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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The chemistry world is exploring globally since 19th century, for alternative solution for conventional solvent which is greener to the process as well as environment. Holbrey et al. [1] described that green chemical technology is based on opportunities to improve processes by using ‘green principles’ in production processes. It can be achieved by reducing or eliminating the waste, improving chemical syntheses, extractions and separations, and reusability of reaction solvents. Several industrial and academic research teams have highlighted the core aspects for green chemistry and they are interested in redesigning the chemical processes to reduce, or eliminate the losses of solvents due to its volatile organic compounds (VOCs).

In 1888, the remarkable discovery was found on potential green technology namely ionic liquid (ILs) by Gabriel and Weiner [2] . The past few years have also witnessed an interest in the use of ILs as a novel class of solvents, and are commonly known as room-temperature ionic liquids (RTILs) [3], [4]. Ever since RTILs exhibit low melting point, high thermal stability and negligible vapor pressure, several research teams had carried out the intense investigation for various applications such as for solvent/catalyst applications, electrolyte/fuel cells, pharmaceutical, separation process and etc. [5]. There were vast number of ILs which had been established for specific (known as task-specified ionic liquids, TSILs) and selective gas separation mainly for CO_2 capture. These ILs are completely composed of ions, there is no solution that they are dissolved in and typically composed of a bulky organic cation; some common examples of cations are imidazolium, and pyridinium. For possible anion to be paired with cation, it could be a halide such as chloride (Cl^-), bromide (Br^-), include organic or inorganic anions such as tetrafluoroborate (BF_4^-) and hexafluorophospate (PF_6^-) [6].

In the present work, the focus is onto the removal for carbon dioxide (CO_2) from natural gas in order to improve the value and the quality of natural gas for its downstream process/application. Up till now, the commercial CO_2 removal process utilizes chemical absorption techniques using alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) as well as N-methyldiethanolamine (MDEA) as solvents [7]. Even though the solvents are capable of removing CO_2 from natural gas, its main drawback namely the high cost of heat regeneration encourage researching to find alternative solvents and ILs have been identified as potential solvents for future betterment.

1.2 PROBLEM STATEMENT

Natural gas, mostly composed of CH_4, contain some complex contaminants such as CO_2, H_2S, CO. CO_2 specifically needs to be removed off due to corrosion to the pipelines as well as the major equipment such as reactor, exchanger and column which then can hinder downstream process and contribute to the environmental hazards once it escapes to the environment. In addition, natural gas is rarely extracted from the earth in a pure state which enough to trunk directly into the pipeline networks for delivery to the consumers. According to Davis [8], the gas normally contains adulterants which run the gamut from water and heavier hydrocarbons to so-called acid gases. Therefore, the removal of these acid gases; CO_2, H_2S, CO and others will improve the value and the quality of natural gas for its downstream process.

Recently, most of the commercial CO_2 scrubbing processes still exploit the organic compound such as alkanolamines which is categorized as volatile organic compounds (VOCs) as the solvents in the process [7]. As a result, the use of VOCs has created major problems due to their volatility to the process itself as well as to the environment. As the solvents running in the process, it will keep evaporate due to its high volatility and this will hold back the solvent recovery system which then can create lost to the plant performance. Besides, in more serious issue to look, VOCs will evaporate to the surrounding and its toxicity will be a source of a number of environmental pollution problems [9].

As a new generation of solvents, RTILs have attracted the attention of the chemists and engineers all over the world to come out with the intense research in order to get a deeper understanding on these unique properties of RTILs. Among the established ionic liquids, imidazolium-based ILs was successfully applied for the

CO_2 removal [5], [7], [10]. Most of them investigated imidazolium-based ILs with 1-butyl-3-methylimidazolium [bmim] ILs such as [bmim][Ac], [bmim][BF_4], [bmim][PF_6] as the chosen ILs. Out of the existing established work, very few of them reported on open literature researching on the effect of 1-hexyl-3-methylimidazolium [hmim] ILs on CO_2 solubility. This work intends to study the effect of longer alkyl chain IL i.e. [hmim] ILs on CO_2 solubility.

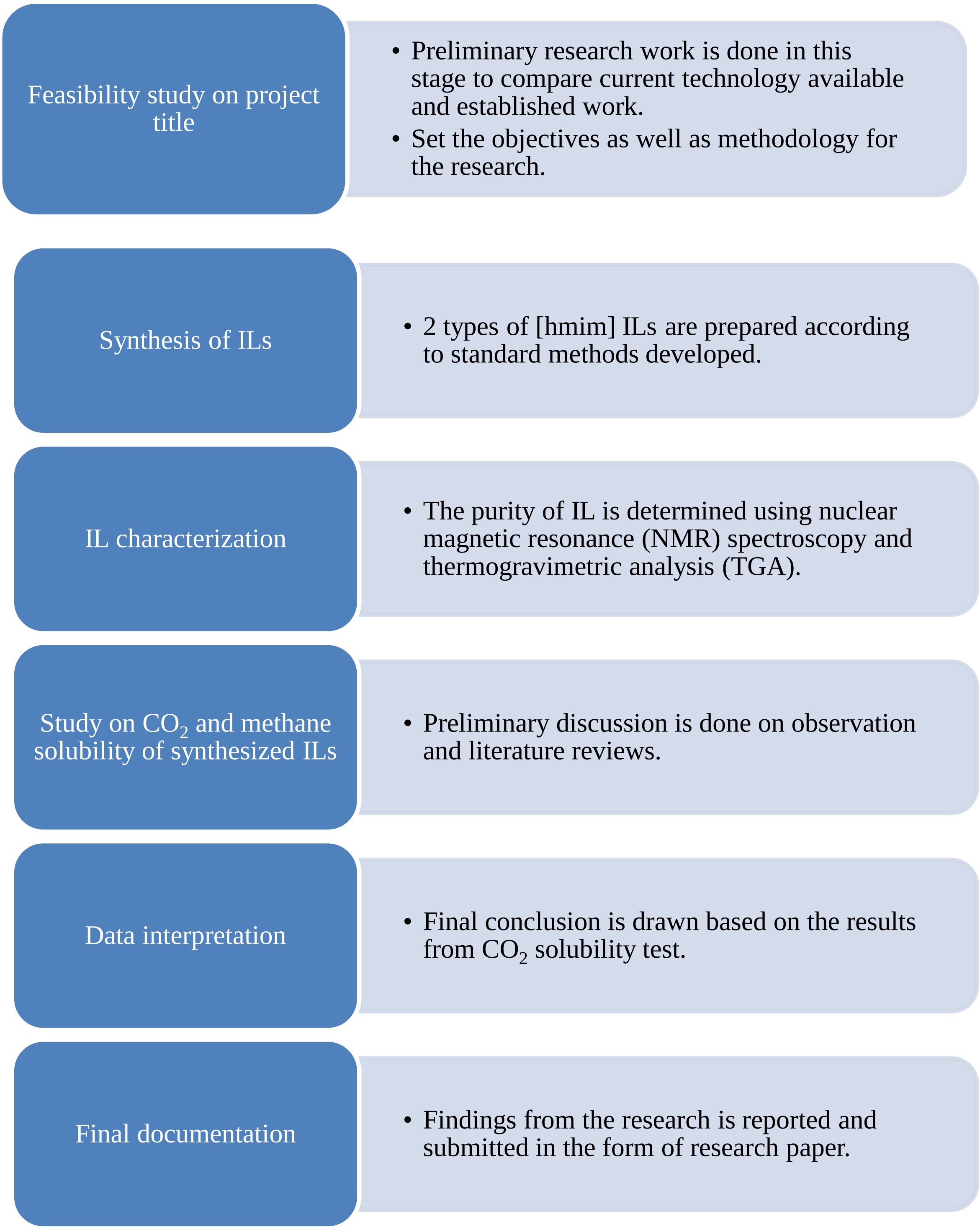
1.3 OBJECTIVES

The objectives of the research are:

1. To synthesize 1-hexyl-3-methylimidazolium [hmim] ionic liquids namely, [hmim][Ac] and [hmim][Tf_2N].
2. To study the effect of anion and pressure onto the solubility of CO_2 in the synthesized ionic liquids.

1.4 SCOPE OF STUDY

To achieve these objectives, this study is divided into several systematic phases in ensuring the research success. The phases can be illustrated in Fig. 1 below:



Feasibility study on project title

- Preliminary research work is done in this stage to compare current technology available and established work.
- Set the objectives as well as methodology for the research.

Synthesis of ILs

- 2 types of [hmim] ILs are prepared according to standard methods developed.

IL characterization

- The purity of IL is determined using nuclear magnetic resonance (NMR) spectroscopy and thermogravimetric analysis (TGA).

Study on CO_2 and methane solubility of synthesized ILs

- Preliminary discussion is done on observation and literature reviews.

Data interpretation

- Final conclusion is drawn based on the results from CO_2 solubility test.

Final documentation

- Findings from the research is reported and submitted in the form of research paper.

Figure 1: Flow chart of project work

1.5 GANTT CHART

Table 1: Gantt chart for FYP1

	Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of project topic	■	■						M I D S E M B R E A K						
2	Preliminary research work		■	■	■	■									
3	Submission of extended report						■								
4	Laboratory & apparatus requisition						■	■							
5	Chemical purchase						■	■		■	■	■	■		
6	Proposal defense									■					
7	Ionic liquids synthesis									■	■	■	■	■	■
8	Submission of interim draft report													■	
9	Submission of interim report														■

Table 2: Gantt chart for FYPII

	Detail/Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
1	Project work continues	■	■	■	■	■	■	■	MIDSEM BREAK	■	■	■	■	■		
2	Submission of progress report									■						
3	Pre-SEDEX											■				
4	Submission of draft report												■			
5	Submission of dissertation													■		
6	Submission of technical paper													■		
7	Oral presentation														■	
8	Submission of project dissertation															■

CHAPTER 2

LITERATURE REVIEW

2.1 CARBON DIOXIDE REMOVAL PROCESS: ABSORPTION

Natural gas generally contains in large quantity of methane (CH_4) together with heavier hydrocarbons such as ethane, isobutene, n-butane, and considerable amount of acid gases such as CO_2, H_2S, and other sulfur components. CO_2 contained in natural gas need to be removed off due to corrosion to the pipelines system and plant equipment, and reduction in heating value of the gas which can lead to product “off-spec”. Basically, to meet end users’ natural gas specification, the CO_2 concentration needs to be approximately 2.5% in the pipelines which can be accomplished in a numbers of ways [11], one of them is absorption.

