

**Synthesis and Characterization of Acetate Based Ionic Liquid for CO<sub>2</sub>  
Removal**

by

Mohd Fauzi bin Yean

Dissertation submitted in partial fulfillment of  
The requirements for the  
**BACHELOR OF ENGINEERING (Hons)**  
**(CHEMICAL ENGINEERING)**

MAY 2011

Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
31750 Tronoh  
Perak Darul Ridzuan

## **CERTIFICATION OF APPROVAL**

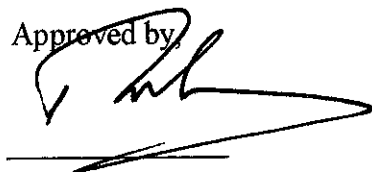
### **Synthesis and Characterization of Acetate Based Ionic Liquid for CO<sub>2</sub> Removal**

by

Mohd Fauzi bin Yean

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

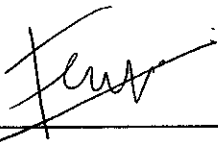


(Assoc. Prof. Dr M Ibrahim A Mutalib)

UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
MAY 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 acknowledgments, and that original work contained herein have not been undertaken or done by unspecified sources or persons.



---

**MOHD FAUZI BIN YEAN**

## ABSTRACT

This report basically discusses the preliminary research done and basic understanding of “**Synthesis and Characterization of Acetate Based Ionic Liquid for CO<sub>2</sub> Removal**”. This project aims at simulation modeling for studying the CO<sub>2</sub> solubility and its behavior towards ionic liquids at room temperature with variable pressure condition. The simulation process part is currently running by using special software for simulation of ionic liquid called **COSMO-RS** software. The simulation process is selecting two types of ionic liquid which are **1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide** and **1-butyl-3-methylimidazolium acetate** as a sample solution for CO<sub>2</sub> removal. This report basically remains consist of four sections. The first section is on the introduction part of the project including background study of the project, problem statement, objectives and scope of study and relevancy of project. The next section is on the literature review. In this section, there will be a brief theory on the ionic liquids regarding the characteristics, conditions and experimental data from journal for CO<sub>2</sub> solubility in ionic liquids. Then this report followed by third chapter which is methodology that covers on the steps and process flow of simulation using **COSMO-RS** software for examining two selected types of ionic liquids. Lastly in final section which is result and discussion part for complete simulation process regarding the selected ionic liquids. Final results are presented by validating some parameters such as interaction energy and sigma profile for completion of simulation data regarding the particular types of ionic liquids that has been selected earlier.

## ACKNOWLEDGEMENT

First and Foremost, the author would like to express the utmost gratitude towards Allah S.W.T for His blessings upon finishing this Final Year Project (FYP). There were many people involved in completing this research project, who had contributed invaluable guidance, advice and assistance. The author would like to express greatest thanks to the Supervisor, Assoc. Prof. Dr M Ibrahim A Mutalib, for his knowledge, guidance and outstanding support throughout the Final Year Project.

The author also would like to take this opportunity to express very sincere thanks to Mr. Kiki Adi Kurnia, the Postgraduate Student of Chemical Engineering Department for his knowledge and guidance in doing a simulation of ionic liquids using COSMO-RS software as well as the calculation parts from the beginning till the end of simulation.

Finally, authors would like to express deepest appreciation to those involved directly or indirectly in the completion of this final year project, Synthesis and Characterization of Acetate Based Ionic Liquid for CO<sub>2</sub> Removal.

## TABLE OF CONTENT

<b>CERTIFICATE OF APPROVAL</b> .....	<b>i</b>
<b>CERTIFICATE OF ORIGINALITY</b> .....	<b>ii</b>
<b>ABSTRACT</b> .....	<b>iii</b>
<b>ACKNOWLEDGEMENT</b> .....	<b>iv</b>
<b>ABBREVIATIONS AND NOMENCLATURE</b> .....	<b>ix</b>
<b>CHAPTER 1: INTRODUCTION</b> .....	<b>1</b>
1.1 Project Background.....	1
1.1.1 Natural Gas.....	1
1.1.2 Carbon Dioxide Content in Natural Gas.....	2
1.1.3 Ionic Liquid as Media for Gas Separation.....	3
1.1.4 Importance of Clean Chemistry.....	4
1.2 Problem Statement.....	6
1.3 Objective.....	6
1.4 Scope of Study.....	7
1.5 Relevancy of Project.....	7
<b>CHAPTER 2: LITERATURE REVIEW</b> .....	<b>8</b>
2.1 Ionic Liquid.....	8
2.1.1 Properties of Ionic Liquids.....	12
2.2 Supercritical Fluids.....	14
2.3 Ionic-Carbon Dioxide System.....	16
2.4 Selection of Ionic Liquid.....	17
2.5 Absorptions of Carbon Dioxide by RTILs.....	19
2.5.1 Physical Absorption of CO <sub>2</sub> .....	20
2.5.2 Chemical Absorption of CO <sub>2</sub> .....	21

<b>CHAPTER 3: METHODOLOGY.....</b>	<b>22</b>
3.1 Research Methodology.....	22
3.2 Process Flow Chart.....	23
3.3 Simulation Tool.....	24
3.3.1 Trend of CO <sub>2</sub> solubility.....	25
3.3.2 Interaction Energy.....	25
3.3.3 Sigma Geometry.....	26
3.3.4 Sigma Profile.....	26
<b>CHAPTER 4: RESULTS AND DISCUSSION.....</b>	<b>27</b>
4.1 CO <sub>2</sub> Solubility Trending.....	27
4.1.1 Evaluation of CO <sub>2</sub> Solubility .....	29
4.2 Interaction Energy of Ionic Liquids.....	30
4.2.1 Evaluation of Interaction Energy.....	31
4.3 Sigma Geometry and Sigma Profile .....	33
<b>CHAPTER 5: CONCLUSION AND RECOMMENDATION.....</b>	<b>36</b>
5.1 Conclusion.....	36
5.2 Recommendation.....	37
<b>REFERENCES.....</b>	<b>38</b>
<b>APPENDICES.....</b>	<b>42</b>
Appendices I : Simulation Data of CO <sub>2</sub> Solubility from COSMO-RS.....	43
for [Bmim][TF <sub>2</sub> N]	
Appendices II : Simulation Data of CO <sub>2</sub> solubility from COSMO-RS.....	46
for [Bmim][Ac]	
Appendices III: Simulation Data of Interaction Energy from COSMO-RS.....	49
for [Bmim][TF <sub>2</sub> N]	
Appendices IV: Simulation Data of Interaction Energy from COSMO-RS.....	52
for [Bmim][Ac]	

## LIST OF FIGURES

Figure 1	: Natural Gas Use by Sector.....	1
Figure 2	: Molecular Structure of Some Popular Anions for Ionic Liquids.....	10
Figure 3	: Molecular Structure of Some Popular Cations for Ionic Liquids.....	11
Figure 4	: Location of Supercritical Region in Phase Diagram .....	14
Figure 5	: Molecular Structure of Selected Ionic Liquids.....	17
Figure 6	: Sample of Experimental Solubility ( <i>PTx</i> ) Data for CO <sub>2</sub> and Ionic.....	19
	Liquids	
Figure 7	: COSMO-RS Software.....	22
Figure 8	: Methodology of Project.....	23
Figure 9	: Simulation using COSMO-RS.....	24
Figure 10	: P-x Diagram for IL.....	25
Figure 11	: Sigma Geometry for CO <sub>2</sub> .....	26
Figure 12	: Graph of Sigma Profile.....	26
Figure 13	: Graph of CO <sub>2</sub> Mol Fraction vs Pressure for [Bmim][TF <sub>2</sub> N] Ionic.....	27
	Liquid	
Figure 14	: Graph of CO <sub>2</sub> Mol Fraction vs Pressure for [Bmim][Ac] Ionic.....	28
	Liquid	
Figure 15	: Graph of Interaction Energy for [Bmim][TF <sub>2</sub> N] Ionic Liquid.....	31
Figure 16	: Graph of Interaction Energy for [Bmim][Ac] Ionic Liquid .....	32
Figure 17	: Graph of Sigma Potential for Ionic Liquids Compound.....	33
Figure 18	: Sigma Geometry of [Bmim][TF <sub>2</sub> N] Compound.....	34
Figure 19	: Sigma Profile of [Bmim][TF <sub>2</sub> N] Compound.....	34
Figure 20	: Sigma Geometry of [Bmim][Ac] Compound .....	35
Figure 21	: Sigma Profile of [Bmim][Ac] Compound.....	35



## LIST OF TABLES

Table 1	: Typical Composition of Natural Gas.....	2
Table 2	: Some Examples of the Most Popular Anions and.....	9
Table 3	: Properties of Ionic Liquids.....	13
Table 4	: Critical Temperature and Pressure of Selected Fluids.....	15
Table 5	: Solubility of CO <sub>2</sub> in [Bmim][TF <sub>2</sub> N] Ionic Liquid Data.....	27
Table 6	: Solubility of CO <sub>2</sub> in [Bmim][Ac] Ionic Liquid Data.....	28
Table 7	: Interaction Energy of [Bmim][TF <sub>2</sub> N] Ionic Liquid Data.....	31
Table 8	: Interaction Energy of [Bmim][Ac] Ionic Liquid Data.....	32

## ABBREVIATIONS AND NOMENCLATURE

CO <sub>2</sub>	Carbon Dioxide
IL	Ionic Liquids
VOC	Volatile Organic Compound
SCF	Supercritical Fluids
Bmim	1-butyl-3-methylimidazole
TF <sub>2</sub> N	bis (trifluoromethylsulfonyl) imide
Ac	Acetate
RTIL	Room Temperature Ionic Liquid
VdW	Van der Waals
HB	Hydrogen Bonding
MF	Misfit



# CHAPTER 1

## INTRODUCTION

### 1.1 Project Background

#### 1.1.1 Natural Gas

Natural gas is a combustible, gaseous mixture of simple hydrocarbon compounds, usually found in deep underground reservoirs formed by porous rock. Natural gas is a fossil fuel composed almost entirely of methane, but does contain small amounts of other gases, including ethane, propane, butane and pentane [1].

Natural gas is used extensively in industrial, electric generation, residential, commercial and others application. Natural gas demand predicted by the Energy Information Administration (EIA) is summarized in figure below:

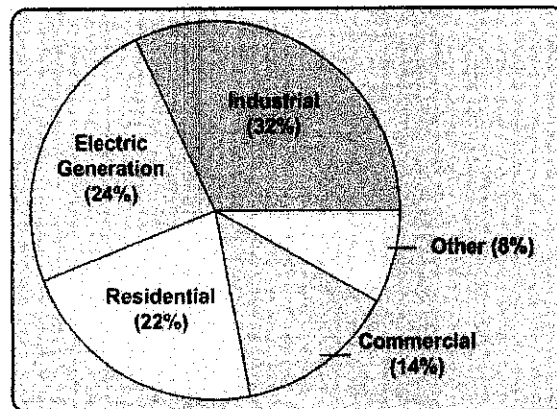


Figure 1 : Natural Gas Use by Sector

However, with much improved distribution channels and technological advancements, natural gas is being used in ways never thought possible. Hence, natural gas is used across all sectors, in varying amounts since it is one of the cleanest, safest, and most useful of all energy sources available in earth [3].



### 1.1.2 Carbon Dioxide Content in Natural Gas

Natural gas is a naturally occurring mixture, consisting mainly of Methane and can also include Ethane, Propane, Butane and Pentane. Commonly, natural gas also contains impurities such as carbon dioxide, hydrogen sulphide and water as well as nitrogen, helium and other trace gases. Those impurities become higher in mole percentage of natural gas composition and affect the quality of natural gas. The typical composition of natural gas is tabulated in Table 1 for references; however the compositions of natural gas vary depending on location and region [3].

Composition in Natural Gas	Mole Percentage (%)
Methane	70-90
Ethane	0-20
Propane	0-20
Butane	0-20
Carbon Dioxide	0-8
Oxygen	0-0.2
Nitrogen	0-5
Hydrogen Sulphide	0-5

Table 1 : Typical Composition of Natural Gas

The increase in demand for energy worldwide has aid the search for alternative sources of primary energy even to the remote part of the globe and the major alternative source with less environmental impact discovered some decade ago is energy from natural gas. Natural gas at its geological conditions in some deposits contain some complex contaminants such as CO<sub>2</sub>, H<sub>2</sub>S, CO, Mercaptan (Acid Gas), which constitute great environmental hazards when get to the atmosphere and also hindered natural gas processes.



### 1.1.3 Ionic Liquid as Media for Gas Separation

The separation and purification of gases has a great importance in a wide variety of application. Separation processes are not only great importance in refineries, but also in the petrochemical, pharmaceutical, chemical and gas processing industries. Gases used in industries demanded to have high purities which resulting to high purities product as required. This step involves one or more separation processes which may include:

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)

Absorption is one of the most common techniques for gas purification [2]. In an absorption system, the gaseous compounds (typically the impurities) are transferred from the gas phase into the liquid solvent. The liquid is then regenerated in a separate step. Many techniques have been employed to improve the mass-transfer efficiency between the phases. Another issue when choosing a solvent for absorption is to consider the solubility of the solvent in the gas phase. If the liquid evaporates into the vapor phase, the “purified” gas will end up contaminated with the absorption solvent [4].

In this separation technique, the choice of solvent is the most important consideration in order to secure the effectiveness of separation process. In order for a new technique to be competitive, it must not only be cost-efficient but also having low energy requirements and does not release volatile organic compounds (VOCs) which might cause additional environmental problem [4]. Ionic liquids have several unique properties of negligible vapor pressure and non-toxicity [8]. In any case, any risk of contaminating the final gas stream with the solvent would be completely eliminated.



#### 1.1.4 Importance of Clean Chemistry

Chemistry has contributed a lot towards human's life but regrettably the delight of human health and the fresh of global environment are threatened from time to time. The compositions of atmosphere are changing by human's rude activities to the earth through the burning of fossil fuels, land-use and emission of volatile organic compounds (VOCs) and greenhouse gases especially CO<sub>2</sub> in VOC are leading our earth to a process of environmental degradation. The use of VOC has exposed to the most of health risks which are acted as irritants and carcinogens. The presence of VOC also contributes towards environmental problem through atmospheric pollution and also causes financial risk as very hard to recover and to dispose all of them completely [9].

