CHAPTER 1

INTRODUCTION

1.1 Natural gas

Natural gas is one of the major types of 'fossil fuels' which could be regarded as a primary energy source for domestic, automobiles and several industrial processes. It also finds another important application, as a 'fuel' for power plants to generate electricity. Natural gas is of great importance, not only as a source of energy but also as a raw material for chemical and petrochemical industry. Most of the researchers firmly believed that natural gas would play a key role for 'clean energy' developments in future. Natural gas contains relatively few undesirable components compared to other fossil fuels which make its use further attractive for keeping the environment benign. Moreover, less number of pollutants is formed on natural gas combustion as compared to coal/oil and also produces virtually no ash particles. It is by far the 'cleanest' of all available fossil fuels and is rapidly gaining importance over oil as an energy source for most of the industrial activities.

The use of natural gas also possessed important advantages including its reasonable fuel efficiency, high product quality and above all requirement of low processing and maintenance cost. Natural gas reserves in Malaysia are ranked at 14th in the world with total 27 gas fields. By January 2008, the natural gas reserves in Malaysia stood at 88 trillion standard cubic feet (tscf). At the current rate of production i.e., 7.01 billion standard cubic feet (bscf) per day, Malaysia's gas reserves could be expected to last for another 36 years. The distribution of total gas reserves in various regions of Malaysia can

be given as: Penunsilar Malaysia (East coast) 38 %, Off-shores of Sabah and Sarawak 14 % and 48 % respectively (Malaysia gas Sdn Bhd, 2009).

1.1.1   Composition of natural gas

Natural gas may be regarded as a mixture of hydrocarbon (compounds of hydrogen and carbon only) and non-hydrocarbon gases. The composition of natural gases varies widely from one region to another based on their geological formation and developments (Kohl and Riesenfeld, 1979). Basically the principle ingredients of natural gas are hydrocarbons and methane (CH_4) is considered to be its major component comprising of 70 to 90 % of its whole composition (Newman, 1985). In addition to CH_4, natural gas also contains varying amounts of other small hydrocarbon molecules such as ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}) and hexane (C_6H_{14}). The organic origin of natural gas explains why it is mainly composed of hydrocarbons. Natural gas also contains some inorganic compounds (non-hydrocarbon portion) as impurities such as carbon dioxide (CO_2), hydrogen sulphide (H_2S) and nitrogen (N_2). The presence or absence of these acid gases (CO_2 and H_2S) makes the natural gas sour or sweet respectively.

The CO_2 contents in natural gas vary widely in various gas fields of the world. For example the amount of CO_2 in natural gas has been found to be as high as 45 % in Kapuni gas field, New Zealand and 54 % in Terrell gas field, Texas (Rojey and Jaffret, 1997). Most recently, the composition of CO_2 in natural gas has been found to be as high as 72 % in some of the Malaysian (Sarawak) gas fields (Darman and Harun, 2006). The production of natural gas from prevailing gas fields is expected to decline in a decade based on the current reserves. Therefore, there is a great need to pay more emphasis for the development of gas reserves with rich CO_2 contents in order to sustain long term future energy challenges as the existing gas fields with low CO_2 contents are rapidly depleting.

1.1.2   Importance of CO_2 removal from natural gas

The presence of high CO_2 contents in natural gas not only results in lowering its heating value but also creates corrosion problems in pipelines during transmission and in processing equipments. The burning of natural gas further leads to the addition of more CO_2 (a greenhouse gas) emissions to the atmosphere which creates serious environmental concern i.e., global warming. Thus the importance of CO_2 removal from natural gas is directly linked to the various problems which are faced during the transmission and industrial processing of natural gas. One of the major applications of natural gas is the synthesis of liquefied natural gas (LNG) especially in Malaysia which is the 2nd largest LNG producer in world. However, during LNG production where natural gas is cooled to -160^oC, the presence of high CO_2 creates blockage problems due to its solidification. Thus it is commercially important and environmentally desirable to remove CO_2 from natural gas prior to its processing.