Absorption process is either physical or chemical phenomenon occurred whereby atoms, molecules or ions enter a bulk phase (solvent) [12]. Several solutes are absorbed from the gas phase into the liquid phase in absorption [13]. Moreover, this approach can be divided in two (2) types of absorption per se; physical absorption and chemical absorption which both of them are commonly used for commercial separation process.

2.1.1 Physical vs. Chemical Absorption

Generally, physical absorption or also called as “physisorption” occurs between a gas mixture and a liquid solvent such as ILs compound. It only involves the transfer of mass that takes place at the interface between the liquid and the gas. This type of absorption depends mainly on the solubility of gasses, pressure and also temperature.

Meanwhile, chemical absorption or “chemisorption” is an employment of chemical reaction between the absorbed and the absorbing substances. Rarely, it combines with the physisorption. This type of absorption depends upon the stoichiometry of the reaction and the concentration of its reactants [12].Table 3 shows the comparison between physisorption and chemisorption [14]:

Table 3: Comparison between physisorption and chemisorption

Physisorption	**Chemisorption**
Solubility proportional to solute partial pressure	Solubility not highly sensitive to solute partial pressure
Low heat of absorption	High heat of absorption
Regenerate by flashing	Need more energy for regeneration
Require multi-stage process to completely remove solute	Easily reduce solute to low level

2.2 IONIC LIQUID TECHNOLOGY

During the recent decade, the chemistry world has witnessed an interest in the use of ILs for the synthetic organic chemistry due to its unique behavior. Morton [15] stated that ILs are essentially non-volatile molten salts with its' melting point less than 100°C and also known as RTILs since the liquid range can span from below 0°C to above 300°C. This remarkable salt compound has demonstrated a significant potential for use in a broad range of applications. The common types of the ILs are based on imidazolium and pyridinium cations with possible anion such as chloride (Cl^-), bromide (Br), tetrafluoroborate (BF_4^-) and hexafluorophospate (PF_6^-) and others [6] as shown in Fig. 2.

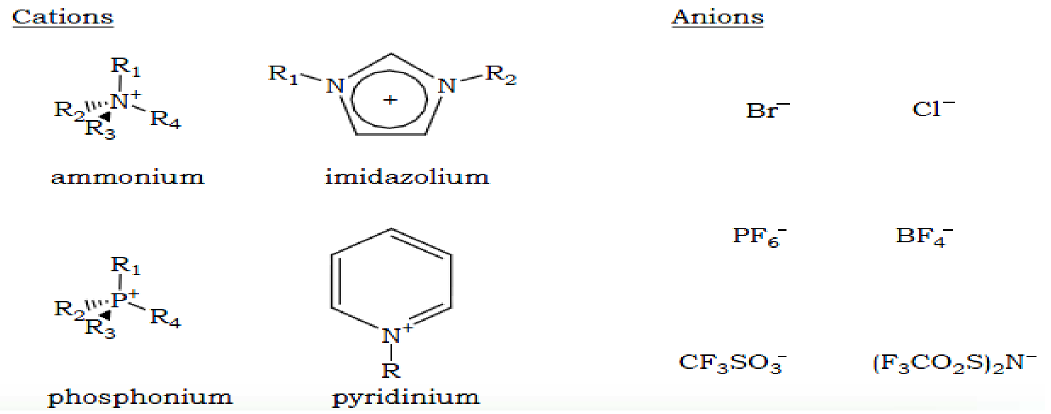


Figure 2: Typical IL cations and anions

The ionic nature of ILs has important impacts for the structure of the liquid on the nanoscopic level. Spectroscopic evidence suggests the presence and importance of the formation of intermolecular cation/anion hydrogen bonds [16]. Favorable and specific anion/cation interactions seem to induce the formation of a persistent anion/cation network.

2.2.1 Solubility of CO_2 in ILs

The non-volatility of ILs avoid contamination of outlet gas stream when ILs are used as absorbent in removing CO_2 from natural gas. This advantage gives ILs huge predominance over the traditional VOCs used in CO_2 removal process [17]. Iwona et al [17] stated that the excellent media for this purpose are imidazolium-based ILs and the same statement been repeated in other reviews [16], [18], [19] based on the result of experimental and theoretical approaches.

At the molecular scale, it was established that the nature of the anion plays a central role for the interaction with CO_2 through specific molecular interactions [10]. In contrast, the cation effects become a secondary role in influencing the solubility of CO_2 in a compound of imidazolium-based ILs. However, Blanchard et al. [20] have found that the increasing of number of the alkyl chain did slightly increase the solubility and it was established by a number of systems involving tetrafluoroborate ($[BF_4]$), hexafluorophosphate ($[PF_6]$), and bis(trifluoromethylsulfonyl)imide ($Tf_2N]$) as the anions. It was proposed that CO_2 molecule can be intercalated in the cavities of the ILs with the conformation of the cation.

Moreover, the strength of this CO_2-anion interaction cannot be solely responsible for the solubility of CO_2 because, as been clarified by Cabaco et al. [10], the strength of anion-cation interaction also affects the available free volume contribution, due to strong Coulombic interaction. Based on the comparative study done by them, it showed that solubility of CO_2 is higher with the IL contains fluorinated anions, such as bis(trifluoromethylsulfonyl)imide ($Tf_2N]$), compared to non-fluorinated anions.

Cadena et al. [19], from the experimental and molecular simulation, have crossed to the conclusion that the association of CO_2 with the anion is the best indicator of CO_2 solubility in imidazolium-based ILs. Besides, the changes in the cation involving the alkyl group are expected to have relatively little influence onto solubility. Due to the strong Coulombic interactions, the underlying fluid structure of the IL is relatively unperturbed by the addition of the CO_2 and this kept the IL stay in its' organized form.

2.2.2 Synthesis of ILs

Generally, the method to synthesize 1-alkyl-3-methylimidazolium ILs is not really complex, it involves two (2) consecutive quaternisation-methatesis/acid-base methods [21]. However, the first step is to afford a precursor of imidazolium-based ILs and has two (2) disadvantages: (a) it is time consuming; and (b) an excess of haloalkane (10-100%) is required to achieve a good yields. Furthermore, the same author explained that, it becomes worst when long-chained derivatives are prepared since high boiling haloalkanes are difficult to remove from the mixture and the alternative way is, synthesizing using microwave (mw) radiation which can easily found in the other literatures [22]. Briefly, the purpose of using microwave is to get a clean process and shorten the reaction times considerably.

Next is the preparation of IL via metathesis with a metal salt or an acid-base neutralization reaction. There are two (2) possible route for the ILs synthesis which is for the first one, it is one-way reaction in which desired ILs are produced directly from its precursor as shown in Fig. 3. As a result, the cation and anion are formed together in the same working step [23].

Meanwhile, the second route, it is a poly-way reaction where desired ILs are synthesized at least two reaction steps involved. First step, the synthesis of the cation as a salt with an easily changeable anion (quaternization) and followed by second step, the anion metathesis.

From the study of Carmicheal et al. [21], they found that after the metathesis and acid-base neutralization reaction, respectively, producing a stoichiometric amount of waste as a contaminant in the mixture. To get the ILs mixture without impurities, which may react with the solutes, the further purification step is needed.

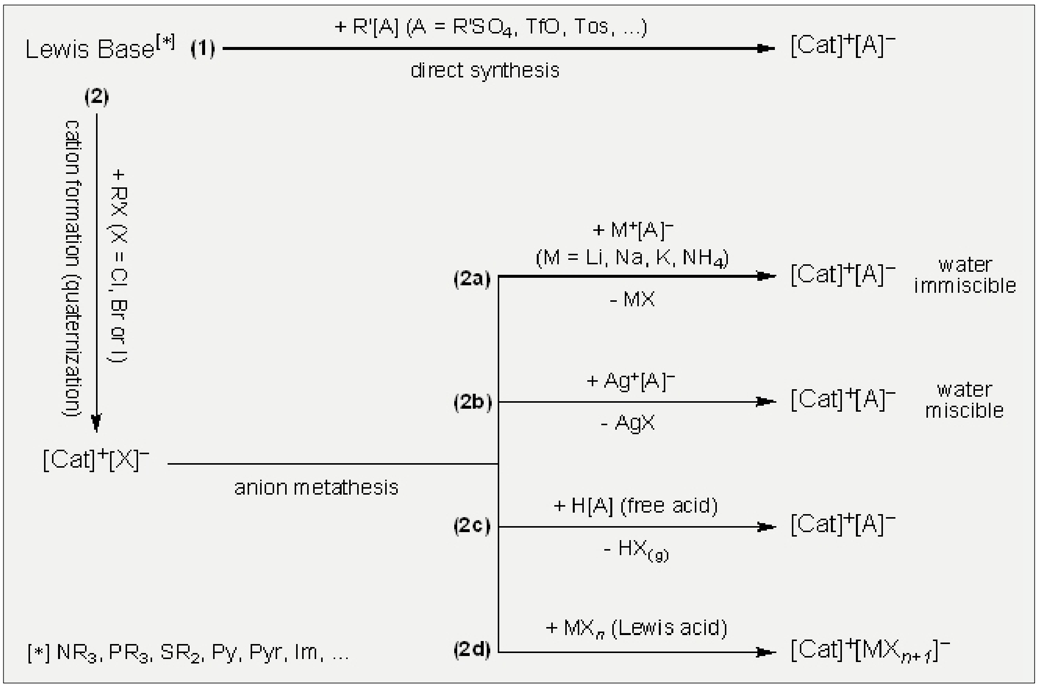


Figure 3: General preparation route for IL synthesis

CHAPTER 3

METHODOLOGY

3.1 SYNTHESIS OF IL MIXTURES

In this present research, all ILs are prepared according to the established methods [5], [7]. Basically, there are two (2) type of imidazolium-based ILs need to be synthesized, namely 1-hexyl-3-methylimidazolium acetate ([hmim][Ac]) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]), from it precursor which is 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]).

