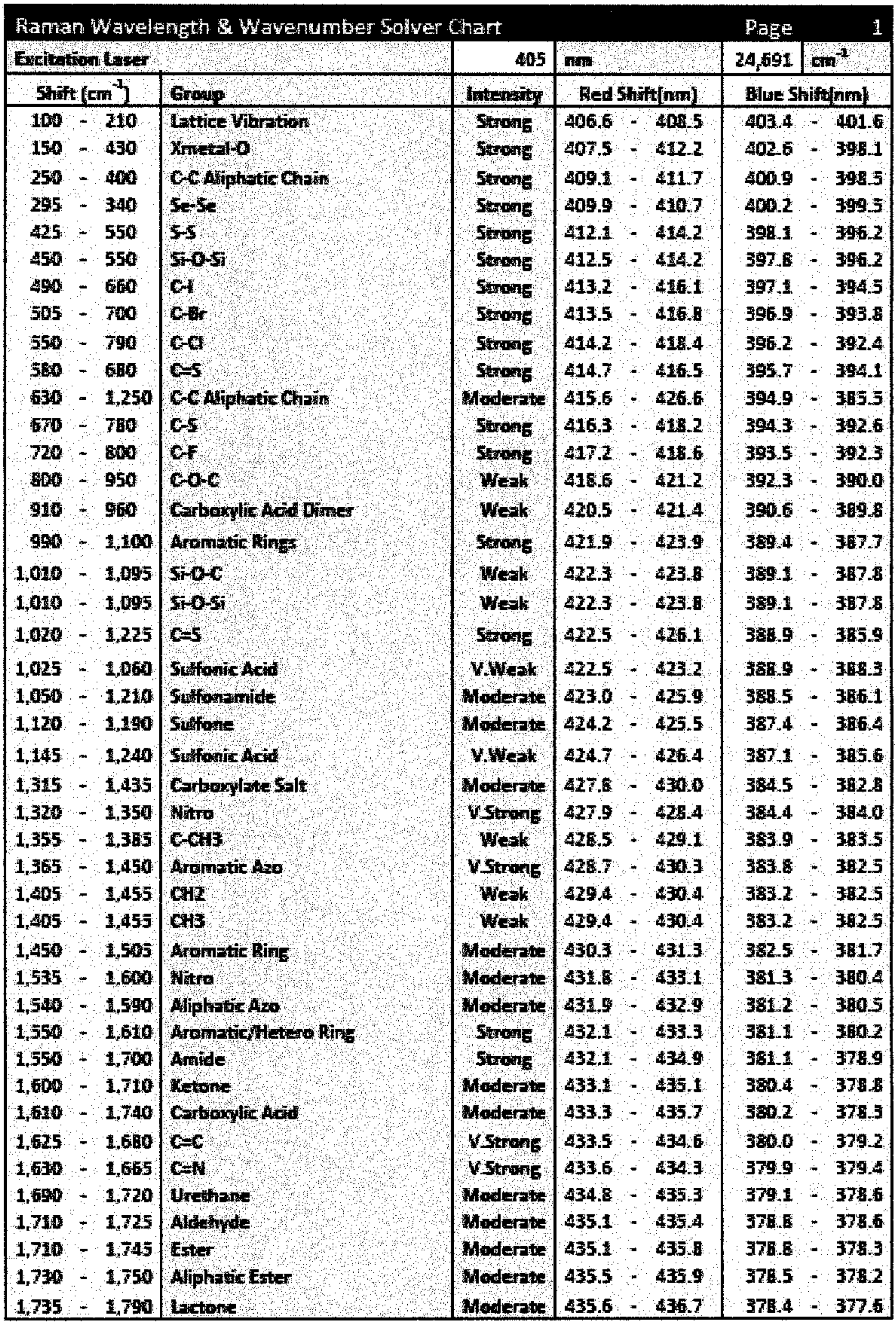
QUARTENIZATION

Propanenitrile imidazolium			3-phenoxylpropyl bromide			ether nitrile imidazolium		
MW	121.137	g/mole	MW	215.09	g/mole	MW	336.227	g/mole
Density	-	g/cm3	Density	1.365	g/cm3	mole	0.087	mole
Mole	0.087	mole	Mole	0.095	mole	mass	29.09666	g
Mass	10.483	g	Vol	15	ml@cm3			

