Separation of CO_2 from Methane Using Ionic Liquids

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(MS in Chemical Engineering)

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4	EME-981	Advanced Fuel Technology	Elective	03	A
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Title: **Separation of Co_2 from Methane Using Ionic Liquids.**

Presented on: **22 Feb 2018** at: **1430 hrs in SCME Seminar Hall**

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Dedication

This thesis is dedicated to my Parents and my Wife

Abstract

When natural gas is produced along with the methane it carries several impurities such as Carbon dioxide (CO_2) and Hydrogen sulphide (H_2S). The CO_2 can form dry ice and hydrates in the pipelines, causes corrosion in supply lines and decreases the calorific value of the gas. The presence of H_2S can cause environmental and health hazards as well. Henceforth the natural gas is pretreated in order to separate the acid gases before the commercial use.

Over the course of time several separation techniques have been developed and deployed for the separation of CO_2 from methane such as Amine scrubbing with suitable amine solution. Membrane separation process is also being used for the separation of the CO_2 from methane using the semi permeable membranes. Recent studies have depicted Ionic Liquids as another potential candidate for the CO_2 separation due to their wide liquid range, high thermal stability and near zero volatility. Ionic Liquids are salts in liquid state at room temperature having melting point below 100 °C. They have high affinity for the CO_2 due to quadrupole moment and physical absorption takes place due to the Vaan der Waals forces.

The purpose of this research is to test CO_2 solubility in the 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF] ionic liquids for the effective CO_2 separation from methane, testing the solubility of CO_2 at different pressure. Preparation and testing of CO_2 solubility in [Bmim][BF_4] ionic liquid based solvent systems. Comparative analysis of the absorption efficiency with the Amine scrubbing processes. Process simulation of the ionic liquid based process for performance and techno-economic evaluation and comparative analysis with conventional amine process using Aspen PLUS® simulator. This work also includes the economic analysis of ionic liquid based natural gas sweetening process.

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Chapter-1

Introduction

1.1 Introduction

Global population was estimated to be 7.2 billion in 2013 and is estimated to be increased up to 9.5 billion by 2050. Demographic trends vary from region to region as developed countries are expected to have a small or negative growth whilst developing countries are expected to have a rise of nearly 70% as per the 2010 demographic values. The increased population however will require more resources and energy thus increasing the demand.

The globalized and more populated world with fast emerging countries requires efficient solutions to meet the growing energy demands in a sustainable way. International organization and corporations use past demographic data and energy trends to predict the future trajectory of the energy use. About 40% increase in energy demand by 2030 is expected [1, 2].

Presently, fossil fuels (oil, gas and coal) are the main contributors in meeting the global energy demand. Being the major source of energy, their high usage has raised environmental concerns because of the emission of greenhouse gas (CO_2). The relation between global warming and CO_2 emission has been reported to be proportional on a multi-decadal scale [3]. Energy productions are responsible for 75% of total stationary CO_2 emissions as shown in Figure 1 [1].

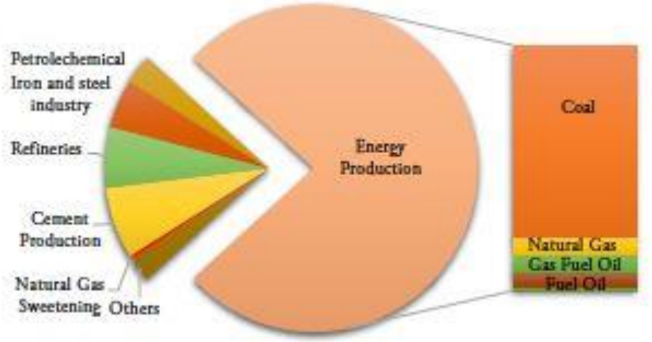


Figure 1. Global stationary CO_2 emitters

Renewable energy technologies have started to emerge as an alternative energy source to meet the global energy demands. They however, face several challenges such as intermittent production, storage during peak production and economic competitiveness with fossil fuels. The economic competence with fossil fuels is evident after the oil prices drop which started in 2014. The energy mix of the future will be linked to the advances in technology, which will enable improvements of renewable energy efficiency, and the exploitation of unconventional gas and oil fields (shale gas, sour gas, tight oil, etc.). As advancements in renewable energy domain are predominantly in solar and wind energy, they will surpass nuclear energy in market share [4], as shown in Figure 2. For now and coming decades fossil fuels will still be playing dominant role and major energy contributors. The coal utilization will remain increasing, while it is expected that the oil production will reach its peak in coming decades.

Natural gas will be the fastest growing energy source in coming 20 years. Natural gas is an affordable source, widely distributed and it is the most environmentally acceptable fossil fuel. Natural gas possesses the highest energy per unit mass decreasing the CO_2 emission per unit of energy produced. It has been reported that natural gas demand will increase up to 35% and in some optimistic scenarios up to 80% by 2035 [5].

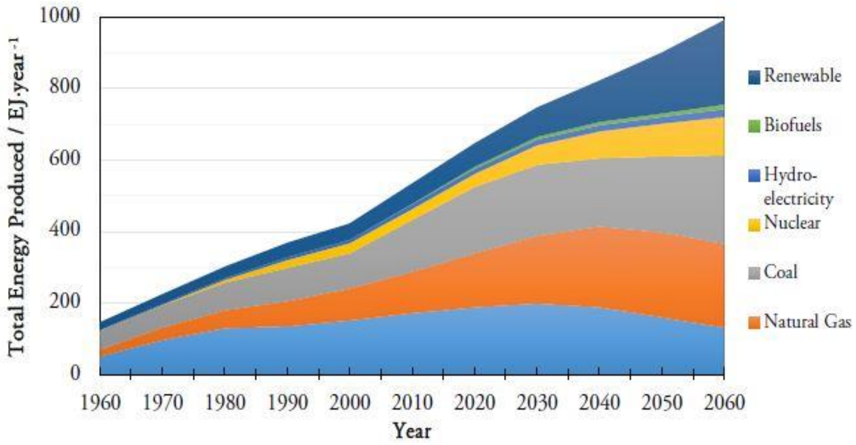


Figure 2. Global energy demand trend [3]

1.2 Natural gas production-

Natural gas is the cleanest burning fossil fuel with relatively lower CO_2 emission per unit of energy produced. Hence, becoming the preferable fuel option for power generation in Organization of Economic Co-operation and development (OECD) countries. According to the 2014 Annual Statistical Bulletin published by OPEC, there were 200 trillion standard cubic meter (SCM) gas reserves worldwide [2].

Two third of the gas reserves are possessed by six countries. Middle east has the largest natural gas volumes with 80 trillion SCM accounting for 40% share and Russia has 24% of the total reserves. Russia, Iran and Qatar have the largest natural gas reserves by the end of 2013. United Arab Emirates has the seventh largest proven gas reserves with 6 trillion SCM. Netherlands has the second largest gas reserves (1.1 trillion SCM) in Western-Europe after Norway with natural gas reserves of 2.7 trillion SCM [2]. Nearly half of these gas reserve contain more than 2% CO_2 and H_2S [6]. Which are known as sour gases when H_2S is present in larger concentration and as acid gases when CO_2 is present in large concentration. Most of the reserves containing large concentrations of these gases are underdeveloped or not being developed at all because of the economic and environmental constrains.

1.3 Motivation

Exploration and production of the gas fields with high percentage of CO_2 becomes necessary to meet the increasing global energy demand, as natural gas can be very essential in meeting the short falls.

While producing natural gas, the sweetening process is usually the costliest part. Traditionally natural gas sweetening is carried out the absorption process globally. The alkanolamine based chemical absorption accounts for the most sweetening processes. However, the chemical absorbents become highly corrosive at high CO_2 loading and can degrade resulting in the foaming production. Besides, the major constrain in the alkanolamine based absorption process is the high regeneration cost, as high reboiler heat duty is required to regenerate the amines. Physical solvents do not pose these problems, but they have relatively much lower CO_2 loading capacity, and they absorb the hydrocarbons too such as methane, which is a valued product. Thich make them unfeasible for the large-scale process. The need to explore and produce more natural gas fields and the existing underperforming fields with high concentration of acid gases require the changes in sweetening technology too. Ionic liquids, being the physical solvents, have shown promising results and can be potential alterative solvents for natural gas sweetening process. The main motivation behind this work is to check their feasibility for industrial scale applications.

Chapter-2

Background and Literature Review

2.1 Natural gas composition

Natural gas is a mixture of hydrocarbons and other components which exist in gas phase at atmospheric conditions. It is mainly composed of methane (CH_4) with a considerable presence of ethane (C_2H_6), propane (C_3H_6), butane (C_4H_{10}), hexane (C_5H_{12}), traces of alkenes and heavier hydrocarbons. Other gases, which are present in large percentages in the raw gas mixture are nitrogen (N_2), carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Some gas composition also includes presence of hydrogen (H_2), helium (He) and argon (Ar). Traces of heavier metals such arsenic, selenium and mercury are also found in some natural gas mixtures. In most of the cases water is present so the gas is assumed to be saturated with water [7]. The composition and percentage of the various components vary from reservoir to reservoir or even with in different wells in a same reservoir.

Among all the components of natural gas mixture, CO_2 and H_2S are of the concern because of the technical challenge they pose along with the Health Safety and Environmental (HSE) issues.

H_2S is a toxic gas, it causes irritation to the eyes at concentrations as low as 50 ppm. It can cause digestive upset and alerted breath when inhaled. The European Union has set the Threshold Limit Value (TLV) of 5 ppm in air for a period of 8 hours time weighted average (TWA) and 10 ppm for a short-term exposure limit (STEL).

CO_2 is a non-toxic gas, but it can cause asphyxia due to oxygen displacement. Further, from the efficiency point of view, the presence of CO_2 decreases heating capacity per volume of gas decreasing the commercial value of the gas. CO_2 is a greenhouse gas and a major contributor of the global warming due to its large emissions [3].

The presence of CO_2 and H_2S in natural gas mixture can cause technical problems by causing corrosion. Both the gases form weak but corrosive acids in the presence of water.

Corrosion is commonly found in stress areas, near welds, parts with high acid concentration (e.g. overhead in the solvent regenerator in an absorption process) or hot equipment like reboiler tubes. Further, the presence of CO_2 and H_2S can cause pipe clog problem due to the hydrate formation [7].

2.2 Natural gas sweetening

As reported earlier, nearly half of the gas reserves contain at least 2% of CO_2 and/or H_2S [6]. Some gas fields have even up to 80% of acid gas presence. Some of them were discovered a few decades ago but the technology at that time was not developed enough produce those sour reservoirs and make them economically and environmentally viable.

The need of producing more complex natural gas reservoirs and comply with stricter regulation has compelled for new engineering processes for the removal of CO_2 and H_2S. Such processes are called natural gas sweetening processes. The variating reservoir conditions and locations have boosted the development of different technologies to coup the variating requirements. However, absorption process has been the preferred one, responsible for 95% of gas sweetening in US alone [8]. Although the important advancements in adsorption and membrane technology are helping increase the use of alternative technologies. Figure 3 presents the schematic of most common gas sweetening processes

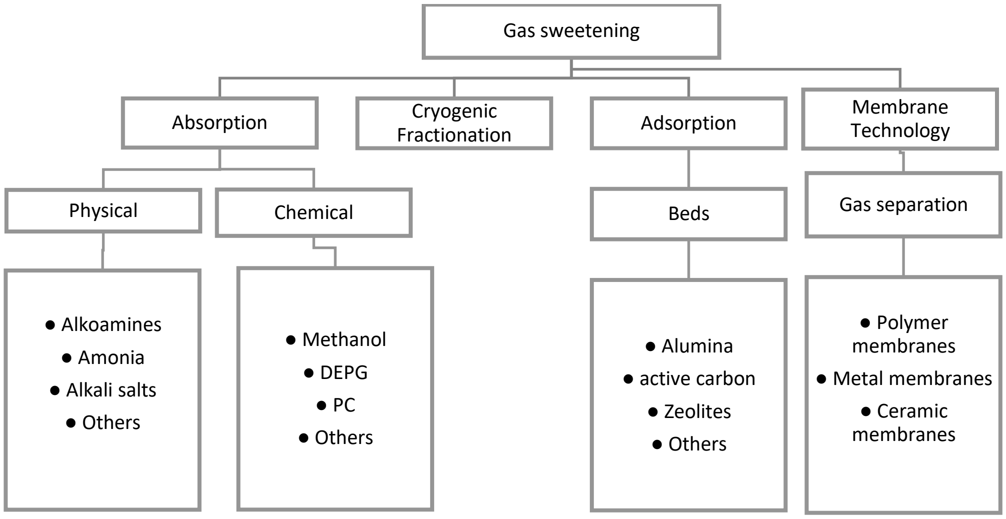


Figure 3. Gas sweetening processes [9]

Most pre-combustion CO_2 capture processes can also be applied for the post combustion CO_2 capture from power plants [10]. The drivers for the CO_2 from natural differs from those in power plants. In the power generation plants CO_2 is produced as the result of exothermic oxidation reaction of the fossil fuel, which releases the energy for the power generation. Hence, CO_2 is a waste in this scenario, energy being the main product. As CO_2 is a greenhouse gas, strong regulations are in place to ensure its controlled emission into the atmosphere to avoid environmental pollution. Therefore, CO_2 must be captured from the flue gases of the power plants. Captured CO_2 can be reused for e.g. enhanced oil recovery or sequestration [11].

The raw natural gas on the other hand contains CO_2 and H_2S as an impurity, which should be removed to avoid the equipment corrosion, hydrate formation and improve the energy capacity per volume of gas. Natural gas sweetening is only responsible for 0.4% CO_2 emission in to the atmosphere as discussed earlier this chapter. Hence, the drivers for CO_2 removal from raw natural gas are rather technical and economic reasons rather than environmental concerns.

2.2.1 Absorption

Gas absorption is the most widely used method for CO_2 removal [12]. Absorption using alkanolamines is very developed and mature technology which has been widely in use since 1931 [13, 14]. The major advantage of wide use of absorption technology is its capability to treat relatively high amount gas and reducing CO_2 to a significantly low concentration.

Absorption process involve either chemical solvents where they chemically react with the acid gases or physical solvents, where they absorb the acid gases in the liquid. Chemical solvents are preferably used because they can reduce the concentration of acid gases to the ppm level.

However, the energy required for the regeneration of the solvent to recover it is relatively high. High energy requirement for solvent regeneration becomes an economical problem when large concentration of acid gases have to be treated. Additionally, the most chemical solvents are water based, hence, the treated gas leaves the gas sweetening unit saturated with water, requiring an additional dehydration step.

Physical solvents on the other hand overcome the drawback of high regeneration energy requirement. As CO_2 is physically absorbed in this type of solvents so lower energy is required for the solvent regeneration. Some physical solvents are selective to either CO_2 or H_2S, which can be beneficial if these gases are going to be processed separately. Though physical solvents require lower energy for regeneration, but they are not capable of reducing the concentration of acid gases significantly as compared to the chemical solvents [15]. Furthermore, the physical solvents can dissolve pentene and higher hydrocarbons during the gas sweetening process.

2.2.1.1 Chemical absorption using amine solvents

Acid gas removal using amine based chemical adsorption is the widely used ad most common sweetening process [8, 16]. This process is also called amine scrubbing. Beside natural gas sweetening amine scrubbing has found its wide use in ammonia process and steam reforming process too [17]. Many alkanolamines, like primary amines monoethanolamine (MEA) and diglycolamine (DGA), secondary amines like diethanolamine (DEA) and diisopropanolamine (DIPA) and tertiary amines like methyldiethanolamine (MDEA) and triethanolamine (TEA) amines have been considered for CO_2 capture [9]. However, monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) are the most typical amines used for natural gas sweetening. Table 1 summarizes the advantages and disadvantages of typical primary secondary and tertiary amine.

Table 1. Advantage and disadvantages of the most commonly used alkanolamines

Amine	Advantages	Disadvantages
Primary Amines (MEA)	• Most reactive • High solution capacity	• High solvent losses • Formation of irreversible heat stable salts. • No selective removal of CO_2 or H_2S. • Highly corrosive
Secondary Amines (DEA)	• Negligible vapor pressure • Loading above stoichiometric ratio at high pressure.	• Numerous irreversible reaction forming corrosive • degradation products
Tertiary Amines (MDEA)	• Selective adsorption of H_2S • Negligible vapor pressure • High molecular weight • Thermally and chemically stable	• Slow reaction

MEA has a high solution capacity because of its low molecular weight. However, its application is nowadays reduced to low acid gas concentration as a result of its high vapor pressure and other operational drawbacks. DEA and secondary amines are preferable option for CO_2 capture [18]. MDEA is relatively much preferred choice for sour gas because of its higher selectivity for H_2S [19].