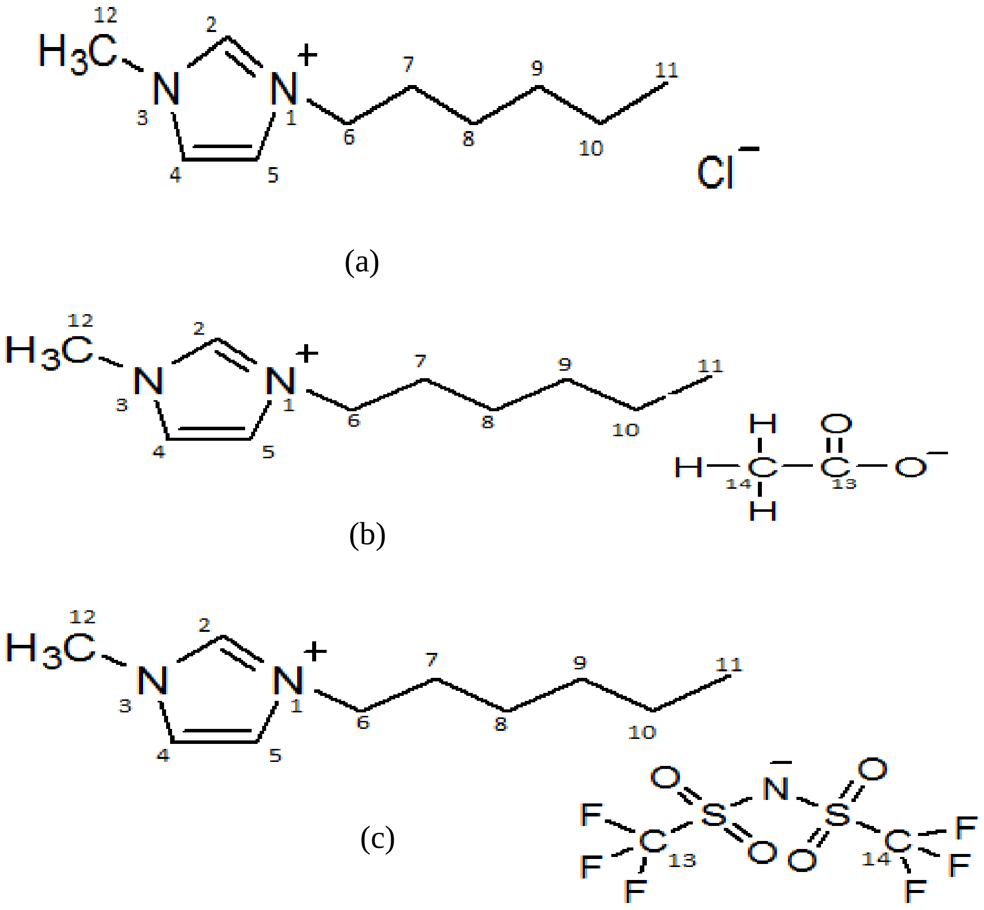


Figure 4: The chemical structure of (a) [hmim][Cl], (b) [hmim][Ac] and (c) [hmim][Tf_2N]

3.1.1 Preparation of 1-hexyl-3-methylimidazolium chloride ([hmim][Cl])

The synthesis of [hmim][Cl] via reflux process:

1. 40 mL of 1-methyl imidazole([mim]) was poured into the 250 mL 3-round neck flask and the setup for reflux process has been prepared which consists of 250 mL 3-neck round flask contained [mim].
2. 60 mL of n-chlorohexane (CH) and 50 mL of ethyl acetate (EA) were injected into the 250 mL 3-neck round flask containing [mim] through septum at one of the mouth of flask.
3. The sample was refluxed at temperature of 70^{o}C for 3 days under inert condition.
4. The whole process was repeated for 2 batches of [hmim][Cl].

Figure 5: The reflux process of [hmim][Cl]

The purification of [hmim][Cl] by re-crystallization:

1. The solvent (upper layer of the solution) was separated from the product (lower layer).
2. Another 50 mL of EA which has been warmed up for 5 minutes in the water bath was poured into [hmim][Cl].
3. The solution then was cooled in an ice bath.
4. The resulting 2-layer solution was separated in which the upper layer was decanted from the flask.

5. The steps above were repeated for 3 times.

The drying process:

1. The product was transferred into Rotary Evaporation (RotaVap) flask and evaporated using RotaVap equipment in order to remove the remaining solvent left in the product as shown in Fig. 6.
2. RotaVap process was left for 5 hours at temperature of 70℃.
3. The empty container was then weighted before the evaporated product was transferred into it.
4. The product was further dried using vacuum oven.
5. Drying process was carried out for 1 day at temperature of 70℃.
6. The sample container was then been weighted again to get the yield of the [hmim][Cl] synthesis.

Figure 6: Separation between solvent and [hmim][Cl] using RotaVap equipment

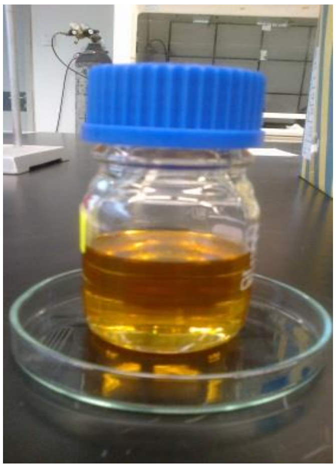


Figure 7: Final product of synthesized [hmim][Cl]

3.1.2 Preparation of 1-hexyl-3-methylimidazolium acetate ([hmim][Ac])

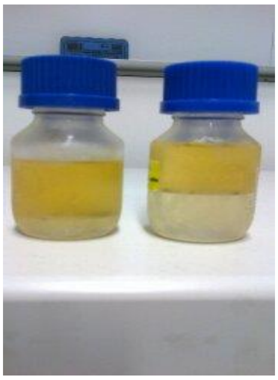
The synthesis of [hmim][Ac]:

1. 50 mL of synthesized [hmim][Cl] was poured into a beaker.
2. About 50 mL of deionized water was added into the beaker and the mixture was stirred until all [hmim][Cl] dissolved.
3. 37g of silver acetate (SA) was added into a round bottom flask.
4. [hmim][Cl] that has been dissolved in water was added into to the round bottom flask.
5. About 20 mL deionized water was added into the flask.
6. The mouth of flask was closed with a stopper.
7. The mixture was stirred at room temperature using a magnetic bar and a magnetic stirrer for 1 day.

Figure 8: Metathesis process of [hmim][Ac]

The purification of [hmim][Ac] by re-crystallization:

1. The resulting solution was then filtered in order to remove solid silver chloride, the by product.
2. The [hmim][Ac] (filtrate) was then evaporated using the RotaVap equipment at 25℃ for 5 hours.
3. Then, about 50mL of dichloromethane was added into the flask containing the product, [hmim][Ac].
4. The mixture was kept in a refrigerator overnight for solvent separation.



F**igure 9**: [hmim][Ac](top layer) mixed with dichloromethane (bottom layer) to extract remaining solid in the solution

5. Then, the resulting mixture was filtered again to separate product with filtrate.
6. The remaining solution was then been evaporated again using RotaVap equipment in order to remove dichloromethane from the solution.
7. After just 1 phase left in the flask during RotaVap, the vacuum pressure was then increased gradually as well as temperature.
8. The empty container was weighted before evaporated product been transfer into it.
9. The product was then transferred into the sample container and been dried out in a vacuum oven at temperature of 60℃ for 24 hours.

10. The sample container been weighted again to get the yield of the [hmim][Ac] synthesis.

Figure 10: Final product of synthesized [hmim][Ac]

3.1.3 Preparation of 1-hexyl-3-methyl bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N])

The synthesis of [hmim][Tf_2N]:

1. 50 mL of synthesized [hmim][Cl] was poured into a beaker.
2. About 50 mL of deionized water was added into the beaker and the mixture was stirred until all [hmim][Cl] dissolved.
3. 37g of lithium bis(trifluoromethylsulfonyl)imide, ($LiTf_2N$) was added into a round bottom flask and followed quickly by addition of deionized water.
4. The solution was then stirred until fully dissolved for 1 day.
5. The resulting solution consists of 2-phase mixture: the top layer is the water and LiCl (aqueous), the bottom is the [hmim][Tf_2N].