METATHESIS

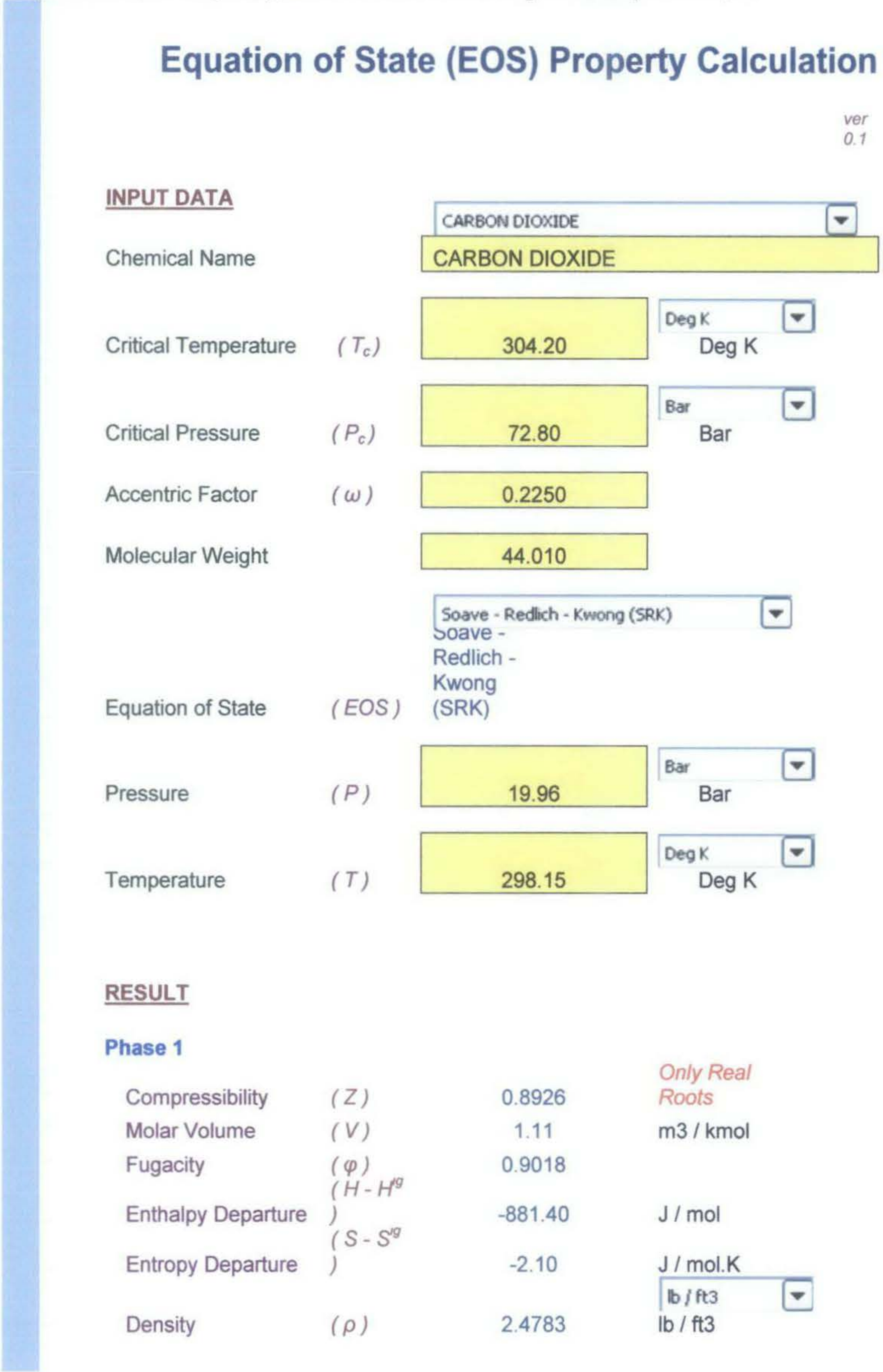
Ether nitrile imidazolium			Sodium DOSS			END PRODUCT		
MW	336.227	g/mole	MW	444.56	g/mole	MW	677.8932	g/mole
mole	0.059484	mole	mole	0.059484	mole	mole	0.059484	mole
mass	20	g	mass	26.44404	g	mass	40.32355	g