In the gas sweetening process the H_2S reacts with any of the amines via direct proton-transfer reaction:

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH+HS- \qquad (2.1)$$

While reacting with alkanolamines the CO_2 molecule follows relatively complex reactive path. It shows two different mechanisms depending on the type of the alkanolamine. The reaction of CO_2 with primary and secondary alkanolamines, which have one hydrogen atom bonded to the nitrogen follows the zwitterion mechanism. Zwitterion mechanism involves formation of a carbamate intermediate which then again reacts with another amine, it follows the following reaction:

$CO_2 + R_1R_2NH \leftrightarrow R_1R_2HN^+COO$ (2.2)

$R_1R_2HN^+COO^- + R_1R_2NH \leftrightarrow R_1R_2H_2N^+ + R_1R_2NCOHO^-$ (2.3)

The overall reaction is:

$CO_2 + 2\ R_1R_2NH \leftrightarrow R_1R_2H_2N^+ + R_1R_2NCOO^-$ (2.4)

As no hydrogen atom is attached to the nitrogen in tertiary alkanolamine, no carbamate is formed during the reaction. Rather, CO_2 hydrolyzes into bicarbonate and free hydrogen can protonate the amine:

$CO_2 + H2O \leftrightarrow H^+ + HCO3^-$ (2.5)
$H^+ + R_1R_2R_3N \leftrightarrow H^+ + R_1R_2R_3N_+H$ (2.6)

The overall reaction is:

$CO_2 + R_1R_2R_3N \leftrightarrow HCO3^- + R_1R_2R_3N^+H$ (2.7)

Oher side reaction might occur during the process. Examples of these sides reactions are the dissociation of bicarbonate into carbonate, or the non-reversible reaction of the amine with other intermediates. But they are usually not considered important for the absorption-desorption process.

The equilibrium of carbamate and bicarbonate in the solution depends on the amount of CO_2 dissolved in the solution. The amount of CO_2 dissolved depends on the partial pressures in the gas phase and of the vapor pressure of acid gases. The vapor pressure of acid gases depends on the temperature. The dissolution of $CO_{2\ \text{hence}}$ the reaction of CO_2 with alkanolamine is enhanced by increasing pressure and decreasing the temperature. When pressure is reduced, and temperature is increased, their actions are reversed, so CO_2 is released back to the gas phase. The typical amine natural gas sweetening process used in industry is shown in Figure 4.

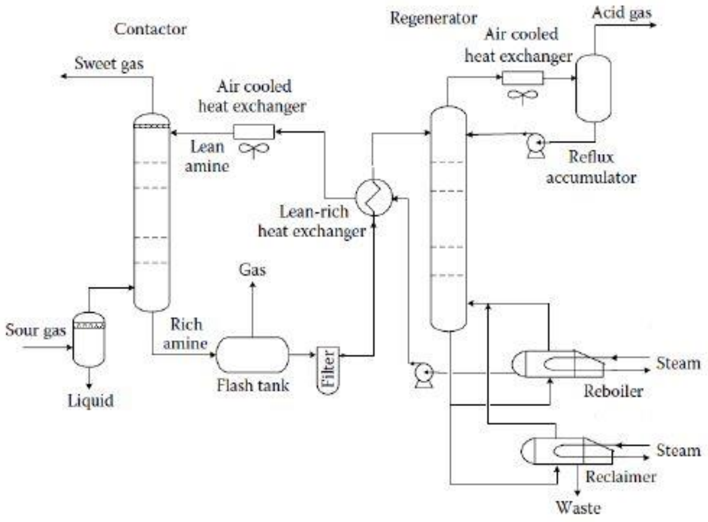


Figure 4. Flow diagram of a typical amine treating process used in industrial plants

2.2.1.2 Chemical absorption using alkali salts

Hot potassium carbonate (K_2CO_3) and its blends with alkanolamine and piperazine have been used for natural gas sweetening [20]. The process has some similarities as that of the with alkanolamines. After the CO_2 and H_2S are dissolved in the aqueous solution they react with K_2CO_3 [21]. The overall reaction is:

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2\,KHCO_3$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3$$

The main drawback of using alkali salts is their lower CO_2 absorption rate in the carbonate-bicarbonate solutions [22].

2.2.1.3 Physical absorption

Physical absorption processes use organic solvents such as dimethylether or polyethylene glycol, methanol, propylene carbonate, sulfolane, N-formylmorpholine and N-methylpyrrolidone. They physically absorb the acid gas components. The removal of CO_2 from natural gas using physical absorption processes depends on the solubility of CO_2 in the solvent. A typical CO_2 removal process using physical solvents is shown in Figure 5

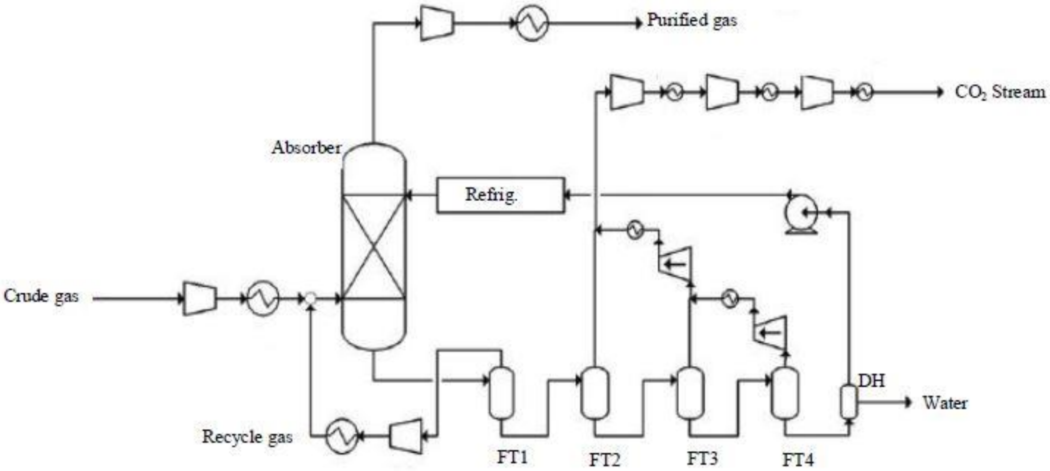


Figure 5. Flow diagram of Selexol process for CO_2 removal from natural gas [23]

The CO_2 solubility depends the partial pressure and on the temperature of the feed natural gas. Higher CO_2 partial pressure and lower temperature increases the solubility of CO_2 in the solvent. After the absorption the enriched solvent with CO_2 in regenerated by the reduction in four flash tanks. The CO_2 rich solvent leaves the absorbed and enters the first flash tank. The rich solvent leaving the absorber also contains absorbed CH_4 and other hydrocarbons. These hydrocarbons are released in the first flash tank and are recycled and introduced again in the absorber along with the natural gas. The solvent leaving the first flash tank is depressurized through the other flash tanks for the subsequent CO_2 removal and solvent regeneration. The lean solvent leaving the last flash tank enters the dehydrator (DH) for water removal, followed by the recycling of the selexol-solvent back to the absorber.

The main advantage of physical solvents is that they require less energy than the alkanolamine process. But to achieve high and reasonable CO_2 solubility with physical solvents, the partial pressure of the CO_2 has to be high. Beside this they physical solvents have high affinity for hydrocarbons can result in hydrocarbon losses during the process.

2.2.2 Adsorption

Adsorption is a process that involves attachment of the gas i.e. CO_2 to the solid surface. Several materials have been used for CO_2 capture using the adsorption process.

These materials include activated carbon alumina, metal organic framework (MOF) and zeolites [24].

The gas adsorbed is desorbed by the pressure swing adsorption (PSA), or by increasing temperature i.e. temperature swing adsorption (TSA). The main advantage of employing the adsorption process for CO_2 removal is the low energy requirement for adsorbent regeneration and the low chance of corrosion. However, the low adsorption capacity and low selectivity make their use unfeasible at the large scale [12]. Instead of the unfeasibility for high scale processes with the current technology, promising highly selective materials and optimized adsorption cycles are being developed for the CO_2 removal from natural gas [24].

2.2.3 Cryogenic Fractionation

Cryogenic fractionation separates CO_2 by condensation. The main advantage is the high pressure of the CO_2 stream, which provides a more economic process for transport and sequestration. However, the selectivity might not be so high, and other problems like the solidification of CO_2 or the formation of azeotropes with ethane and propane make this technology challenging. Cryogenic separation is more suitable for CO_2 capture from oxyfuel process, where purified oxygen is used for combustion [12].

2.2.4 Membrane Technology

Membrane technology is the emerging alternative to the akanolamine based absorption process. Membrane is the perm-selective barrier and facilitates the flow of one component and restricts the flow of other(s). The development of new polymeric and inorganic materials and transport facilitated membranes have increased the possible applications of membrane technology for natural gas sweetening. The chemical and mechanical stability and the performance deterioration over time are the main challenges faced by this technology [24]. Researchers are trying to overcome these challenges to fully exploit the potential use of membrane technology by developing new efficient materials and membranes

Some researchers have found the hybrid combination of membrane technology followed by the chemical absorption for bulk CO_2 removal as a feasible process [25].

2.3 Ionic Liquids

Ionic liquids are the salts which are in liquid state at room temperature having melting points below 100°C. Their molecular structure is preferably unsymmetrical with distributed ionic charge, so that the inter-ionic interactions are spread leading to the low melting point. The ionic liquids are highly tunable as there is a large diversity of ionic liquids. At least a million ionic liquids can be synthesized [26]. By choosing correct cation-anion pair, their molecular structure can be designed so its properties i.e. yield, selectivity, substrate solubility and product separation etc. can be tuned to meet the requirements for any certain process.

The interest in the applications of ionic liquids began in late 1990s, after Seddon [27], Freemantle [28, 29] and Huddleston *et al.* [30] described them as novel solvents for green technology between 1997 and 1998. However, the first work about ionic liquids in literatures dates back to 1888, when S. Gabriel and J. Weiner reported the melting point of ethanolammonium nitrate between 52 - 55°C [31]. But the work of Walder in 1914, who synthesized the low melting ethylammonium nitrate ionic liquid with melting point around 13 - 14°C, is usually accepted as the first work on ionic liquids in literature [32]. A more extended overview on the development of ionic liquid technology including their -successful industrial application is given by Plechkova and Seddon [33]. Until 1997, only 432 articles were published, while the total number published by the end of 2014 rose up to more than 46700 according to Scopus, and almost 10000 patents on the use of ionic liquids have been filed. The reason of high attention towards ionic liquids is their remarkable properties such as nearly negligible volatility [27, 29], high thermal stability [34], chemical stability [26] and the tunable nature. Ionic liquids have been employed in various fields in chemistry, electrochemistry and in mechanical, chemical and biochemical engineering [33, 35, 36]. One of the most successful uses of ionic liquids is alternative solvents as replacements for volatile organic compounds. In this respect, intensive work has been made in synthesis and in separation technology [37-39].

2.3.1 CO_2 solubility in ionic liquids

The solubility of CO_2 in ionic liquids has been widely studied for many applications especially for the carbon capture. The interest in this area started after

Blanchard *et al.* reported high CO_2 solubility in imidazolium-based ionic liquids [37]. The solubility of CO_2 in ionic liquids has been extensively studied in imidazolium-based ionic liquids pairing with different anions, including [PF6], [BF4], [Tf2N-] and others [38-41]. Besides, other ionic liquids based on cations like pyridinium, pyrrolidinium, phosphonium and ammonium- based have also been investigated [42-44].

Table 2. List of anions and their chemical structure

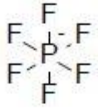
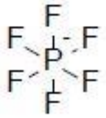
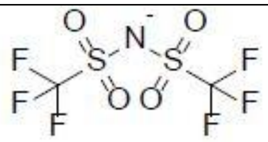
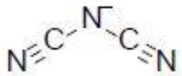
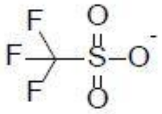
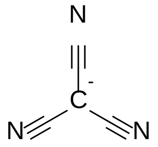
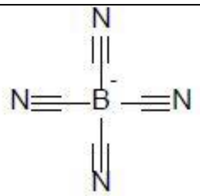
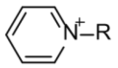
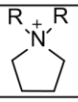
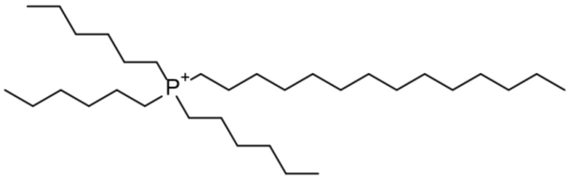
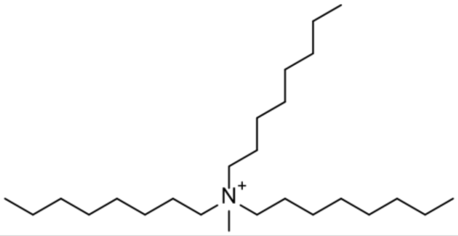
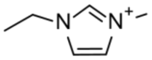
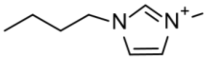
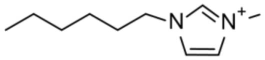
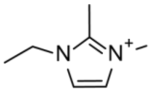
Anion	Name	Structure
$[PF_6^-]$	Hexafluorophosphate	
$[BF_4^-]$	Tetrafluoroborate	
$[Tf_2N^-]$	bis(trifluoromethylsulfonyl)amide	
[dca]	dicyanamide	
[TfO]	trifluoromethanesulfonate	
[tcm]	tricyanomethanide	
[TCB]	tetracyanoborate	

Table 3. List of cations and their chemical structure

Cation	Name	Structure
[$C_n$pyr]	pyridinium	
[C_nPyrr]	pyrrolidinium	
[$P_{6,6,6,14}$]	trihexyltetradecylphosphonium	
[$N_{8,8,8,1}$]	trioctylmethylammonium	
[emim]	1-ethyl-3-methylimidazolium	
[bmim]	1-butyl-3-methylimidazolium	
[hmim]	1-hexyl-3-methylimidazolium	
[emmim]	1-ethyl-2,3-dimethylimidazolium	

It was reported that increasing the length of alkyl chain of cation increase the solubility of CO_2 [45]. Though the improvement is not significant [46]. Attempts to increase the CO_2 in ionic liquids by several researchers involved the addition of CO_2-philic group. [47-49]. For example, for the liquid behavior it can be observed in literature that the addition and selection of ions effects the overll properties. The presence of a certain specie in anion or cation can hugely impact the properties of IL. It was also reported that the presence of fluorine can highly enhance the performance. Reseachers observed the presence of fluorine increase capturing capabilities of the IL [47-49].

The study of the effect of anion and cation on the solubility of CO_2 in ionic liquids concluded that solubility of CO_2 in ionic liquid was more influenced by the anion than the cation [43, 50]. The solubility of CO_2 in ionic liquids having anions with fluorinated groups as compared to the ionic liquids with anions having sulfate or ether groups [48]. The solubility of ionic liquids with 1-buty-3-methylimidazolium (Bmim) cation increased with the following order $[NO_3] < [dca] < [BF4] < [PF_6] < [Tf2N]$ [50].

The work of Kazarian *et al.* [51] suggested that the interaction between the CO_2 molecule and ionic liquid are Lewis acid-base type. Where the CO_2 acts as the acid and the anion serves as the Lewis base. However, in few cases the experimental data varies from this hypothesis for example $[BF_4]$ anion is stronger base than $[PF_6]$ but the solubility of CO_2 in $[Hmim][PF_6]$ is greater as compared to the $[Hmim][BF_4]$ [52]. Therefore, the free volume has been suggested as the dominant factor for CO_2 solubility together with other entropic factors [53, 54].

From the extensive studies conducted by various researchers it was demonstrated that ionic liquids have high absorption capacity for CO_2. Studies have also suggested that CH_4 has low solubility in ionic liquids [55-57]. Therefore, ionic liquids could be attractive alternative solvents for the natural gas sweetening processes.