The purification of [hmim][Tf_2N] by washing:

1. The top layer was poured out from the solution.

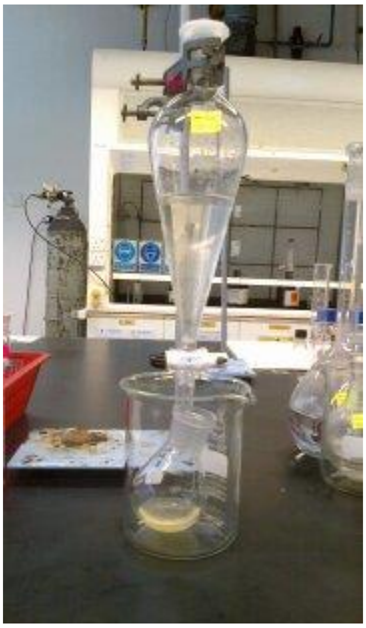


Figure 11: The product [hmim][Tf_2N]was separated from the aqueous LiCl

2. About 50 ml of water was added to the product solution, and the mixture was shaken gently.
3. The solution was left to settle until 2 phase layer is clearly seen.
4. The top phase which is the aqueous phase was then poured into the beaker and a few drop of 1 M silver nitrate, $AgNO_3$ solution was added to it. If any white precipitate spotted on the top of solution, the solution needs to be washed again with water.
5. The procedure 1 till 3 was repeated until no more white precipitate formed or the aqueous phase becomes very clear after addition of $AgNO_3$.

The drying process:

1. After the washing process, the product of [hmim][Tf_2N] was evaporated using RotaVap equipment at 70℃ for 5 hours.
2. The empty container was weighted before evaporated product was transferred into it.
3. Then, the final product was transferred into the sample container followed by drying in a vacuum oven at 70℃ for 3 days.

4. The sample container was then been weighted again to get the yield of the [hmim][Tf_2N] synthesis.

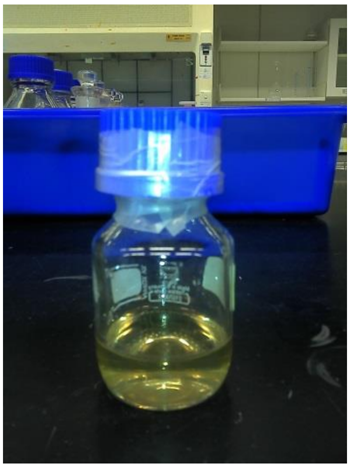


Figure 12: Final product of synthesized [hmim][Tf_2N]

3.2 CHARACTERIZATION OF ILS

After synthesize process, the ILs sample undergone the characterization process in order to confirm its characteristic. Based on the methods developed and reported in the established literature [7] and [5], the purity of the ILs will be determined by nuclear magnetic resonance (NMR) spectroscopy. Meanwhile, measurement for chloride content in the ILs will be done using Ion Chromatography (IC) in order to trace the amount of unreacted chloride from the precursor [hmim][Cl]. Other than that, the decomposition temperature of each ILs is determined by thermogravimetric analyzer (TGA).

3.2.1 Purity analysis

The purity analysis was carried out by using nuclear magnetic resonance (NMR) spectroscopy and the analysis using TopSpin 3.0 software. In NMR, 5 to 10 mg of sample is dissolved in approximately 0.7 cm^3 of deuterated methanol solvent (MeOH). The ^1H and ^{13}C NMR spectra are recorded at room temperature and reported in parts per million (ppm) references with TMS as an internal standard. The process was done at ambient temperature.

3.2.2 Chloride content

The chloride content was determined by ion chromatograph (Metrohm Model 761 Compact IC) Metrosep A Supp 5-150 analytical column (150mm × 4.0mm) and a Metrosep A Supp 4/5 guard column (4.0mm × 5mm) at ambient condition. The injection volume was 0.020 cm^3. A mixture of (3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$) was used as eluent and the regenerating solution was 1.0 M H_2SO_4. 4 different concentration of standard solution for chloride were prepared; 200 ppm, 100 ppm, 50 ppm, and 10 ppm. Each IL sample was prepared by dissolving 0.39g for [hmim][Ac] and 0.16g for [hmim][Tf_2N] in 40 cm^3 of acetonitrile before being diluted to 100 cm^3 with deionized water. The result was analyzed using Metrodata IC Net 2.3 software.

Figure 13: Ion chromatograph (Metrohm Model 761 Compact IC)

3.2.3 Thermal analysis

The decomposition temperature of the ionic liquids was determined using thermogravimetric analyzer (TGA, Perkin Elmer Pyris V-3.81). A sample of about 5 mg is used in a platinum pan under nitrogen atmosphere. Heating rates of $10^oC.min^{-1}$ is used for the thermal decomposition study.

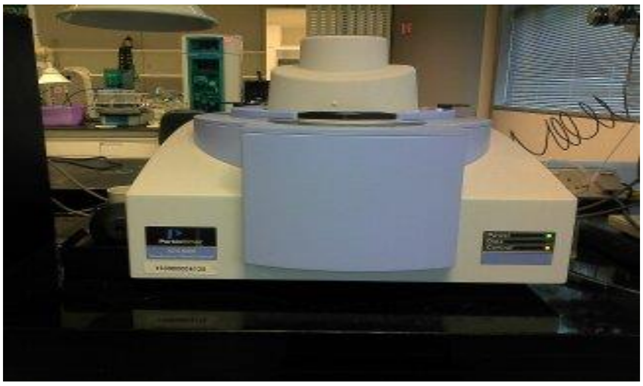


Figure 14: Thermogravimetric analyzer (TGA, Perkin Elmer Pyris V-3.81)

3.2.4 Water content

The water content of [hmim][Ac] and [hmim][Tf_2N] were determined by using coulometric Karl Fischer autitrator, Mettler Toledo DL39 with CombiCuolomat fritless Karl Fischer reagent (Merck). Both ILs were tested by injecting 1mL of both samples individually into the equipment.

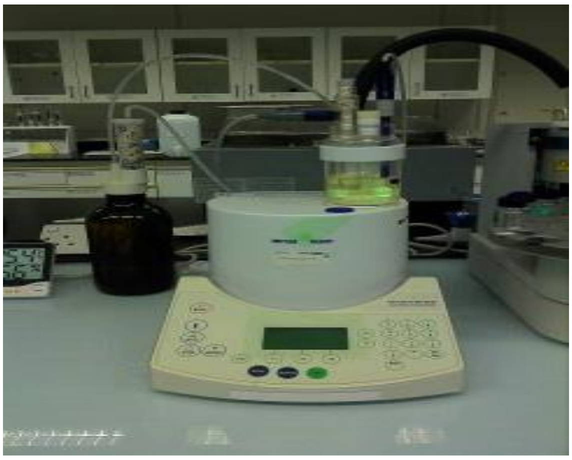


Figure 15: Karl Fischer autitrator (Mettler Toledo DL39)

3.3 CO_2 SOLUBILITY

The experimental method used for this gas solubility measurement is based on isochoric saturation technique whereby a known quantity of a gaseous solute is put into contact with precisely determined quantity of degassed solvent at a constant temperature inside a solubility cell of accurately known volume. When thermodynamic equilibrium is achieved, the pressure above the solvent is constant and is directly related to the solubility of the gas in the solvent. The carbon dioxide gas used in the measurement has the mole fraction purities of 0.99995.

The quantity of IL introduced into the solubility cell, V_{liq}, is determined gravimetrically. The amount of solute (CO_2) present in the liquid solution, n_2^{liq}(subscript 2 stands for solute and subscript 1 stands for solvent), is calculated by difference between two pVT measurement, the first when the gas is introduced into the vessel with the volume V_v and the second after thermodynamic equilibrium is reached:

$$n_2^{liq} = \frac{p_{ini}V_v}{Z_2(p_{ini},T_{ini})RT_{ini}} - \frac{p_{eq}(V_{tot}-V_{liq})}{Z_2(p_{eq},T_{eq})RT_{eq}} \qquad (1)$$

where p_{ini} and T_{ini} are the pressure and temperature in the first pVT determination, and p_{eq} and T_{eq} are the pressure and temperature at equilibrium. V_{tot} is the total volume of the equilibration cell and Z_2 is the compressibility factor for the pure gas. The solubility can then be expressed in mole fraction:

$$x_2 = \frac{n_2^{liq}}{n_1^{liq}+n_2^{liq}} \qquad (2)$$

or as the Henry's law constant:

$$K_H = \lim_{x2\to 0}\frac{f_2(p,T,x_2)}{x_2} \cong \frac{\varphi_2(p_{eq},T_{eq})p_{eq}}{x_2} \qquad (3)$$

where f_2 is the fugacity of the solute and φ_2 its fugacity coefficient which can be calculated using SRK equation of state.

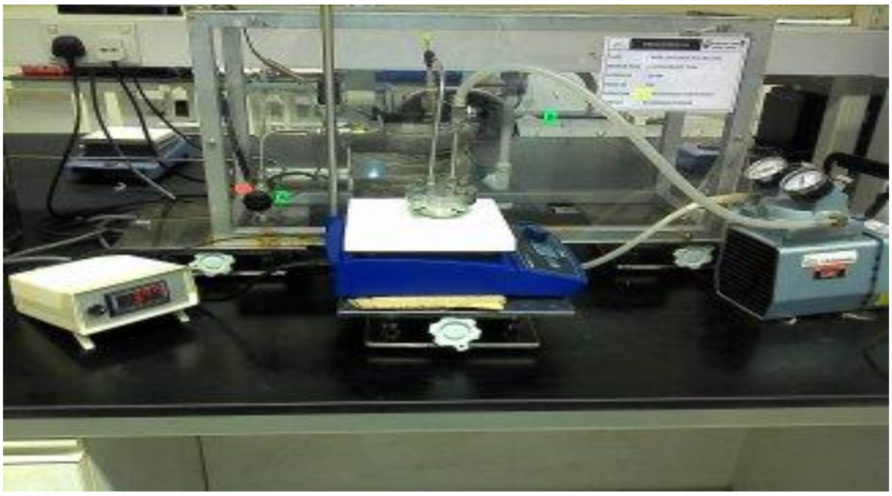


Figure 16: CO_2 solubility cell

3.4 CHEMICALS AND EQUIPMENT

The chemicals and equipment used in this research are listed in the tables below:

Table 4: List of chemicals used for IL synthesis

No.	Chemical Name	Purity (%)
1	1-methylimidazole	99
2	n-chlorohexane	99
3	Ethyl acetate	99
4	Lithium bis(trifluoromethylsulfonyl)imide	99
5	Silver acetate	99

Table 5: List of equipment used in the synthesis

No.	Equipment	Purpose
1	Solubility cell	Measure the CO_2 absorption in ILs
2	Nuclear magnetic resonance (NMR)	Establish the purity of ILs
3	Refrigerator	Cool the synthesized ILs
4	Vacuum oven	Dry the synthesized ILs
5	Karl Fischer autotitrator	Measure the water content of ILs
6	Ion chromatograph	Measure the chloride content in ILs
7	Thermogravimetric analyzer	Measure the degradation temperature for ILs

CHAPTER 4

RESULT AND DISCUSSION

4.1 WATER CONTENT

The water content of [hmim][Ac] and [hmim][Tf_2N] were analyzed by coulometric Karl Fischer autitrator, Mettler Toledo DL39 with CombiCuolomat fritless Karl Fischer reagent (Merck) at ambient temperature and the result is presented in the Table 6.