Typically, the solvents are volatile organic compounds or VOCs. Solvents play an extremely important role in many industrial processes, acting as medium for chemical reactions and extraction of products. The environment and health concerns are added to public acted as a driving force to the scientific community towards the development of novel processes. Several benefits of green chemistry involve economical, energy efficient, less wastes, safer product and provide competitive advantages. Some efforts are underway to overhaul chemical's policy, most probably by the recent European Union's new chemicals policy, Registration, Evaluation and Authorization of Chemicals (REACH), the focus also must be on overhauling the way chemicals are designed from the outset [10]. As an example, some of the regulations that address the use and control of VOC emissions in Europe can be cited as:

- Environmental Protection Act 1990<sup>a</sup>
- Control of Substances Hazardous to Health (COSHH) regulations.<sup>a</sup>
- Pollution Prevention and Control Regulations 2000<sup>a</sup>
- Health and Safety at Work Act 1974<sup>a</sup>
- EU Solvents Directive (1999/13/EC)<sup>a</sup>



Clean chemistry is an approach to the design, manufacture and use of chemical products to intentionally reduce or eliminate chemical hazards. In order to reduce the amount of volatile organic solvent used in industry, ionic liquids have received the increasing attention as solvent for reaction process [11]. This interest also refers to the ionic liquid also known as “green solvents” as their potential through non-volatile character, high thermal and chemical stability [12].

Besides ionic liquids, supercritical fluids are also good candidates for replacing VOCs. In the past few years, supercritical fluids have attracted interest as solvent for both analytical and chemical process applications. They possess interesting combinations of solvent properties such as high diffusivity and liquid like solvating properties which make them attractive for variety of uses [13]. Supercritical fluids behave either like a gas or a liquid, depending on the values of thermodynamic properties. This tuning of properties and other advantageous properties of supercritical fluids led to innovative technologies. Among the most studied supercritical fluids is carbon dioxide,  $\text{CO}_2$  which is cheap, easily available, non-flammable, non-toxic and has mild critical pressure [9].

The supercritical  $\text{CO}_2$  (sc  $\text{CO}_2$ ) is environmentally acceptable as an alternative to conventional solvent for reaction chemistry so called Green Technology. In addition, supercritical fluids can lead to reactions which are difficult or even impossible to achieve in conventional solvents [14]. It is not surprising that an increasing interest in environmentally benign processes based simultaneously on ionic liquids and supercritical carbon dioxide (sc $\text{CO}_2$ ). The compounds extraction from the ionic liquids medium using sc $\text{CO}_2$  results that there is no detectable amount of ionic liquids will be present in the supercritical phase and the extracted product will be free of any contamination of both the ionic liquids and sc $\text{CO}_2$ . Therefore, it is clear that the use of ionic liquids and  $\text{CO}_2$  as combined solvents for reactions and separations having a potential to be the solvent replacement of VOCs in industry.



## 1.2 Problem Statement

Natural gas is mainly used as a fuel or as a raw material for petrochemical industries. Recently, the average amount of CO<sub>2</sub> present in natural gas reservoir was found to be as high as 46 and 72% in Peninsular and Sarawak, respectively. Its presence can reduce the fuel value of natural gas besides creating corrosion problem in pipes during transmission. In order to remove CO<sub>2</sub> a technique which is absorbing CO<sub>2</sub> with ionic liquids is strongly proposed.

A newly introduced ionic liquids, possesses unique properties such as high thermal stability, extremely low vapor pressure and less corrosive which makes it a good candidate as solvent replacement in the CO<sub>2</sub> separation processes. Currently, several ionic liquids have been tested experimentally and were found to be successful in absorbing CO<sub>2</sub>. However, more fundamental studies are required to synthesize better and more practical ionic liquids as options besides characterizing their properties required for engineering applications.

## 1.3 Objective of Study

The objectives of this project are as follow:

1. To understand the fundamental of carbon dioxide, CO<sub>2</sub> absorption principle in ionic liquids.
2. To develop a predictive method for estimating the carbon dioxide, CO<sub>2</sub> solubility in ionic liquids at room temperature with variable of pressure conditions.
3. To acquire the simulation data of CO<sub>2</sub> solubility in selected ionic liquids based on experimental data published form the relevant journal.
4. To select the best set of simulation data and model for CO<sub>2</sub> solubility in selected ionic liquids in terms of interaction energy and sigma profile.
5. To validate the complete simulation results by comparing the experimental results from the relevant journal.





## 1.4 Scope of Study

This project would cover the simulation of CO<sub>2</sub> solubility in selected ionic liquids as a research for CO<sub>2</sub> absorption in natural gas. Nowadays, natural gas contains a lot of amount of carbon dioxide, CO<sub>2</sub>, in the reservoir. Removal of the acid gases like CO<sub>2</sub> from the natural gas streams is very important process. CO<sub>2</sub> is non-combustible and its presence lowers the fuel value of the natural gas. Currently, the most widely used technology for the removal of acid gases from natural gas is absorption using aqueous alkanolamines as the absorbent or solvent. However, there were few drawbacks such as degradation of the aqueous amine solution, high enthalpy of reaction and significant corrosion and fouling problems in the process.

Alternatively, newly introduced CO<sub>2</sub> absorption with ionic liquid, possesses unique properties such as high thermal stability and less corrosive. In view of the above research, this project is actively considering the ionic liquids as a promising alternative technique. Ionic liquids are liquids that comprised entirely of ions. They also possessed a number of unique properties such as high chemical stability, wide liquid temperature range (approximately 300K), good solvents for polar, non-polar, organic and inorganic compounds, non detectable vapour pressure and almost zero flammability. Thus, this technique is strongly proposed and the best way for CO<sub>2</sub> absorption.

## 1.5 Relevancy of Project

The unique properties of ionic liquids has recently generated considerable interest and also has a great potential in oil and gas as well as in chemical industries. Environmental concern frequently center on the most safe handling and solving the critical problem of carbon dioxide, CO<sub>2</sub> composition in natural gas. The knowledge regarding the unique properties of ionic liquids provides insight into the chemical and physical absorption that exist between solute and solvent molecules. On the other hand, the unique properties of ionic liquids such as high chemical stability are very useful in designing separation and purification equipment.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Ionic Liquid

Ionic liquids (ILs) are a class of neoteric solvents that composed solely of large heterocyclic organic cations and organic or inorganic anions. Basically, ionic liquids are organic salts with a melting point low enough to be liquid at room temperature as result of low lattice energy [13,14]. Due to their highly asymmetrical chemical structure and weak columbic forces, packing of the molecules in the crystal lattice is very difficult and therefore crystallization is prevented which result to low melting point (below 100<sup>0</sup>C) as compared to other inorganic salt [5].

The number of cations and anions that can be selected for the design of an ionic liquid is enormous. The turnable properties of ionic liquid through an endless combination and modification of anions and cations, classified them as “designer solvent” [16]. This property allows the design of solvents for the development of more efficient and sustainable processes and products. However, process of choosing the right combination of both cations and anions is difficult and tough. Seddon estimated that there are at least one million types of binary ionic liquid and 10<sup>18</sup> ternary ionic liquids that are potentially possible to be selected [7]. For comparison, about 600 molecular solvents are in use today [17].

In general, ionic liquids have many properties that are similar to conventional organic solvents such as good salvation qualities. Additionally, they have also a wide temperature range (approximately 300<sup>0</sup>C) over which they remain liquids [4]. These properties are dependent on the cation and the anion combination. Researchers have shown that adjusting the structure of either the anion or the cation can have large effects on many properties including melting points, viscosities, densities and gas & liquid solubilities [18,19,20].



The first water-stable ionic liquids (ILs), was developed in 1992, included 1-ethyl-3-methyl imidazolium  $\text{BF}_4$  and 1-ethyl-3-methyl imidazolium  $\text{MeCO}_2$  [12]. Up to now, there are three different generations of ionic liquids that are known; 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> generation. The 1<sup>st</sup> generation comprised of chloroaluminate ionic liquids [7] while the 2<sup>nd</sup> generation is made of air and moisture stable ionic liquids [11] including 1-ethyl-3-methyl imidazolium  $\text{BF}_4$  and finally the 3<sup>rd</sup> generation is recently discovered task specific ionic liquids [13].

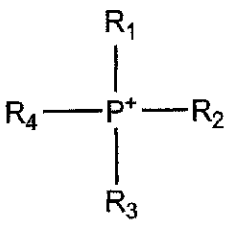
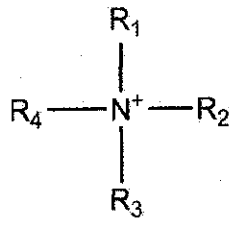
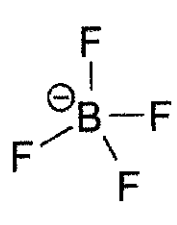
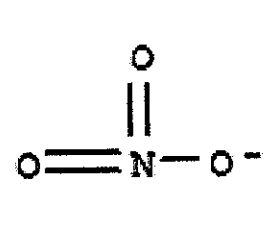
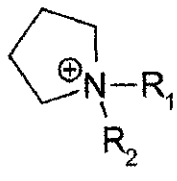
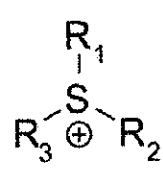
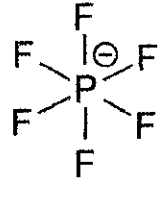
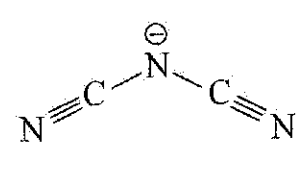
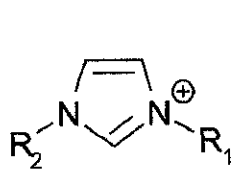
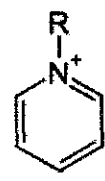
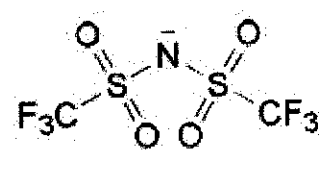
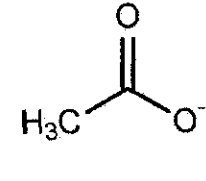
Cation Family		Anion Family	
 <p>Tetraalkyl-phosphonium</p>	 <p>Tetraalkyl-ammonium</p>	 <p>Tetrafluoroborate</p>	 <p>Nitrate</p>
 <p>Pyrrolidinium</p>	 <p>Sulfonium</p>	 <p>Hexafluorophosphate</p>	 <p>Dicyanamide</p>
 <p>Imidazolium</p>	 <p>Pyridinium</p>	 <p>Bis (trifluoromethylsulfonyl) imide</p>	 <p>Acetate</p>
<p>Note – <math>R_1, R_2, R_3, R_4</math> : H, methyl, ethyl, propyl...</p>			

Table 2 : Some Examples of the Most Popular Anions and Cations



In general, ionic liquids have both organic and inorganic material solvency power. Their non-volatile character, high thermal & chemical stability and recoverability make them potentially attractive as compared to conventional organic solvent [19]. They have been commonly recognized as a versatile alternative to conventional organic solvent [5]. Besides that, ionic liquid observed to have significant different in phase behavior compared to normal organic liquids. It shows very high solubility of water and carbon dioxide and very solubility of hydrogen.

The structural heterogeneity of ionic liquids including thermodynamic modeling, dynamics, and transport understanding the role of the anion-cation interactions in modulation of side-chain aggregation and control of the nature of nonpolar domains has important applications in industrial separation chemistry including gases separation, carbon dioxide capture and in IL-based catalytic systems [21]. Therefore, ionic liquids show a great potential for the separation of gases especially for carbon dioxide and hydrogen.

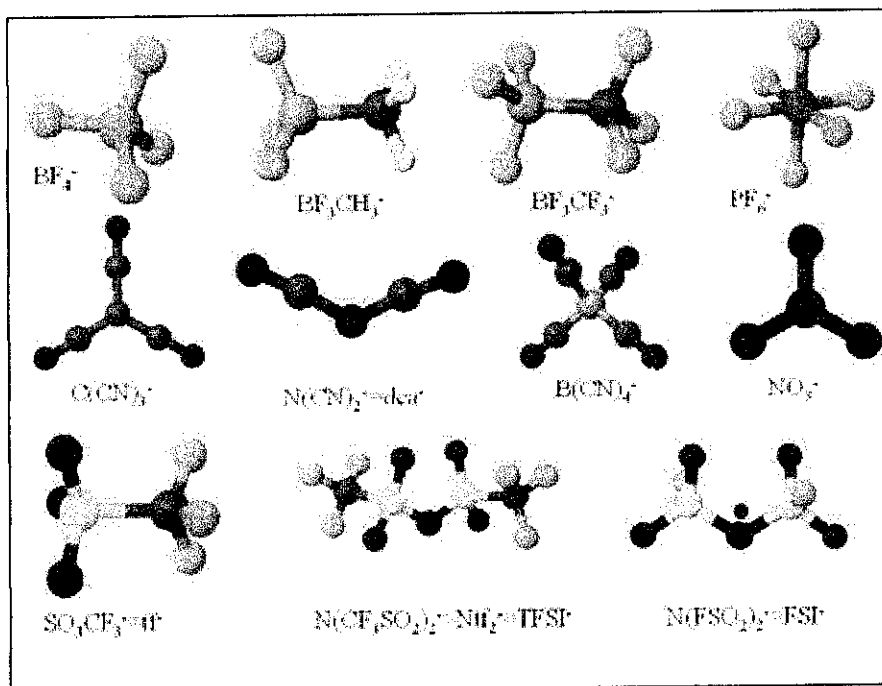


Figure 2 : Molecular Structure of Some Popular Anions for Ionic Liquids

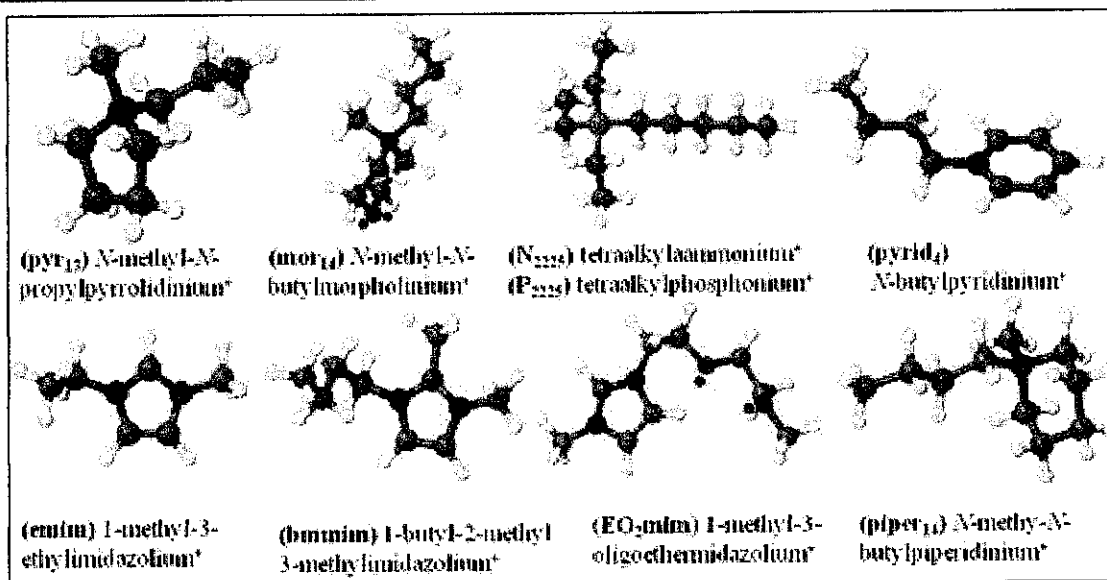


Figure 3 : Molecular Structure of Some Popular Cations for Ionic Liquids

This unique property has allowed ionic liquids to be studied as reaction media, catalysts and novel solvents in several potential applications such as gas separations, media for cleaning operations, electrolytes/fuel cells, and heat-transfer fluids. The very low vapor pressure of ionic liquids makes them further attractive for gas separations as they show almost no solubility in the gaseous phase. The wide range of ionic liquids applications in electrochemical technologies such as solvent-free electrolytes in various devices and processes, such as rechargeable lithium batteries, fuel cells, chemical sensors, electrochemical capacitors, dye-sensitized solar cells and the electrodeposition [22, 23].