1.2   Overview of the current processes for CO_2 removal

A wide range of processes are currently available for the separation of CO_2 from natural gas such as adsorption, membrane technology, cryogenic methods and absorption. Each method has its own advantages and disadvantages which are discussed in detail as follows:

1.2.1   Adsorption

Adsorption is a surface phenomenon in which a gas or liquid (solute) accumulates on the surface of a solid or a liquid (adsorbent) which results to form a film of molecules or atoms (adsorbate). The most common industrial adsorbents which are used to remove CO_2 from natural gas include activated carbon, zeolites, carbon molecular sieves, silica gel and alumina. The removal of CO_2 using this process follows two steps: i) adsorption of gas in the adsorbents to achieve saturation, and ii) regenartion step to reuse the adsorbents. The adsorption process can be categorized into two methods based on the

technique used for regeneration step i.e., pressure swing adsorption (PSA) and thermal swing adsorption (TSA). In PSA, the regeneration of adsorbents is achieved by reducing the system pressure, however, in TSA the temperature of system is increased at constant pressure to shift the adsorption equilibrium to assist the adsorbent regeneration (Burchell et al., 1997).

Mainly, the PSA method is adopted for gas separations with high concentration in gas mixtures (bulk separations) such as hydrogen separation, air separation and even in air drying. However, PSA has a disadvantage of high pressure and vacuum requirements which contribute in increasing the operating cost of the process. The development of PSA process for the removal of CO_2 from natural gas is still under progress. The primary applications of TSA include purification of gaseous mixtures by separating undesired components which are present in low concentrations e.g., removal of H_2S, mercaptans, organic sulfides and disulfides from natural gas (Kohl and Riesenfeld, 1979). The main obstacles in using TSA is the large time requirement for adsorption cycle, limitation due to cooling of adsorbent bed, high energy requirements and large heat losses (Burchell et al., 1997). The process of adsorption is not attractive for large-scale separation of CO_2 due to its limited capacity and low CO_2 selectivity in available adsorbents.

1.2.2   Membrane technology

The membrane technology introduces the application of a thin barriers commonly known as "membrane" that selectively allow certain gases to permeate. There are various types of membranes based on materials, pore sizes and applications. The most commonly available commercial membranes are made from polymeric and ceramic materials. Two different mechanisms have been proposed in separating components from gaseous mixtures using membrane technology such as diffusion and pore flow (Baker, 2004). The membrane process has been widely used for hydrogen recovery from purge gases in ammonia synthesis, refinery and natural gas dehydration as well as acid gas removal from natural gas. The use of membrane technology also offers a few advantages such as membranes are usually compact and lightweight, and the process requires low

maintenance cost.   However, high capital cost and low performance of membrane systems for bulk CO_2 removal make the use of membranes restricted. The presence of CO_2 in feed stream may cause swelling on the membrane pores which would no longer act to selectively separate the components from gas mixture. In addition to this, the membrane systems also have problems to withstand high operating conditions of temperature and pressure (Baker, 2004).

1.2.3   Cryogenic methods

Cryogenic separation processes are commonly used with the objective to liquefy and purify the gases at very low temperature. The working principle of this separation method is based on freezing point difference of each constituent of feed gas mixtures. Even though the cryogenic method has good economics for bulk gas separations with $CO_2 > 10\%$, this method is rarely applied as the separation of gaseous mixture as it is greatly influenced by the composition of its each component (Mc Kee, 2002). The use of cryogenic method for natural gas sweetening, could be more advantageous as liquid CO_2 is recovered which is easy to transport and requires no more energy for compression. However, the main disadvantage of cryogenic separation is its high energy consumption mainly required for the refrigerant compressor. This process also requires the removal of water and other condensable gases before the gas stream is cooled in order to avoid their freezing and eventual blockage of process equipments. Moreover, an additional separation is required at sweetening stage since about 10% of hydrocarbon components are also present together with CO_2. These two additional separation steps bring upon extra cost and contribute to overall high cost of installations (Mc Kee, 2002).
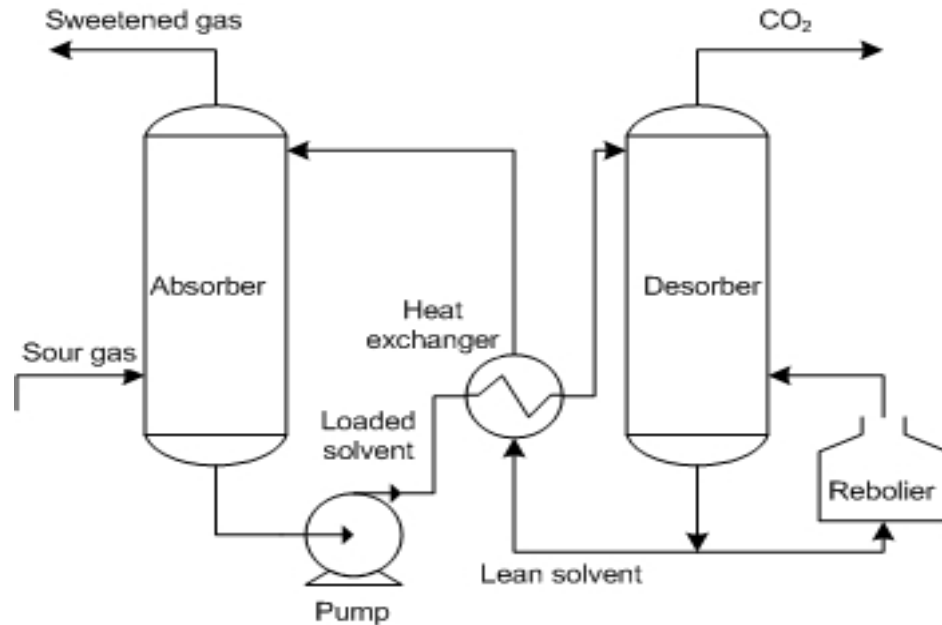
1.2.4   Absorption