RAMAN Interpretation Table



Raman Wavelength & Wavenumber Solver Chart			Page	1
Excitation Laser		405	nm	24,691 cm^{-1}
Shift (cm^{-1})	**Group**	**Intensity**	**Red Shift(nm)**	**Blue Shift(nm)**
100 - 210	Lattice Vibration	Strong	406.6 - 408.5	403.4 - 401.6
150 - 430	Xmetal-O	Strong	407.5 - 412.2	402.6 - 398.1
250 - 400	C-C Aliphatic Chain	Strong	409.1 - 411.7	400.9 - 398.5
295 - 340	Se-Se	Strong	409.9 - 410.7	400.2 - 399.5
425 - 550	S-S	Strong	412.1 - 414.2	398.1 - 396.2
450 - 550	Si-O-Si	Strong	412.5 - 414.2	397.8 - 396.2
490 - 660	C-I	Strong	413.2 - 416.1	397.1 - 394.5
505 - 700	C-Br	Strong	413.5 - 416.8	396.9 - 393.8
550 - 790	C-Cl	Strong	414.2 - 418.4	396.2 - 392.4
580 - 680	C=S	Strong	414.7 - 416.5	395.7 - 394.1
630 - 1,250	C-C Aliphatic Chain	Moderate	415.6 - 426.6	394.9 - 385.5
670 - 780	C-S	Strong	416.3 - 418.2	394.3 - 392.6
720 - 800	C-F	Strong	417.2 - 418.6	393.5 - 392.3
800 - 950	C-O-C	Weak	418.6 - 421.2	392.3 - 390.0
910 - 960	Carboxylic Acid Dimer	Weak	420.5 - 421.4	390.6 - 389.8
990 - 1,100	Aromatic Rings	Strong	421.9 - 423.9	389.4 - 387.7
1,010 - 1,095	Si-O-C	Weak	422.3 - 423.8	389.1 - 387.8
1,010 - 1,095	Si-O-Si	Weak	422.3 - 423.8	389.1 - 387.8
1,020 - 1,225	C=S	Strong	422.5 - 426.1	388.9 - 385.9
1,025 - 1,060	Sulfonic Acid	V.Weak	422.5 - 423.2	388.9 - 388.3
1,050 - 1,210	Sulfonamide	Moderate	423.0 - 425.9	388.5 - 386.1
1,120 - 1,190	Sulfone	Moderate	424.2 - 425.5	387.4 - 386.4
1,145 - 1,240	Sulfonic Acid	V.Weak	424.7 - 426.4	387.1 - 385.6
1,315 - 1,435	Carboxylate Salt	Moderate	427.8 - 430.0	384.5 - 382.8
1,320 - 1,350	Nitro	V.Strong	427.9 - 428.4	384.4 - 384.0
1,355 - 1,385	C-CH3	Weak	428.5 - 429.1	383.9 - 383.5
1,365 - 1,450	Aromatic Azo	V.Strong	428.7 - 430.3	383.8 - 382.5
1,405 - 1,455	CH2	Weak	429.4 - 430.4	383.2 - 382.5
1,405 - 1,455	CH3	Weak	429.4 - 430.4	383.2 - 382.5
1,450 - 1,505	Aromatic Ring	Moderate	430.3 - 431.3	382.5 - 381.7
1,535 - 1,600	Nitro	Moderate	431.8 - 433.1	381.3 - 380.4
1,540 - 1,590	Aliphatic Azo	Moderate	431.9 - 432.9	381.2 - 380.5
1,550 - 1,610	Aromatic/Hetero Ring	Strong	432.1 - 433.3	381.1 - 380.2
1,550 - 1,700	Amide	Strong	432.1 - 434.9	381.1 - 378.9
1,600 - 1,710	Ketone	Moderate	433.1 - 435.1	380.4 - 378.8
1,610 - 1,740	Carboxylic Acid	Moderate	433.3 - 435.7	380.2 - 378.3
1,625 - 1,680	C=C	V.Strong	433.5 - 434.6	380.0 - 379.2
1,630 - 1,665	C=N	V.Strong	433.6 - 434.3	379.9 - 379.4
1,690 - 1,720	Urethane	Moderate	434.8 - 435.3	379.1 - 378.6
1,710 - 1,725	Aldehyde	Moderate	435.1 - 435.4	378.8 - 378.6
1,710 - 1,745	Ester	Moderate	435.1 - 435.8	378.8 - 378.3
1,730 - 1,750	Aliphatic Ester	Moderate	435.5 - 435.9	378.5 - 378.2
1,735 - 1,790	Lactone	Moderate	435.6 - 436.7	378.4 - 377.6