Ionic liquids are also suitable to replace organic/traditional solvents in catalytic processes, hydrogenation and polymerization reactions. Together with the exploration of potential applications, the interest in their synthesis and physical properties increased remarkably. The former necessitates for reducing the impurities in the ionic liquids that originates from the synthesis method (for example, small amounts of chloride, water and other impurities) may affect significantly a number of physical properties of ionic liquids.



### 2.1.1 Properties of Ionic Liquids

According to Eliane, most of the intrinsic properties of ionic liquids derive from the Coulombic attraction forces between the ions. She claimed that not only the vanishingly low pressure that is characteristic of ionic liquids but for instance, also the melting point temperature. However, other effects such as Van de Waals and hydrogen bonding interactions and rotation of the alkyl chain length of the cation also influences the properties of ionic liquids. They are all closely related with the combination of cations and anions [9].

In term of the melting point, there is no reliable way to predict the precise of organic salts. However, in general ionic liquid exhibit low melting point (<373 K) and a wide temperature interval as a liquid (~200 K) [17]. This low melting point is a result of the chemical composition of Ionic Liquids which contains larger asymmetric organic cations compared to their inorganic counterparts of molten salts. The asymmetric decreases the lattice energy and increases the melting point as in resulting of ionic medium. In some cases, anions play relatively important role in lowering the melting point. Larger the anion, lower the melting point [18]. In extent, increase in the alkyl chain length of the cation from methyl to butyl or hexyl is also result to decrease of the melting point [9].

Viscosity is a key property of ionic liquids which is the ionic liquids tend to have higher viscosity than conventional solvents but the value of the viscosity varies tremendously with chemical structure, composition, temperature and the presence of solutes or impurities. Usually, ionic liquids have manageable viscosity between the pressure of 7 to 11 Pa/s at room temperature, 298 K [17]. However, it has long been appreciated that small amounts of water can have a big impact on the viscosity of ionic liquids, even small amount of water can cause the viscosity to drop quite a bit [19]. The effect of the components on the physical properties of ionic liquids of room-temperature that has been studied can be used for development of engineering design.



Summary of some important properties of ionic liquids that need to be taken account for chemical reactions are described in the table as shown below:

Property	Cation	Anion
Melting Point	Decreases with increasing size of the cation and decreasing symmetry	Decreases with increasing size of the anion
Water Solubility	Hydrophobicity increases with increasing alkyl chain length <sup>b</sup>	Strongly affected by the anion type
Polarity	Strongly affected by the cation type	Less influenced by the anion choice
Viscosity	Increases with increasing cation type	Affects with no defined pattern
Density	Decreases with increasing cation size	Affects with no defined pattern
Conductivity	Increasingly alkyl chain length decreases the conductivity	No effect
Diffusion Coefficient	Increasingly alkyl chain length decreases the cation diffusion coefficient	Slightly increasing with increasing anion size
Gases Solubility	Little influence	Strongly affected by the anion type

**Table 3 : Properties of Ionic Liquids**



## 2.2 Supercritical Fluids

A supercritical fluid is a substance with both gas and liquid like properties. It is a material which can be either liquid or gas, used in a state above the critical temperature and critical pressure where gases and liquids can coexist. Supercritical behavior only occurs when substance is above its critical temperature and pressure. In the phase diagram of pure substances, the region where a supercritical fluid is found can be seen in figure as below:

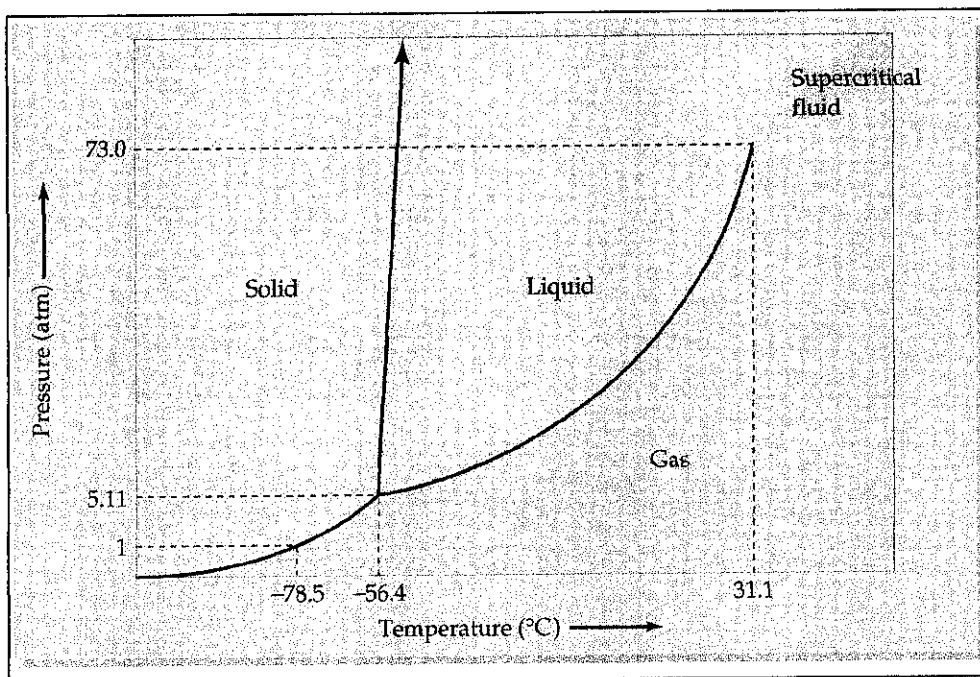


Figure 4 : Location of Supercritical Region in Phase Diagram

In figure above, the coexistence curve of gas-liquid is well known as the bubble curve. By moving upwards along the bubble point curve, the temperature and pressure is increasing simultaneously and here where the liquid phase becomes less dense and gas phases becomes denser. This is happen due to thermal expansion of liquid phase and the rise of pressure in gas phase. Eventually, the densities of the two phases converge and become identical, making the distinction between gas and liquid not possible, ending the bubble point curve at the critical point [9].





A supercritical fluid (SCF) has both the gaseous property of being able to penetrate anything and the liquid property of being able to dissolve materials into their components. Supercritical fluid has high thermal motion and it is possible to change the density widely (from low like a gas to high like a liquid), therefore we can control many properties whose function is expressed by density [13]. Comparing the liquids, the properties of supercritical fluid are greatly influenced on the slight pressure change which is possible to control the properties as solvent just using one fluid. The solvent strength of supercritical fluid is a function of densities in which involves temperature and pressure. The relationship between pressure, temperature and density may be describe by an equation of state which is a number developed by various worker.

Generally, density and solvating power of supercritical fluid is increasing at higher pressure for a given temperature, while reduction in density and solvent strength was observed with increasing temperature at constant pressure [11]. In addition, supercritical fluids exhibit significantly lower viscosities than liquids (typically an order of magnitude), which provides favorable flow properties. This allows supercritical fluids to penetrate matrices with low permeability more readily than conventional solvent [11]. Because of their tunable properties, the supercritical fluids can be used in various applications with different nature of compounds. Below is the critical temperature and pressure of selected fluid which commonly found in industries. From Table 4, it shows that CO<sub>2</sub> have the lowest critical temperature compared to others types of solvents.

Solvent	Critical Temperature, T <sub>c</sub> (°C)	Critical Pressure, P <sub>c</sub> (bar)
CO <sub>2</sub>	31.1	73.8
Ethane	32.2	48.8
Ethylene	93.0	50.4
Cyclohexane	280.3	40.7
Toluene	318.6	41.1
Benzene	289.0	48.9
Water	374.2	220.5

Table 4 : Critical Temperature and Pressure of Selected Fluids



### 2.3 Ionic-Carbon Dioxide System

Supercritical carbon dioxide (scCO<sub>2</sub>) is the most widely used solvent in various supercritical fluid industries, such as waste water treatment, solvent for extraction, polymer manufacturing and etc [12]. This is due to its non flammability, non toxicity, non polarity, low critical temperature and pressure values and of course its low price in the market [13]. In the original form of gas phase, carbon dioxide is volatile, non-viscous, non-conducting, non-polar and unable to dissolve large and unsaturated compounds. When it had been used under supercritical conditions, however, the solubility of organic compounds in CO<sub>2</sub> improves considerably.

The scCO<sub>2</sub> is always been used in a lot of separation processes. Supercritical carbon dioxide has been found to be able to extract or precipitate substance without any cross-contamination [7,13,14,15]. CO<sub>2</sub> can easily be removed from the ionic liquid by simple depressurization whereas ionic liquid is not soluble in CO<sub>2</sub> [17]. Therefore, there is no contamination of product with ionic liquid can take place. Blanchard and Brennecke [24] show that numerous type of organic compound, polar or non polar, volatile or non volatile with a variety of functional group can all be extracted from the ionic liquid [Bmim][PF<sub>6</sub>] with scCO<sub>2</sub>.

In addition, ionic liquids can be considered as a good solvent for carbon dioxide, CO<sub>2</sub>. Mainly the anion type and its interactions with CO<sub>2</sub> molecules affect the extent of dissolution [9,18]. Negligible expansion of the liquid phase is detected when the CO<sub>2</sub> dissolve in the ionic liquids [9,15,19]. The strong interactions that keep the molecules of the ionic liquid close inhibit expansion when CO<sub>2</sub> is dissolved, increasing the density of the mixture. Ionic liquids and carbon dioxide, CO<sub>2</sub> combination in reaction and extraction media has known to be very attractive. The advantage of both having non-toxic, non flammable and cheap in prices of CO<sub>2</sub> make them highly demanded in industries.



## 2.4 Selection of Ionic Liquid

In this study, two ionic liquids were selected for simulation modeling approach which are 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, [Bmim][TF<sub>2</sub>N]. Both these ionic liquids are examined at room temperature, 298.15 K with variable of pressure condition. Then, those selected ionic liquids are known as room temperature ionic liquid, RTIL since their operating condition is at room temperature, 298.15 K. Structural variations in the cations and anions of both selected ionic liquids that enhance or diminish solubility are identified. Figure below shows the molecular structure of both ionic liquids.

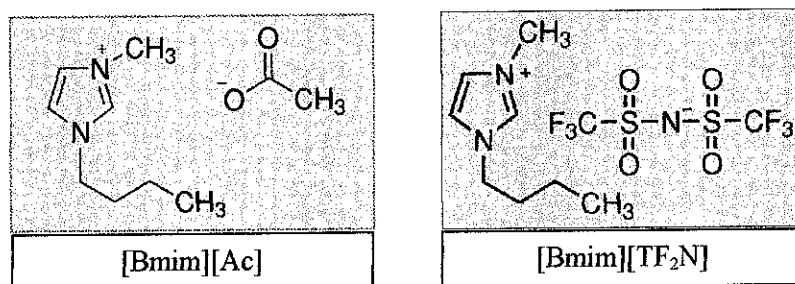


Figure 5 : Molecular Structure of Selected Ionic Liquids

The 1-butyl-3-methylimidazolium, [Bmim] cation as one sample of imidazolium cation family is widely used in recent years due to high stability in ionic liquids compound compared to other ionic liquids containing the cation family such as pyridinium and sulfonium [20]. [Bmim] cation is regarded as a common model cation for the analysis of structural variations in the ring cations within imidazolium family [23]. [Bmim] cation also generally has high value in the lengths of alkyl chain that enhance the solubility of CO<sub>2</sub> in that particular ionic liquid. Based on data available towards this selected cation seems to indicate that the longer the alkyl chain in ionic liquids, the higher the free volume within ionic liquids and consequently the higher the solubility of CO<sub>2</sub> in ionic liquids rather than only having high stability property in the ionic liquids compound.



Besides that, the acetate, [Ac] and bis (trifluoromethylsulfonyl) imide, [TF<sub>2</sub>N] anion is widely used in recent years in researching the solubility of CO<sub>2</sub> in ionic liquids due to high stability in ionic liquid compound compared to other anions such as methylsulfate, CH<sub>3</sub>OSO<sub>3</sub><sup>-</sup> and tetrafluoroborate, BF<sub>4</sub><sup>-</sup> [14]. In general, the ionic liquids containing these anions are actually very highly electronegative in which having strong negative charge within them [21] and the solubility of CO<sub>2</sub> is very high in these types of anions. This is due to the strong interaction between CO<sub>2</sub> and negative charge of anions in the increasing temperature and pressure [16].

The anions are less amenable to systematic structural variation but usually have larger impact on gas solubility. The presence of fluorine-containing anions or fluoroalkyl group is also taking place in the CO<sub>2</sub> solubility in ionic liquid results [24] but it presents lesser effect compared to electronegative of anions. However, those behaviors of anion are yet poorly understood. Some authors emphasize the role of the interactions between the CO<sub>2</sub> with [Ac] and [TF<sub>2</sub>N] anion [7,11,12,13] while others identify the large free volume of the ionic liquids as a factor responsible that can be considered for higher solubility of CO<sub>2</sub>. Hence, the result of high solubility of CO<sub>2</sub> in this research is developed by the combination of acetate, [Ac] and bis (trifluoromethylsulfonyl) imide, [TF<sub>2</sub>N] anion with 1-butyl-3-methylimidazolium, [Bmim] cation as a good pair to absorb CO<sub>2</sub>.