Absorption is a basic chemical engineering unit operation which is probably the most established technique for gas separation processes. This process may be defined in which, atoms, molecules, or ions of one substance enter into the bulk phase of another substance. In other words, we can say that absorption is basically a process where molecules of one

phase (gas) are taken directly into another phase (liquid). Since the foundation of modern industry until the present time, absorption of gases in liquids has been of great interest to chemical and process engineering (Zarzycki and Chacuk, 1993). The major advantage of using absorption is its flexibility of absorber to handle wide range of feed rates. The absorption systems may be classified into physical absorption i.e., without any chemical reaction and chemical absorption.

In physical absorption, the dissolved gas develops weak interactions with solvent which helps in the recovery of solvents through desorption i.e., removal of gas from a liquid solution. Typical examples of physical absorption include ammonia in water and hydrocarbons in oil. In chemical absorption, the absorbed substances undergo chemical reactions with the solvents which help to achieve high loadings but on the other hand leading to excessive energy consumption to recover solvents. In many technologically important processes, the chemical absorption is used instead of the physical process, e.g. absorption of carbon dioxide using alkanolamines such as monoethanolamine (MEA) diethanolamine (DEA) and N-methyldiethanolamine (MDEA). Figure 1.1 shows a typical process flow diagram for a CO_2 absorption plant, which includes the gas absorbtion section (absorber) as well as solvent regeneration section (desorber).

The basic operation of the process starts when a feed gas containing CO_2 is introduced at the bottom of absorber which interacts with solvent flowing counter currently across the column. The CO_2 lean gas (sweetened gas) proceeds up through the absorber whereas at the bottom, CO_2 rich liquid (loaded solvent) is collected and pumped to the top of desorber for solvent regeneration. The loaded solvent on its way to desorber also exchanges heat with CO_2 lean solvent to improve the process economics. The CO_2 loaded solvent travels down in the desorber against the upward flow of its vapor mixture generated from reboiler. The vapor stream picks up more CO_2 from loaded solvent while travelling through the desorber and leaves out at the top. The two main factors which can greatly improve the performance of absorption process are solvent characteristics and flexible design of absorber/desorber to with stand wide range of operating conditions.

Figure 1.1: A schematic diagram for a simplified absorption-desorption unit used to remove CO_2 from sour natural gas (Ref: M. M. Mshewa, 1995)