Equation of State (EOS), used to calculate compressibility Factor, Z.



Equation of State (EOS) Property Calculation

ver 0.1

INPUT DATA

		CARBON DIOXIDE	
Chemical Name		CARBON DIOXIDE	
Critical Temperature	(T_c)	304.20	Deg K Deg K
Critical Pressure	(P_c)	72.80	Bar Bar
Accentric Factor	(ω)	0.2250	
Molecular Weight		44.010	
		Soave - Redlich - Kwong (SRK)	
Equation of State	(EOS)	Soave - Redlich - Kwong (SRK)	
Pressure	(P)	19.96	Bar Bar
Temperature	(T)	298.15	Deg K Deg K

RESULT

Phase 1

			Only Real Roots
Compressibility	(Z)	0.8926	
Molar Volume	(V)	1.11	m3 / kmol
Fugacity	(φ)	0.9018	
Enthalpy Departure	$(H - H^{ig})$	-881.40	J / mol
Entropy Departure	$(S - S^{ig})$	-2.10	J / mol.K
Density	(ρ)	2.4783	lb / ft3 lb / ft3

Phase 2

Compressibility	(Z)
Molar Volume	(V)
Fugacity	(φ)
Enthalpy Departure	$(H - H^{ig})$
Entropy Departure	$(S - S^{ig})$
Density	(ρ)