The water content in [hmim][Tf_2N] was recorded quite high (18722ppm) compared to [hmim][Ac] (376.71 ppm), and this is probably because of longer exposure to the atmosphere during the metathesis process. In addition, $LiTf_2N$ is highly soluble in water, it able to capture the moisture rapidly after been exposed to the surrounding during the synthesis. However, the high water content in [hmim][Tf_2N] had essentially no effect towards the CO_2 solubility as been reported in the established literature [24]. They reported that the resulting bonding of hydrogen from water with the anion does not eliminate the [Tf_2N] anion/CO_2 interactions. Therefore, although with high water content, the synthesized [hmim][Tf2N] still can be utilized for the CO_2 solubility testing.

Table 6: Water content in synthesized ionic liquids

Ionic liquid	Water content (ppm)
[hmim][Ac]	376.71 (0.04%)
[hmim][Tf_2N]	18722 (1.87%)

4.2 CHLORIDE CONTENT

All result for chloride content for both [hmim][Ac] and [hmim][Tf_2N] were analyzed using Metrodata IC Net 2.3 software and presented in Table 7.

Table 7: Chloride content in synthesized ionic liquids

Ionic liquid	**Chloride content (ppm)**
[hmim][Ac]	0.550
[hmim][Tf_2N]	953.3

For [hmim][Ac] , the amount of chloride content in IL detected by IC is 0.550 ppm which is nearly none unreacted chloride contained. This means that, the synthesis process for this IL is almost complete whereby almost all the chloride ions in precursor [hmim][Cl] been exchanged with acetate coming from silver acetate. The peak detected at 5.262 min is the peak from acetate composition in the solvent.

For [hmim][Tf_2N] , the amount detected is 953.3 ppm which is much higher compared to [hmim][Ac]. The high amount of chloride is resulted from incomplete ion exchange of precursor into product. These traces can be minimized or reduced by prolong the reaction period in ensuring the complete anion exchange between chloride ions and Tf_2N ions.

4.3 THERMAL ANALYSIS

The thermal stability of the ILs is reported in terms of start temperature (T_s) and decomposition temperature (T_d) at heating rate of 10°C.min^{-1} as shown in Table 8. The decomposition of the ILs begins at T_s and T_d is determined by the intersection between the baseline weight from the beginning of the measurement and the tangent of the weight against temperature curve as decomposition occurs.

Table 8: Start temperatures (T_s) and decomposition temperatures (T_d) of [hmim][Ac] and [hmim][Tf_2N] at heating rates of 10°C.min^{-1}

Ionic liquid	**T_s (°C)**	**T_d (°C)**
[hmim][Ac]	220.87	273.25
[hmim][Tf_2N]	426.31	484.26

The possible explanation is [hmim][Ac] still have a significant amount of impurities in its matrix structure such as dichloromethane and water molecules with the boiling point of 39°C and 100°C respectively. Despite of these impurities, [hmim [Ac] was still reliable to continue with the CO_2 solubility since it still has the degradation temperature above 200°C [25] as shown in Fig. 17.

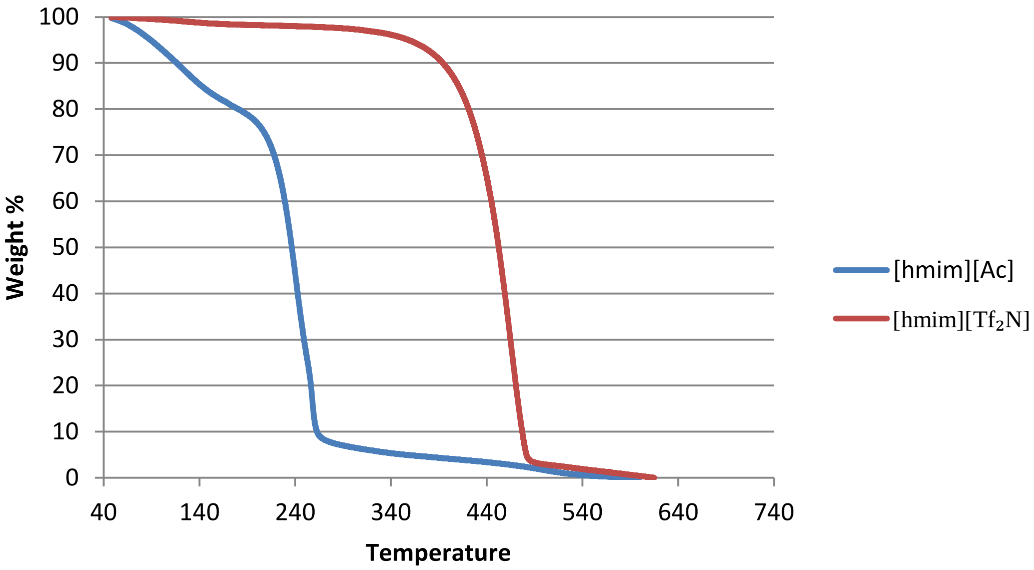


Figure 17: Plot of thermal decomposition of [hmim][Ac] and [hmim][Tf_2N] at heating rate of 10°C.min^{-1}.

4.4 PURITY ANALYSIS

NMR analysis was performed in order to analyze the purity level of the samples i.e.; [hmim][Cl], [hmim][Ac] and [hmim][Tf$_2$N]. All the samples were dissolved in acetonitrile as a solvent aiming at detecting the existence of ^{1}H and ^{13}C spin in the samples. The NMR results are as follow:

[hmim][Cl]:

^{1}H NMR (500 MHz, CH_3CN): δ 10.0580 [s, 1H, (2)], 7.8198-7.7849 [d, 2H, (4,5)], 4.2452 [d, 2H, (6)], 3.9277 [t, 3H, (12)], 1.2095 [m, 6H, (7,8,9)], 0.7856 [t, 3H, (11)].

^{13}C NMR (500MHz, CH_3CN): δ 136.6770 (2), 122.9136, 121.6424 (4,5), 116.8928 (solvent), 48.4805 (6), 30.1561 (12), 29.1090 (7,8), 24.7330 (9), 21.4685 (10), 12.6956 (11).

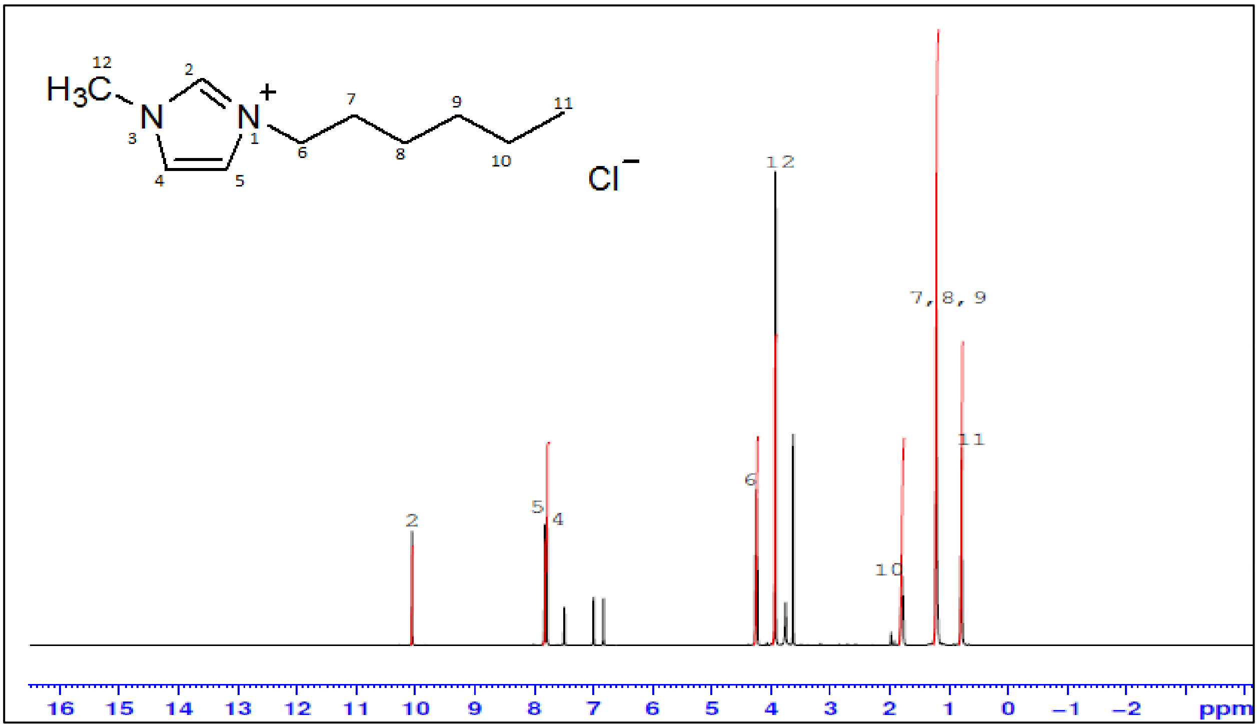


Figure 18: ^{1}H NMR (CH_3CN) of ionic liquid [hmim][Cl]