1.3 Solvents

There is a wide range of solvents which are used for different seperation processes and can be classified based on their origin (organic/inorganic) and intrinsic charateristics (physical/chemical). Some of the most commonly used solvents for CO_2 absorption process are illustrated in Figure 1.2 along with a new class of solvents known as ionic liquids.
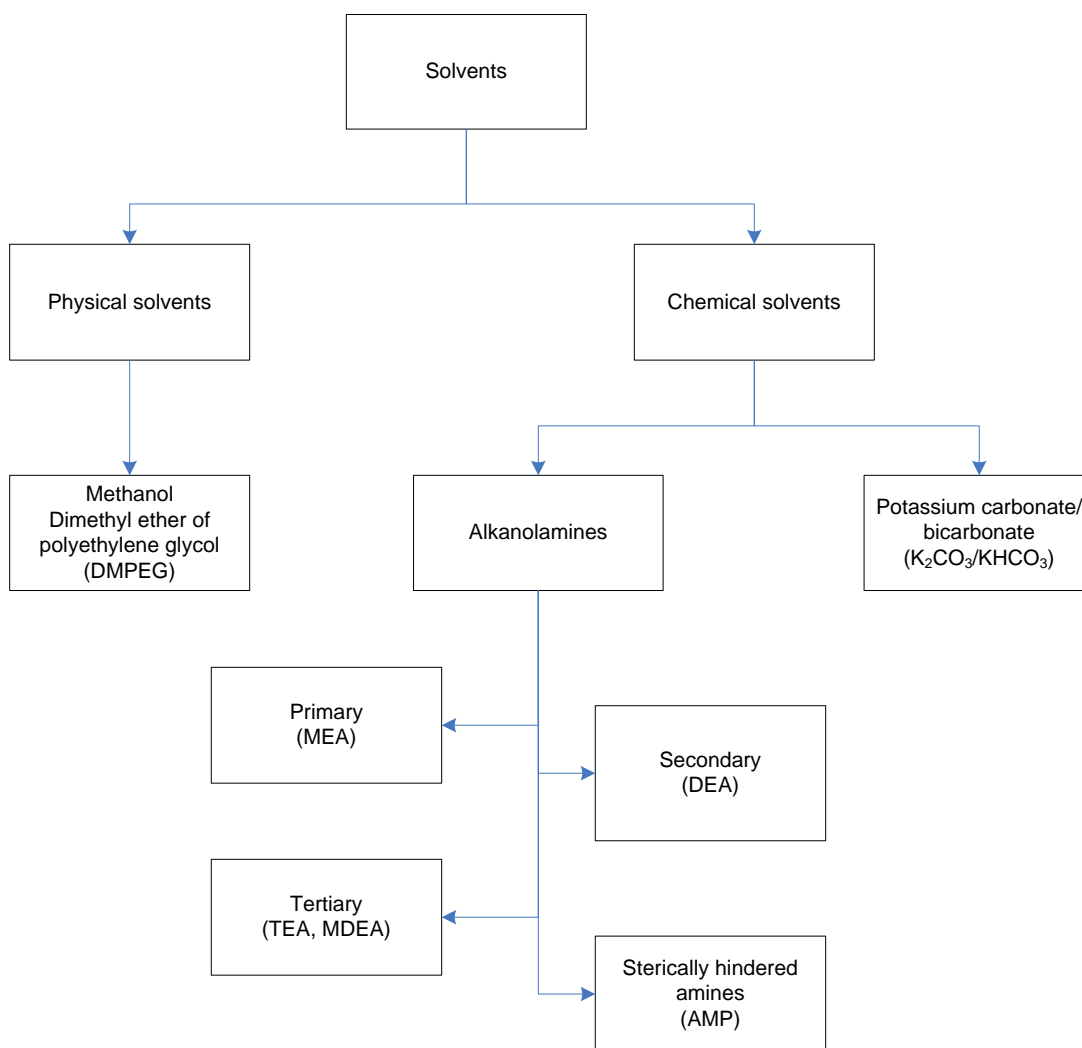
Figure 1.2. Various types of physical, chemical solvents and ionic liquids.

1.3.1 Physical solvents

Physical solvents are usually organic and highly polar in nature. The solubility of acid gases such as CO_2 in these solvents is considered to be directly proportional to the partial pressure of target gas in feed stream. The physical solvents appear to be more cost effective when acid gas impurities constitute a considerable fraction of the total gas stream. Moreover, these solvents may be more economical when the extreme purity of treated gas is not required. As mentioned above, physical solvents do not undergo chemical reactions. Therefore, there are fewer chances for the formation of intermediates

or any kind of by-products and easiness of regeneration. Physical solvents can be regenerated by a mere reduction in system pressure which is economical as compared to high thermal energy required for chemical solvent recovery. In Table 1.1, some of the physical solvents used in industry are given along with the commercial processes in which these solvents are utilized.