Although both anion and cation influence the CO<sub>2</sub> solubility in ionic liquids but the anion has the higher and stronger influence towards CO<sub>2</sub> solubility compared to cation in the ionic liquid compound [7,11,12,13]. The dominance of cation can be dramatically influenced by the anions paired to it for determine the solubility of CO<sub>2</sub> as the anion-CO<sub>2</sub> interaction being dominant by the secondary location some CO<sub>2</sub> molecules adopt at higher pressures is actually closer to the partial positive on N<sub>3</sub> (nitrogen with the methyl substituent) instead of the acidic C<sub>2</sub> hydrogen. Overall, the effect of alkyl chain length within the [Bmim] cation has a very minor effect on CO<sub>2</sub> solubility [25].



## 2.5 Absorptions of Carbon Dioxide by RTILs

The worldwide research on thermodynamic and transport properties of room-temperature ionic liquids (RTILs) and their mixtures with various chemicals has been conducted since past several years for possible applications of this new class of compounds [26,27,28]. Among others, one of the promising applications with RTILs is a nonvolatile or so-called “green” solvent for capturing unwanted compounds such as CO<sub>2</sub> in the exhaust gas stream of power plants. Although there are commercial organic solvents to capture these flue gases at the present, new RTIL solvents may provide viable and more environmentally friendly alternatives. The capture and sequestration of carbon dioxide in the power plant are urgently needed in order to reduce anthropogenic CO<sub>2</sub> accumulations in the atmosphere [29].

CO <sub>2</sub> (1) + [bmim][Ac] (2)			CO <sub>2</sub> (1) + [bmim][Tf <sub>2</sub> N] (2)		
T/K	P/MPa	100x <sub>1</sub>	T/K	P/MPa	100x <sub>1</sub>
298.1	0.0102	16.2	298.2	0.0100	0.4
298.0	0.0503	25.1	298.1	0.0500	1.5
298.2	0.1003	27.5	298.0	0.0998	3.0
298.1	0.3994	32.6	297.9	0.3998	10.7
298.1	0.7001	35.7	298.2	0.6998	17.4
298.1	0.9996	38.3	298.2	0.9997	23.4
298.3	1.3002	40.6	298.1	1.2999	28.7
298.1	1.5000	42.0	298.1	1.4995	31.7
298.1	1.9994	45.5	298.1	1.9998	39.0

Figure 6 : Sample of Experimental Solubility (*PTx*) Data for CO<sub>2</sub> and Ionic Liquids

As often stated elsewhere, effectively capturing acid or sour gases from exhaust gases requires very strong absorption because of the relatively small partial pressures of these gases in the gas stream. The strong absorption means that the gas absorption needs to be “chemical” absorption which is involved reversible chemical complex formation instead of the simple “physical” absorption which is no chemical reactions involved would be practical for high pressure gas absorption. It is well-known that CO<sub>2</sub> possesses relatively high solubility in RTILs compared with the case of hydrocarbons [30]. However, most reported cases for CO<sub>2</sub> seem to be the physical absorption [30,31,32].



### 2.5.1 Physical Absorption of CO<sub>2</sub>

Physical absorption is about absorbents allow a gas to permeate a solid or liquid under one set of conditions, and desorbs under others. The rate of absorption or desorption is temperature and pressure dependent. Smaller differences in conditions require less energy, but require more absorbent to capture CO<sub>2</sub> at an equivalent rate. The solid absorbent such as activated carbon is passed through the gas stream and the CO<sub>2</sub> is held on the surface of the particles by surface forces with no chemical reactions get involved [33]. Once collected, the particles are heated and desorbing the CO<sub>2</sub>.

Absorption of CO<sub>2</sub> in most current physical solvent systems occurs at high partial pressure of CO<sub>2</sub> and low temperatures. The solvents are then regenerated by either heating, pressure reduction, or a combination of both. The interaction between CO<sub>2</sub> and the absorbent is weak relative to chemical solvents, decreasing the energy requirement for regeneration. The capacity can be higher than chemical solvents, since it is not limited by the stoichiometry of the chemical system. Physical solvent scrubbing of CO<sub>2</sub> is well established. The use of IIs as solvents for CO<sub>2</sub> absorption has been of great interest in recent years, and much work is being carried out to explain the behavior of CO<sub>2</sub>-IIs systems [34,35,36].

A physical solvent selectively absorbs CO<sub>2</sub> without a chemical reaction. The loading that can be achieved depends upon the solvent being used, the partial pressure of CO<sub>2</sub> in the gas stream, and the temperature, with higher partial pressures and lower temperatures being more favorable. Based on physical solvents, capacity is generally proportional to CO<sub>2</sub> partial pressure. The weaker bonding between CO<sub>2</sub> and this solvent allows the CO<sub>2</sub> to be separated from the solvent in a stripper by reducing the total pressure. Since the main problem with physical solvents is that their capacity is best at low temperatures, it is necessary to cool the syngas before capturing CO<sub>2</sub>. Overall, most reported cases of CO<sub>2</sub> absorption seem to be physical absorption [33].



## 2.5.2 Chemical Absorption of CO<sub>2</sub>

The most commonly used technology today for low concentration CO<sub>2</sub> capture is absorption with chemical solvents. This chemical absorption process is involving the reversible chemical complex reaction [33] and has been used commercially for the removal of acid gas impurities from process gas streams. The problems of scale, efficiency, and stability become barriers when chemical solvents are used for high volume gas flows with a relatively smaller fraction of valuable product. The processes require large amounts of material undergoing significant changes in conditions, leading to high investment costs and energy consumption.

As chemical reactions occur, more CO<sub>2</sub> is driven from the gas phase into the solution due to the lower chemical potential of the liquid phase compounds at this temperature. When the solution has reached the intended CO<sub>2</sub> loading, it is removed from contact with the gas stream and heated to reverse the chemical reaction and release high-purity CO<sub>2</sub>. The flue gas must first be cooled and treated to remove reactive impurities such as sulfur, nitrogen oxides, and particulate matter. Otherwise, these impurities may react preferentially reducing the capacity for CO<sub>2</sub>, or irreversibly poisoning the solvent. This process modularity of CO<sub>2</sub> gas chemical absorption can achieve a considerable reduction in energy consumption [37].

The resulting pure CO<sub>2</sub> stream is recovered at pressures near atmospheric pressure. The degradation and oxidation of the solvents over time produces products that are corrosive and may require hazardous material handling procedures. Hence, the solvent like ionic liquids at room temperature can be proposed for CO<sub>2</sub> absorption since it may provides viable and more environmental friendly alternatives as a solution of this issue. A case of the CO<sub>2</sub> and 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] system is observed having high solubility of CO<sub>2</sub> with the chemical absorption can be the best knowledge [33] as a new solvent in CO<sub>2</sub> absorption process.



## CHAPTER 3

### METHODOLOGY

#### 3.1 Research Methodology

The current method used for the prediction and screening of CO<sub>2</sub> solubility in ionic liquids is COSMO-RS that also known as a quantum-chemical based method. COSMO-RS is the universal theory to accurately predict a wide range of properties in complex liquid mixtures such as solubility of gases, phase behavior and vapor pressure. Those characteristics of measurement are very important and significant towards the research of this project that involved CO<sub>2</sub> and ionic liquids for examining the level of CO<sub>2</sub> solubility in ionic liquids. The solubility of CO<sub>2</sub> in ionic liquids of widely varying structures at room temperature, 298.15K and the relative polarity of ionic liquids can be predicted using COSMO-RS as well for further discussion regarding interaction energy in ionic liquids. The trends in CO<sub>2</sub> solubility are explained in the light of molecular interactions qualitatively through sigma profiles and sigma-potentials of ionic liquids.



Figure 7 : COSMO-RS Software





### 3.2 Process Flow Chart

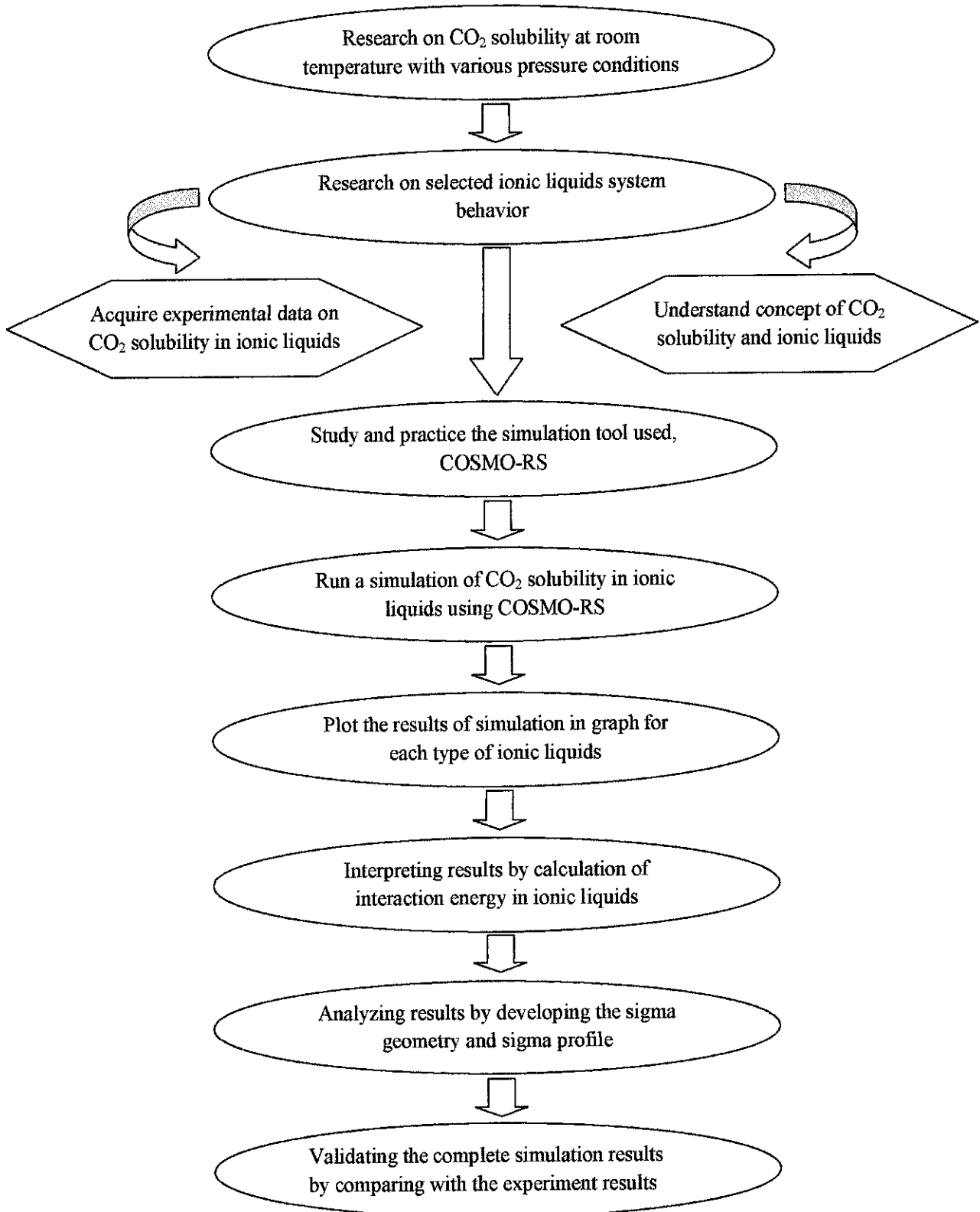


Figure 8 : Methodology of Project



### 3.3 Simulation Tool

In this study, the simulation process is currently running by using special software for simulation of ionic liquid called **COSMO-RS** or other name **COSMOtherm** that able to compute all kinds of thermodynamical data relevant to chemical process engineering, chemical and environmental analytics and life science thermodynamic modeling. The simulation process is selecting two types of ionic liquid which are **1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide** and **1-butyl-3-methylimidazolium acetate** as a sample absorbent for CO<sub>2</sub> removal. The main variables for this simulation process are temperature and pressure which is the condition of those two ionic liquids must be at room temperature, 25°C @ 298K together with multiple values of pressure conditions.

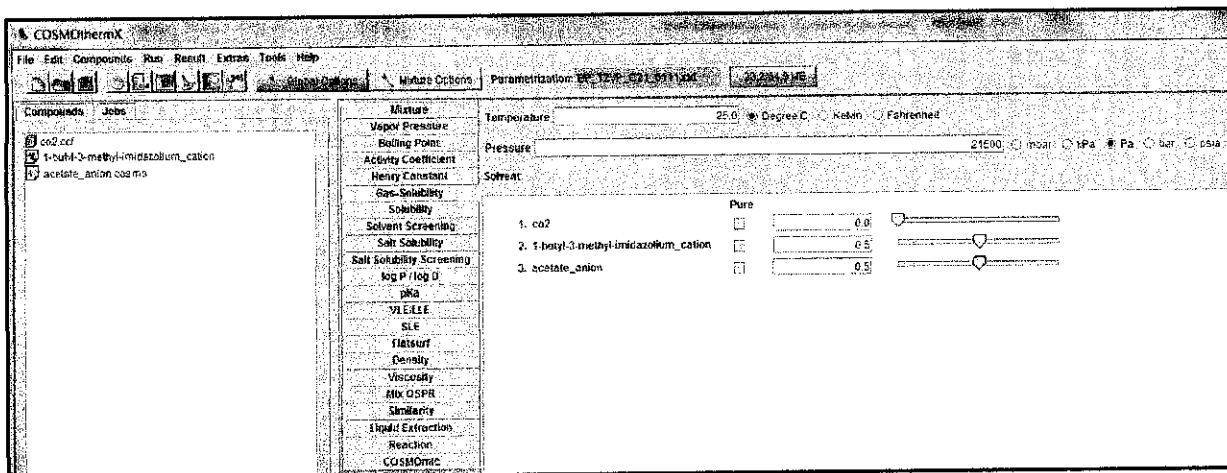
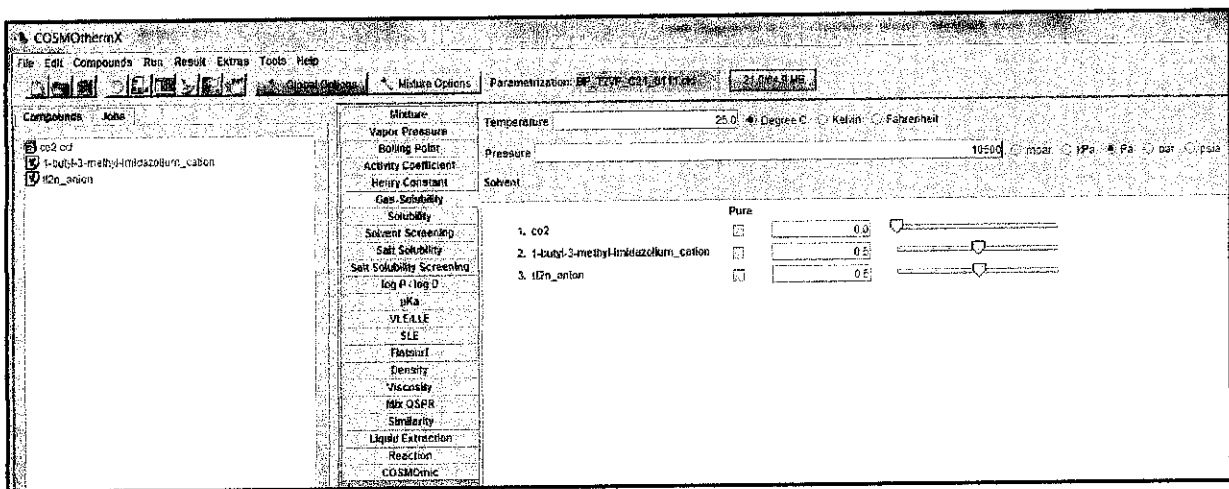


Figure 9 : Simulation using COSMO-RS



### 3.3.1 Trend of CO<sub>2</sub> solubility

The trend of CO<sub>2</sub> solubility in ionic liquids is the graph plotting results of simulation in which acquiring the experimental data from journal in order to identify the types of absorption occurred either it involves a physical absorption or chemical absorption.. It can be more easily seen and understand by using a P-x diagram in which the various conditions of pressure (MPa) is plotted against the CO<sub>2</sub> mole fraction at room temperature, 25°C @ 298K.