2.4 Aim of the study

The aim of this study is to provide better insight in to the CO_2 capture using ionic liquids for natural gas sweetening applications. Testing of CO_2 solubility in 1-butyl-3-methyl-imidazolium tetrafluoroborate $[Bmim][BF_4]$ ionic liquid on lab scale. This study will also involve task specific extensive experimentation for evaluation of the potent solvent system for CO_2 capture with focus on natural gas sweetening as main application, that may involve the mixtures of ionic liquid $[Bmim[BF_4]$ with different solvents including acetone and ethanol etc. Preparation and testing of hybrid solvents by mixing ionic liquid $[Bmim][BF_4]$ with amine for CO_2 solubility analysis. Further this study will focus on modeling the CO_2 solubility in ionic liquid $[Bmim][BF_4]$ and its mixtures using Aspen PLUS®. Process simulations will be performed for evaluation of the proposed solvent system for industrial application. Comparative analysis of the proposed solvent system with conventional amine process for performance evaluation. Economic analysis to check the economic feasibility of the proposed solvents involving ionic liquid. The purpose of lab-based experimentation and techno-economic evaluation is to check the applicability and feasibility of ionic liquids for industrial scale natural gas sweetening process as the replacement for conventional alkanolamines.

Chapter-3

Materials and Methodology

This chapter includes details about the materials used for this study. Beside the materials, the experimental setup, experimentation methodology and approach for the process simulation is also discussed in this chapter.

3.1 Materials

The details of the ionic liquid and other solvents used for the experimental study in this work are given below in Table 4

Table 4. Materials used for experimentation

Material	Purity	Supplier
1-butyl-3-methylimidazolium tetrafluoroborate	>98%	Sigma Aldrich
Diethanolamine	>98%	Daejung Korea
Acetone	99%	Sigma Aldrich
Ethanol	99%	Lab Grade

3.2 Experimentation methodology

The experiments were conducted in controlled lab environment. The details for the experimentation methodology including the experimental setup, experimentation procedure and measurement of the CO_2 solubility are discussed in detail in section below.

3.2.1 Experimental setup: Isochoric Equilibrium Cell

The apparatus used for the CO_2 solubility measurements in this study has already been used by various researchers [58-60]. The apparatus used is called isochoric equilibrium cell or isochoric saturation technique. In this technique a known about of gaseous solute is put in contact with a precisely known amount of the solvent at a constant temperature inside an equilibrium cell of accurately known volume. The CO_2 solubility was measured from the pressure drop in the system, as ionic liquids have negligible vapor pressure, therefore, the pressure inside the system was contributed by the pressure of CO_2. The experimental setup consists of a stainless-steel equilibrium cell, a gas reservoir and constant temperature water bath. The maximum operating pressure limit for this experimental setup was known to be around 8 bar, and the experiments were performed at a maximum pressure of 6 bar for safety purposes. The dimensions of the equilibrium cell are given in 5 and schematic diagram of the experimental set up is shown in Figure 6, where (a) corresponds to the equilibrium cell while (b) to the gas reservoir.

Table 5. Dimensions of the equilibrium cell

Parameter	Value	Unit
Inner diameter of the reactor	42	mm
Height of the reactor	40	mm

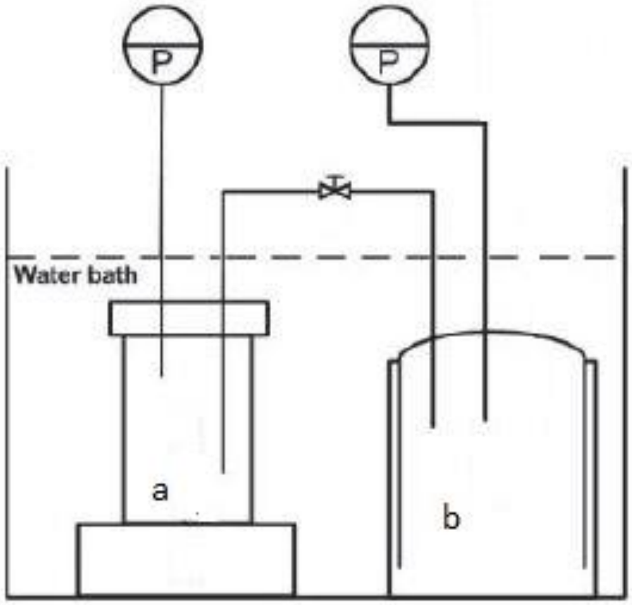


Figure 6. Isochoric Equilibrium Cell. (a) represents the equilibrium, (b) represents the gas reservoir

3.2.2 Gas solubility measurement

For the CO_2 solubility measurement, the isochoric saturation technique was used. During the solubility measurement experiments, the volume of the system was held constant so was the temperature. The temperature was maintained at 30°C using constant temperature water bath. And the pressure difference was recorded during the gas absorption into the liquid solvent. Ionic liquids have negligible vapor pressure, ensuring that the pressure exerted inside the equilibrium cell is solely due to the CO_2. First a known amount of the solvent was introduced in to the equilibrium cell at the constant temperature, then the CO_2 was introduced at a constant pressure into the equilibrium cell from the gas reservoir, whose volume is known. An initial reading of the system pressure is noted when the gas is introduced in the system, after that the gas starts dissolving in to the solvent, resulting in the system pressure drop. After a certain amount of time the system pressure remains stable and equilibrium is attained and no further gas in absorbed by the solvent. After the equilibrium is attained at a given operating pressure, the final pressure reading is noted. The process is repeated again by increasing the pressure, taking the initial pressure reading when gas is introduced and the final pressure reading when equilibrium is attained, and no further pressure drop is observed. The number of moles of CO_2 dissolved are calculated by using PVT relation. The number of moles of CO_2 dissolved in to the solvent are calculated by following equation,

$$nCO_2 = \frac{(P^0_{CO_2} - Pvapor)VG}{Z_1RT} - \frac{(P^e_{CO_2} - Pvapor)VG}{Z_2RT} \tag{3.1}$$

Where, $P^0_{CO_2}$ is the initial pressure, $P^e_{CO_2}$ is the equilibrium pressure, $Pvapor$ is vapor pressure, VG is the volume of gas, Z_1 and Z_2 are the compressibility factors, R is the universal gas constant, T is the temperature and nCO_2 is the number of moles of CO_2 absorbed.

From the CO_2 solubility, CO_2 loading in the solvent can be calculated using following relation

$$xCO_2 = \frac{nCO_2}{n(solvent)} \tag{3.2}$$

Where nCO_2 moles of CO_2 and $n(solvent)$ is the number of moles of the solvent.

3.2.3 Calibration of the experimental setup

Before starting the experimentation, solubility measurement apparatus was calibrated to check the reliability of the results. The calibration experiments were performed by testing in CO_2 solubility in pure ionic liquid [Bmim][BF_4] 30°C and pressures up to 5 bar using the procedure explained above in this chapter. All experiments were repeated at least 3 times. The CO_2 solubility measured by the isochoric saturation method were in good agreement with the literature. Hence, it was assumed that the equipment is reliable for the main experimentation. The details of the calibration experiments are given in Table 6

Table 6. Comparison of the measured CO_2 solubility with the literature

Pressure (bar)	Measured CO_2 Loading	Literature	Reference
1	0.0159	0.0162	[61]
1	0.0161	0.0160	[61]
1	0.0161	0.01591	[61]
6	0.078	0.077	[62]

3.3 Process modeling and simulation

Modeling and simulation was performed for performance evaluation of the conventional DEA based process and the ionic liquid based process. Further another reason was to model the CO_2 solubility in ionic liquid and its solvent mixtures. Simulations were carried out using Aspen PLUS® simulator (version 8.4). The simulation study gave an insight in to the process conditions, to determine the efficiency and applicability of the said process. For performance evaluation study discussed in detail in Chapter 4, first the base model with conventional DEA as a case study was simulated and compared with the reference model from literature. Then the process with DEA+[Bmim][BF_4] was modeled and compared. The details for the parameters used for simulation of DEA and ionic liquid [Bmim][BF_4] are given in subsequent section.

3.3.1 Modeling of diethanolamine (DEA)

The properties of the species involved in the testing were modelled too. The nRTL method was employed for this purpose. The property parameters of IL were entered. DEA existed as a registered component in the simulation software.. This property package has been commonly adopted by many researchers for the simulation of the DEA based scrubbing process. This package is also most recommended and reliable in terms of the modelling and simulation of DEA. Besides the prior performance of the IL when modeled was promising as well. The reaction chemistry for the DEA based sweetening process is comprised of both the equilibrium as well as kinetic reactions [63].

The equilibrium reactions are as defined as:

$$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+ \tag{R1}$$

$$2H_2O \leftrightarrow HCO^+ + OH^- \tag{R2}$$

$$HCO_3^- + H_2O \leftrightarrow H3o^+ + CO_3^{-2} \tag{R3}$$

the kinetic reactions are defined as:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \tag{R4}$$

$$HCO_3^- \leftrightarrow CO_2 + OH^- \tag{R5}$$

$$DEA + CO_2 + H_2O \leftrightarrow DEACOO^- + H_3O^+ \tag{R6}$$

$$DEACOO^- + H_3O+ \leftrightarrow DEA + CO_2 + H_2O \tag{R7}$$

The equilibrium constant K_{eq} for equilibrium reaction from R1 to R3 is estimated as follows, where A, B, C and D are reaction parameters

$$\ln(k_{eq}) = A + \frac{B}{T} + C.ln(T) + D.T \tag{3.3}$$

The reaction rate for the kinetic reactions R4 to R7 is determined using the power law expression as follows:

$$r = kexp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i$$

(3.4)

The values for parameters in Eq. (3.3) i.e. (A, B, C and D) are given in Table 7, while the parameters for the equation (3.4) i.e. (*k* and *E*) are given in Table 8.

Table 7. Parameters for the equilibrium reactions [63]

Reaction	*A*	*B*	*C*	*D*
R1	-13.3373	-4218.71	0	9.871E+03
R2	132.899	-13445.9	-22.4773	0
R3	216.	-12431.7	-35.4819	0

Table 8. Parameters for the kinetic reactions [63]

Reaction	*K*	*E* (J/kmol)
R4	4.32E+13	5.547E+07
R5	2.38E+17	1.233E+08
R6	6.48E+06	2.123E+07
R7	1.43E+17	4.813E+07

3.3.2 Modeling of ionic liquid [Bmim][BF_4]

The ionic liquids, though having a lot of research focus and attention in multiple disciples for various application, are not available in the Aspen Plus® data bank, because the thermodynamic data available about the ionic liquids is very scarce. The ionic liquid was modeled using electrolyte nonrandom two-liquid model. Ionic liquid was created as a new user defined component, whose properties and interaction with other components was defined.

Properties are very important for modeling of any specie[64]. These properties here are entered in correlation. Those corellations have already been studied by many authors. Who have suggested to use the aforementioned method for property definition. They are also essential for a process simulation. The scalar properties for the [Bmim][BF_4] ionic liquid were obtained from literature, and are given in Table 9

Table 9. Scalar properties of the ionic liquid [Bmim][BF$_4$]

MW	T_b	T_c	P_c	V_c	ω	Z_c	$\Delta H_f^{\ominus}$	$\Delta H_c^{\ominus}$	T_m	*Ref*
226.02	632.3	886.1	27.4	655.4	0.5276	0.2434	-1221.8	-5335	192.1	[65]

Beside the critical properties, the temperature dependent properties such as heat capacity, density and viscosity were calculated from the equations given in Table 10. The parameters for the temperatures dependent properties were obtained from the literature.

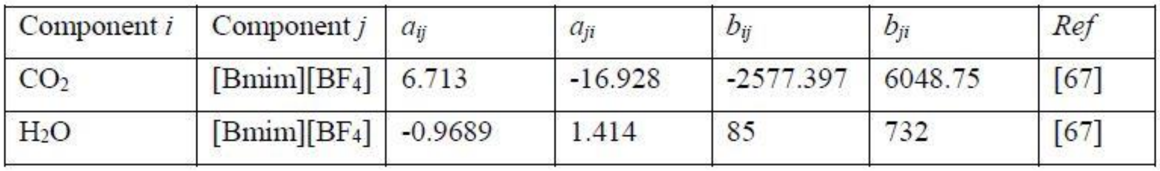
Table 10. Equations for the Temperature Dependent properties

Property	Specific equation	Notation description	Ref
Vapor pressure	$\ln P_i^s = \frac{C_{2_I}}{T + C_{3_I}}$	P_i^s is the vapor pressure in Pa, T is in k, $C_{1_I} - C_{3_I}$ are equation coefficients	[65]
Heat capacity	$C_{Pi} = C'_{1i} + C'_{2i}T + C'_{3i}T^2$	C_{Pi} is molar heat capacity in J.kmol^{-1}.k^{-1} and C'_{1i}-C'_{3i} are equation coefficients	[66]
Density	$\rho_i = \frac{M_i P_{ci}}{RT_{Ci}[Z_i^{*,RA}(1 + d_i(1 - T_r)]^{[1+(1-T_r)^{2/7}]}}$	ρ_i is density in g.cm^{-3}, T_{Ci} and P_{Ci} are critical temperature and pressure, $Z_i^{*,RA}$ and d_i are equation coefficients	[67]
Viscosity	$ln\eta_i = A_i + \frac{B_i}{T} + C_i lnT$	η_i is the liquid viscosity in mPa.s and A_i, B_i, C_i are equation coefficients	[65]

Surface tension	$\sigma_i = C''_{1i}(1-\frac{T}{T_{Ci}})^{(C''_{2i}+C''_{2i}T_{ri}+C''_{4i}T_{ri}^2+C''_{5i}T_{ri}^3)}$	σ_i is the surface tension in mN.m^{-1} and $C''_{1i} - C''_{5i}$ are th equation coefficients	[66]
Thermal conductivity	$\lambda_i = C''_{1i} + C''_{2i}T + C''_{3i}T^2$	λ_i is the liquid thermal conductivity in W.m^{-1}.K^{-1} and C''_{1i}- C''_{3i} are equation coefficients	[66]

Ionic liquid was modeled using the electrolyte non-random two-liquid model (NRTL). The NRTL binary interaction parameters for the ionic liquid [Bmim][BF$_4$] with CO$_2$ and H$_2$O, used in the NRTL model were also obtained from the literature and is given in Table 11

Table 11. NRTL binary parameters of [Bmim][BF$_4$] with CO$_2$ and H$_2$O



Component *i*	Component *j*	a_{ij}	a_{ji}	b_{ij}	b_{ji}	*Ref*
CO$_2$	[Bmim][BF$_4$]	6.713	-16.928	-2577.397	6048.75	[67]
H$_2$O	[Bmim][BF$_4$]	-0.9689	1.414	85	732	[67]

Chapter-4

Results and Discussions

This chapter includes the experimental results for CO_2 solubility in the ionic liquid, ethanol-ionic liquid solvent mixtures, acetone-ionic liquid solvent mixture and DEA-ionic liquid solvent mixtures. The experiments were conducted at constant temperature of 303 K and pressures ranging from 1 to 6 bar. The isochoric equilibrium cell was used for the solubility measurement, solubility was calculated from the CO_2 pressure drop in the system. The temperature was maintained by immersing the system in the isothermal water bath.

After the measured CO_2 solubility through experimentation, the modeling of ionic liquid and modified solvent mixtures using ASPEN PLUS is discussed. Measured solubility is compared with solubility data obtained by modeling and simulation. The ionic liquid and modified solvent systems were simulated at the similar parameters temperature and pressure i.e. 303 k and 1-6 bar. The data was verified for further case study analysis and performance evaluation for the potential use of modified ionic liquid solvent system for the natural gas sweetening process.

Further, the case study was carried out for performance evaluation of the conventional alkanolamine based industrial natural gas sweetening process and modified ionic liquid process. The base model was developed using ASPEN PLUS software and verified with the literature. Ionic liquid modified process was modeled using the same software. The results were compared and analyzed for the performance evaluation of the conventional process and modified process. The evaluation was carried out in terms of the natural gas purity, purity of the acid gas leaving the stripper section and the regeneration energy required to carry out the solvent regeneration process in the stripper section etc.

Furthermore, this chapter includes the economic analysis for the modified ionic liquid process for the natural gas sweetening on the industrial scale. The economic analysis provides a broader view for the applicability of the proposed solvent system on the industrial scale.

4.1 Measured solubility of CO_2

The measured solubility of CO_2 was measured and calculated using isochoric equilibrium cell. The equipment was calibrated by measuring the solubility of CO_2 in pure ionic liquid at varying pressures. The solubility results obtained were then compared to the literature and were observed to be in good agreement. The experiments were performed at constant temperature of 303 K. After the equipment was calibrated the CO_2 solubility was measured and calculated for different solvents and their prospective mixtures with the ionic liquid [Bmim][BF_4].