Table 1.1. Physical solvents used in commercial separation processes.

Physical solvents	Trade names (Liscensor)
Methanol (CH_3OH)	Rectisol (Lurgi)
N-methyl-2-pyrrolidone (NMP)	Morpysorb
N-formylmorpholine (NFP)	Purisol (Lurgi)
Propylene carbonate (PC)	Fluor solvent (Fluor Daniel)
Di-methyl ether of Propylene glycol (DMPEG)	Selexol (Union Carbide)
Tri-butyl phosphate (TBP)	Estassolvan (IFP/Uhde)

Refs: Kohl and Riesenfeld (1979), Henni A., 2002.

The main disadvantage of using physical solvents could be attributed to their potential of low vapor pressure which makes them highly volatile. As mentioned above most of the physical solvents are organic in nature and are categorized as highly volatile organic compounds (VOCs). Therefore, the use of these solvents leads to their excessive losses when applied for the treatment of gases at high operating pressures. Moreover, physical solvents may also absorb some of the major components (hydrocarbons) of the natural gas which is being treated for acid gas removal. On the other hand, this tendency of physical solvents to absorb hydrocarbon gases may be advantageous depending on the objective of the process (Shah, 1989). In other words, physical solvents can be used in processes which involve the removal of hydrocarbons from gas mixtures.

The cost and efficiency of any physical absorption process greatly depends on physical properties of the solvent utilized. The density, viscosity, surface tension and vapor pressure of solvents are the most important physical properties that have to be considered in evaluating an existing solvent or designing a new solvent. There is a significant effect

of these properties on the size of absorption equipment and the operating cost of the process (Baker et al., 1991). Most of the solubility characteristics which are considered for the selection of solvents are: high selectivity and thermal stability, reasonable vapor pressure to sustain against high pressure requirements, less affinity for light hydrocarbons and low energy consumption for regeneration procedures. Unfortunately, most of the known physical solvents used to date do not fulfill the above mentioned criteria. Therefore, in the design and development of absorption process, a compromise could be made between the physical and solubility characteristics of the solvents.

1.3.2   Chemical solvents

Chemical solvents effectively remove acid gases from feed gas mixture through a classical acid-base reaction between the target gas and solvent. In this way, chemical solvents can attain high loading gas capacity even with low partial pressure of treated gas. The most commonly used chemical solvents are aqueous solutions of alkanolamines which are made by reacting ammonia with a number of alcohol molecules. These ammonia derivatives can be subdivided into three different classes depending on the number of substituent groups on the nitrogen atom. These include primary alkanolamines (MEA) in which one hydrogen atom of the ammonia molecule is replaced by an ethanol group, secondary alkanolamines (DEA) in which two ethanol groups are present in the molecular backbone and trertiary alkanolamines (MDEA) in which all hydrogen atoms have been replaced by either alkyl or alkanol groups. Some of the developed commercial processes using alkanolamine solutions of specific concentrations are shown in Table 1.2.

Table 1.2: Chemical solvents (Alkanolamines) used in commercial separation processes.

Aqueous alkanolamines	Concentration (wt. %)	Trade names (Liscensor)
Monoethanolamine (MEA)	20-35	ECO-amine (Fluor Daniel)
Diethanolamine (DEA)	20-30	SNPA-DEA
Diglycolamine (DGA)	40-60	ECO-amine (Fluor Daniel)

Ref: Henni A., 2002.

All types of aqueous alkanolamine solutions exhibit different behaviors when come in contact with CO_2 due to their molecular structure. Primary and secondary alkanolamines form carbamate species during reaction with CO_2 according to the following overall reaction:

$$2Am + CO_2 \rightleftharpoons AmH^+ + AmCOO^- \tag{1.1}$$
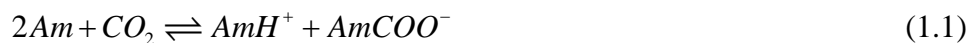
Aqueous solutions of tertiary amines do not form carbamates when react with CO_2 and the reaction of ternary amines with CO_2 is considered a hydrolysis catalyzed reaction as follows:

$$Am + CO_2 + H_2O \rightleftharpoons AmH^+ + HCO^{-3} \tag{1.2}$$
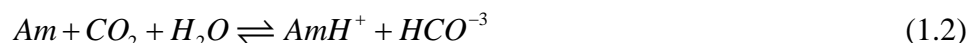
Recently, the addition of a primary or secondary alkanolamines as an activator to aqueous MDEA solutions became a subject of great interest to many researchers working on CO_2 removal from sour natural gas. The rationale of using these aqueous ternary blends is based on the ability to take the advantages of both types of amines i.e., to obtain high rates of CO_2 absorption with lower heat requirements for regeneration of solvents. Most recently, another activator has been introduced in the industry which is a cyclic di-amine known as piperazine (PZ). A general mechanism for the influence of activator in aqueous amine solution on the CO_2 solubility was initially proposed by Astarita et al. (1981) which is represented as follows:

$$CO_2 + activator \rightleftharpoons Intermediate \tag{1.3}$$

$$Intermediate + OH^- \rightleftharpoons Activator + HCO^{-3} \tag{1.4}$$

The gas treatment process using PZ activated MDEA aqueous solution was patented by BASF in early 80s (Appl et al., 1982) and it has proven to be a successful solvent for the bulk removal of carbon dioxide. Over the past decade most attention was paid towards exploring the kinetics and mechanism of adding PZ in aqueous MDEA solutions. The

most important information for an optimal design and operation of an absorption unit is the thermodynamic equilibrium and solution characteristics along with mass transfer related issues i.e., hydrodynamics and kinetics. However, the information available in the literature on CO_2 absorption in PZ activated MDEA solutions is limited to atmospheric and low pressure operating conditions.

1.3.3   Ionic liquids (ILs)

Ionic liquids (ILs) are generally defined as 'molten salts' having melting temperature lower than $100^{o}C$, considering the boiling point of water as standard. Most of the ILs are 'liquid at room temperature' and are commonly known as room-temperature ionic liquid (RTILs). Most of the liquids with which we are familiar are molecular e.g., water, ethanol, and benzene whereas ILs are solely comprised of ions i.e., organic cations and organic/inorganic anions (Wilkes, 2002). A large number of ILs can be synthesized due to the possibility of varying alkyl chain length of cations and obtaining different combinations for cations and anions. It has been estimated that approximately 10^{18} (one quintillion) ILs can be made if their binary and ternary combinations are included (Brennecke and Maginn, 2001). Although there are various options to obtain new types of ILs, the true algorithm of finding a perfect combination of IL for a particular application is still to be explored. Across the world, scientists and engineers are exploring ILs with new combinations of ions and predicting physical and thermodynamic properties from their structure (Rogers and Voth, 2007).

The classification of ILs is generally based on the types of cations, some of the examples of these common classes are given in Figure 1.3. These classes include imidazolium, quaternary ammonium, pyrrolidinium and pyridinium. The anions are indicated by X^- such as tetrafluoroborate $[BF_4]$, hexafluorophosphate $[PF_6]$, bis(trifluoromethylsulfonyl) imide $[(CF_3SO_2)2N]$ or $[Tf_2N]$, triflate $[CF_3SO_3]$, acetate $[CH_3CO_2]$, trifluoroacetate $[CF_3CO_2]$, dicyanamide $[(CN)2N]$, nitrate $[NO_3]$, chloride $[Cl]$, bromide $[Br]$, or iodide $[I]$. The imidazolium based ILs with anions; $[BF_4]$, $[PF_6]$ and $[Tf_2N]$ are the most widely studied solvents in the field of separation processes specifically for CO_2 removal