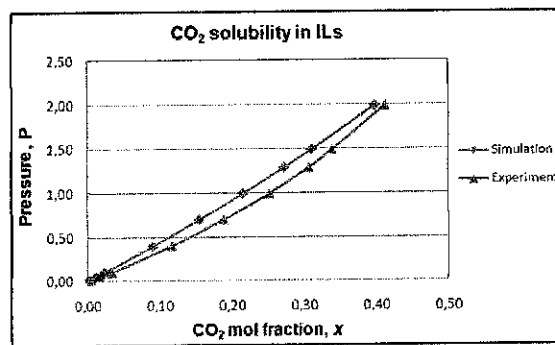


Figure 10 : P-x Diagram for IL

### 3.3.2 Interaction Energy

The interaction energy in COSMO-RS is the presentation of interaction between molecules of ionic liquids compound. It consists of three types of energy which are van der waals energy, hydrogen bonding energy and misfit energy that measured in unit of kJ/mol. The total interaction energy is very important for determining the strength of CO<sub>2</sub> solubility in the particular types of ionic liquids and the formula for total interaction energy calculation as followed:

$$\Delta H_{total} = H_{mix} - (H^{\circ}_{CO_2} + H^{\circ}_{IL})$$

$H_{mix}$  = interaction energy of CO<sub>2</sub> and ionic liquids mixture compound

$H^{\circ}_{CO_2}$  = interaction energy of CO<sub>2</sub> pure compound

$H^{\circ}_{IL}$  = interaction energy of ionic liquids pure compound



### 3.3.3 Sigma Geometry

Sigma geometry is a three-dimension (3-D) molecule compounds model consisting of several color representations for each molecule in the compound. There are three basic color representations which are blue for very positive charge, green for neutral charge and red for very negative charge.

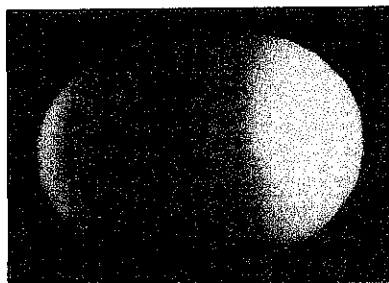


Figure 11 : Sigma Geometry for CO<sub>2</sub>

### 3.3.4 Sigma Profile

Sigma profile is the representation of chemical compound characteristics or behavior based on the peak presentation either in polar area or non polar area. The region of  $-1 < x < 1$  in sigma profile graph represents the non polar area and having neutral charge within the compound which is stable composition of molecules. The region of lower than  $-1$  having positive charge while higher than  $1$  (negative charge) in sigma profile and both of them are polar area.

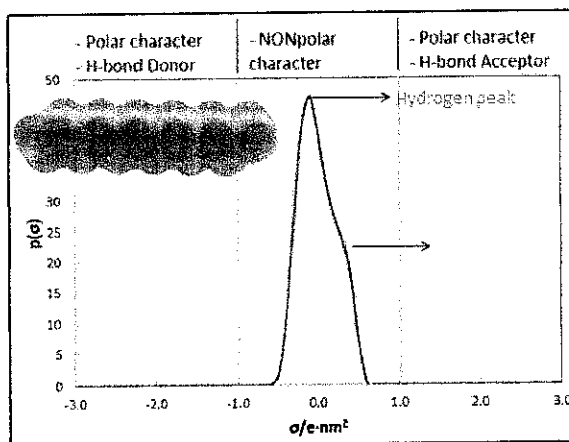


Figure 12 : Graph of Sigma Profile



## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 CO<sub>2</sub> Solubility Trending

The table and graph below are the result of simulation using COSMO-RS software for 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, [Bmim][TF<sub>2</sub>N] ionic liquid. The experimental data is taken from the journal for simulation in order to determine the solubility of CO<sub>2</sub> in the [Bmim][TF<sub>2</sub>N] ionic liquid. Both the experimental [33] and simulation data are plotted in a graph in order to be taken for comparison both of them. There are good agreement results even though a little bit differences of CO<sub>2</sub> mol fraction data can be seen from the graph might be due to error during the experiment or simulation process in software.

Pressure (Mpa)	CO <sub>2</sub> mol fraction (experiment)	CO <sub>2</sub> mol fraction (simulation)
0.00955	0.0050	0.002245
0.04935	0.0175	0.011554
0.09905	0.0335	0.023088
0.39705	0.1165	0.090285
0.69600	0.1885	0.154396
0.99435	0.2520	0.215237
1.28782	0.3065	0.272187
1.49075	0.3385	0.309957
1.98730	0.4115	0.397249

Table 5 : Solubility of CO<sub>2</sub> in [Bmim][TF<sub>2</sub>N] Ionic Liquid Data

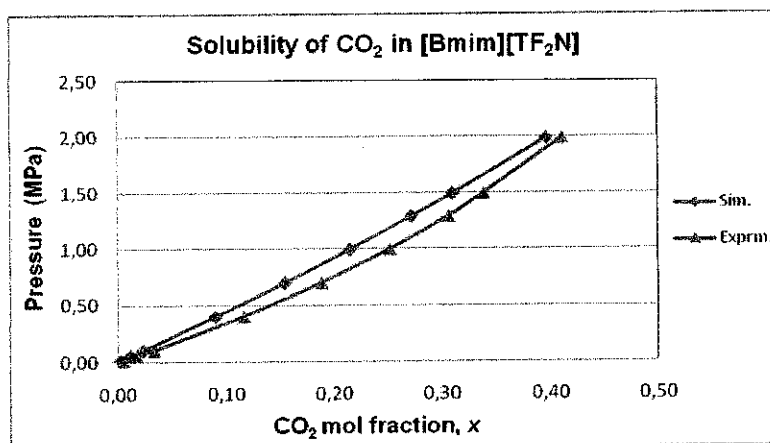


Figure 13 : Graph of CO<sub>2</sub> Mol Fraction vs Pressure for [Bmim][TF<sub>2</sub>N] Ionic Liquid



The table and graph below are the result of simulation using COSMO-RS software for 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] ionic liquid. The experimental data is taken from the journal too for simulation in order to determine the solubility of CO<sub>2</sub> in the [Bmim][Ac] ionic liquid. Both the experimental [33] and simulation data are plotted in a graph in order to be taken for comparison both of them. There are huge differences of CO<sub>2</sub> mol fraction data and a deviation from experimental data can be seen from the graph due to chemical absorption has occurred in the reaction.

Pressure (MPa)	CO <sub>2</sub> mol fraction (experiment)	CO <sub>2</sub> mol fraction (simulation)
0.0102	0.1620	0.002278
0.0503	0.2510	0.011171
0.1003	0.2750	0.022115
0.3994	0.3260	0.084541
0.7001	0.3570	0.142473
0.9996	0.3830	0.195897
1.3002	0.4060	0.245888
1.5000	0.4200	0.277263
1.9994	0.4550	0.350250

Table 6 : Solubility of CO<sub>2</sub> in [Bmim][Ac] Ionic Liquid Data

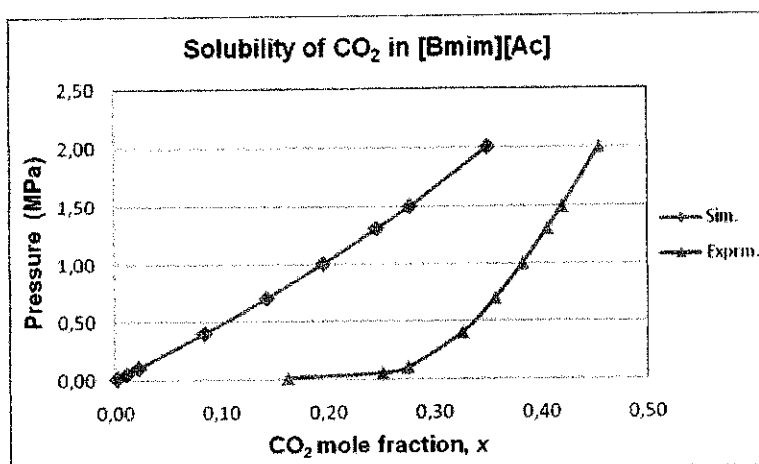


Figure 14 : Graph of CO<sub>2</sub> Mol Fraction vs Pressure for [Bmim][Ac] Ionic Liquid



#### 4.1.1 Evaluation of CO<sub>2</sub> Solubility

To establish trends due to structural variations in the anions with the same cation in the model ionic liquids, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, [Bmim][TF<sub>2</sub>N] and 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] are used. The cation [Bmim] is regarded as a representation model cation that having long alkyl chain ring in which can enhance solubility of CO<sub>2</sub>. As the best knowledge, the cation modifications might diminish CO<sub>2</sub> solubility in ionic liquid if there are having the presence of hydroxyl, phenyl and ether but in this case, they do not. Then, cation is highly can contribute to high solubility of CO<sub>2</sub>.

The result showed that COSMO-RS predicts a different data of CO<sub>2</sub> solubility in two type of ionic liquid which is containing two different anions, [TF<sub>2</sub>N] anion and [Ac] anion. The combination of [Bmim] cation and [TF<sub>2</sub>N] anion is showing a good agreement towards the experimental data from journal and it can be said that a physical absorption has occurred within [Bmim][TF<sub>2</sub>N] compound since the COSMO-RS can only predicts the physical properties of ionic liquids but not the complex reaction within it. Meanwhile, the combination of [Bmim] cation and [Ac] anion is showing a deviation between simulation data and experimental data from journal and it explained that the complex chemical reaction has occurred within it known as chemical absorption.

Anions are less amenable to systematic structural variation but usually have larger impact on CO<sub>2</sub> solubility. The presence of fluorine in [TF<sub>2</sub>N] anions shows the lower result of CO<sub>2</sub> solubility compared to the presence of strong hydrogen bonding reaction in [Ac] anion due to the factor of electronegative order. The more electronegative of anion, the higher the possibility of CO<sub>2</sub> will be attracted and the solubility of CO<sub>2</sub> will be high. Therefore, the order of electronegative for anion mainly is a factor to determine which one is having higher CO<sub>2</sub> solubility.



## 4.2 Interaction Energy of Ionic Liquids

In order to obtain the accurate data for solubility of CO<sub>2</sub> in both [Bmim][TF<sub>2</sub>N] and [Bmim][Ac] ionic liquid, nine iteration of data has been done by simulation of software with the nine different assumption of CO<sub>2</sub> solubility for each ionic liquid. The interaction energy is very important information which is presenting the strength of interaction between among molecules within ionic liquids compound. In COSMO-RS, the total interaction energy consists of three types energy which are misfit energy ( $H_{MF}$ ), hydrogen bonding energy ( $H_{HB}$ ) and Van der Waals energy ( $H_{VDW}$ ). The result of nine iterations will be obtained in the term of total energy interaction for each both ionic liquid using the equation below:

$$\Delta H_{total} = H_{mix} - (H^{\circ}_{CO_2} + H^{\circ}_{IL})$$

$H_{mix}$  = interaction energy of CO<sub>2</sub> and ionic liquids mixture compound

$H^{\circ}_{CO_2}$  = interaction energy of CO<sub>2</sub> pure compound

$H^{\circ}_{IL}$  = interaction energy of ionic liquids pure compound

For further discussion of total interaction energy in both [Bmim][TF<sub>2</sub>N] and [Bmim][Ac] ionic liquid, the comparison between each pure ionic liquid and mixture of ionic liquid will be done in terms of three components of interaction energy which are molecular fusion energy ( $H_{MF}$ ), hydrogen bonding energy ( $H_{HB}$ ) and Van der Waals energy ( $H_{VDW}$ ). The pure ionic liquid is the condition where no presence of CO<sub>2</sub> in the ionic liquid molecular component while mixture of ionic liquid is the condition where the presence of CO<sub>2</sub> taking apart in the ionic liquid molecular component. The pure CO<sub>2</sub> is also very important data to be taken as a consideration during determining the total interaction energy for obtaining the accurate data of CO<sub>2</sub> solubility.