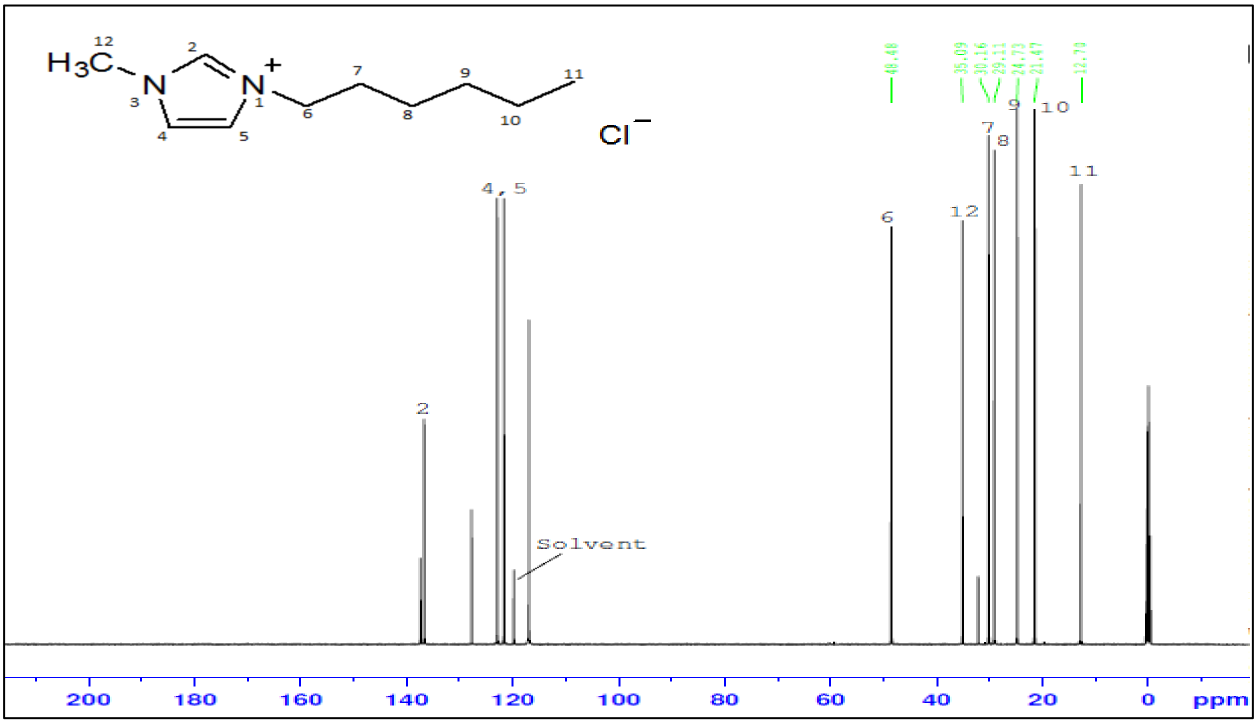


Figure 19: ^{13}C NMR (CH_3CN) of ionic liquid of [hmim][Cl]

[hmim][Ac]:

^{1}H NMR (500 MHz, CH_3CN): δ 9.8771 [s, 1H, (2)], 7.5134-7.2922 [d, 2H, (4,5)], 5.7765 [d, 2H, (6)], 4.2133 [d, 2H, (7)**],** 4.0166 [t, 3H, (12)], 3.6727-3.5662 [d, 2H, (8,9)], 1.8991 [t, 3H, (14)], 1.3766 [d, 2H, (10)], 0.8211 [t, 3H, (11)].

^{13}C NMR (500MHz, CH_3CN): δ 174.74 (13), 128.13 (2), 123.17 (4), 121.74 (5), 117.89 (solvent), 50.13 (6), 48.84 (12), 35.23 (7), 29.41 (8), 25.07 (9), 23.03 (14), 21.80 (10), 12.97 (11).

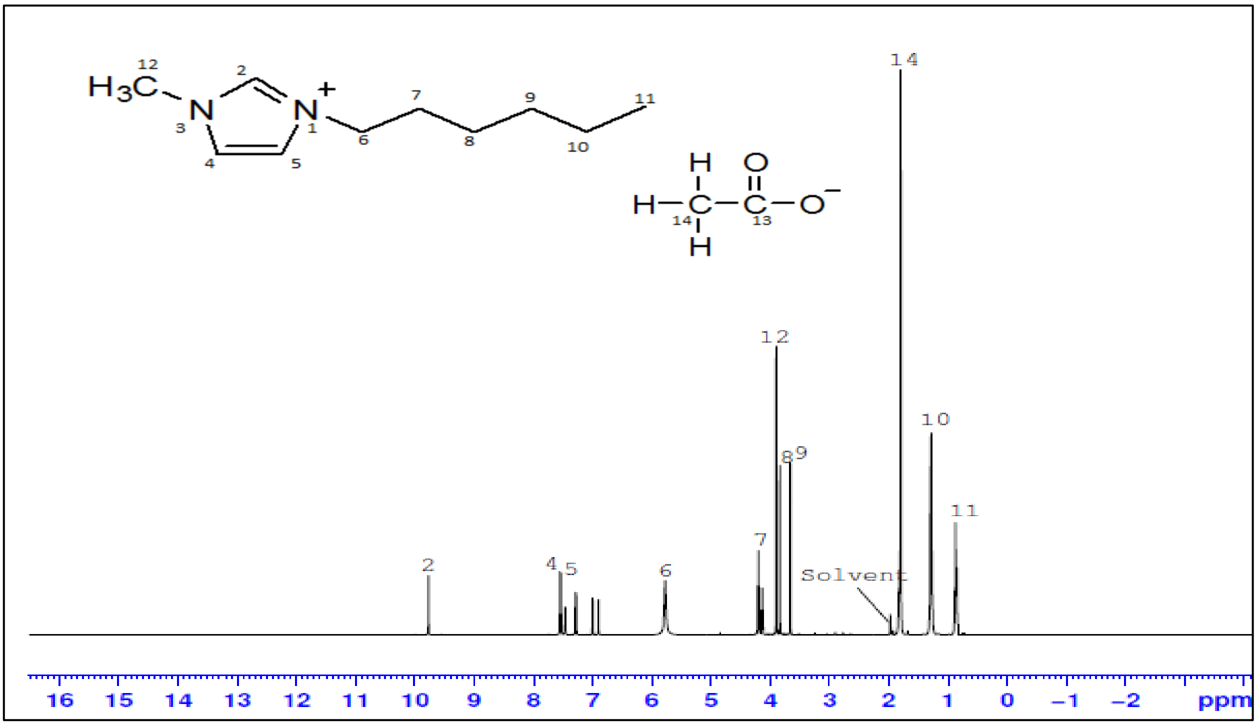


Figure 20: ^{1}H NMR (CH_3CN) of ionic liquid [hmim][Ac]

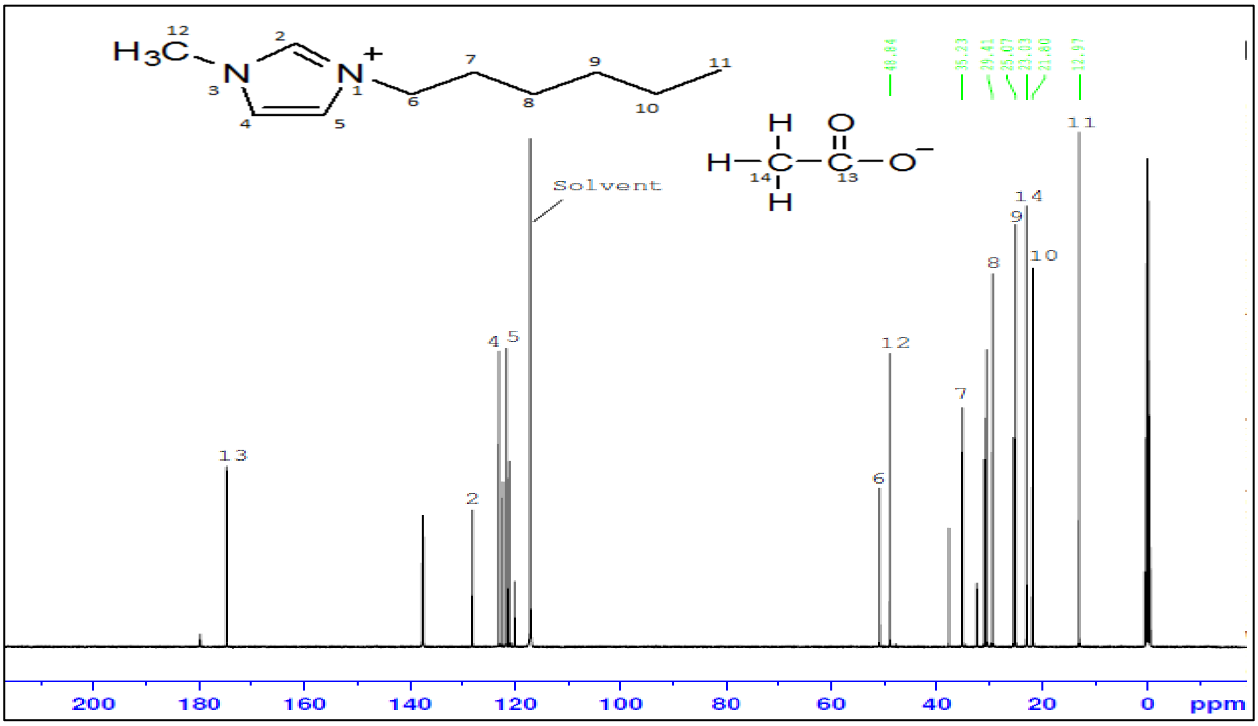


Figure 21: ^{13}C NMR (CH_3CN) of ionic liquid of [hmim][Ac]

[hmim][Tf$_2$N]:

^{1}H NMR (500 MHz, CH$_3$CN): δ 8.5123 [s, 1H, (2)], 7.4214-7.4112 [d, 2H, (4,5)], 4.2013 [d, 2H, (6)], 4.1877 [t, 3H, (12)], 1.8323[d, 2H, (7)**]**, 1.3855-1.2587[d, 2H, (8,9,10)**]**, 0.8854 [t, 3H, (11)].