(Husson-Borg et al., 2003; Byung-Chul and Outcalt, 2006; Shiflett and Yokozeki, 2007; Shin et al., 2008). Above all, the extensively investigated IL for CO_2 solubility study is 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$ (Shiflett and Yokozeki, 2005). Currently, much attention is being paid towards the synthesis of new ILs which could have great potential to absorb large amounts of carbon dioxide.
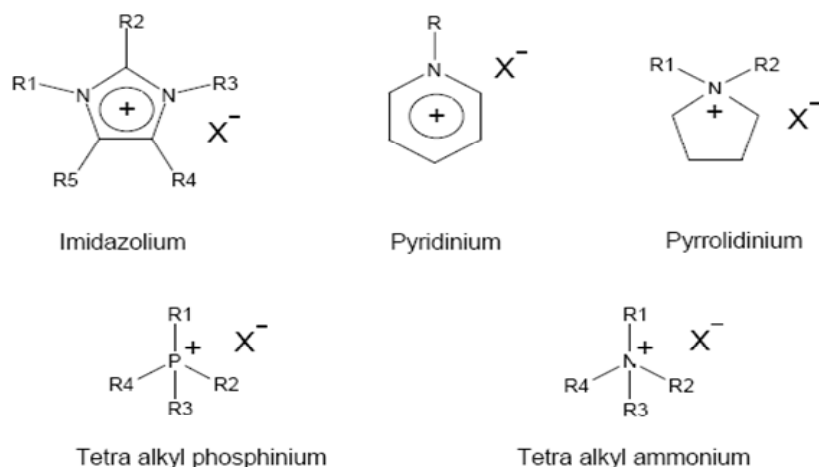
Figure 1.3: Schematic examples for different classes of ILs based on the type of cations with varying alkyl chain length.

[R = (methyl, ethyl, butyl, hexyl, octyl, or decyl) and X^- are anions = $[BF_4]$, $[PF_6]$, $[Tf_2N]$, $[CF_3SO_3]$, $[CH_3CO_2]$, $[CF_3CO_2]$, $[(CN)2N]$, $[NO_3]$, $[Cl]$, $[Br]$, $[I]$ etc.]

The selection of various types of cations and anions in making ILs serves to 'tailor' the peculiar properties of these solvents for a particular application. Therefore, ILs are also known as 'designer solvents' as their physicochemical properties can easily be tuned by combining various types of anions or cations. Researchers have shown that adjusting the structure of either the anion or the cation can have large effects on many properties including melting points, viscosities, densities, gas and liquid solubilities (Seddon et al., 2000; Anthony et al., 2001 and 2002). Ionic liquids have received much attention both from the industrial and academic communities due to their unique properties such as wide liquidus range, negligible vapor pressure and high thermal stability. A major advantage of using ILs over the traditional solvents is their negligible volatility which decreases the

risk of solvent loss to the atmosphere, suggesting that ILs could be inherently benign than the traditional organic solvents.

1.4   Problem statement

The composition of CO_2 in natural gas varies widely depending on the geological locations where it is produced as mentioned in Section 1.1.1. The presence of CO_2 in natural gas has several disadvantages including the lowering calorific value, corrosion of pipelines and process equipments. This problem would persist until CO_2 is partially or completely removed from natural gas prior to being sent to downstream for its utilization in various processes. Thus, it is commercially important and environmentally desirable to remove CO_2 from natural gas. Mostly, the removal of CO_2 from natural gas is performed through absorption process using physical or chemical solvents at atmospheric or low pressure conditions i.e., 1-2 bar. This leads to high energy consumption for reducing natural gas exploration pressure i.e., 70-100 bar to atmospheric pressure. After the removal of CO_2 from natural gas at low pressures, additional energy is required for recompression of treated gas for transmission purposes. Therefore, there is a great need to design and develop an absorption process for the bulk removal of CO_2 from natural gas at its exploration conditions i.e., low temperature and high pressure (LTHP). The knowledge of thermophysical properties of solvents is also essential for the rational design of gas absorption units. The introduction of new solvents with unique properties and generating gas liquid equilibrium (GLE) data using pure and binary mixtures of CO_2 and CH_4 at LTHP conditions is currently a key issue. However, most of the experimental solubility data is available at low pressures and using single/pure gases, which could not be used in the design and development of high pressure absorbers.

1.5   Research objectives

The potential application of imidazolium based ILs for bulk removal of CO_2 from natural gas at its exploration conditions in comparison to existing alkanolamine solvents was investigated. A summary of main objectives of the present research are as follows:

- To determine the thermophysical properties including density, isobaric coefficients of thermal expansion, viscosity, surface tension, refractive index and thermal stability of solvents such as aqueous MDEA solutions, aqueous PZ solutions, aqueous solutions of MDEA/PZ and imidazolium based ILs. The experimental data is then used for developing empirical correlations of all the measured properties based on their result outcomes to understand a relationship between the structure and properties of respective solvents.