4.1.1 Solubility of CO_2 in pure ionic liquid [Bmim][BF_4]

The solubility of CO_2 in ionic liquid [Bmim][BF_4] was determined by measuring the pressure drop in the isochoric equilibrium cell at constant temperature of 303 K. A known amount of [Bmim][BF_4] was first introduced in the equilibrium cell. Then a known amount of the CO_2 was introduced in the cell until the system reached 1 bar system pressure. The ionic liquids have negligible vapor pressure, so it was considered that the total pressure in the equilibrium cell is due to the pressure of CO_2. After the equilibrium was achieved, the pressure drop was measured as difference between initial system pressure and final system pressure. The pressure drop in the system occurred because a certain amount of CO_2 has been absorbed in the liquid phase of [Bmim][BF_4]. when the CO_2 was introduced and after the system achieved equilibrium. The CO_2 solubility was then calculated. Once the system was stable, the pressure was increased to 2 bar. After the system attained equilibrium certain pressure drop was observed in the system and the CO_2 was measured. Similar procedure was repeated for pressure up to 6 bar and CO_2 solubility was measured and plotted against the increasing pressure. The CO_2 was calculated as mol CO_2/mol ionic liquid. Figure 7 illustrates the loading of CO_2 in [Bmim][BF_4] a function of increasing pressure.

It can be observed in the Figure 7 that the CO_2 loading increased as the pressure was increased showing a linear relation between the solubility and CO_2 pressure in the system. Ionic liquid [Bmim][BF_4] shows favorable CO_2 solubility with linear increase with respect to the increasing pressure. This favor can be associated with the presence of anion [BF_4]. This has already been suggested by various researchers through experimental and simulation data [35, 41].

4.1.2 Solubility of CO_2 in pure Ethanol

The solubility of CO_2 was measured in pure ethanol to check its potential use as mixture component with [Bmim][BF_4] for CO_2 capture. The CO_2 solubility was measured at constant 303 K temperature and pressure ranging from 1 bar to 6 bar. The results are plotted as CO_2 loading against the increasing pressure. The trend can be observed in Figure 7. The solubility of CO_2 increases linearly with increasing pressure in pure ethanol. The CO_2 loading in pure ethanol and pure [Bmim][BF_4] was compared to examine the difference. Experimental results showed that ethanol has CO_2 loading much higher than that of the pure ionic liquid. Being a cheaper and easily available solvent ethanol can be mixed with ionic liquid to check the mixture performance and examine the potential of the said mixture for CO_2 and as an alternative sweetening solvent.

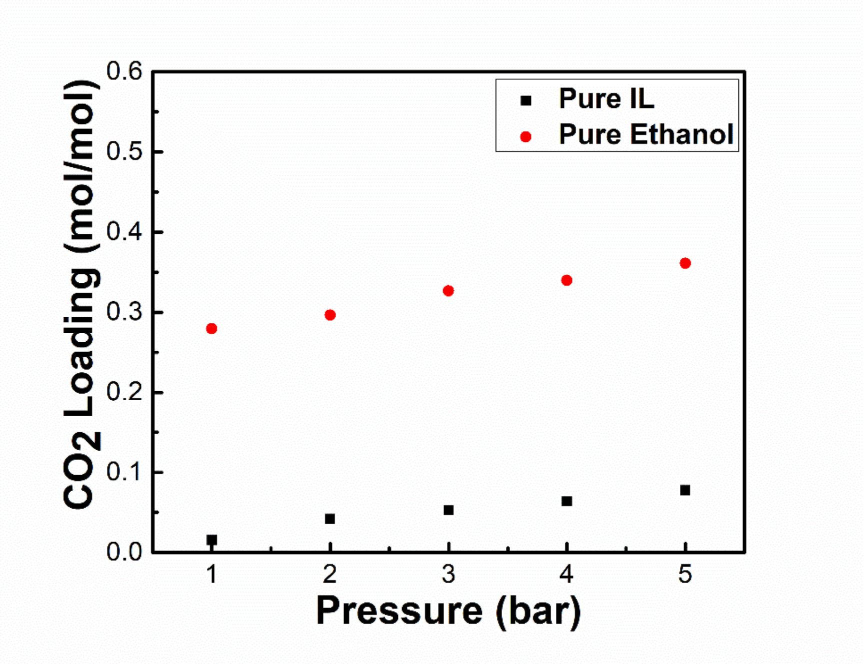


Figure 7. Measured CO_2 loading in pure [Bmim][BF4] and pure ethanol

4.1.3 Solubility of CO_2 in ethanol and [Bmim][BF_4] mixtures

Ionic liquid has relatively low CO_2 solubility, to use it on industrial scale for CO_2 capture its effect was studied by preparing the mixture at different [Bmim][BF_4] ionic liquid with ethanol, which is relatively much cheaper and has good CO_2 solubility. To study the effect of presence of ionic liquid on CO_2 solubility in ethanol and vise versa, two different solvent mixtures were prepared with 30% ionic liquid and 50% ionic liquid. Similar experimental procedure was followed as described before in this chapter. Experiments were carried out at the constant 303 K temperature and pressures ranging from 1 bar to 6 bar. The solubility results of the said mixtures are then compared with solubility of CO_2 in pure ionic liquid and pure ethanol to check the effect and potential of mixture as CO_2 separation media. The comparison is given in figure 8.

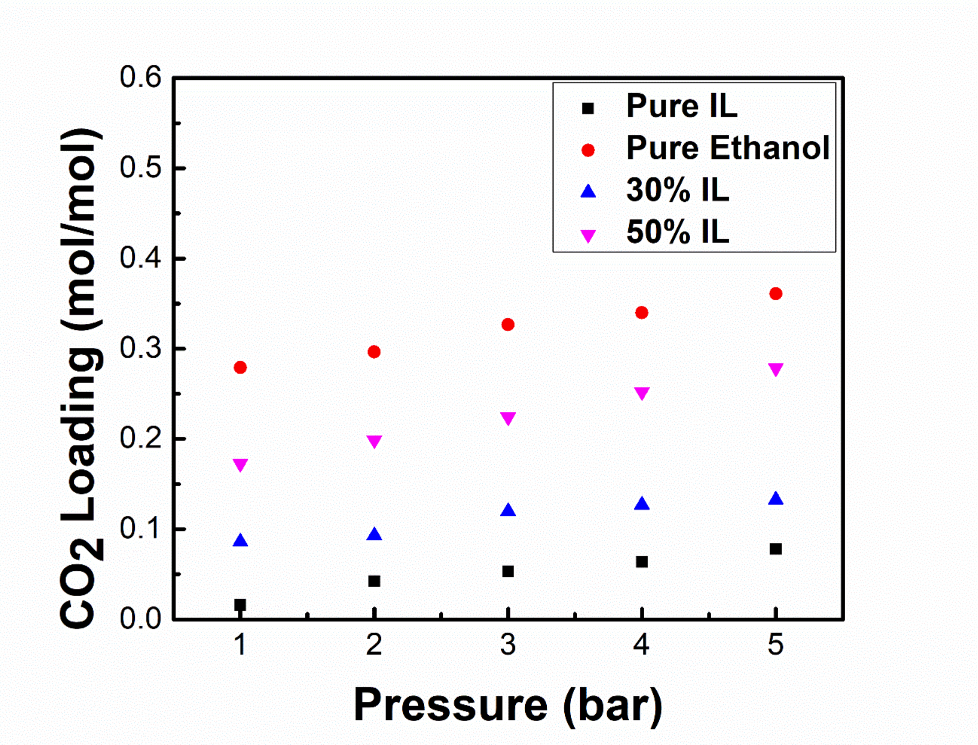


Figure 8. Comparison of measured CO_2 loading in solvent mixtures of [Bmim][BF_4] and ethanol with different compositions

After comparison of the CO_2 loading in ionic liquid and ethanol mixtures with CO_2 in pure ethanol and pure [Bmim][BF_4] it was observed that ethanol had relatively higher CO_2 loading as compared to the pure [Bmim][BF_4] as similar experimental conditions. With addition of the ionic liquid in ethanol the CO_2 solubility relatively dropped. In mixture of ethanol and 30% [Bmim][BF_4] the solubility of CO_2 sufficiently dropped as compared to the pure ethanol. When [Bmim][BF_4] concentration was increased to 50%, an increase in CO_2 solubility was observed as compared to the mixture with 30% [Bmim][BF_4] concentration. Still the presence of ionic liquid with ethanol did not affect the CO_2 solubility in positive direction. The decrease in CO_2 solubility in the mixture of [Bmim][BF_4] and ethanol makes this solvent system unviable for the practical use.

4.1.4 Solubility of CO_2 in pure acetone

The solubility of CO_2 in pure acetone was studied following the similar experimental procedure. The experiments were performed at constant 303 K and pressure ranging from 1 bar to 6 bar. The CO_2 solubility in acetone was studied to check and compare the viability and performance of [Bmim][BF_4] and acetone mixture. The solubility of CO_2 in pure acetone is plotted as CO_2 mole loading versus pressure. The trend can be seen in Figure 9.

The experimental results show increase in the CO_2 solubility with increasing temperature. The trend observed was similar as that of the other solvents in terms of the increase in CO_2 solubility with increasing temperatures. Further the CO_2 loading in pure acetone and pure [Bmim][BF] was compared to check the difference. The pure acetone has twice the CO_2 loading as compared to the pure ionic liquid. The effect on the CO_2 loading after they are mixed is studied too to check the viability of the solvent system for use in practical CO_2 capture applications.

4.1.5 Solubility of CO_2 in acetone and [Bmim][BF_4] mixtures

To study the CO_2 solubility performance in the mixtures of [Bmim][BF_4] and acetone, four mixtures were prepared with varying [Bmim][BF_4] concentrations. The mixtures were prepared with [Bmim][BF_4] concentrations of 10%, 20%, 50% and 75%. The experiments were performed separately for each composition. Similar experimental approach was followed as described before at constant 303 K temperature and pressure varying from 1 bar to 6 bar. The comparative solubility results in terms of CO_2 loading are plotted against pressure in Figure 10.

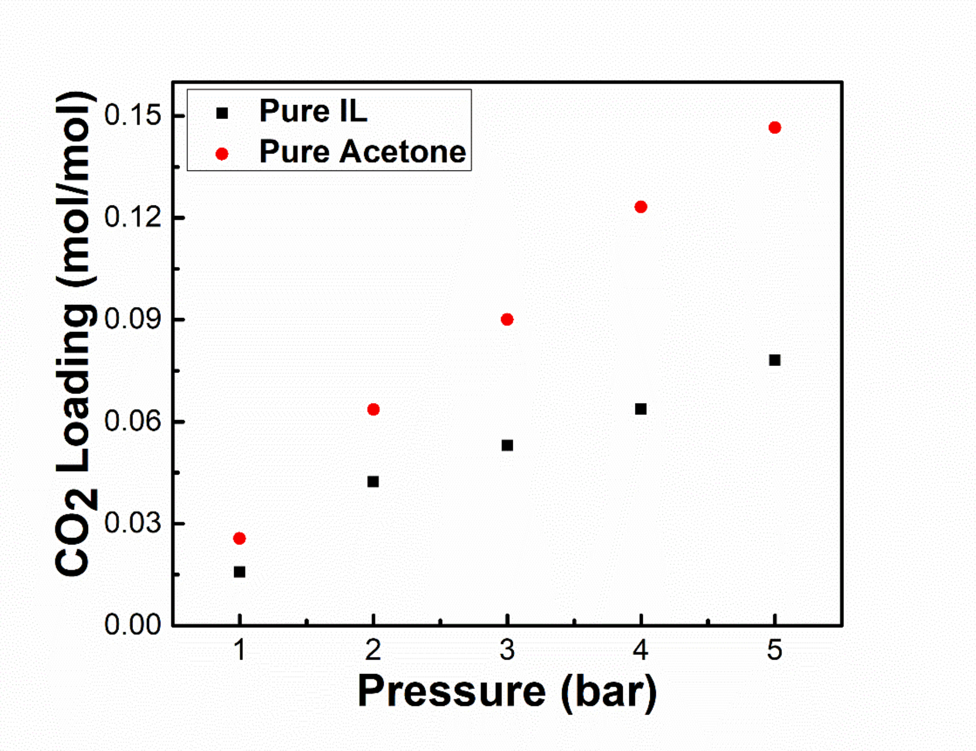


Figure 9. Measured CO_2 loading in pure [Bmim][BF4] and pure acetone

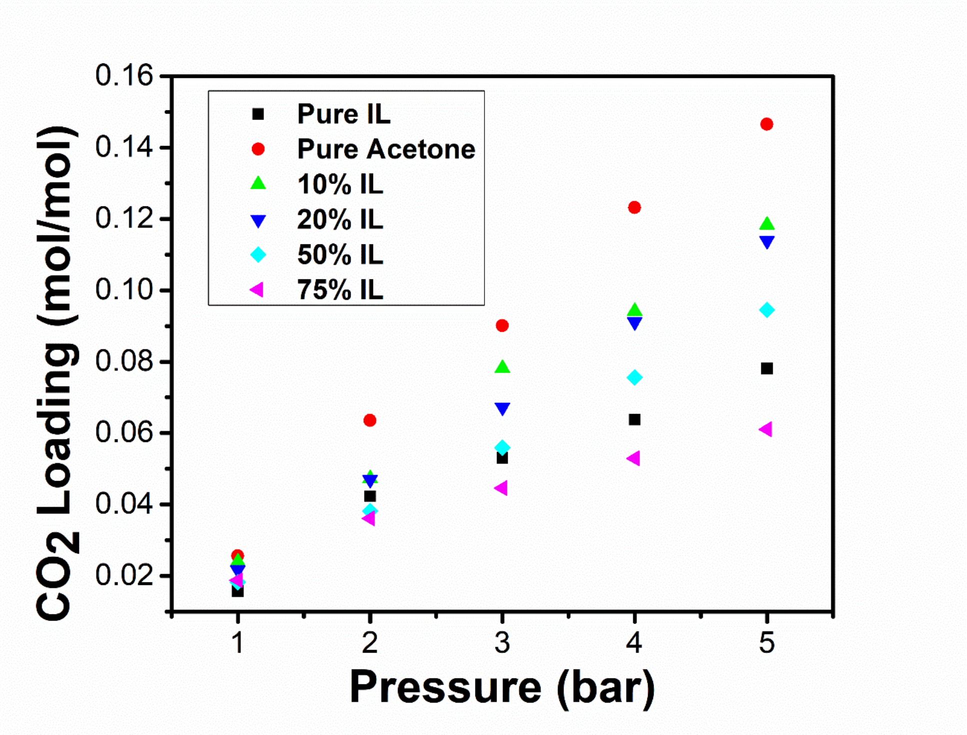


Figure 10. Measured CO_2 loading in mixtures of [Bmim][BF_4] and acetone at different compositions

As discussed before, pure acetone has CO_2 loading much higher than the pure [Bmim][BF_4]. When mixture with 10% [Bmim][BF_4] was tested, it showed a slight decrease in CO_2 loading as compared to the pure acetone. When the mixture with 20% [Bmim][BF_4] was tested, the CO_2 loading further decreased. The mixture of acetone and [Bmim][BF_4] was showing no increase or improvement in the CO_2 loading. The CO_2 loading in mixture with 50% [Bmim][BF_4] concentration further decreased. In this mixture the loading was close to that of the pure ionic liquid up to 3 bar pressure, when pressure was further increase slight increase was in CO_2 loading was observed but overall loading was still considerably lower than the pure acetone. When mixture with 75% [Bmim][BF_4] was tested, the CO_2 loading less than the pure ionic liquid was observed. The experiments showed that when ionic liquid is mixed with acetone, the CO_2 loading was decreasing with increasing ionic liquid concentration, up to the point that it even fell below the CO_2 loading of pure ionic liquid. As acetone has much higher CO_2 loading than the [Bmim][BF_4], in the solvent mixture when concentration of [Bmim][BF_4] was increased, the CO_2 loading decreased. The reduction in CO_2 loading can be associated with the decrease in acetone concentration in the. Similar behavior has been reported by Zhigang *et al.* [62]. From the experimental results it was concluded that the mixture of acetone with [Bmim][BF_4] cannot be used for the CO_2 capture, as the mixture was showing no positive or promising results.

4.1.6 Solubility of CO_2 in diethanolamine [DEA]

Alkanolamines have been widely used since1931 for CO_2 capture. They have high CO_2 loading and are relatively cheaper than the ionic liquids. However, they require high regeneration energy, are unfavorably degradable and show higher solvent loss during the natural gas sweetening process. On the other hand, the excellent properties of ionic liquids such as thermally stability, nonvolatility and tunable chemistry which are perceived to be helpful in reducing the regeneration energy. It was reported by several researchers that the mixtures of ionic liquid and amine considerably positive response in for CO_2 capture. To check the effect and performance of ionic liquid and alkanolamine mixture in terms of the CO_2 loading, the experiments were performed.