### 4.2.1 Evaluation of Interaction Energy

Iteration	CO <sub>2</sub> mol%	$\Delta H_{CO_2-[Bmim][TF_2N]}$	VdW	HB	MF
1	0,002245	-1,4213	-2,153210	0,001530	0,730240
2	0,011554	-1,4050	-2,136300	0,011460	0,718760
3	0,023088	-1,3840	-2,113810	0,022370	0,705240
4	0,090285	-1,2530	-1,974750	0,091680	0,621030
5	0,154396	-1,1128	-1,827400	0,165400	0,532990
6	0,215237	-0,9631	-1,671820	0,243520	0,441310
7	0,272187	-0,8059	-1,510540	0,325410	0,347400
8	0,309957	-0,6909	-1,393670	0,384980	0,280230
9	0,397249	-0,3850	-1,088160	0,542400	0,107940

Table 7 : Interaction Energy of [Bmim][TF<sub>2</sub>N] Ionic Liquid Data

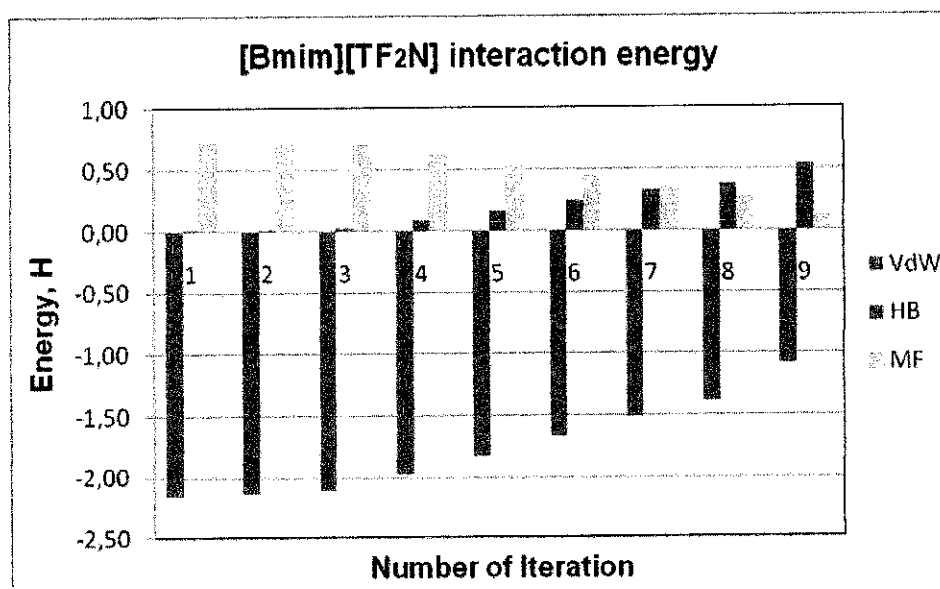


Figure 15 : Graph of Interaction Energy for [Bmim][TF<sub>2</sub>N] Ionic Liquid

From the graphs above, we can see that Van der walls energy in all iteration is the highest value regardless the sign of negative in the mixture of [Bmim][TF<sub>2</sub>N] interaction energy component but there are showing hydrogen bonding energy tends to get increase slightly while the others two get decrease in the last iteration. However, Van der walls energy still the dominant component in the mixture of [Bmim][TF<sub>2</sub>N] interaction energy.



Iteration	CO <sub>2</sub> mol%	$\Delta H_{CO_2-[Bmim][Ac]}$	VdW	HB	MF
1,000000	0,002278	-1,296130	-3,806770	0,013200	2,497390
2,000000	0,011171	-1,312890	-3,768090	0,037560	2,416440
3,000000	0,022115	-1,327440	-3,717130	0,068610	2,318680
4,000000	0,084541	-1,417890	-3,413550	0,257350	1,728290
5,000000	0,142473	-1,495180	-3,107600	0,451420	1,143210
6,000000	0,195897	-1,558020	-2,802010	0,648960	0,569380
7,000000	0,245888	-1,608520	-2,494000	0,852690	-0,000950
8,000000	0,277263	-1,632920	-2,288300	0,991450	-0,375220
9,000000	0,350250	-1,665310	-1,769430	1,352120	-1,301100

Table 8 : Interaction Energy of [Bmim][Ac] Ionic Liquid Data

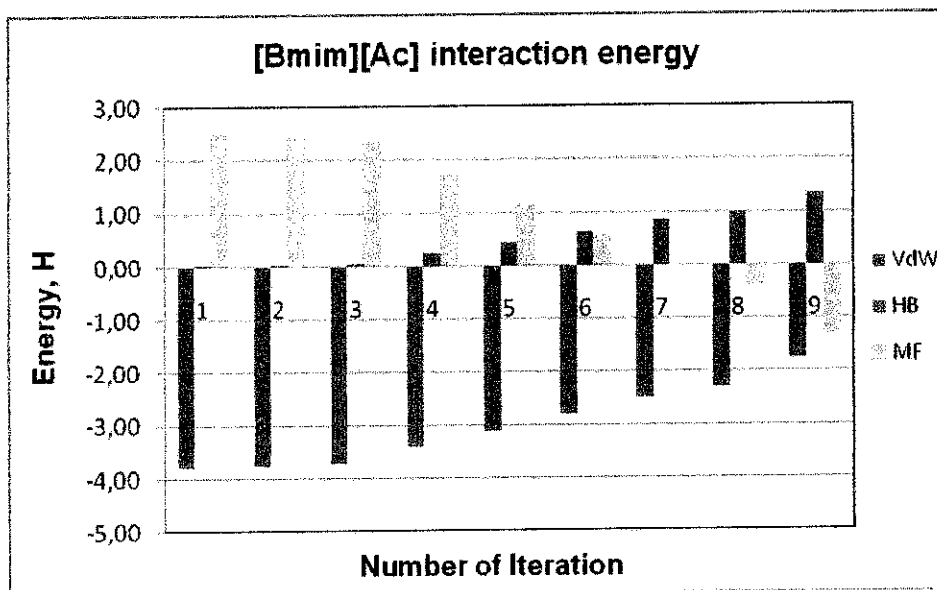


Figure 16 : Graph of Interaction Energy for [Bmim][Ac] Ionic Liquid

From the graphs above, we can see that Van der Waals energy in all iteration is the highest value regardless the sign of negative in the mixture of [Bmim][Ac] interaction energy component but there are showing hydrogen bonding energy highly increase while the others two get decrease drastically in the last iteration. Hence, hydrogen bonding energy is taking place and will be the dominant component in the mixture of [Bmim][Ac] interaction energy.



### 4.3 Sigma Geometry and Sigma Profile

Sigma geometry is a three-dimension (3-D) molecule compounds model consisting of three basic color representations which are blue for very positive charge, green for neutral charge and red for very negative charge. Meanwhile, sigma profile is the representation of chemical compound characteristics or behavior based on the peak presentation either in polar area or non polar area. The region of  $-1 < x < 1$  in sigma profile graph represents the non polar area and having neutral charge while the region of lower than -1 having positive charge, then the region of higher than 1 in sigma profile having negative charge and both charges actually are polar area with different properties.

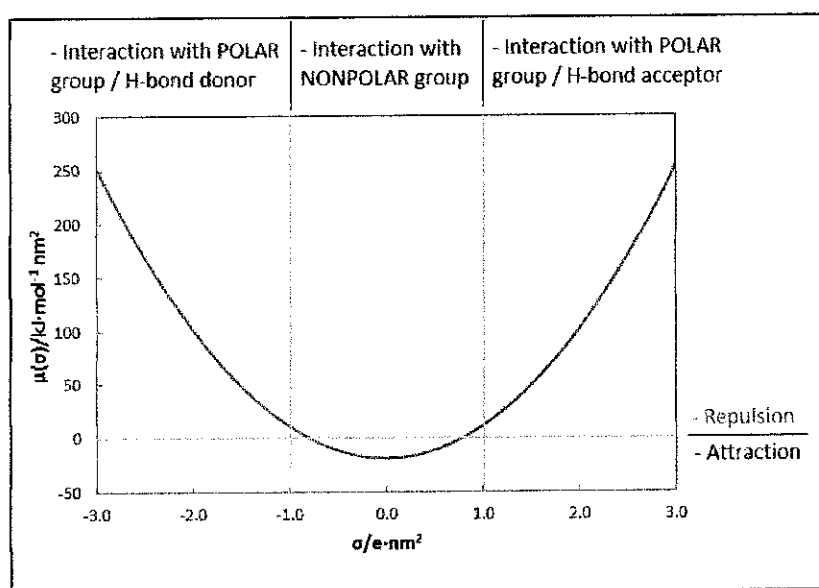


Figure 17 : Graph of Sigma Potential for Ionic Liquids Compound

There are two key interactions criteria for both polar and non polar region:

- The overlapping within non polar area is attractive interaction. The higher overlapping area or total peak area leads to higher interaction.
- The overlapping within the polar area is repulsive interaction. For H-bond group, the interaction is acceptor-donor and vice versa instead of the overlapping peak.

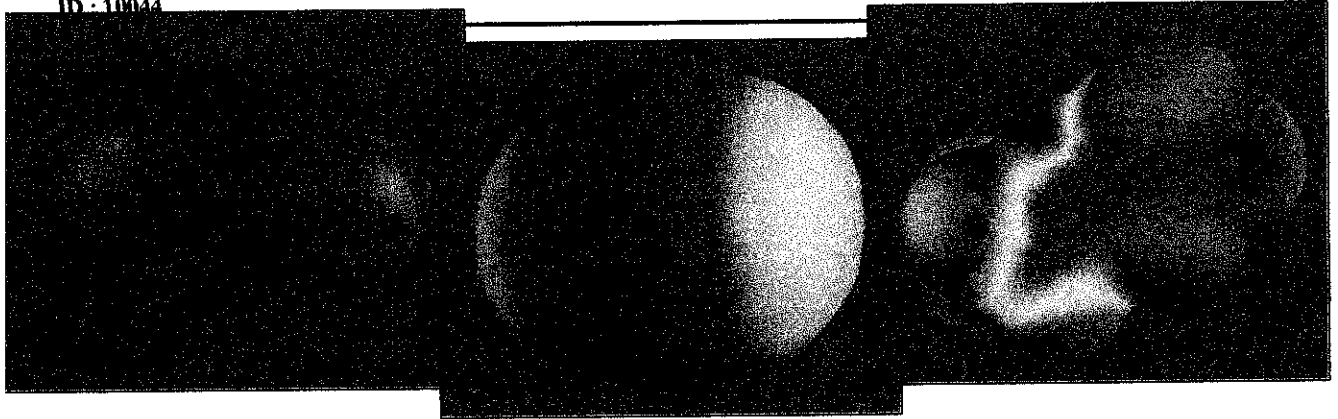


Figure 18 : Sigma Geometry of [Bmim][TF<sub>2</sub>N] Compound

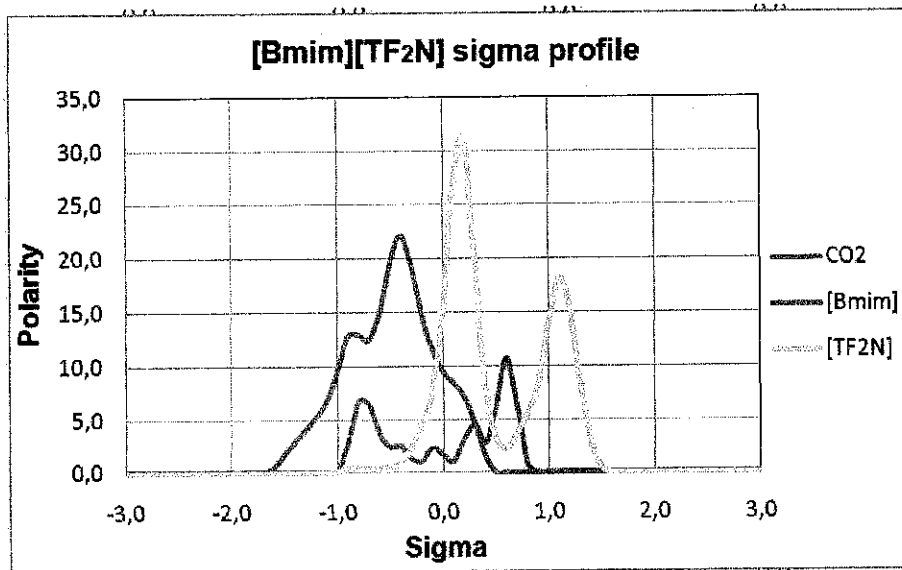


Figure 19 : Sigma Profile of [Bmim][TF<sub>2</sub>N] Compound

Ionic liquids 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, [Bmim][TF<sub>2</sub>N] presents peak and unresolved peak within non polar area. The [Bmim] cation presents moderate electropositive charge in the left hand side polar area and H-bond becomes a donor to [TF<sub>2</sub>N] anion. The [TF<sub>2</sub>N] anion presents strong electronegative-charge in the right hand side polar area and becoming H-bond acceptor from [Bmim] cation and CO<sub>2</sub>. The higher interaction between [TF<sub>2</sub>N] anion and [Bmim] cation compared to CO<sub>2</sub> has proved Van der Waals is the dominant in interaction energy.

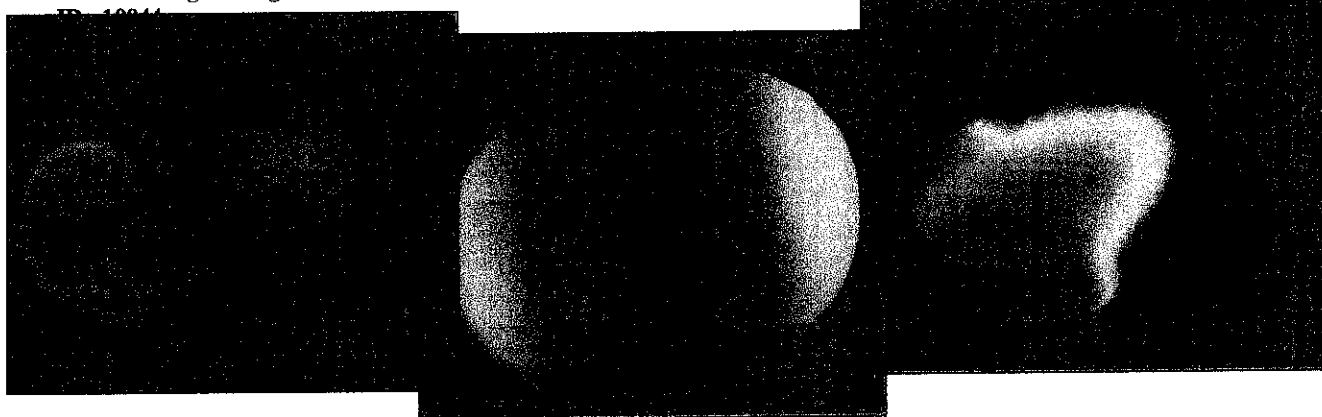


Figure 20 : Sigma Geometry of [Bmim][Ac] Compound

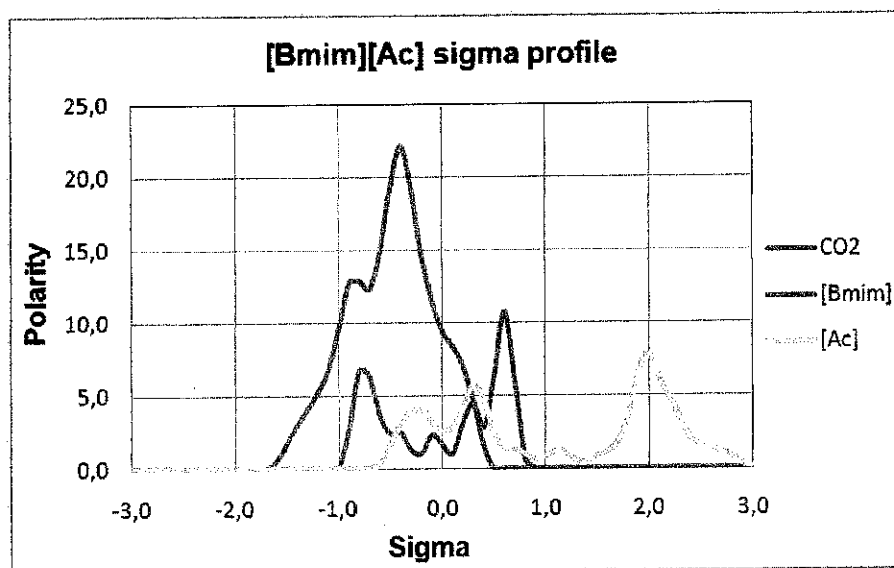


Figure 21 : Sigma Profile of [Bmim][Ac] Compound

Ionic liquids 1-butyl-3-methylimidazolium acetate, [Bmim][Ac] presents peak and unresolved peak within non polar area. The [Bmim] cation presents moderate electropositive charge in the left hand side polar area and H-bond becomes a donor to [Ac] anion. The [Ac] anion presents very strong electronegative-charge in the right hand side polar area and becoming H-bond acceptor from CO<sub>2</sub>. The higher interaction between [Ac] anion and CO<sub>2</sub> compared to [Bmim] cation has proved hydrogen bonding is the dominant in interaction energy.