- To measure experimental solubility of CO_2 in aqueous MDEA solutions, PZ activated aqueous MDEA solutions and ILs using a high pressure gas solubility apparatus and to correlate the gas liquid equilibrium solubility data through extended Henry's law constant and an equation of state to determine other thermodynamic parameters such as enthalpy, Gibbs free energy and entropy of solutions.

- To study the effect of temperature, pressure, concentration of amines and nature of ILs on the solubility CO_2 with the motive to examine the potential application of ILs for bulk CO_2 removal through a simple design of absorption/desorption process.

- To investigate the effect of CH_4 presence on the solubility of CO_2 in aqueous solutions of MDEA and ILs using binary mixtures CO_2/CH_4 with rich CO_2 contents at exploration conditions of natural gas i.e., low temperatures and high pressures.

1.6 Scope of study

The main scope of this work is to systematically investigate the basis for potential application of imidazolium based ILs to remove CO_2 from natural gas at its exploration conditions with a perspective to replace the existing conventional alkanolamines. The development of a fundamental understanding between thermophysical properties of solvents and their solubility affinity for CO_2 on the basis of experimental outcomes is

considered in the present work. This fundamental information could be extended to modify or develop a process using ILs for the separation of CO_2 from natural gas at high pressure conditions before it is sent to downstream for further processing. In the present work, thermophysical properties of aqueous MDEA/PZ solutions and ILs are experimentally measured. The performance of these solvents for bulk removal of CO_2 from feed gas stream was examined at high pressure using a static equilibrium based approach. For this purpose, first of all the physical properties of all the studied solvents have been measured and correlated. Secondly, the performance of those solvents for the separation of gases was determined by interacting them with CO_2 and its binary mixtures with CH_4 at temperatures of 303.15 K, 318.15 K and 333.15 K and pressures up to 90 bar. Finally, the CO_2 solubility potential of ILs in comparison to alkanolamines was investigated by reprocessing the recycled ILs which were obtained after desorption of CO_2 by reducing the system pressure.

1.7   Thesis layout

The layout for remaining chapters is as follows:

The main purpose of Chapter 2 is to present a detailed literature survey in the field of measuring physical properties of various solvents and their potential applications for CO_2 solubility. This chapter is divided into three main sections. In the first section the literature related to the determination of thermophysical properties of alkanolamines and ILs is summarized. In second part, a description of various techniques typically used in literature to measure gases solubility in liquids, while focusing more on the technique used in this work is included. The final part of this chapter contains the research work related to the solubility of CO_2 in the conventional solvents and ILs.

Chapter 3 presents about the listing of various materials used in this work such as solvents and gases along with their origins and purities. It also includes results for the extent of PZ solubility in water and amount of impurities present in ILs after purification. The details of all the apparatuses used in this study are also given in this chapter along with their calibration techniques and experimental procedures. It also describes the design

and specifications of high pressure gas solubility apparatus which is used to measure the solubility of CO_2/CH_4 in the solvents. It also highlights the working procedure, methodology and basis for solubility calculations to measure solubility of gases in solvents.

The analysis and results/discussion for thermophysical property measurements of all the studied solvents are presented in Chapter 4. These results include the densities, viscosities, surface tension, refractive index and thermal decomposition of aqueous MDEA solutions, aqueous PZ solutions, PZ activated aqueous MDEA solutions and ILs. The empirical correlations developed for the properties of the studied solvents based on their experimental results are also discussed. This chapter also addresses the effects of amine concentrations and anion types of ILs on their measured properties for a wide range of temperatures.

Chapter 5 focuses on the application of studied solvents for CO_2 separation systems at low temperature and high pressure conditions. The experimental results for CO_2 solubility in solvents such as aqueous MDEA/PZ solutions and imidazolium based ILs have been discussed. This chapter also covers the theory behind the gas-liquid interactions for physical and chemical absorption systems. The details for the effect of CH_4 presence on the solubility of CO_2 in aqueous MDEA solutions and ILs at total system pressures of 90 bar has been presented. The potential application of ILs in gas separation systems and its easiness for regeneration have also been elaborated by measuring the CO_2 solubility in recycled ILs. It also highlights some of important thermodynamic properties for CO_2 solubility in solvents using extended Henry's law constant and Peng-Robinson equation of state (PR-EOS) approach. Finally, in chapter 6 the conclusions of present research work are summarized and a few recommendations are made for future work.