The experiments were first performed using 30 wt% DEA aqueous solution at constant 303 K temperature and pressure ranging from 1 bar to 6 bar. The 30 wt % DEA aqueous was used because it is the concentration widely used for CO_2 capture on industrial scale. The experiments were performed in isochoric equilibrium cell following the procedure described before in this chapter. The results are plotted as CO_2 loading against the pressure in Figure 11.

The CO_2 is absorbed in DEA following a chemical reaction explained in chapter 2. It follows the zwitterion mechanism, which if the most widely accepted model for CO_2 absorption in the alkanolamines. The CO_2 loading in the 30 wt% DEA aqueous solution increased with increasing CO_2 pressure. Further the CO_2 loading in 30 wt% DEA solution and pure ionic liquid were compared to check the difference. It can be observed in Figure 15 that the DEA aqueous solution has considerably higher CO_2 loading as compared to the pure [Bmim][BF_4].

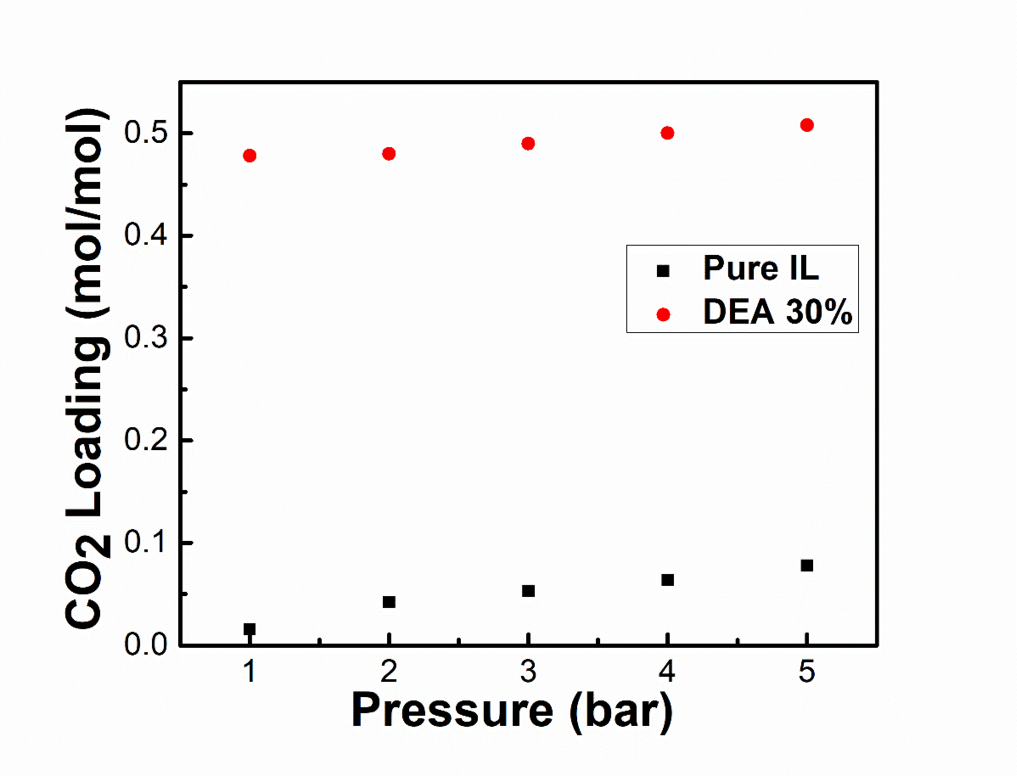


Figure 11. Measured CO_2 loading in 30 wt% DEA and pure [Bmim][BF4]

4.1.7 Solubility of CO_2 in DEA and [Bmim][BF_4] mixtures

To check the performance of ionic liquid and DEA solutions in terms of the CO_2 loading, different aqueous solutions with varying [Bmim][BF_4] concentrations were prepared and tested. The solvents comprised of 70% water and 30% [Bmim][BF_4] +DEA. The solvent was overall 30wt% with varying concentrations of ionic liquid and DEA. The first solvent was prepared with 20% [Bmim][BF_4] and tested using the isochoric equilibrium cell at constant 303 K temperature and pressure ranging from 1 bar to 6 bar. The subsequent solvents were prepared with increasing concentration of the [Bmim][BF_4] to 30%, 40%, 50%, 60% and 70%. Each solvent was tested experimented and analyzed separately at the similar experimental conditions and following the similar procedure to examine the effect of increasing [Bmim][BF_4] concentration on the CO_2 loading. This scheme was also followed to check the optimum solvent composition for effective CO_2 capture. The results of the CO_2 solubility analysis in varying [Bmim][BF_4] +DEA aqueous mixture are given in Figure 12.

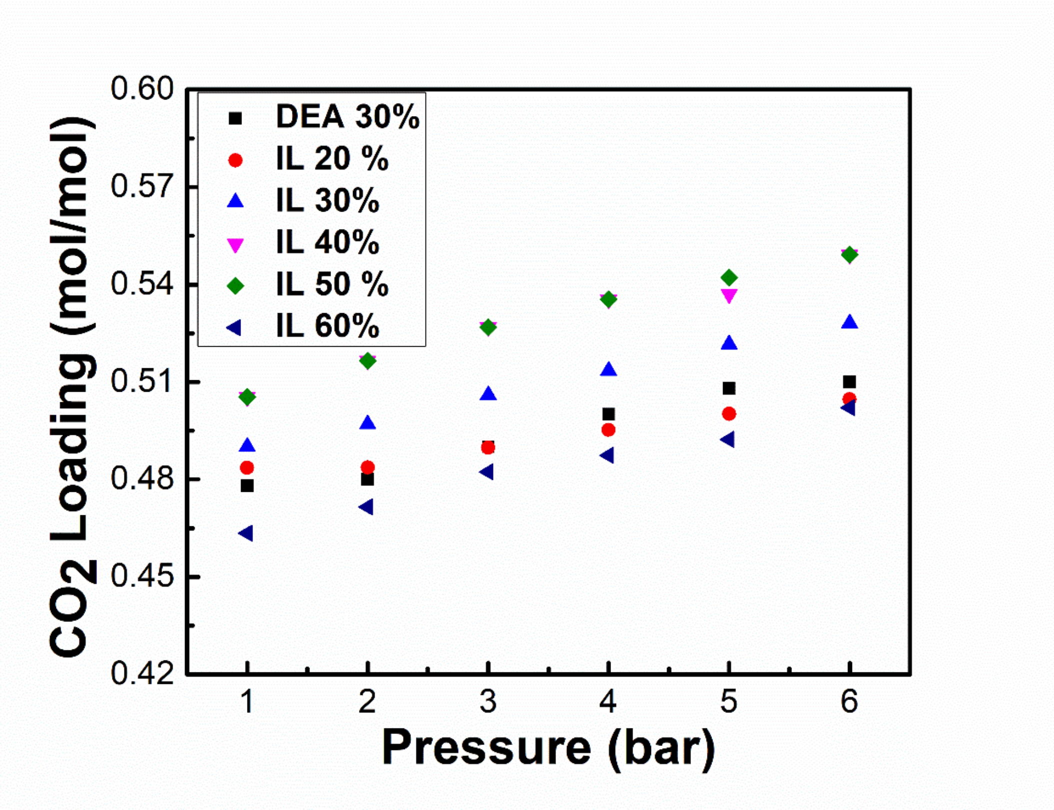


Figure 12. Measured CO_2 loading in DEA + [Bmim][BF_4] mixtures with varying IL concentration

The CO_2 loading results for different solvent compositions were compared with CO_2 loading in standard 30 wt% DEA aqueous solution. The solvent with 20% [Bmim][BF_4] showed lower CO_2 loading as compared to the 30 wt% DEA aqueous solution. The [Bmim][BF_4] concentration was increased to 30% and increased CO_2 loading was observed. In the solvent with 40% [Bmim][BF_4], CO_2 loading further increased. At 50% [Bmim][BF_4] concentration highest CO_2 loading was observed. When the concentration of [Bmim][BF_4] was increased to 60%, a sharp decrease in the CO_2 loading was observed, at 70% [Bmim][BF_4] concentration, the CO_2 loading further declined. The relation of CO_2 loading with the varying concentration of [Bmim][BF_4] at 6 bar pressure is given in Figure 13. It can be observed that highest CO_2 loading was obtained at 50% [Bmim][BF_4] concentration and a sharp decrease in the CO_2 loading followed as the concentration was increased to 60% and then 70%.

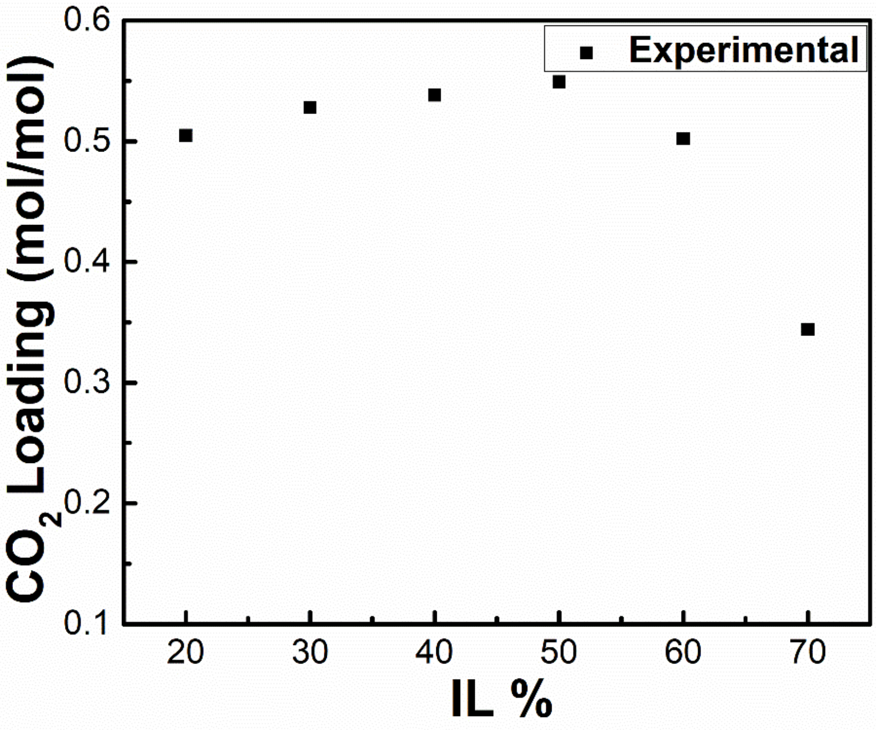


Figure 13. Measured CO_2 loading capacity in different DEA + [Bmim][BF_4] mixtures

4.1.8 Solubility of CO_2 in modified [Bmim][BF_4]+DEA+H_2O solvent system

The initial experimental results with varying [Bmim][BF_4] concentration in 30% wt% [Bmim][BF_4]+DEA aqueous solution showed that the solvent with 50% [Bmim][BF_4] had the highest CO_2 loading. After the extensive experimentation and varying the concentration of [Bmim][BF_4], DEA and H_2O. It was observed that the solvent scheme with 30% [Bmim][BF_4], 30% DEA and 40% H_2O had the highest CO_2 loading. This scheme was termed as the modified solvent system. The CO_2 loading in modified solvent is plotted against the pressure in Figure 14.

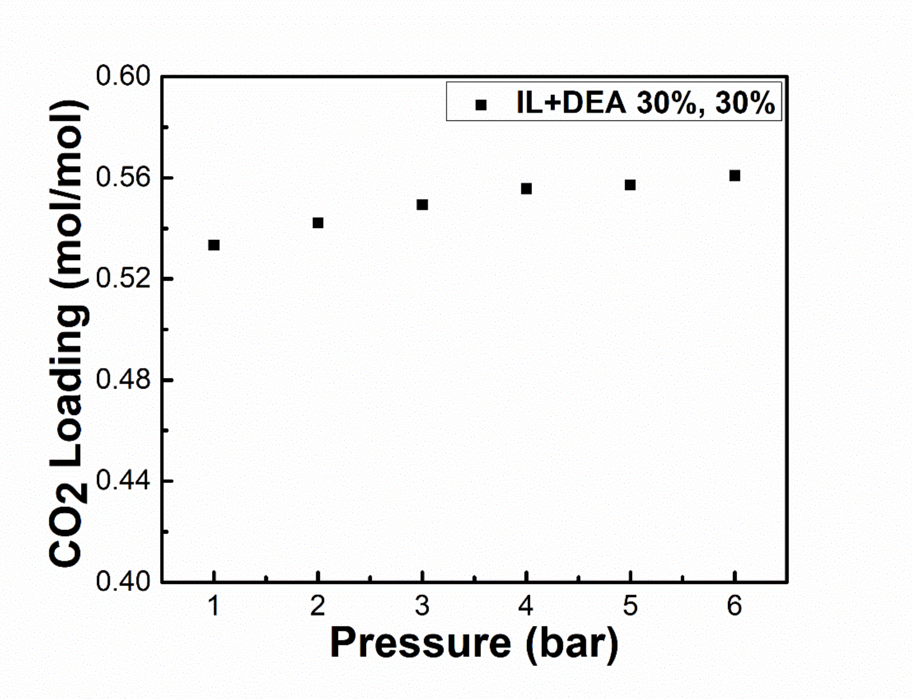


Figure 14. Measured CO_2 loading in modified DEA+[Bmim][BF_4] solvent mixture

4.1.9 Comparison of solubility of CO_2 in modified solvent system with [Bmim][BF_4] and DEA mixtures at varying concentrations

The CO_2 loading capacity in the modified solvent system was compared to the other solvent schemes with varying [Bmim][BF_4] concentrations. The comparison is shown in Figure 15. The CO_2 loading in modified solvent was observed to be relatively higher as compared to the other solvent compositions. The increased CO_2 loading gave a promising scenario for use in the practical CO_2 capture process. This scheme was selected as the final composition to be further analyzed.

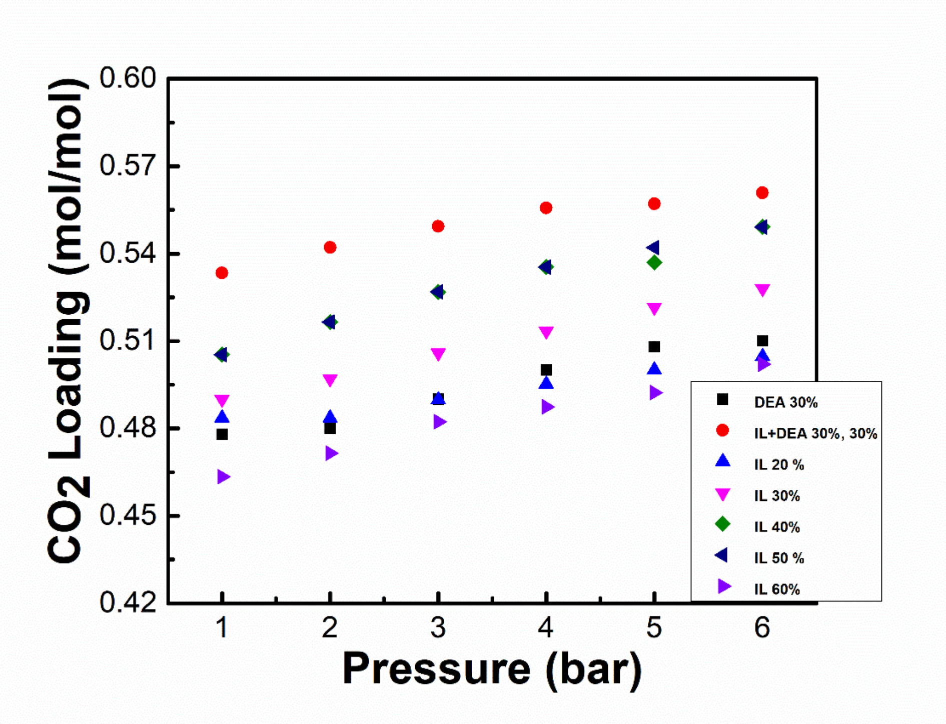


Figure 15. Measured CO_2 loading in modified DEA+[Bmim][BF_4] and other colvent compositons of DEA+[Bmim][BF_4] compositions

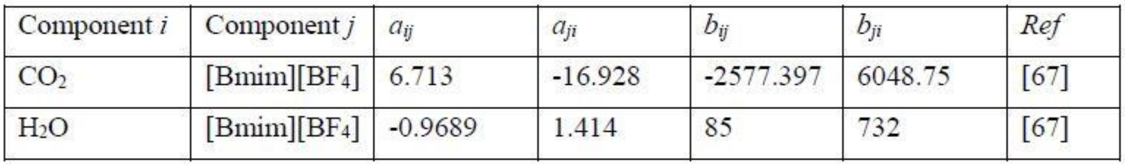
4.2 Simulated solubility of CO_2

The simulation study was carried out using ASPEN PLUS® simulation software (version 8.4). For DEA the default electrolyte nonrandom two-liquid (eNRTL) parameters and physical property correlations available in ASPEN PLUS® were used to model the CO_2 solubility. The ionic liquid [Bmim][BF_4] was added as a user defined component. The scalar properties, temperature dependent properties and binary interaction data used in the modeling were obtained from literature which is given in Table 12-13

Table 12. Scalar property parameters used in the simulation

MW	T_b	T_c	P_c	V_c	ω	Z_c	ΔH_f^{θ}	ΔH_c^{θ}	T_m	*Ref*
226.02	632.3	886.1	27.4	655.4	0.5276	0.2434	-1221.8	-5335	192.1	[67]

Table 13. NRTL binary parameters of CO_2 and H2O with [Bmim][BF4]



Component *i*	Component *j*	a_{ij}	a_{ji}	b_{ij}	b_{ji}	*Ref*
CO_2	[Bmim][BF_4]	6.713	-16.928	-2577.397	6048.75	[67]
H_2O	[Bmim][BF_4]	-0.9689	1.414	85	732	[67]

To simulate the ionic liquid eNRTL method was used. The column was modeled by Radfrac (an equilibrium stage model).