---

## CHAPTER 5

### CONCLUSION & RECOMMENDATION

#### 5.1 Conclusion

This project is actively considering the ionic liquids as a promising alternative technique for CO<sub>2</sub> absorption. Newly introduced CO<sub>2</sub> absorption with ionic liquid that begins with the synthesis of ionic liquids reaction by selecting the imidazolium as cation while the bis (trifluoromethylsulfonyl) imide and acetate as anion for the simulation process using COSMO-RS software. The project is also undergoing further process by taking some additional information regarding literature review of absorption principle, as well as the types of potential ionic liquids. The proposed method to be used currently is the simulation of potential ionic liquids for CO<sub>2</sub> removal. Characterization of the ionic liquids will be complete done in the end of the simulation.

Trends in solubility and selectivity as a function of the chemical structure of cations and anions were analyzed. In general, solubility in ILs containing fluorine containing anions was higher than ILs containing other anions such as acetate, borate, sulphate, halogenide. Sigma profiles and sigma-potentials of solvents are valuable tools for a priori solvent characterization. Gas-liquid interactions were described qualitatively through sigma-potentials of ILs and quantitatively through activity coefficients. The combinatorial activity coefficients were correlated with the molar volume of ILs. Solubility of CO<sub>2</sub> and selectivity for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> separations decrease with an increase in temperature. CO<sub>2</sub> is much more soluble than methane and nitrogen and therefore the solubility of CO<sub>2</sub> in ionic liquid and temperature will play the key role in solvent selection for CO<sub>2</sub> capture. Low melting point ionic liquids with such cations and fluorine-containing anions may be investigated further experimentally. COSMO<sub>therm</sub> is a promising preliminary tool for fast screening and design of ILs for such purpose as it readily provides a number of pertinent.



## 5.2 Recommendation

COSMO*therm* is a promising preliminary tool for fast screening and design of ILs for such purpose as it readily provides a number of pertinent information. Even though the prediction, as a whole, succeeded to simulate all the experimental data from respective journal but COSMO*therm* cannot reproduce some of the trends that appear in experimental solubility data. Therefore, there are needed some recommendations that can be done in order to increase the accuracy of data obtained from simulation as stated below:

- Quality of prediction needs be improved by considering fugacity correction, considering interactions between ions in the treatment of ILs and improved parameterizations of COSMO-RS.
- It is recommended for a simulation to be ran at temperature of 283.15, 298.15, and 323.15 K since ionic liquids (ILs) of widely varying structures at those temperature as well as the molar volumes and the relative polarity of ILs.
- Database regarding the types of ionic liquids in the COSMO*therm* need to be upgraded from time to time so that the required ionic liquids for simulation are available and can be ran easily.
- Other factors and parameters regarding the absorption of CO<sub>2</sub> should be studied further in order to obtain the accurate data of ionic liquids properties as a reference for upcoming research.
- Need an alternative or support simulation tool that can examine both physical and chemical absorption of CO<sub>2</sub> since the COSMO*therm* can only predict the physical absorption for ionic liquids.
- Provide a specific guideline and tutorial on COSMO*therm* for variable properties of ionic liquids prediction so that the simulation process will become smooth and can save the time.



## REFERENCES

1. Kohl, A. L. and Riesenfeld, F. C., Gas Purification. 4 th edition. 1985, Houston, TX: Gulf Publishing Company
2. Seader, J. D., Separation Process Principles. 1998, New York: Wiley
3. Jennifer Lynn Anthony (2004), Gas solubilities in ionic liquids: experimental measurements and applications, *University of Notre Dame*
4. Zhang, S.J, Chen, Y.H,Rex. X.F.R, Zhang, J.M., Zhang X.p., Solubility pf CO<sub>2</sub> in sulfonate ionic liquids at high pressure, *J.Chem. Eng. Data.* 2005, 50, 230-233.
5. Aki, S.N.V.K, B.R.,Saurer, E.M.,Brennecke,J.F. High pressure phase behavior of CO<sub>2</sub> with imidazolium-based ionic liquids, *J. Phys. Chem. B* **2004**, *108*, 20355-20365
6. Eliane KUHNE (2008), Fluid Phase Behavior of Ionic Liquid-Based Systems of Interest for Green Processes: Measurements and Modelling, State University of Campinas
7. J.D. Holbrey, K.R. Seddon, Ionic liquids, *Clean Products & Process* 1 (1999) 223-236
8. J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D.Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, *Green Chmistry* 3(2001) 156-162
9. Poliakoff & Darr, 'New Directions in Inorganic and Metal-Organic Coordination Chemictry in Supercritical Flids '*Chem Rev,1999, 99,495-541*'
10. L.A Blancard, E.J Beck Marginand joad919991
11. Seddon, K.R., Stark, A., and Torres, M. J., Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.*, **2000** *72(12): 2275-2287*
12. Anthony, J. L., Maginn, E. J., and Brennecke, J. F., Solution thermodynamics of imidazolium-based ionic liquids and water. *J.Phys. Chem. B*, **2001**. *105: 10942-10949*





13. Anthony, J. L., Maginn, E. J., and Brennecke, J. F., Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B*, **2002**, *106*(29): 7315-7320
14. Wilkes, J. S. and Zaworotko, M. J., Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J. Chem. Soc.-Chem. Commun.*, **1992**, (13):965-967.
15. A.E.Visser, R.P.Swatloski, W.M. Reichert, R. Mayton , S.Sheff , A. Wierzbicki, J.H. Davis, Jr. and R.D. Rogers, *Chemical Communications*, **2001**, 135-136
16. M.D. Bermejo, A. Martina, G. Focod, M.J. Coceroc, S.B.Bottini , C.J. Peters, Application of a group contribution equation of state for the thermodynamic modeling of the binary systems CO<sub>2</sub>-1-butyl-3-methylimidazolium nitrate and CO<sub>2</sub>-1-hidroxy-1-propyl-3-methylimidazolium nitrate, *J.of Supercritical Fluids* **50** (2009) 112-117
17. Manish S, Kelkar and Edward J. Maginn, "Effect of Temperature and Water Content on the Shear Viscosity of the Ionic Liquids". *Journal of Photochemistry and Photobiology, A: Chemistry*, **2004**, *165*(1-3), 229-240
18. E.M.S.N.V. Saurer, K. Aki, J.F> Brennecke, Removal of ammonium bromide, ammonium chloride, and zinc acetate from ionic liquid/organic mixtures using carbon dioxide, *Green Chemistry* **8** (2006) 141-143
19. Bianca Breure, Susana B Bottini, Geert Jan Witkamp and Cor J. Peter, Thermodynamic Modeling of the Phase Behavior of Binary Systems of Ionic Liquids and CO<sub>2</sub> with the Group Contribution Equation of State, *J. Phys. Chem.B* **2007**, *111*, 14265-14270
20. A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke, *Chem. Commun.*, **2003**, *5*, 572-573
21. E.W. Castner Jr. and J.F. Wishart, *J. Chem. Phys.* **132** (2010), p. 120901-1.
22. In: A. Kokorin, Editor, *Theory, Properties, New Approaches*, InTech (2011)
23. In: A. Kokorin, Editor, *Applications and Perspectives*, InTech (2011)
24. L.A. Blanchard, D. Hancu, E.J. Beckman and J.F. Brennecke, *Nature*, **1999**, *399*, 28-29



25. Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. Anion Effects on Gas Solubility in Ionic Liquids. *J. Phys. Chem. B* **2005**, *109*, 6366–6374
26. *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2003.
27. Plechkova, N. V.; Seddon, K. R. *Chem. Soc. ReV.* **2008**, *37*, 123–150.
28. Magee, J. W.; Frenkel, M. IUPAC project (2003-020-2-100), NIST Ionic liquids database, 2005; <http://ilthermo.boulder.nist.gov/ILThermo/mainmenu.uix>.
29. Maginn, E. J. Design and Evaluation of Ionic Liquids as Novel CO<sub>2</sub> Absorbents, *Quarterly Technical Report to DOE*. December 31, 2004; January 31, 2005; May 31, 2005; August 16, 2005; November 20, 2005; January 12, 2006
30. Brennecke, J. F.; Anderson, J. L.; Maginn, E. J. Gas Solubilities in Ionic Liquids, In *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003; p 81-92.
31. Costa Gomes, M. F. *J. Chem. Eng. Data* **2007**, *52* (2), 472–475.
32. Shiflett, M. B.; Yokozeki, A. *J. Phys. Chem. B* **2007**, *111* (8), 2070–2074
33. A. Yokozeki,<sup>\*</sup>† Mark B. Shiflett,<sup>‡</sup> Christopher P. Junk,<sup>‡</sup> Liane M. Grieco,<sup>‡</sup> and Thomas Foo<sup>‡</sup> *DuPont Fluoroproducts Laboratory, Chestnut Run Plaza 711, Wilmington, Delaware 19880 and DuPont Central Research and DeVelopment, Experimental Station, Wilmington, Delaware 19880 ReceiVed: June 16, 2008; ReVised Manuscript ReceiVed: October 14, 2008*
34. Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. Guide to CO<sub>2</sub> separations in imidazoliumbased room-temperature ionic liquids. *Ind. Eng. Chem. Res.* 2009, *48*, 2739–2751.
35. Huang, J.; R  uther, T. Why are ionic liquids attractive for CO<sub>2</sub> absorption? An overview. *Aust. J. Chem.* 2009, *62*, 298–308.



- 
36. Bara, J. E.; Camper, D. E.; Gin, D. L.; Noble, R. D. Roomtemperature ionic liquids and composite materials: platform technologies for CO<sub>2</sub>
37. Process Simulation of CO<sub>2</sub> Chemical Absorption Based on Self-Heat Recuperation Technology for Pre-Combustion Process Akira Kishimoto, Yasuki Kansha, Chiro Fushimi, Atsushi Tsutsumi\* Collaborative Research Center for Energy Engineering, Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-Ku, Tokyo, 153-8505, Japan [a-tsu2mi@iis.u-tokyo.ac.jp](mailto:a-tsu2mi@iis.u-tokyo.ac.jp) capture. Acc. Chem. Res. 2010, 43 (1), 152–159



---

## **APPENDICES**

Appendices I : Simulation Data of CO<sub>2</sub> Solubility from COSMO-RS for [Bmim][TF<sub>2</sub>N]

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-im	0,0	0,0	
2	tf2n_anion	0,0	0,0	
3	co2	-2,64869639	-0,41374166	0,002245
Gas Solubility at T = 298,15 K and p = 9,55000 kPa at given concentration XS={0.5 0.5 0.0} - job 1				
Gas Solubility at T = 298,15 K and p = 49,35000 kPa at given concentration XS={ 0.5 0.5 0.0 }				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-im	0,0	0,0	
2	tf2n_anion	0,0	0,0	
3	co2	-1,93726258	-0,40961481	0,011554
Gas Solubility at T = 298,15 K and p = 49,35000 kPa at given concentration XS={0.5 0.5 0.0} - job 2				
Gas Solubility at T = 298,15 K and p = 99,05000 kPa at given concentration XS={ 0.5 0.5 0.0 }				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-im	0,0	0,0	
2	tf2n_anion	0,0	0,0	
3	co2	-1,63661586	-0,40546222	0,023088
Gas Solubility at T = 298,15 K and p = 99,05000 kPa at given concentration XS={0.5 0.5 0.0} - job 3				
Gas Solubility at T = 298,15 K and p = 397,05000 kPa at given concentration XS={ 0.5 0.5 0.0 }				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	tz2n_anion	0,0	0,0	
3	co2	-1,04438561	-0,38061584	0,090285

Gas Solubility at T = 298.15 K and p = 397.05000 kPa at given concentration XS={0.5 0.5 0.0} - job 4

**Gas Solubility at T = 298.15 K and p = 696.00000 kPa at given concentration XS={0.5 0.5 0.0}**

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	tz2n_anion	0,0	0,0	
3	co2	-0,81136471	-0,35584885	0,154396

Gas Solubility at T = 298.15 K and p = 696.00000 kPa at given concentration XS={0.5 0.5 0.0} - job 5

**Gas Solubility at T = 298.15 K and p = 994.35000 kPa at given concentration XS={0.5 0.5 0.0}**

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	tz2n_anion	0,0	0,0	
3	co2	-0,66708326	-0,33134057	0,215237

Gas Solubility at T = 298.15 K and p = 994.35000 kPa at given concentration XS={0.5 0.5 0.0} - job 6

**Gas Solubility at T = 298.15 K and p = 1287.82000 kPa at given concentration XS={0.5 0.5 0.0}**

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	t2n_anion	0,0	0,0	
3	co2	-0,56513213	-0,30747073	0,272187
Gas Solubility at T = 298.15 K and p = 1287.82000 kPa at given concentration XS={0.5 0.5 0.0} - job 7				
Gas Solubility at T = 298.15 K and p = 1490.75000 kPa at given concentration XS={0.5 0.5 0.0}				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	t2n_anion	0,0	0,0	
3	co2	-0,50869911	-0,29108827	0,309957
Gas Solubility at T = 298.15 K and p = 1490.75000 kPa at given concentration XS={0.5 0.5 0.0} - job 8				
Gas Solubility at T = 298.15 K and p = 1987.30000 kPa at given concentration XS={0.5 0.5 0.0}				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	1-butyl-3-methyl-iml	0,0	0,0	
2	t2n_anion	0,0	0,0	
3	co2	-0,40093678	-0,2517275	0,397249
Gas Solubility at T = 298.15 K and p = 1987.30000 kPa at given concentration XS={0.5 0.5 0.0} - job 9				

