

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a review on related research work in the field of measuring thermophysical properties of solvents and their potential application for the separation of carbon dioxide (CO₂) from natural gas. The knowledge of solvent properties such as density, isobaric coefficients of thermal expansions, viscosity, surface tension, refractive index and thermal stability are essential in providing the basic understanding for the process developments. The nature of solvents used could be organic or inorganic depending on their base components as well as the physical or chemical intrinsic characteristics. Di-methyl ether of propylene glycol also commercially known as Selexol is one of the popular physical solvents used for commercial separation processes. Among the chemical solvents such as aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA) and piperazine (PZ) are also of great interest for the removal of CO₂ from sour natural gas. The distinctive properties of MDEA such as low vapor pressure and low enthalpy of absorption have contributed to its preferential use for CO₂ removal compared to other alkanolamines. Most recently, ionic liquids (ILs) have gained some attention as potential solvents for gas separation processes due to their peculiar properties such as negligible vapor pressure, high thermal and chemical stability, wide liquidus range and high affinity for the absorption of selective gases. There are a large number of various types of ILs available, however, imidazolium based ILs with [BF₄], [PF₆] and [Tf₂N] anions have received most attention due to their potential for the removal of CO₂ from natural gas.

2.2 Thermophysical properties of solvents

The measurement of thermophysical and transport properties of solvents including density, viscosity, surface tension, refractive index and thermal decomposition to set the feasible temperature operating range plays a key role in the development and design of a separation process (Fredlake et al., 2004). The knowledge of these basic physical properties of solvents can be further used to derive other properties such as isobaric coefficients of thermal expansions and excess volumetric properties (Maham et al., 1994; Hawrylak et al., 2000). Moreover, the knowledge of physical properties of process solvents are also important for understanding the rate and mechanism of mass transfer and modeling of absorbers and regenerators as these properties greatly affect the liquid-film transfer coefficients (Al-Ghawas et al., 1989).

2.2.1 Density

Density of any substance is an important physical property which is defined as ‘mass per unit volume’. The knowledge of densities for various solvent plays a key role in developing a basic understanding for solute-solvent interactions. Moreover, the density data for binary and ternary solvent systems could be further used to calculate their excess volumetric properties which are useful for providing a basic understanding of their molecular interactions. There are various empirical correlations to determine volumetric properties of binary and ternary solvents such as Redlich-Kister equation which describes the functionality of both concentration and temperature (Aguila-Hernández et al., 2001).

The density measurements for pure MDEA using various types of pycnometers have been performed with wide variation in the uncertainty of measured values (Al-Ghawas et al., 1989; Wang et al., 1992; Li and Shen 1992; Paul and Mandal 2006a). However, the densities of pure MDEA were measured using a densimeter (DMA 45, Anton Paar) with high accuracies of $\pm 3 \times 10^{-2} \text{ kg.m}^{-3}$ (Henni et al., 2000; Aguila-Hernández et al., 2001). The densities for binary mixtures of MDEA + water with concentrations 10, 20, 30, 40 and 50 (wt.%) has been investigated using Gay-Lussac pycnometers (Al-Ghawas et al.

1989; Rinker et al., 1994). Most recently the densities of pure MDEA and aqueous MDEA solutions i.e., MDEA + water have been reported at four different temperatures i.e., 295 K, 308 K, 318 K and 333 K using a densimeter (DMA 4500, Anton Paar) with an accuracy of $\pm 5 \times 10^{-2} \text{ kg.m}^{-3}$ (Pouryousefi and Idem, 2008). Recently, the addition of PZ as an activator in aqueous MDEA solutions to enhance its performance of as absorbent has gained widespread attention. The densities of aqueous PZ solutions and aqueous MDEA + PZ solutions have been measured at specific concentrations used for acid gas solubility studies (Derks et al., 2005 and 2008; Samanta and Bandyopadhyay, 2006; Paul and Mandal, 2006b).