^{13}C NMR (500MHz, CH$_3$CN): δ 135.54 (2), 123.35 (13), 121.97 (14), 120.87 (4), 118.76 (5), 117.04 (water), 115.66 (solvent), 49.25 (12), 35.52 (6), 30.46 (7), 29.25 (8), 25.04 (9), 21.79 (10), 12.91 (11).

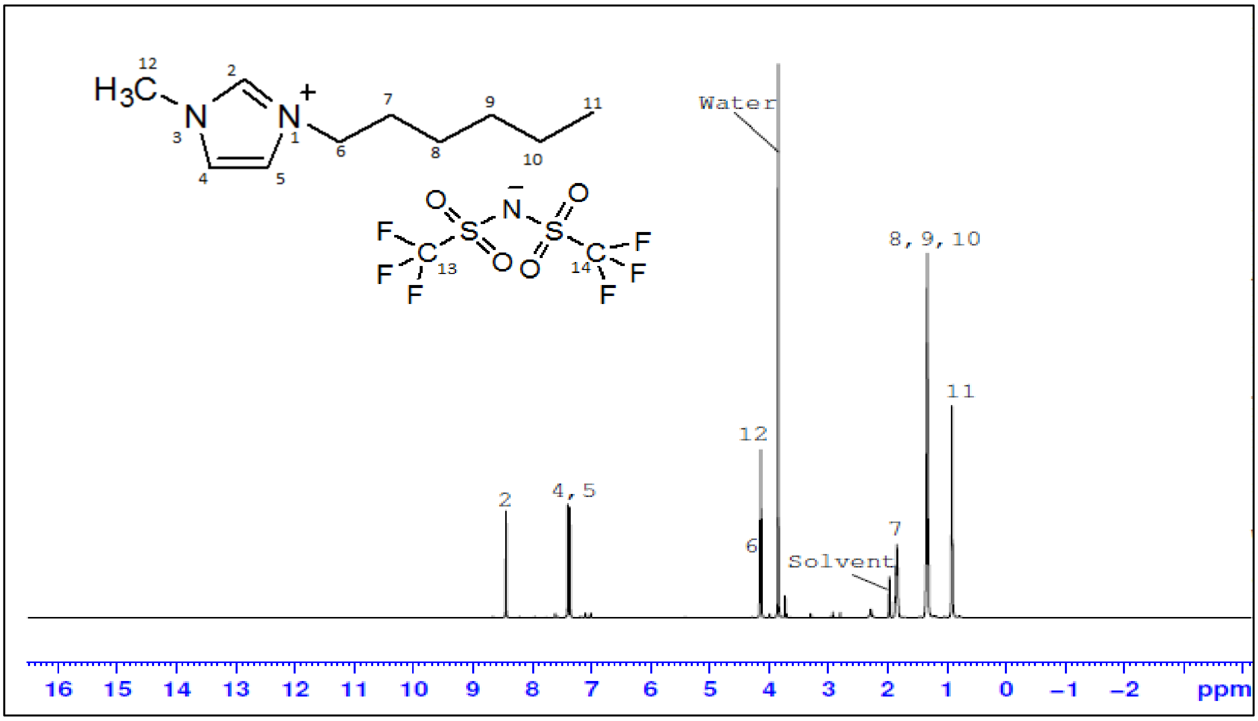


Figure 22: ^{1}H NMR (CH$_3$CN) of ionic liquid [hmim][Tf$_2$N]

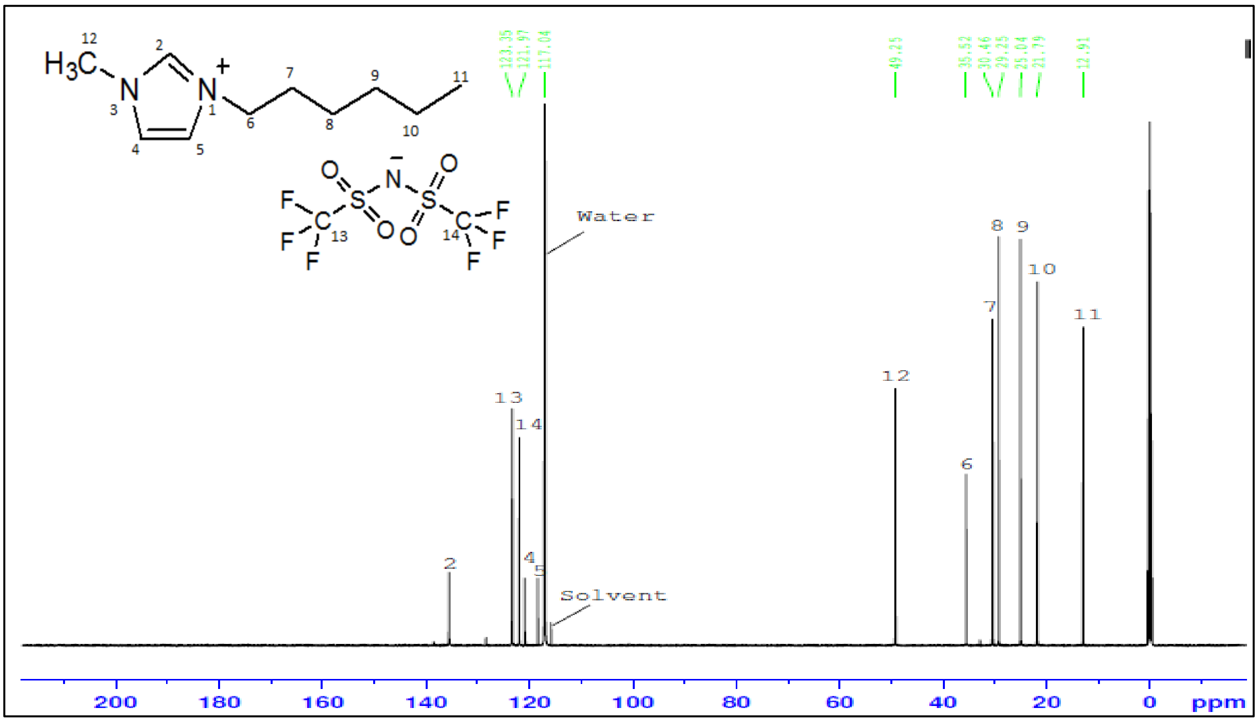


Figure 23: ^{13}C NMR (CH_3CN) of ionic liquid of [hmim][Tf_2N]

4.5 CO_2 SOLUBILITY

In the present work, the solubility of CO_2 in two imidazolium ionic liquids; [hmim][Ac] and [hmim][Tf_2N] were investigated and the CO_2 solubility result at ambient temperature 25°C and at pressure range of 5-20 bar using isochoric saturation technique were recorded and presented in Table 9 . Mole fractions of CO2 and KH for both ionic liquids were calculated using Eq. (2) and (3) respectively. The details of the solubility characteristics of CO_2 in the synthesized imidazolium based ionic liquids are discussed in the following sections.

Table 9: The CO_2 solubility of [hmim][Ac] and [hmim][Tf_2N] at temperature of 25°C

[hmim][Ac] + CO_2		
Pressure (bar)	Mole fraction of CO_2, x_{CO2}	Henry's law constant, K_H (bar)
3.11	0.1541	43.57±0.2
5.73	0.1572	
7.32	0.1765	
10.53	0.1922	
16.55	0.212	
[hmim][Tf_2N] + CO_2		
3.82	0.1756	28.39±0.2
5.96	0.2198	
7.52	0.2880	
11.42	0.3223	
17.53	0.3821	

4.5.1 The effect of pressure

Fig. 24 illustrates that the mole fraction of CO_2 absorbed in both ionic liquids are clearly affected by pressure. As expected, increasing in pressure will increase the mole fraction of CO_2 for both IL. Analysis of the solubility data in Fig. 24 showed that there is almost a smooth linear relation between the CO_2 solubility and the pressure up to 16.55 bar for [hmim][Tf_2N] which indicating the solubility of CO_2 happens physically. If the measurement continues up to 60 bar, the graph will keep increase linearly as been reported in the literature [26]. Unlike [hmim] [Tf_2N], [hmim][Ac] give relatively low values compared to [hmim][Tf_2N]. This is because CO_2 solubility was influenced by its chemical absorption behavior [10]. With increased number of alkyl chain, the absorption was difficult to happen because of bulky structure of [hmim][Ac]. However, the values seem to be too low (as will be discussed in detail below).