4.2.1 Solubility of CO_2 in DEA and [Bmim][BF_4] mixtures

The solubility of CO_2 was modeled at similar temperature and pressure parameters as that of the experimental procedure i.e. 303 K and pressure ranging from 1 bar to 6 bar. The solubility was first modeled with 30 wt% DEA aqueous solution with pure CO_2. Then the solvent composition was varied as 30 wt% [Bmim][BF_4]+DEA aqueous solution, with varying [Bmim][BF_4] concentrations, following the same composition used in the experimental analysis. The simulated CO_2 solubility is given as CO_2 loading against increasing pressure in Figure 16.

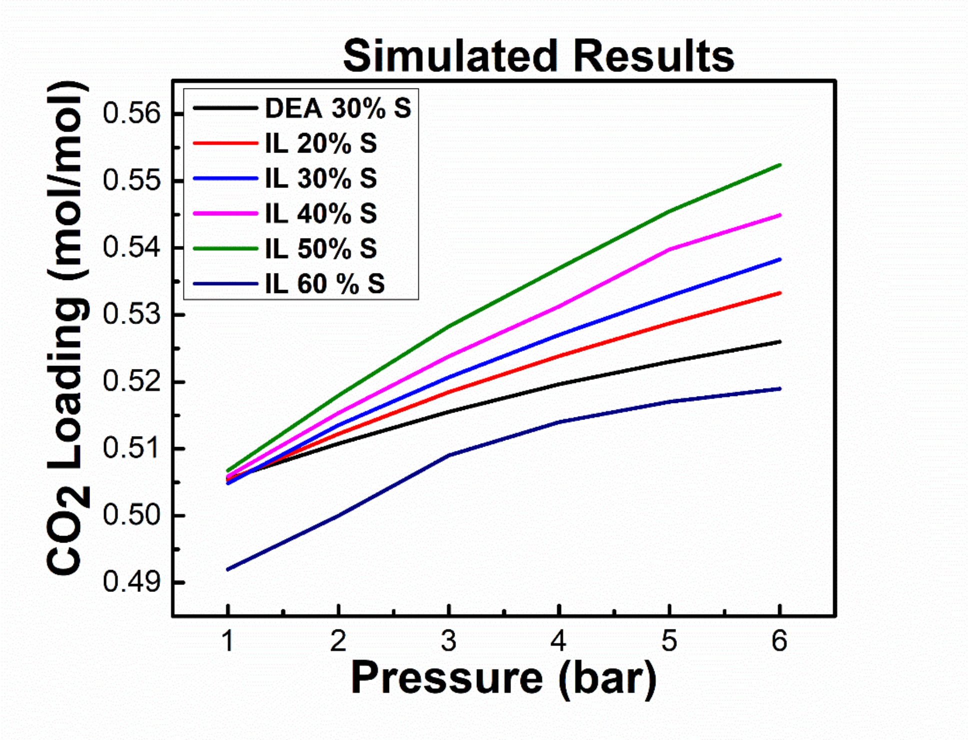


Figure 16. Simulated CO_2 loading in DEA+[Bmim][BF_4] with varying [Bmim][BF_4] compositions

The CO_2 solubility in solvent with 20% [Bmim][BF_4] concentration slightly increased as compared to the solubility in 30 wt% DEA aqueous solution. In solvent with 30% [Bmim][BF_4] concentration, further increase in CO_2 loading was observed. The CO_2 loading kept increasing with increasing [Bmim][BF_4] concentration in the solvent. At 50% [Bmim][BF_4] concentration, highest CO_2 loading was obtained. But as the [Bmim][BF_4] concentration was increased to the 60%, decline in the CO_2 loading was observed. This declined further sharpened in solvent containing 70% [Bmim][BF_4]. Hence, it was established that solvent with 50% [Bmim][BF_4] concentration has the maximum CO_2 loading. The CO_2 loading data obtained via simulations follows the same trend as that of the experimentation, showing increase in CO_2 loading in increasing [Bmim][BF_4] concentration and then decline after the concentration is increased to 60%. The trend of increasing CO_2 loading with varying [Bmim][BF_4] concentration and then decline after reaching the maximum loading capacity at 6 bar and 303 K is shown in Figure 17.

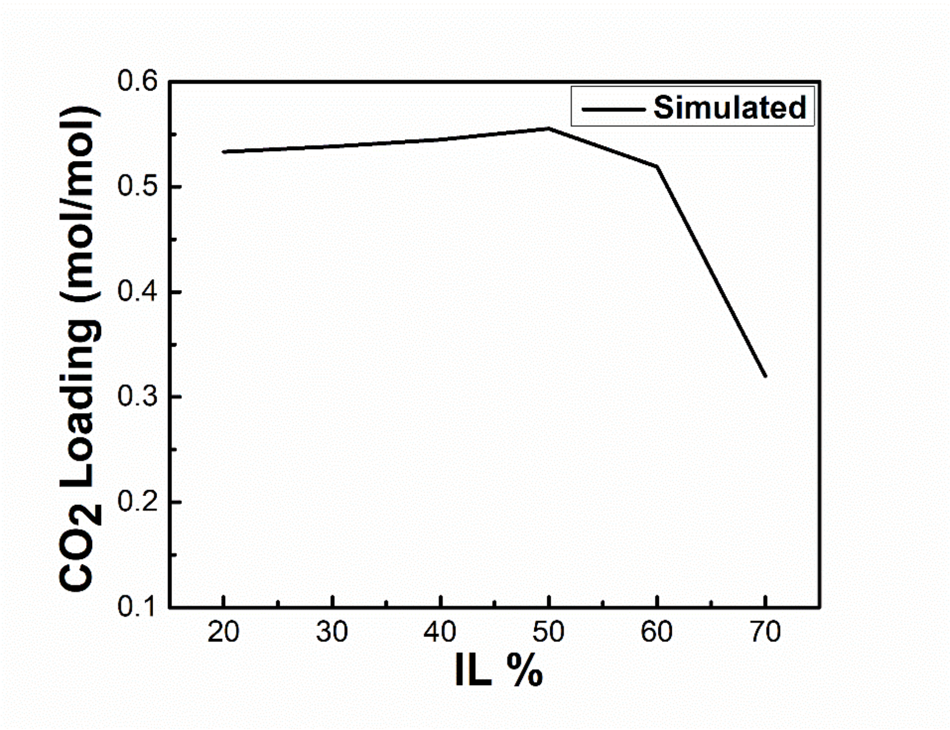


Figure 17. Simulated CO_2 loading capacity in DEA+[Bmim][BF4] with varying [Bmim][BF_4] compositions

4.2.2 Solubility of CO_2 in modified [Bmim][BF_4]+DEA+H_2O solvent system

Following the similar scheme as that of the experimentation, the concentrations of [Bmim][BF_4]. DEA and H_2O were varied to check the performance of the new solvent compositions in terms of the CO_2 loading. The modified solvent system comprises of 30% [Bmim][BF_4]+ 30% DEA + 40% H_2O. Likewise, the modified solvent system shown highest CO_2 loading capacity as compared to the other solvent compositions and scheme. The CO_2 loading in modified solvent system is shown in Figure 18.

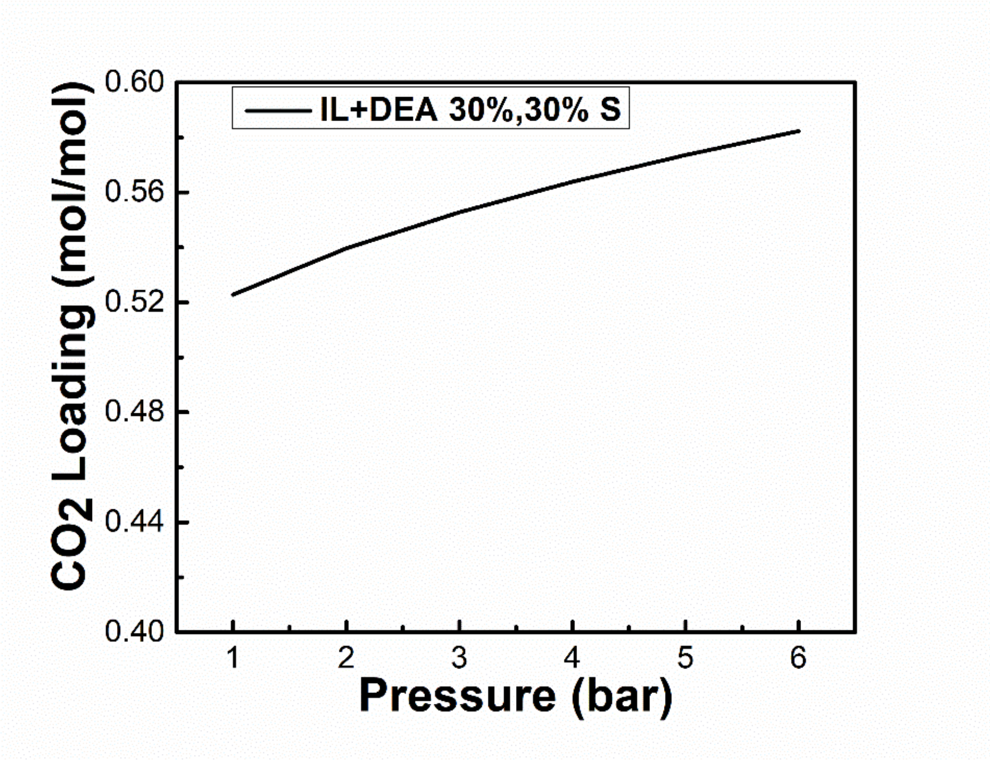


Figure 18. Simulated CO_2 loading in modified DEA+[Bmim][BF4] solvent

4.2.3 Comparison of solubility of CO_2 in modified solvent system with [Bmim][BF_4] and DEA mixtures at varying concentrations

The CO_2 loading for the modified solvent system was compared with the other solvent systems with 30% wt aqueous solutions with carrying [Bmim][BF_4] concentration. It can be seen in Figure 19 that the CO_2 loading in modified solvent system is relatively much higher as compared to the other solvents. It can be analyzed that the new formulated composition has much higher CO_2 loading as compared to the conventionally used 30 wt% DEA aqueous solution.

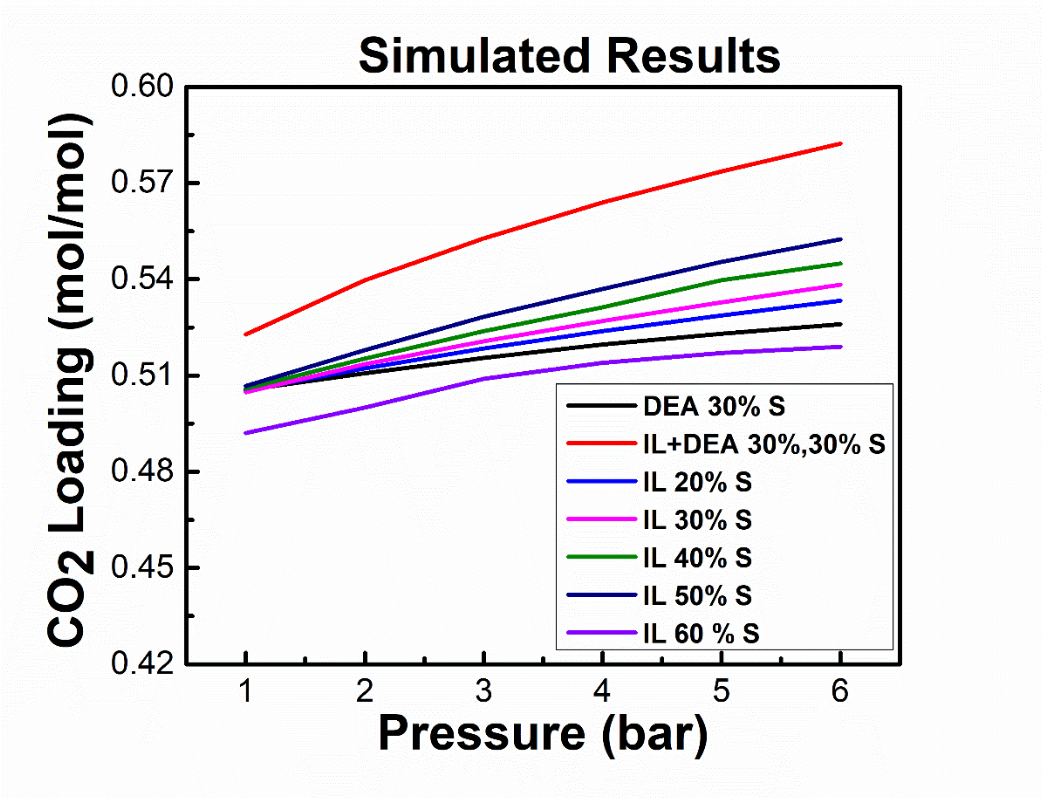


Figure 19. Simulated CO_2 loading in modified DEA+[Bmim][BF4] solvent and DEA+[Bmim][BF4] solvents with varying compostions

After the experimentation, it was confirmed via simulations too that the new solvent system can be an efficient replacement for conventional amines. This new composition was hence selected for further analysis and performance evaluation.

4.3 Comparison of experimented and simulated solubility of CO_2

The CO_2 solubility data obtained through experimentation was compared to the data obtained by the simulation study. The comparison showed mean deviation of less than 10%, which shows that the experimented and simulated data are in good agreement. The comparison between the experimented and simulated CO_2 loading in 30 wt% DEA aqueous solution is given in Figure 20.

Figure 20 shows the comparison of measured and simulated CO_2 loading in solvent with 20% [Bmim][BF_4] too with mean deviation less than 10%. Results depicting the increase in CO_2 loading with increasing CO_2 pressure in the system, following the similar trend. Further comparison of the experimented and simulated CO_2 loading in different solvent compositions of DEA and [Bmim][BF$_4$] are depicted in Figure 20, depicticting the overall comparison of measured and simulated CO$_2$ loading at different solvent compositions.