Most of the published work related to the density measurements of alkanolamines lacks in obtaining data points for a wide range of temperature and use of apparatus with high reliability and precision. In general, a decrease in the density of pure and aqueous MDEA solutions has been observed with an increase in temperature. Moreover, the density of MDEA + water increased with an increase in MDEA concentration. Although there is a considerable work reported in literature, the availability of density data for binary and ternary systems of aqueous solutions of MDEA/PZ is limited to the specific temperatures and concentrations.

Huddleston et al. (2001) reported the densities of $[\text{C}_4\text{mim}]$ based ILs with different anions such as $[\text{Cl}]$, $[\text{I}]$, $[\text{BF}_4]$, $[\text{PF}_6]$ and $[\text{Tf}_2\text{N}]$ at temperature 298 K. The main motive of their study was to investigate the effect of anions on the densities of ILs having a common cation. They found an increase in the density of IL with an increase in molar mass of its anion. Pereiro et al. (2007) studied the effect of increase in alkyl chain length of cations on the densities of ILs. For this purpose they measured the densities of $[\text{C}_4\text{mim}]$, $[\text{C}_8\text{mim}]$ and $[\text{C}_{12}\text{mim}]$ based ILs with a common anion i.e., $[\text{PF}_6]$ at temperatures ranging from 273.15 K to 343.15 K. They observed that the densities of ILs slightly decrease with an addition of each $(-\text{CH}_2)$ group to the alkyl chain length of IL cation. They also showed that the density of all studied ILs decrease with an increase in temperature. Holbery and Seddon (1999) investigated imidazolium based ILs with $[\text{BF}_4]$

anion and concluded that the density of ILs decrease linearly with increasing temperature but at a rate less than that for molecular organic solvents.

In general, the ILs are associated with varying contents of some impurities such as water and chloride. The water contents present in the ILs are either due to ineffective drying after their preparation or due to absorption from the atmospheric air and chloride contents come during ion exchange synthesis step especially in imidazolium based ILs. Seddon et al. (2000) investigated the influence of water and chloride contents of ILs on their physical properties such as density and viscosity. They concluded that the density and other physical properties of imidazolium based ILs is significantly affected due to the presence of these impurities. Therefore, it is of utmost importance to assess and report the purity of ILs along with their density data. However, in most of the research work, the density measurements of ILs are demonstrated without mentioning their impurities.

2.2.2 Viscosity

Apart from density, viscosity is another important physical and transport property of fluids. The viscosity of a fluid may be simply considered as a 'direct measure of its internal friction' i.e., the fluid tends to oppose any dynamic change in proportion to the applied shearing force. The dynamic viscosity of fluids is generally reported as viscosity of fluid with units of mPa.s or cP. However, kinematic viscosity ($\text{m}^2.\text{s}^{-1}$ or stokes) of fluids represents the ratio of dynamic viscosity and their densities at corresponding temperatures. The viscometers which have been used by various researchers to measure the kinematic viscosities of liquids are namely Ostwald, Cannon-Fenske, Ubbelohde and Cannon-Ubbelohde. These viscometers work on the principle of efflux time required for a liquid to flow through a U-shaped glass capillary. The dynamic viscosities of liquids can also be directly measured using a cone and plate (Brookfield viscometer) and rotational (SVM 3000, Stabinger, Anton Paar) viscometers.

The viscosity of pure MDEA has been reported by (Al-Ghawas et al., 1989; DiGuillo et al., 1992; Rebolledo-Libreros and Trejo, 2006). However, the work was restricted to

some specific temperatures. The viscosity values for binary mixtures of MDEA + water with concentrations 20, 30, 40 and 50 (wt.%) have been measured but only at four different temperatures i.e., 303 K, 313 K, 323 K and 333 K (Li and Lie et al., 1994). The viscosities of binary and ternary systems of aqueous PZ and MDEA solutions have also been reported by the same research groups who measured the densities of these solutions (Derks et al., 2005 and 2008; Samanta and Bandyopadhyay, 2006; Paul and Mandal, 2006a). Most of them found that the viscosities of aqueous MDEA/PZ solutions decrease with an increase in temperature. On the other hand, they found that the viscosity of these solutions increase with an increase in amine concentration.