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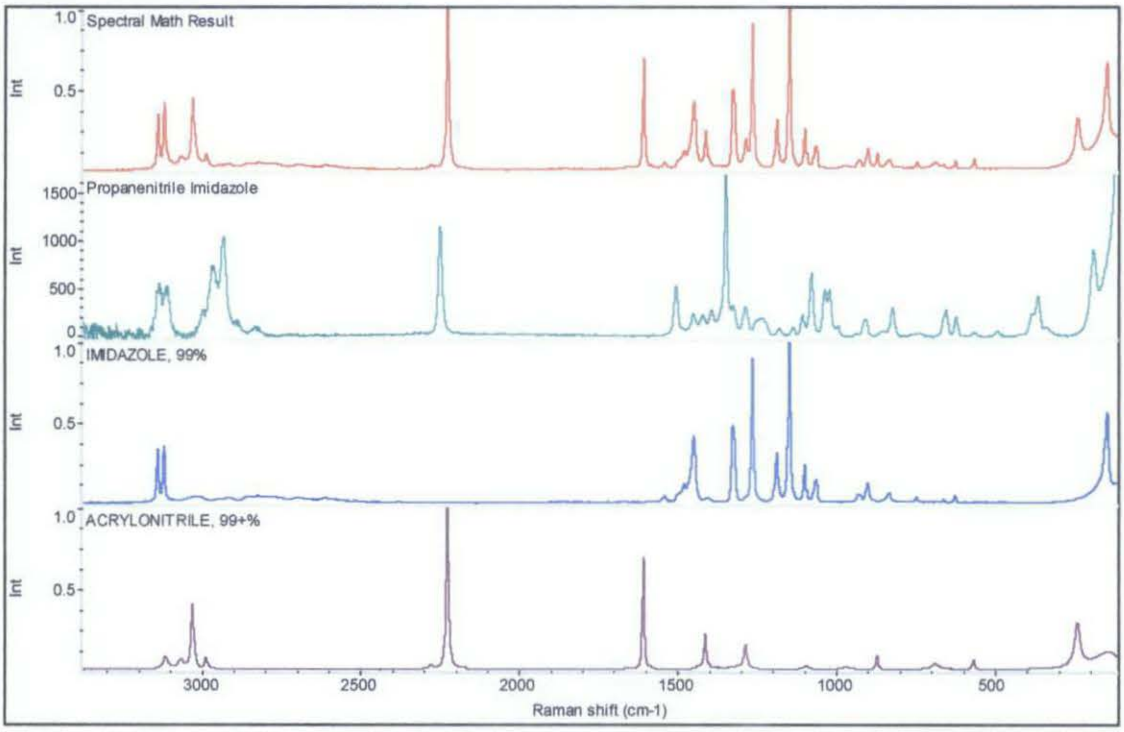
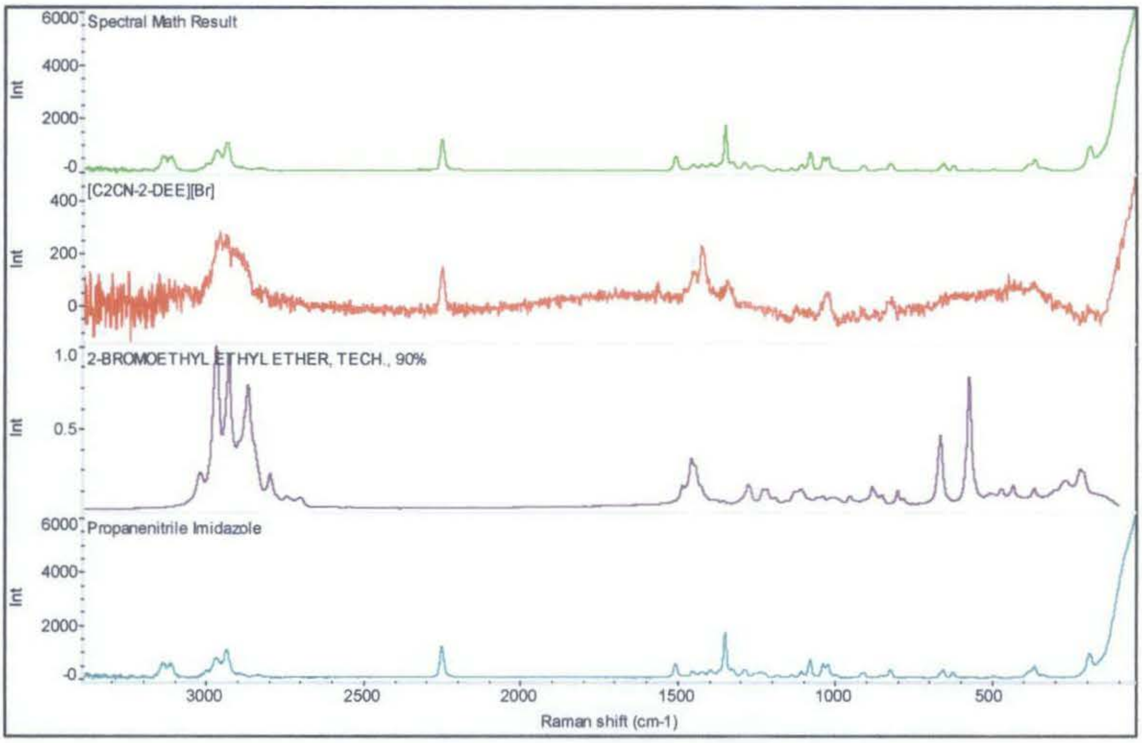
RAMAN Analysis for intermediate reactions

- **Alkylation**



- **Quaternization process of [C_2CN-2-Deeim][Br]**



- **Quaternization of [C$_2$CN-Pr-3-Pheim][Br]**