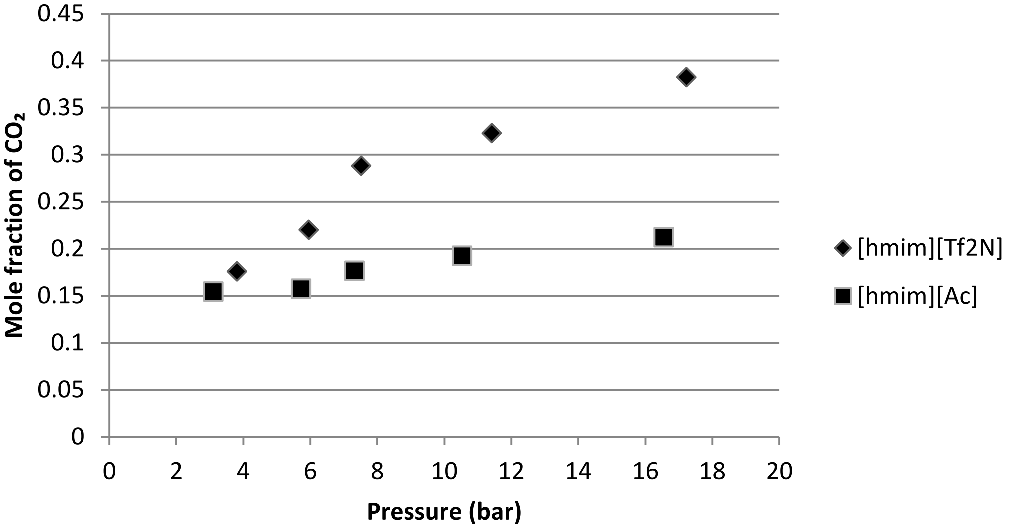


Figure 24: CO_2 solubility in term of mole fraction of CO_2 in ■ [hmim][Ac] and ♦[hmim][Tf_2N]at 25°C

Based on Henry's law, the solubility of a gas in a liquid is proportional to the partial pressure of the gas above the surface of the liquid. The Henry's law constants for the solubility of CO_2 in imidazolium ionic liquids were calculated and presented in the Table 9. [hmim][Tf_2N] shows the lower values compared to [hmim][Ac] at temperature of 25°C. A high value in K_H indicates the low gas solubility and vice versa.

4.5.2 Effects of anions in ionic liquids

A lot of studies done indicate that CO_2 solubility in ionic liquids depend primarily on the strength of interaction of the CO_2 with the anion while the cation just a secondary effect. In this work, author keeps the cation of [hmim] but used [Tf_2N] and [Ac] anions in order to investigate whether the statement is applicable for [hmim] cation ionic liquid.

In Fig. 24, [hmim][Tf_2N] gives the higher solubility values compared to [hmim][Ac] in term of the mole fraction. The author believes that, this is due to the fluorinated anion and also molar mass of the ionic liquids itself. Kanakubo et al. [27] used X-ray diffraction to study the interaction of ionic liquids [bmim][PF_6] with CO_2 and found that CO_2 molecules are preferentially solvated to the anion rather than the cation. However, for [hmim][Ac] the CO_2 solubility values were too low. It is believed that [hmim][Ac] should give high solubility due to the chemical complexion between the solvent and the solute. The mechanism of chemical absorption for [hmim][Ac] had briefly explained by Yunus et al. [28] whereby the acetate anion removes the acidic proton at 2-position in the imidazolium ring to form acetic acid and carbene. As the acetic acid vaporizes from the system, the negatively charged carbene will chemically bond with CO_2. They also reported that the disadvantage of using acetate anion is that the amount of energy required to remove the CO_2 from solvent is much larger than the solvent without this functional group. This error may cause by the significant amount of impurities such as silver acetate in the solution which affect the absorption ability of [hmim][Ac].

Based on this work, CO_2 molecules are more favor to attach at the surface of [hmim][Tf_2N] due to strong interaction of CO_2 with the fluoroalkyl chains at the anion side. Further support of this result was provided by literature done by Pringle et al. [29], who compared the CO_2 solubility in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [emim][Tf_2N] with 1-ethyl-3-methylimidazolium bis(methanesulfonyl)imide, [emim][Nmes]. Their observation stated that fluorinated anion result in higher value of CO_2 solubility and proven that through fluorination method, it could increase the CO_2 philicity of the ionic liquid. To have the clear view, CO_2 solubility values of both of synthesized ionic liquids were compared with non-fluorinated anion [hmim] taken from the literature and presented in Fig. 25.

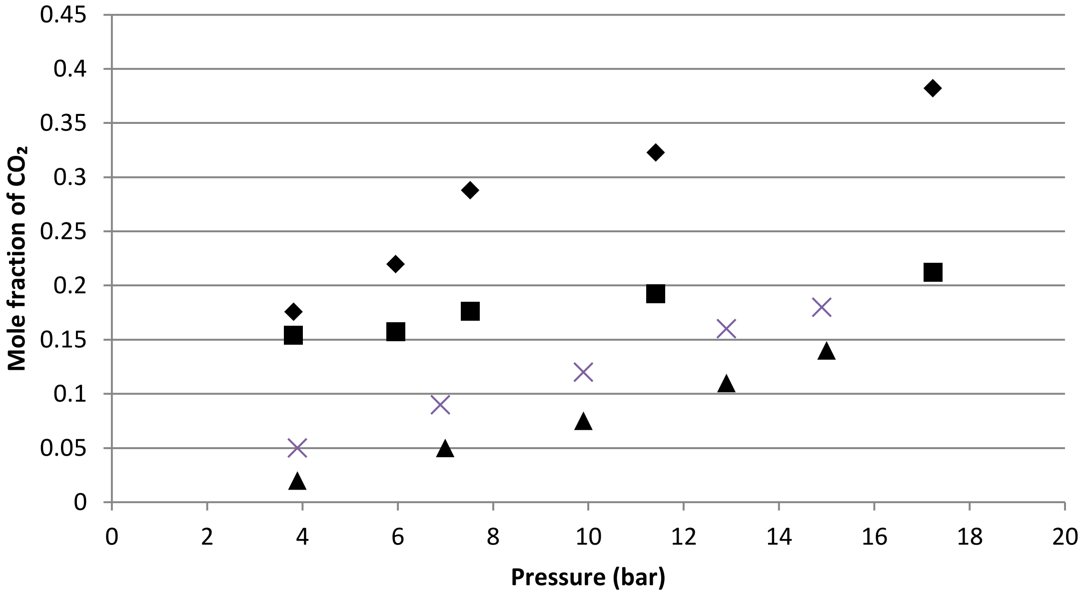


Figure 25: Comparison of CO_2 solubility in synthesized ionic liquids with imidazolium ionic liquids from literature. ▲[bmim][IAAC] [30],■ [hmim][Ac], ♦ [hmim][Tf_2N], × [bmim][SUC] [30].

Author had used solubility of 1-butyl-3-methylimidazolium acetate [bmim][Ac], 1-butyl-3-methylimidazolium iminoacetic acid acetate [bmim][IAAC], and 1-butyl-3-methylimidazolium succinamate [bmim][SUC] from established work done by Yokozeki et al. [30] to compare with the ionic liquids from this work. Nonetheless, [bmim] cation was used for the comparison, author believes that it still comparable due to the nature of cations play a minor role in determining the CO_2 solubility in these ionic liquids [28]. Fig. 25 clearly indicates that [hmim][Tf_2N] give the higher solubility in the order of; [bmim][IAAC] < [bmim][SUC] < [hmim][Ac] < [hmim][Tf_2N].

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

As a conclusion, the objectives of this research paper were to synthesize ILs namely, [hmim][Ac] and [hmim][Tf$_2$N] and to study the solubility of CO_2 in the synthesized ionic liquids by isochoric saturation technique. This is in line with the purpose of searching for the other alternative in substituting the commercial solvent used in removing carbon dioxide (CO_2) from natural gas feed with greener solvent, towards process as well as to the environment.

The solubility of CO_2 in [hmim][Ac] and [hmim][Tf$_2$N] and the anion effect onto solubility have been investigated. Both ionic liquids were prepared based on the quaternization and metathesis method from the precursor [hmim][Cl]. After the desired product formed, both ILs were undergone the purification process by thoroughly washing them using the suitable solvent in order to ensure all the unreacted or by-product are completely removed from its matrix. The characterization steps were carried out in ensuring the purity of both synthesized IL is at acceptable range for solubility test. The purity and chloride content were checked and analyzed using the Nuclear Magnetic Resonance and Ion Chromatograph respectively.

The solubility of CO_2 in both [hmim][Ac] and [hmim][Tf$_2$N] was measured at 25°C for the pressure range of 5 bar – 20 bar. The measured CO_2 solubility values in the studied ionic liquids increase with the pressure. From the literature, the anions of the ionic liquids have pronounced effect on the CO_2 capacity and the amount CO_2 absorbed was enhanced by the presence of the fluorinated anion molecules in the liquids. As expected, ILs that contains higher level of fluorination has better CO_2 solubility. Consequently, in the range of ionic liquids studied, imidazolium based ionic liquids with fluorinated anions can be regarded as potential as solvent for the separation of CO_2 from natural gas.

5.1 RECOMMENDATION

Based on this work, some recommendations for future works have been suggested to improve the methodology as well as the CO_2 solubility of [hmim][Ac] and [hmim][Tf_2N].

The ability of synthesized ionic liquids should be tested also with pure methane gas in resemblance for natural gas, more preferably, with the mixture of methane and CO_2 so that the result will be more relevant for the real situation. In this study, only CO_2 gas was tested onto the ionic liquids due to time constraint and restriction of equipment used.

Other than that, both ionic liquid should be tested for the range of temperatures and pressures. Hence, the enthalpy and entropy of ionic liquids can be established.

In order to make this work more relevant, run the sample taken from current solvent used by industrial such as alkanolamines for CO_2 solubility and compare with the result from synthesized ionic liquids.

Lastly, both ionic liquids can be blended together or embedded with solid carrier such as zeolite, silica and carbon molecular sieve in order to have a larger surface area for the absorption process hence, will improve the performance.

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