Huddleston et al. (2001) presented the viscosities of [C₄mim] based ILs with a wide range of fluorinated and non-fluorinated anions at temperature of 298 K. In their results, they showed that the viscosities of ILs are two or more orders of magnitude greater than most of the traditional organic solvents (methanol, ethanol) and are more comparable to the viscosity values of typical oils (soybean oil). At any particular temperature, the viscosities of ILs seem to be more viscous than soybean oil but somewhat less viscous than glycerin (Law and Watson, 2001). In general, a decrease in viscosities of ILs has been found with an increase in temperature due to the diminishing effect on the strength of interactions between their cations and anions.

2.2.3 Surface tension

Surface tension is another important property to be considered in the design of gas separation systems such as absorption columns. The interfacial tension values of solvents greatly affect the hydrodynamics and mass transfer rate of acid gases during the absorption process. The surface tension values of solvents also help to understand the undesirable formation of foam during absorption of acid gases in solution of aqueous alkanolamines. The problem of foaming is associated with the dispersion of a gas in a liquid and depends on the characteristic and chemical structure of the components used for each system under study (Li and Lie, 1994).

The surface tension for binary mixtures of MDEA with water was measured by Rinker et al. (1994) with amine concentrations 10, 20, 30, 40 and 50 (wt.%) using a Rosano surface tensiometer. They presented only four data points for each concentrations of studied system at temperature ranging from 293.15 K to 353.15 K with interval of 20 K. They reported that the surface tension of aqueous MDEA solutions decreases with an increase in temperature and amine concentrations. Alvarez et al. (1998) measured the surface tension of pure as well as the binary mixtures of MDEA with water for a wide temperature ranging from 298.15 K to 323.15 K using a Traube stalagmometer but with specific amine concentrations with deviations in measurements less than ± 0.4 %. Recently, Águila-Hernández et al. (2007) have also measured surface tension of pure MDEA and MDEA + water with concentrations up to 50 wt.% using FTA 200 contact angle system through a pendant drop method at temperatures of 313.15 K and 333.15 K.

The surface tension measurements for aqueous PZ solutions with concentrations 4.3, 8.6, 12.9 (wt.%) were performed by Derks et al. (2005) at only two temperatures i.e., 293.15 K and 313.15 K. Paul and Mandal (2006b) reported the surface tensions of PZ activated aqueous MDEA solutions for a wide temperature range from 293 K to 323 K, however, they limited their study for the overall amine concentrations of 30 wt.%.

The surface tension measurements for [C₄mim], [C₈mim], and [C₁₂mim] based ILs with anions [BF₄], [PF₆], [Cl] and [Br] were performed by Law and Watson (2001) at temperature range of 290 K to 340 K. They correlated the experimental surface tension values of the studied ILs and suggested that a linear decrease of surface tensions with an increase in temperature. The surface tension of [C₄mim][PF₆] was investigated by a large number of researchers as it is one of the basic and most widely synthesized IL (Freire et al., 2007; Jiqin et al., 2007; Kilaru et al., 2007; Pereiro et al., 2007; Zhang et al., 2007; Ghatee and Zolghadr, 2008; Yi et al., 2008). However, a systematic investigation for the surface tension measurements of imidazolium based ILs is still limited.

2.2.4 Refractive index

The refractive index for binary mixtures of MDEA + water with specific amine concentrations have been measured by Pouryousefi and Idem, (2008) at temperatures of 295 K, 308 K, 318 K, 333 K using ATAGO FRX-5000 refractometer. They observed a linear decrease in the refractive index values of aqueous MDEA solutions with an increase of temperature. However, the values of refractive index were found to be increased with MDEA concentration in their binary mixtures with water. The refractive index data of aqueous PZ solutions and PZ activated MDEA solutions is not available in published literature.