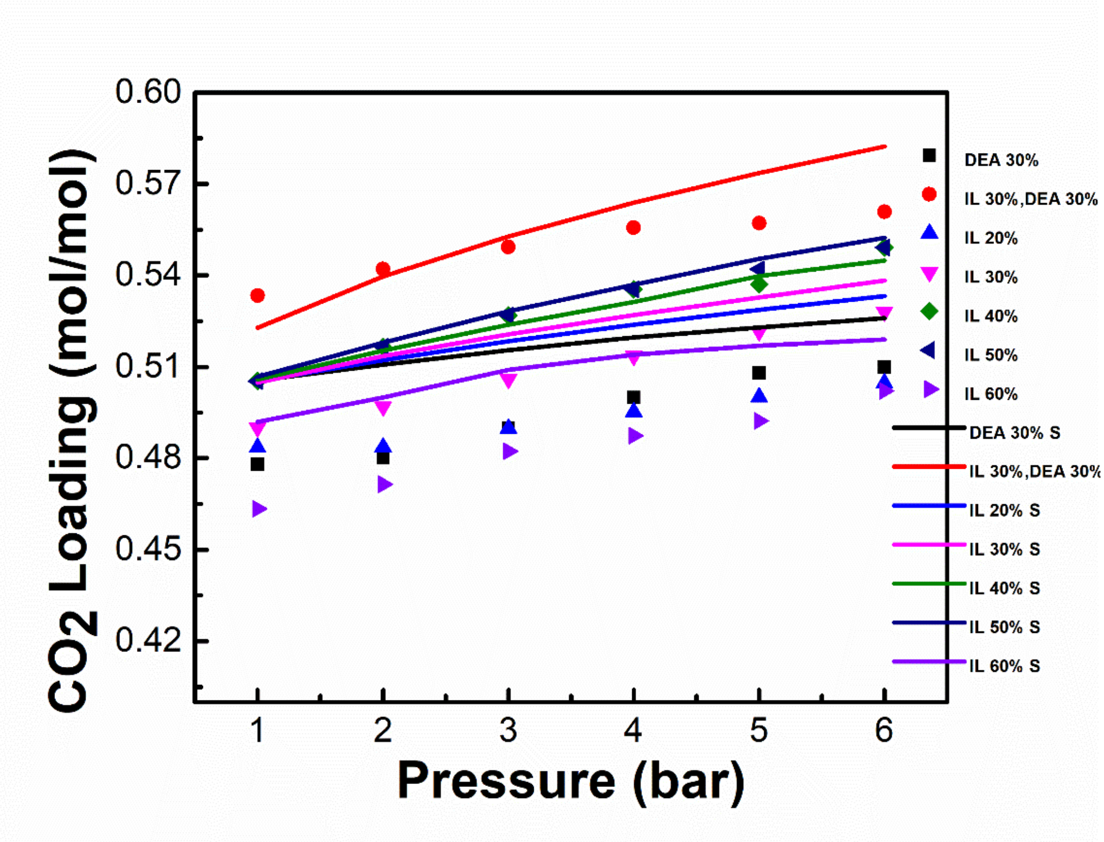


Figure 20. Comparison of measured and simulated CO2 loading in DEA+[Bmim][BF4] solvent with varying[Bmim][BF4] compositions

Figure 20 depicts the CO$_2$ loading in different solvent systems including the modified DEA+[Bmim][BF$_4$] system. The comparative analysis of the measured and simulated CO$_2$ loading was conducted to check the reliability of the results obtained through simulation study. As based on the results of process simulation, further study about energy analysis and cost estimation would be conducted. The comparative analysis showed the reliability of the results obtained via simulations. Further, the similar trend of the increasing CO$_2$ loading with increasing the concentration of [Bmim][BF$_4$] in both i.e. experimentation and simulation can be observed in the Figure 21, as the CO$_2$ starts rapidly decreasing when the concentration of [Bmim][BF$_4$] is increased from 50% to 60% and then to the 70%. As DEA has higher CO_2 loading, the significant decrease of DEA concentration in the solvent mixture decrease the number of moles of DEA available for the reaction, resulting in the decrease of CO_2 loading.

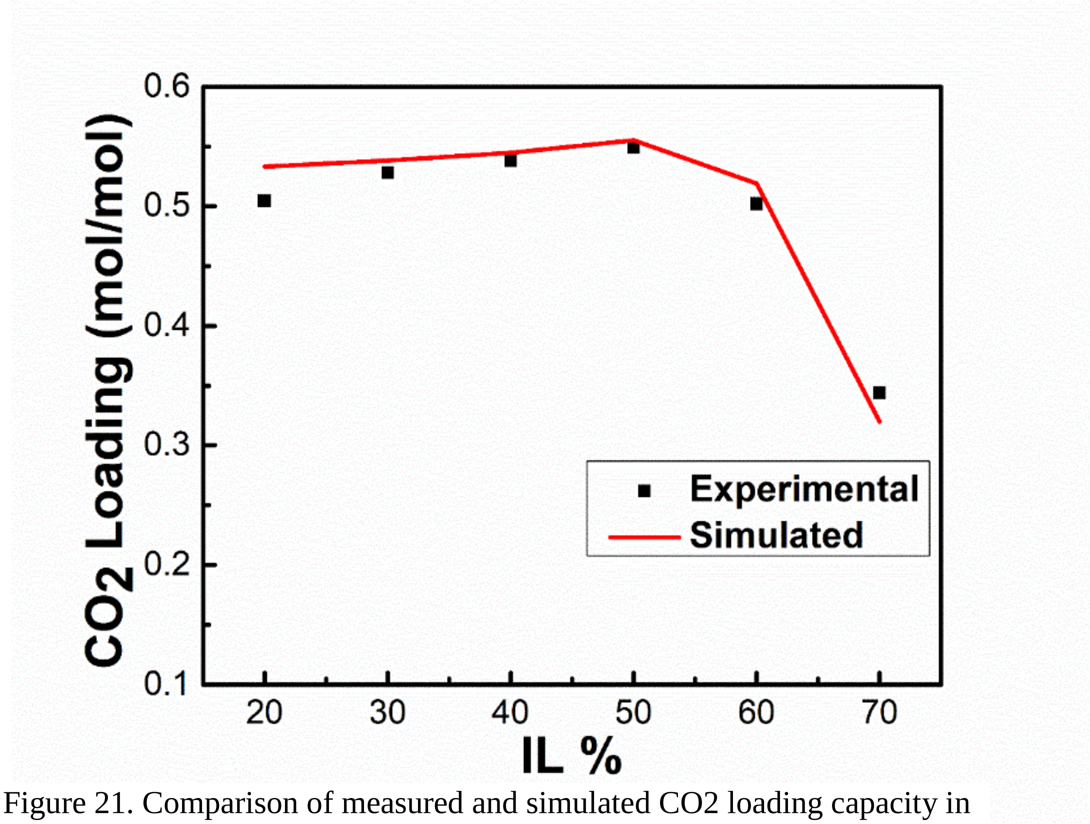


Figure 21. Comparison of measured and simulated CO2 loading capacity in DEA+[Bmim][BF4] solvent with varying [Bmim][BF4] compositions

4.3 Case study: Process simulation and performance evaluation

After the ionic liquid was successfully modeled using the ASPEN PLUS Simulation software, and results were verified by performing comparative analysis with the results obtained through the experimentation. After the validation of the CO_2 solubility result, process simulation was carried out for comparative performance evaluation and comparison of the conventional DEA based natural gas sweetening with the modified DEA+[Bmim] [BF_4] solvent.

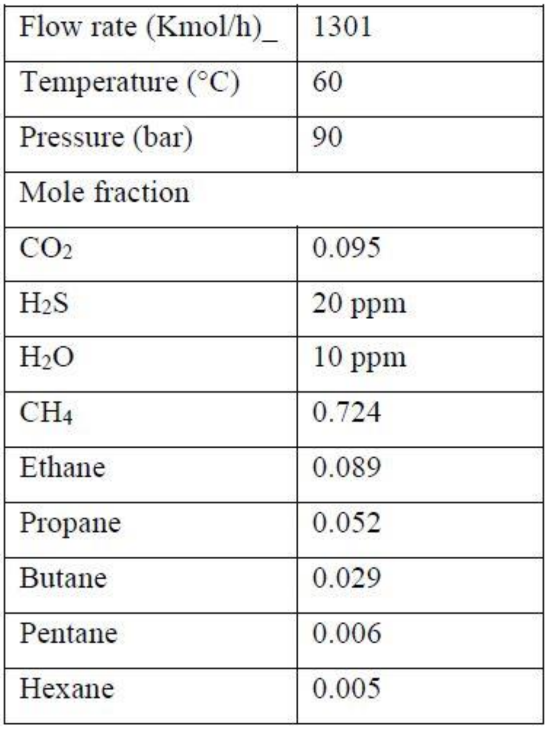
In any conventional alkanolamine based natural gas sweetening process, by far the most expensive aspect is the regeneration heat duty; cost of solvents, electricity for pumps and cooling is also high but not to a lesser extent. The performance evaluation will focus on the regeneration heat duty consumption including other parameters in the base model using 30% DEA and modified DEA+[Bmim][BF_4] model. A detailed cost analysis is also carried out to check the viability of the modified process for the industrial applicability of the ionic liquid based solvent system for the natural gas sweetening process. The case study is based on the work carried out by L. Peters *et al.* [68].

4.3.1 Modeling and validation of the base model

The base model is based on the work by L. Peters *et al.* [68]. The base model for the case study was simulated using ASPEN PLUS (version 8.4). For the simulation of base model amine property package using the equations and parameters described in Chapter 2 were used. The model is based on eNRTL. The simulation was carried out following the similar absorber-desorber scheme used in the literature.

The solvent composition of the base model is 30% DEA and 70% H_2O. The specification set for the sweet gas stream leaving the absorber was with less than 5% CO_2 content, and for the acid gas stream leaving the stripper column was with CO_2 purity of more than 90%. The parameters and composition of the feed crude natural gas are given in Table 14

Table 14. Summary of Feed gas conditions



Flow rate (Kmol/h)_	1301
Temperature (°C)	60
Pressure (bar)	90
Mole fraction	
CO_2	0.095
H_2S	20 ppm
H_2O	10 ppm
CH_4	0.724
Ethane	0.089
Propane	0.052
Butane	0.029
Pentane	0.006
Hexane	0.005

The natural gas after it is produced from the reservoir. The gaseous mixture is directed to the sweetening facility. The removal of acid gas so that the gas can further be supplied is performed. This removal involves the separation of CO_2 up to a certain amount. This amount usually varied from country to country. First, the gas is put through the column. The solution is showered where it separates the CO_2. The purified gas now leaves the column. The solvent is regenerated after its processed through stripper. There, the DEA and the gas are separated and processed for further use.

The solvent inlet conditions and parameters for absorber and stripper column are given in Table 15

Table 15. Absorber and stripper operating conditions

	Unit	Value
Absorber		
Solvent flow rate	kmol/h	3161.49
Solvent inlet temperature	°C	33
Solvent inlet pressure	Bar	90
Stages		18
Stripper		
Column pressure	Bar	2.1
Stages		14

The detailed process flow sheet for the base model is given in Figure 22.

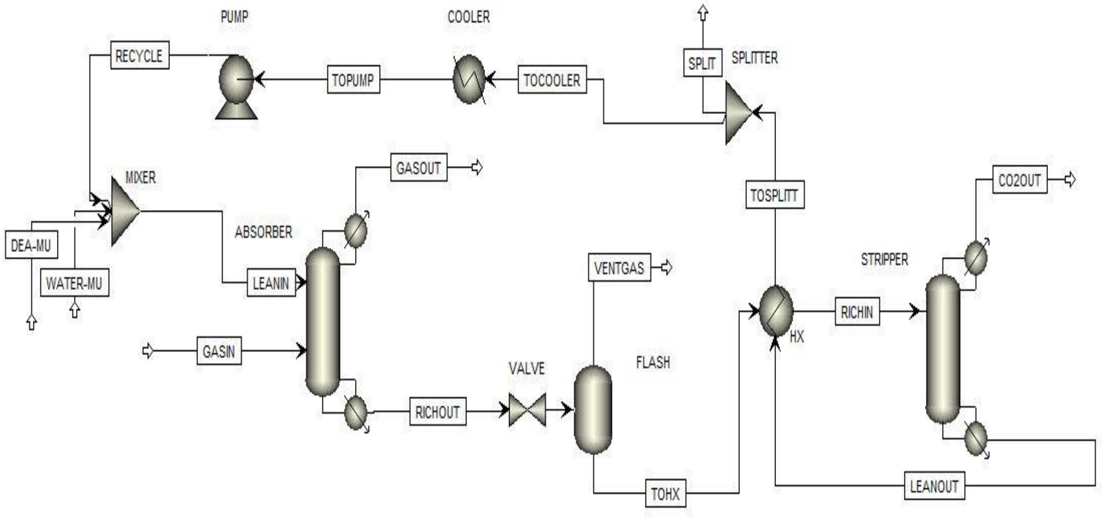


Figure 22. Detailed flow sheet of the base model with 30% DEA solution

After the base case model was simulated the results were compared and varified with the work of L. Peters *et al.* [68]. The comparativer analysis was carried out to check the validation of process simulation of the base case, which would be used for further perrormance evaluation and study. A detailed comparison of the base case model simulation results with the simulation results of L. Peters *et al.* [68] can be seen in table 16

Table 16. Comparison and summary of base model with reference model

Parameter	This work (base model)	L. Peters *et al.*
Solvent inlet flow rate (kmol/h)	3161.49	3161.49
Gas inlet flow rate (kmol/h	1301	1301
Sweet gas flow rate (kmol/h)	1164.31	1180.63
Sweet gas purity (%)	>90	>91
Sweet gas pressure (bar)	90	89.5
Sweet gas temperature (°C)	36.709	33.3

Acid gas purity (%)	92	97.7
Acid gas temperature (°C)	25	25
Acid gas pressure (bar)	1.299	1.3
Reboiler heat duty (kj/kg)	2934.42	3076

After comparative analysis of the result summary of the base model with the reference model of the case study, base model was in good agreement with the reference model. The sweet gas flow rate, purity, temperature and pressure were approximately the same. Acid gas purity, pressure and temperature were also same as of the base model. The reboiler heat duty was slightly different but within the acceotable limit of below 10% deviation. This proved the validity of the model for further performance based analysis.

4.3.2 Process simulation and evaluation of DEA+[Bmim][BF$_4$] based modified process

The DEA+[Bmim][BF$_4$] based modified model was simulated using the same ASPEN PLUS simulation software. To simulate the modified process, default parameters and physical properties for DEA were used, details of which are already mentioned in Chapter 3 in detail. Ionic liquid [Bmim][BF$_4$] was defined as user-defined component, the property parameters required for the simulation are given in Chapter 3, along with the detailed property parameter for ionic liquid [Bmim][BF$_4$] used in the study. The crude natural gas composition was same for the based model, which are summarized in Table 14. The modified process has a composition of 30% DEA, 30% [Bmim][BF$_4$] and 40% H_2O. The operating parameters and details of the absorber and stripper column are given in Table 17.

Table 17. Absorber and stripper conditions for modified DEA+[Bmim][BF$_4$] process

	Unit	Value
Absorber		
Solvent flow rate	kmol/h	1826
Solvent inlet temperature	°C	33
Solvent inlet pressure	Bar	90

Stages		18
Stripper		
Column pressure	Bar	2.1
Stages		14

The operating conditions for process evaluation of the modeified process were not changed in order to study the performance and compare with the base model. Further, to check and study the prossiblity of integration of the modified process in to the existing alkanolamine based naturlal gas sweetening plants. The process flow sheet for the DEA+[Bmim][BF_4] based modified process is given below is Figure 23

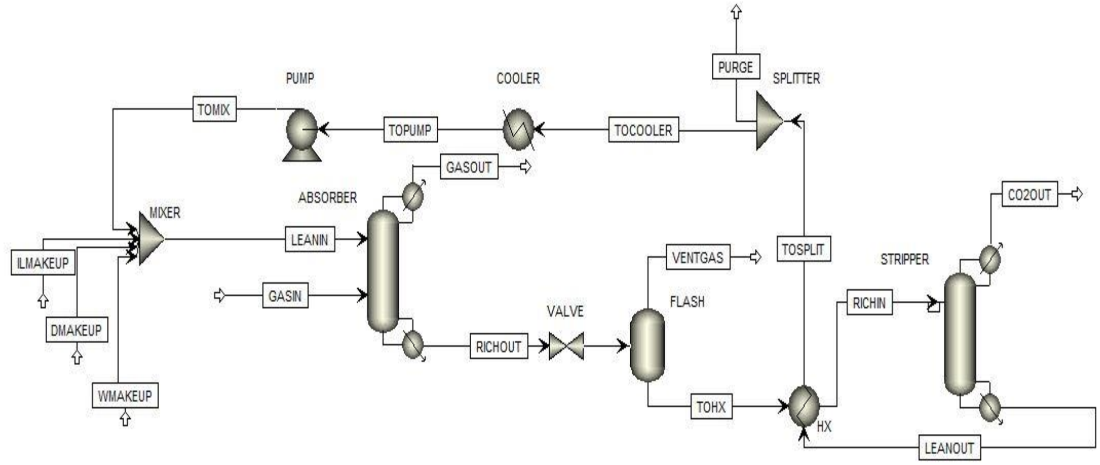


Figure 23. Detailed process flow sheet of the modified DEA+[Bmim][BF4] system

Likewise the conventional process, the crude natural gas enters the absorber column at bottom, while lean solvent enters at the top of the column in the counter-current mode. The CO_2 present in the crude natural gas chemically reacts with the DEA while physically absorbing in to the ionic liquid present in the solution. After the CO_2 is absorbed in to solution, sweet natural gas leaves at the top of the absorber and is processed for further use. The rich DEA+[Bmim][BF_4] solution leaves the absorber at bottom. The pressure of the CO_2 enriched solution is decreased to nearly atmosphere pressure after it passes through the valve and in to the flash separator, where gas is splitted from the liquid. The rich solvent is then preheated in the cross heat exchanger through the lean solvent coming form the stripper, and enters the stripper column. In the stripper the temoerature is increased about 125 °C, the CO_2 is stripped off and the DEA is regenerated through the reversible reaction. The CO_2 leaves at the of the stripper while hot lean DEA+[Bmim][BF_4] solution leaves at the bottom of the stripper column. The lean solvent then flows through the cross heat exchanger, pre heating the CO_2 rich solution flowing towards the stripper, and after passing through the heat exchanger the lean solvent is again repressurized, and cooled to match the absorber inlet conditions and make up DEA, water and ionic liquid are added to account for the losses, if any.