Appendices II : Simulation Data of CO<sub>2</sub> Solubility from COSMO-RS for [Bmin][Ac]

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	co2	-2.64268496	-0.36222524	0,002278
2	acetate_anion	0,0	0,0	
3	1-butyl-3-methyl-iml	0,0	0,0	
Gas Solubility at T = 298.15 K and p = 10.20000 kPa at given concentration XS={0.0 0.5 0.5} - job 1				
<b>Gas Solubility at T = 298.15 K and p = 50.30000 kPa at given concentration XS={0.0 0.5 0.5}</b>				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	co2	-1.95191622	-0.3569541	0,011171
2	acetate_anion	0,0	0,0	
3	1-butyl-3-methyl-iml	0,0	0,0	
Gas Solubility at T = 298.15 K and p = 50.30000 kPa at given concentration XS={0.0 0.5 0.5} - job 2				
<b>Gas Solubility at T = 298.15 K and p = 100.30000 kPa at given concentration XS={0.0 0.5 0.5}</b>				

Nr	Compound	log10(x_sol)	ln(gamma)	CO2 mol %
1	co2	-1.65530892	-0.34988437	0,022115
2	acetate_anion	0,0	0,0	
3	1-butyl-3-methyl-iml	0,0	0,0	
Gas Solubility at T = 298.15 K and p = 100.30000 kPa at given concentration XS={0.0 0.5 0.5} - job 3				
<b>Gas Solubility at T = 298.15 K and p = 399.40000 kPa at given concentration XS={0.0 0.5 0.5}</b>				



Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	co2	-1,07293306	-0,30895608				0,084541
2	acetate_anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 399.40000 kPa at given concentration XS={ 0.0 0.5 0.5 } - job 4							
Gas Solubility at T = 298.15 K and p = 700.10000 kPa at given concentration XS={ 0.0 0.5 0.5 }							

Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	co2	-0,84626831	-0,26962139				0,142473
2	acetate_anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 700.10000 kPa at given concentration XS={ 0.0 0.5 0.5 } - job 5							
Gas Solubility at T = 298.15 K and p = 999.60000 kPa at given concentration XS={ 0.0 0.5 0.5 }							

Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	co2	-0,70797253	-0,2319289				0,195897
2	acetate_anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 999.60000 kPa at given concentration XS={ 0.0 0.5 0.5 } - job 6							
Gas Solubility at T = 298.15 K and p = 1300.20000 kPa at given concentration XS={ 0.0 0.5 0.5 }							

Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	CO2	-0.60926304	-0.19628567				0,245888
2	acetate anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 1300.20000 KPa at given concentration XS={0.0 0.5 0.5} - job 7							
Gas Solubility at T = 298.15 K and p = 1500.00000 KPa at given concentration XS={0.0 0.5 0.5}							

Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	CO2	-0.55710763	-0.1734443				0,277263
2	acetate anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 1500.00000 KPa at given concentration XS={0.0 0.5 0.5} - job 8							
Gas Solubility at T = 298.15 K and p = 1999.40000 KPa at given concentration XS={0.0 0.5 0.5}							

Nr	Compound	log10(x_sol)	ln(gamma)				CO2 mol %
1	CO2	-0.455622	-0.11973118				0,35025
2	acetate anion	0,0	0,0				
3	1-butyl-3-methyl-iml	0,0	0,0				
Gas Solubility at T = 298.15 K and p = 1999.40000 KPa at given concentration XS={0.0 0.5 0.5} - job 9							

Appendices III: Simulation Data of Interaction Energy from COSMO-RS for [Bmim][TF<sub>2</sub>N]

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring	P (Pa)
1	co2	-6.64477	4.25507	-495306.52512	-6.60623	4.17793	0.0	-10.78416	0.0	17992.0
2	1-butyl-3-methyl-iml	-9.99519	-30.97625	-1111468.4753	-22.27675	15.44102	-2.38983	-36.64589	-4.21235	
3	tf2n anion	-3.63827	-29.91091	-4798440.6659	-20.0527	13.47894	-2.38646	-32.4317	0.0	

Compound properties at T = 298.15 K in mixture x(1)=0.0022 x(2)=0.4989 x(3)=0.4989 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.0022 x(2)=0.4989 x(3)=0.4989**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring	P
1	co2	-6.6385	4.25617	-495306.51884	-6.60316	4.17592	0.0	-10.77908	0.0	18037.0
2	1-butyl-3-methyl-iml	-10.01162	-30.97913	-1111468.49173	-22.27744	15.43361	-2.38483	-36.64465	-4.21235	
3	tf2n anion	-3.63022	-29.9095	-4798440.65785	-20.03878	13.47688	-2.38153	-32.42111	0.0	

Compound properties at T = 298.15 K in mixture x(1)=0.0116 x(2)=0.4942 x(3)=0.4942 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.0116 x(2)=0.4942 x(3)=0.4942**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring	P
1	co2	-6.62816	4.25798	-495306.50851	-6.59877	4.17365	0.0	-10.77242	0.0	18113.0
2	1-butyl-3-methyl-iml	-10.04063	-30.98421	-1111468.52074	-22.28176	15.42097	-2.37932	-36.6425	-4.21235	
3	tf2n anion	-3.60142	-29.90446	-4798440.62905	-20.01789	13.47827	-2.37613	-32.40743	0.0	

Compound properties at T = 298.15 K in mixture x(1)=0.0231 x(2)=0.4885 x(3)=0.4885 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.0231 x(2)=0.4885 x(3)=0.4885**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,56714	4,26867	-495306,44748	-6,57163	4,1595	0,0	-10,73113	0,0
2	1-butyl-3-methyl-imid	-10,22101	-31,01581	-1111468,70111	-22,30731	15,34316	-2,3446	-36,62903	-4,21235
3	ft2n anion	-3,4315	-29,87469	-4798440,45913	-19,88848	13,48602	-2,34154	-32,32313	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,0903 x(2)=0,4549 x(3)=0,4549 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,0903 x(2)=0,4549 x(3)=0,4549**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,50598	4,27938	-495306,38632	-6,54274	4,14455	0,0	-10,68729	0,0
2	1-butyl-3-methyl-imid	-10,41719	-31,05018	-1111468,8973	-22,33401	15,26097	-2,3078	-36,61467	-4,21235
3	ft2n anion	-3,25382	-29,84356	-4798440,28145	-19,75041	13,49512	-2,30462	-32,23398	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,1544 x(2)=0,4228 x(3)=0,4228 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,1544 x(2)=0,4228 x(3)=0,4228**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,44506	4,29006	-495306,3254	-6,51212	4,1288	0,0	-10,64092	0,0
2	1-butyl-3-methyl-imid	-10,63153	-31,08773	-1111469,11164	-22,36221	15,17389	-2,26883	-36,59933	-4,21235
3	ft2n anion	-3,06687	-29,81081	-4798440,0945	-19,60318	13,50627	-2,26547	-32,14011	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,2152 x(2)=0,3924 x(3)=0,3924 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,2152 x(2)=0,3924 x(3)=0,3924**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,38619	4,30037	-495306,26654	-6,48028	4,11244	0,0	-10,59272	0,0
2	1-butyl-3-methyl-iml	-10,85811	-31,12742	-1111469,33822	-22,39022	15,08438	-2,22793	-36,58351	-4,21235
3	f2n anion	-2,88045	-29,77814	-4798439,90807	-19,44979	13,51823	-2,22448	-32,04285	0,0

Compound properties at T = 298.15 K in mixture x(1)=0.2722 x(2)=0.3639 x(3)=0.3639 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.2722 x(2)=0.3639 x(3)=0.3639**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,34562	4,30748	-495306,22597	-6,45715	4,10059	0,0	-10,55774	0,0
2	1-butyl-3-methyl-iml	-11,02641	-31,15691	-1111469,50652	-22,41045	15,01942	-2,1982	-36,57196	-4,21235
3	f2n anion	-2,7455	-29,7545	-4798439,77312	-19,33766	13,52787	-2,19464	-31,97251	0,0

Compound properties at T = 298.15 K in mixture x(1)=0.3100 x(2)=0.3450 x(3)=0.3450 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.3100 x(2)=0.3450 x(3)=0.3450**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,24783	4,32461	-495306,12817	-6,39641	4,06959	0,0	-10,466	0,0
2	1-butyl-3-methyl-iml	-11,47846	-31,23611	-1111469,95857	-22,46156	14,8504	-2,11963	-36,54171	-4,21235
3	f2n anion	-2,40072	-29,6941	-4798439,42835	-19,04147	13,5556	-2,11579	-31,78899	0,0

Compound properties at T = 298.15 K in mixture x(1)=0.3972 x(2)=0.3014 x(3)=0.3014 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298.15 K in mixture x(1)=0.3972 x(2)=0.3014 x(3)=0.3014**

Appendices IV: Simulation Data of Interaction Energy from COSMO-RS for [Bmim][Ac]

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,41287	4,2957	-495306,29321	-6,48547	5,95776	0,0	-12,44322	0,0
2	1-butyl-3-methyl-iml	-5,70807	-30,22517	-1111464,18818	-29,74657	33,46829	-21,86356	-41,83054	-4,21235
3	acetate anion	14,10321	-45,52693	-600464,50646	-23,02753	16,25708	-21,81127	-17,47334	0,0
Compound properties at T = 298,15 K in mixture x(1)=0,0023 x(2)=0,4989 x(3)=0,4989 - energies are in kJ/mol - pressure is in kPa - area is in nm^2 - volume is in nm^3 - job 1									
<b>Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,0023 x(2)=0,4989 x(3)=0,4989</b>									

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,40781	4,29658	-495306,28815	-6,48608	5,94611	0,0	-12,4322	0,0
2	1-butyl-3-methyl-iml	-5,77924	-30,23764	-1111464,25935	-29,77725	33,39423	-21,84563	-41,80622	-4,21235
3	acetate anion	14,16293	-45,51647	-600464,44675	-23,013	16,26184	-21,80484	-17,47	0,0
Compound properties at T = 298,15 K in mixture x(1)=0,0112 x(2)=0,4944 x(3)=0,4944 - energies are in kJ/mol - pressure is in kPa - area is in nm^2 - volume is in nm^3 - job 1									
<b>Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,0112 x(2)=0,4944 x(3)=0,4944</b>									

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,39117	4,2995	-495306,27152	-6,48595	5,93206	0,0	-12,41801	0,0
2	1-butyl-3-methyl-iml	-5,89927	-30,25867	-1111464,37938	-29,82226	33,30105	-21,8312	-41,7737	-4,21235
3	acetate anion	14,28078	-45,49582	-600464,3289	-22,98267	16,27131	-21,78822	-17,46575	0,0
Compound properties at T = 298,15 K in mixture x(1)=0,0221 x(2)=0,4889 x(3)=0,4889 - energies are in kJ/mol - pressure is in kPa - area is in nm^2 - volume is in nm^3 - job 1									
<b>Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,0221 x(2)=0,4889 x(3)=0,4889</b>									

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,29513	4,31632	-495306,17547	-6,4844	5,84814	0,0	-12,33255	0,0
2	1-butyl-3-methyl-iml	-6,5853	-30,37886	-1111465,06541	-30,08659	32,7417	-21,73615	-41,58133	-4,21235
3	acetate anion	14,95563	-45,37759	-600463,65405	-22,81034	16,32419	-21,69453	-17,44	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,0845 x(2)=0,4577 x(3)=0,4577 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,0845 x(2)=0,4577 x(3)=0,4577**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,20288	4,33248	-495306,08322	-6,47999	5,76532	0,0	-12,24531	0,0
2	1-butyl-3-methyl-iml	-7,28134	-30,5008	-1111465,76145	-30,34609	32,18439	-21,63836	-41,38909	-4,21235
3	acetate anion	15,62993	-45,25946	-600462,97975	-22,63254	16,37924	-21,59825	-17,41353	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,1425 x(2)=0,4288 x(3)=0,4288 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,1425 x(2)=0,4288 x(3)=0,4288**

Nr	Compound	mu	log10(p)	E_COSMO+DE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,1145	4,34797	-495305,99485	-6,47265	5,68441	0,0	-12,15707	0,0
2	1-butyl-3-methyl-iml	-7,98375	-30,62386	-1111466,46386	-30,59882	31,63433	-21,53928	-41,19869	-4,21235
3	acetate anion	16,30157	-45,14179	-600462,3081	-22,44999	16,43638	-21,49979	-17,38658	0,0

Compound properties at T = 298,15 K in mixture x(1)=0,1959 x(2)=0,4021 x(3)=0,4021 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0,1959 x(2)=0,4021 x(3)=0,4021**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-6,0311	4,36258	-495305,91145	-6,46252	5,60439	0,0	-12,06692	0,0
2	1-butyl-3-methyl-iml	-8,69295	-30,7481	-1111467,17306	-30,84633	31,08497	-21,43569	-41,00852	-4,21235
3	acetate anion	16,96873	-45,02491	-600461,64095	-22,26311	16,49543	-21,39965	-17,35889	0,0

Compound properties at T = 298,15 K in mixture x(1)=0.2459 x(2)=0.3771 x(3)=0.3771 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0.2459 x(2)=0.3771 x(3)=0.3771**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-5,97769	4,37194	-495305,85804	-6,45411	5,55198	0,0	-12,00609	0,0
2	1-butyl-3-methyl-iml	-9,17351	-30,83229	-1111467,65362	-31,00823	30,72199	-21,36613	-40,88243	-4,21235
3	acetate anion	17,41528	-44,94668	-600461,19439	-22,13402	16,53655	-21,33045	-17,34011	0,0

Compound properties at T = 298,15 K in mixture x(1)=0.2773 x(2)=0.3614 x(3)=0.3614 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0.2773 x(2)=0.3614 x(3)=0.3614**

Nr	Compound	mu	log10(p)	E_COSMO+dE+Mu	H_int	H_MF	H_HB	H_vdW	E_Ring
1	co2	-5,85231	4,3939	-495305,73266	-6,42735	5,42291	0,0	-11,85026	0,0
2	1-butyl-3-methyl-iml	-10,39716	-31,04667	-1111468,87727	-31,404	29,81685	-21,18535	-40,56778	-4,21235
3	acetate anion	18,53468	-44,75057	-600460,075	-21,7974	16,64488	-21,15056	-17,29172	0,0

Compound properties at T = 298,15 K in mixture x(1)=0.3503 x(2)=0.3249 x(3)=0.3249 - energies are in kJ/mol - pressure is in kPa - area is in nm<sup>2</sup> - volume is in nm<sup>3</sup> - job 1

**Molecule/Conformer properties at T = 298,15 K in mixture x(1)=0.3503 x(2)=0.3249 x(3)=0.3249**