The modified solvent based process is modeled following the similar procedure, as in common practice for the conventional amine processes. Summary of the process simulation for modified solvent system is given in Table 18

Table 18. Result summary of modified DEA+[Bmim][BF4] process

Parameter	Value
Solvent inlet flow rate (kmol/h)	1826
Gas inlet flow rate (kmol/h	1301
Sweet gas flow rate (kmol/h)	1176.74
Sweet gas purity (%)	>90
Sweet gas pressure (bar)	90
Sweet gas temperature (°C)	42
Acid gas purity (%)	91
Acid gas temperature (°C)	37.019
Acid gas pressure (bar)	1.3
Reboiler heat duty (kJ/kg CO_2)	2231.55

4.3.3 Performance based comparative analysis of DEA based process and DEA+[Bmim][BF_4] based modified process

The DEA based model, which was selected and simulated as he base model for the performance evaluation was compared with the modified DEA+[Bmim][BF_4]

based process for comparative evaluation. The performance evaluation of the modified process was carried out to check its feasibility with the conventional DEA process for a same crude gas composition at similar operating parameters. As the modified solvent has given promising results in terms of CO_2 loading capacity, its performance study will give an insight to the future prospect and possible utility of the ionic liquid and amine blends based solvent systems for natural gas sweetening. A detailed comparison of the DEA based process and DEA+[Bmim][BF_4] based modified process is given in Table 19. The comparison is discussed in detail below with respect to different parameters.

Table 19. Performance based result summary of DEA based process and DEA+[Bmim][BF_4] based process

Process parameter	DEA based process	DEA+[Bmim][BF_4] based process
Solvent feed flow rate (kmol/h)	3161.49	1826
Sweet gas flow rate (kmol/h)	1164.31	1176.74
Sweet gas purity (%)	90	90
Sweet gas temperature (°C)	36.709	53
Sweet gas pressure (bar)	90	90
Acid gas flow rate (kmol/h)	132.137	132
Acid gas purity (%)	92	91
Acid gas temperature (°C)	25	36.869
Acid gas pressure (bar)	1.299	1.299
Lean loading	0.0632	0.0246
Cooled lean solvent temperature (°C)	122.94	116.94
Hot rich solvent temperature (°C)	68.92	63.282
Reboiler temeperature (°C)	123.628	116.946
Reboiler heat duty (kJ/kg CO_2)	2934.42	2231.55

Lean loadings of DEA based process and DEA+[Bmim][BF_4] process were studied to acquire minimum regeneration heat duty. Meanwhile process to achieve the same CO_2 removal capacity as of the DEA based process. To obtain it the loadings should be considered. Loading before the reacgtion have crucial effect of the performance of solvent. The lean laoding plays a key role in the solvent regeneration heat duty. The reduction in heat duty significantly reduces th energy demand for the over all process. Because as duscussed in earlier chapters that the rapid energy demand and better aternaguves for traditiona methods. The energy demand can further be reduced by Due to the lower lean loading, the DEA+[Bmim][BF_4] process requires less heat duty for same level of the acid gas purity and solvent regeneration.

The DEA+[Bmim][BF_4] based process has lower solvent-specific demand as compared to the DEA based process. As demonstrated by the experimental as well as simulated results the DEA+[Bmim][BF_4] based process has higher CO_2 loading capacity as compared to the DEA based process, which result in lower solvent-specific demand. Lower solvent specific demand result in decreased solvent circulation rate, which in turn results in lower regeneration sensible heat. With the decrease in specific solvent demand, the powers of solvent pumps decrease, resulting in saving a small amount of the electricity. Further the reduction of circulatinng solvent flow rate also decreases the cooling water demand of lean cooler and DEA recovery section. Beside the circulating solvent flow rate, lower temperature of the lean solvent out of rich-lean heat exchanger, also cuts the cooling water demand for lean solvent cooler. As it can be noted in the Table 19 that for DEA+[Bmim][BF_4] process has lower lean solvent temperature as compared to the DEA based process.

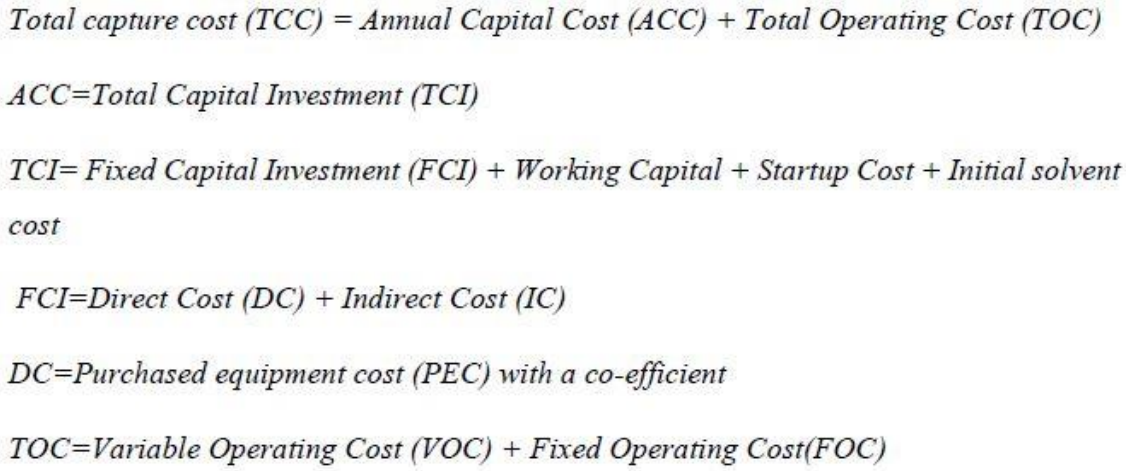
DEA+[Bmim][BF_4] based modified process requires less energy thn aminees. Therefore the alernative options, the possible replacements for the capture systems. According to the data obtained through performance evaluation of both the said process, the DEA+[Bmim][BF_4] based process requires 23.95% less regeneration heat duty as compared to the DEA based process. The reduction in regeneration heat duty can be attributed to the decrease of sensible and latent heat during the regeneration process. The sensible heat is decreased because the heat capacity of the DEA+[Bmim][BF_4] modified solvent is lower than the 30% DEA solution because the heat capacity of ionc liquid is lower than the water and the solvent flow rate for the modified DEA+[Bmim][BF_4] is lower than the DEA process because of the higher CO_2 loading as discussed earlier. The decrease in the latent heat can be attributed to the reduction of the vapor pressure of solvent due to the presence of ionic liquid in it, as ionic liquid has negligble vapor pressure, this results in decrease amout of water being vaporized during the process.

From the performance evaluation it can be concluded that DEA+[Bmim][BF_4] based modifed process is more potent for natural gas sweetning process as compared to the DEA base process, because it requires less regeneration heat duty which is the main cost contributor for the conventional amine bases process, modified process requires less specific solvent due to relatively higher CO_2 loading which in turn will result in reduced cooling water demand and reduced electricity cost.

4.4 Economic evaluation of the DEA+[Bmim][BF_4] based process

For any process to be feasible and applicable on the industrial scale for practical applications the economic evaluaton is a necessary step. After the successful performance evaluation of the modified DEA+[Bmim][BF_4] process, the economic analysis was performed to check the economical feasibility of the process.

There was many metrices to measure the cost of CO_2 capture processes, but in this study the CO_2 capture cost was selected. For this purpose the cost model used by Huang *et al.* [67] was used. All costs are in USD. The break down of the CO_2 capture cost calculation and model and methodology are as below;



Total capture cost (TCC) = Annual Capital Cost (ACC) + Total Operating Cost (TOC)

ACC=Total Capital Investment (TCI)

TCI= Fixed Capital Investment (FCI) + Working Capital + Startup Cost + Initial solvent cost

FCI=Direct Cost (DC) + Indirect Cost (IC)

DC=Purchased equipment cost (PEC) with a co-efficient

TOC=Variable Operating Cost (VOC) + Fixed Operating Cost(FOC)

The purchased equipment cost (PEC) was updated to the year 2008 with the Chemical Engineering Cost Index. The year 2008 for cost update was considered for a raltive comparative analysis on the basis of cost, because most of the related studies are carried out with resepect to the year 2008. The direct (DC) and indirect cost (IC), fixed capital investement (FCI), total capital investement (TCI) were calculated on the based of purchased equipment cost. The annual captial investement (ACC) was computd by equation to a constant series of payments for every year of the project life. Project life was selected to be 25 years with 7500 working hours per year, as are used in common practice within the literature.

Table 20. Composition of Total Capital Investment (TCI) in USD

Direct Cost (DC)	**Percentage of PEC**	**Cost ($)**
Purchased Equipment	100	502309.2
Purchased Equipment Installation	10	50230.92
Instrumentation and Control	20	100461.8
Piping	30	150692.8
Electrical	5	25115.46
Building and Building services	10	50230.92
Yard Improvements	10	50230.92
Land	5	25115.46
Miscellaneous	2	10046.18
	Total DC	964433.7
Indirect cost (IC)	**Percentage of DC**	
Engineering and supervision	15	144665
Contingency	11	106087.7
Procurement cost	2	19288.67
	Total IC	270041.4
	Percentage of FCI (DC+IC)	
Working capital	15	185171.3
Startup Cost	1	12344.75
Initial Solvent cost		186818.6
TCI *sum of above costs*		1618810

From the total capital investement (TCI), annual captital cost (ACC) was calculated as a series of payments, using following equation,

$$ACC = \frac{TCI}{((1 + ir)^n - 1)/ir(1 + ir)^n}$$

Where *ir* denotes the interest rate, which is 8% in this study, and *n* denotes project lifetime which is 25 years.

Therefore, from above equation , the ACC= 247910.7 USD

As the total capture cost (TCC) is calculated as the sum of annual capture cost (ACC) and total capture cost (TOC), the total operating cost (TOC) is further calculated as the sum of variable operating cost (VOC) and fixed operating cost (FOC) with te addition of the distribution and marketing cost and research and development (R&D) cost calculated with the fixed percentages of the sum of the fixed operating cost (FOC) and variable operating cost (VOC).

The prices for the utilities i.e. reboiler steam, cooling water, process water and electricity and the solvents i.e. ionic liquid [Bmim][BF_4], DEA and water are given in Table 21.

Table 21. Cost for the solvents and utilities

	Value	Unit	Source
Cost for diethanolamine	2400	Dollar/t	[68]
Cost for ionic liquid [Bmim][BF_4]	6600	Dollar/t	[67]
Cost for reboiler steam	14.5	Dollar/t	[68]
Cost for electricity	0.07	Dollar/kWh	[68]
Cost for cooling water	0.01	Dollar/t	[68]
Cost for process water	0.5	Dollar/t	[68]
Direct Labour	15	Dollar/h	[68]

The detailed compostion and break down of the total operating cost is given below in Table 22. Total operating cost was calculated for one year assuming 7500 working hours.

Table 22. Composition of total operating cost (TOC)

Variable Operating Cost (VOC)	**UNIT PRICE**	-	**Amount**	**COST ($)**
DEA Make up, US$/ton	2400		0.020763	373725
IL-make up US$/ton	6600		0.020761	1027660
Steam cost US$/ton	3.66		20.846	572222.7
Cooling water cost US$/ton	0.0329		703	173465.3
H_2O make up cost US$/ton	0.04		0.178462	53.5386
Electrical cost US$/kWh	0.06		222	99900
Miscellaneous operating materials	2% of VOC			44940.52
			TOTAL	2291967
Fixed Operating Cost (FOC)	**Composition**	-		**COST**
Local tax	1% of FCI			12344.75
Insurance	1% of FCI			12344.75
Maintenance (M)	3% of FCI			37034.25
Operating labor (OL)	34.65 US$/h		7500	259875
Laboratory costs	20% of OL			51975
Supervision	20% of OL			51975
Plant Overheads	50% of OL			129937.5
Operating Supplies	15% of M			5555.138
Administrative cost	15% of OL			38981.25
			TOTAL	600022.6
Distribution & Marketing	0.5% of (FOC+VOC)			14459.95
R&D cost	5% of (FOC+VOC)			144599.5
TOC	*sum of all above costs*			3051049

From the sum of annual capital cost and total operating cost, total capture cost (TCC) was obtained to be **$ 3,298,959**. The total capture cost (TCC) being the sum of annual capital cost, as the fix sum of total capital investment per anum and total annual cost being calculated by the working capacity of the plant for one year i.e. 7500 hours; the CO_2 capture cost can be calculated by dividing the total capital cost by the total amount of CO_2 captured per anum, the total amount of CO_2 captured and cost of capture/t of CO_2 is given in Table 23.

Table 23. Calculation of CO_2 capture cost/ton

CO_2 capture/h 5.1287 t/h

Total operating hours /year 7500

Total CO_2 captured/ year = CO_2 captured/h x total operating hours/yr

38465.55 t/yr = 5.1287 ton/h 7500

CO_2 capture cost (Dollar/tonne) = Total capture cost (TCC) / Total CO_2 captured

\$ 85.764/tonne CO_2 \$3,298,959 38465.55 t

From the economic evaluation as elaborated in this chapter the capture cost was calculated to be \$85.764/t CO_2. The difference of calculation criteria. The cost is affected by many factors. Still the cost of \$85.764/t is reasonable and in near appriximation among other researchers. The cost can further be reduced if the cost of ionc liquidss reduce. Because that is the significant amount of the overll process. The cost comparison with other researchers is given in Table 24.

Table 24. Comparison of CO_2 capture cost with other researchers

This work	Other researchers			
	Hassan *et al.* [69]	Raynal *et al.* [70]	Mores *et al.* [71]	Huang *et al.* [67]
\$85.76/ton CO_2	\$55/t CO_2	74€/t CO_2	\$112/t CO_2	\$70/t CO_2

It is worth mentioning that total operating cost (TOC) covers more than 80% of the total capture cost (TCC) for CO_2 capture. In the total operating cost (TOC) main sinks for the electrical power consumption are the pumps. Steam is consumed as the heat source for the reboiler. The steam cost is the dominating factor in the total operating cost (TCC) contributing a major portion. Hence, illustrating the importance of reducing the regeneration heat duty, which in the case of modified DEA+[Bmim][BF_4] process is

23.95% less than the conventional DEA process, hence reducing the operating cost as predicted. However, the total capital investment (TCI) in case of modified DEA+[Bmim][BF_4] process is higher than the conventional DEA process, because of the high cost of the ionic liquids. Still the cost analysis shows that the modified solvent system as proposed can be used for the natural gas sweetening process on industrial scale.

4.5 Conclusions

Techno-economic performance of ionic liquid based CO_2 capture processes was assessed through this study. The evaluation is based on the measured CO_2 solubility analysis and process simulation results, taking a conventional DEA based natural gas sweetening process as the base reference case.

The modified [Bmim][BF_4]+DEA based solvent with 30% [Bmim][BF_4], 30% DEA and 40% H_2O has been found to have maximum CO_2 loading. It was found that the CO_2 loading of amines increases when mixed with ionic liquid. Through process simulation and evaluation, it has been concluded that the ionic liquid based modified solvent is potent and applicable for natural gas sweetening process on industrial scale.

The modified DEA+[Bmim][BF_4] requires 23.94% less regeneration heat duty as compared to the conventional DEA base process, hence it is more energy efficient. Besides, the ionic liquid based process was found to be better than DEA based process in terms of specific solvent demand, circulated solvent and cooling water demand.

Although ionic liquid has a high price, the total capture cost of IL based process is still reduced as solvent cost occupies a smaller portion of the total cost. The IL based process is better than the conventional DEA based process in terms of the circulated solvent, cooling water demand and regeneration heat duty. The IL-based solvents could result in energy saving and cost efficient natural gas sweetening processes on industrial scale in future.

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