The refractive indices of [C₄mim] based ILs with [BF₄], [Br] and [I] were presented by Kim et al. (2004) at temperature range from 293.2 K to 323.2 K using Abbe refractometer 3T (Atago Co.) with measuring accuracy of $\pm 10^{-4}$. They reported that the temperature effect on refractive index of ILs is almost negligible as in case of [C₄mim][BF₄], the refractive index decreased from 1.4227 to 1.4172 when a temperature was raised from 293.2 K to 323.2 K. However, they observed that the refractive index values are highly dependent on the type of IL anion i.e., refractive index values were found to be in decreasing order of effect of [BF₄], [Br] and [I]. The refractive index of [C₆mim][Tf₂N] has been measured by Pereiro et al. (2006) at temperatures between 288.15 K to 318.15 K with an interval of 5 K. They reported that the refractive index values of studied IL using an automatic refractometer (ABBEMAT-HP Dr. Kernchen) with high precision of $\pm 10^{-5}$. However, the information related to the impurities which could be associated with these ILs is missing in the literature which is an obstacle to comment on the reliability of data.

2.2.5 Thermal stability

The knowlegde of thermal stability of solvents is extremely crucial for the design of an absorption and regeneration units in gas separation processes. The solvents, which have high thermal stability, could be utilized within a wide range of temperature conditions due to their minimum risk of losses and decompositions. The degradation analysis on 50

wt.% aqueous MDEA solution has been investigated using a gas chromatograph (GC) and gas chromatograph-mass spectrophotometer (GC-MS) by Chakma and Meisen, (1988). The compounds which they found in a partially degraded MDEA are: methanol, ethylene oxide, trimethylamine, ethylene glycol, 2-(dimethylamino)ethanol, 1,4-dimethylpiperazine, *N*-(hydroxyethyl) methylpiperazine, triethanolamine, and *N,N*-bis(hydroxyethyl) piperazine. The samples of partially degraded aqueous MDEA solution were obtained by a reaction of known volume of MDEA solution with CO₂ in an autoclave at temperature 453 K.

Later, Chakma and Meisen (1997) extended their work to understand the mechanism of reaction between CO₂ and aqueous MDEA solutions with concentrations ranging from 20 to 50 wt.%. They obtained the degraded samples by reacting aqueous solutions of MDEA with CO₂ in autoclave at temperatures ranging 373 K to 473 K and gas partial pressures up to 42.4 bar. For the analysis of degraded samples of MDEA, they used the same approach as adopted by Chakma and Meisen, (1988). They compared the kinetics of MDEA degradation with the results of Barth et al., (1984) for DEA, and concluded that MDEA degrades quite slowly than DEA under the comparable conditions of CO₂ partial pressures and reaction temperatures.

Most recently, Reza and Trejo (2006) also carried out an experimental investigation on the degradation of 30 wt.% of aqueous solutions of MDEA, DEA and AMP in the presence of CO₂ and H₂S at temperature 473 K. They also analyzed the partially degraded samples of aqueous alkanolamines using gas chromatography technique. They concluded that aqueous solutions of MDEA degrade at a slower rate than DEA under similar experimental conditions. Tokuda et al. (2005) investigated the kinetics of decomposition for 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([C₄mim][BF₄]) using thermogravimetric analyser. Their main objective was to identify the effects of contaminants on the decomposition temperatures of the studied IL. For this purpose, they added water and NH₄Cl to the IL and measured the mass loss using a constant heating rate of 10°C per minute. They found that the decomposition of the studied IL is significant decreased with an addition of contaminants up to 10 wt.%.

Although most of the alkanolamines and ILs have great potential as solvents for gas treatment processes at wide temperatures. The thermal stability and decomposition data for most of these solvents are still scarce. However, most of the published research work is related to the analysis of degraded amines or effects of contaminants in ILs with the objective to understand the kinetics of degradation mechanism.

2.3 Methods for measuring gases solubility in solvents

For the solubility measurements of various gases in solvents especially ILs, two different approaches so far have been adopted namely vapor liquid equilibrium (VLE) solubility cell and gravimetric microbalance. Among these, VLE approach has been extensively used for the solubility measurements of gases in order to gain insight into the high pressure phase behavior of various gases in solvents. The vapor liquid equilibrium approach can be further categorized into: i) Isochoric saturation technique, ii) High pressure view cell technique (synthetic method) and iii) High pressure VLE apparatus (static method). In isochoric saturation technique, a known quantity of gaseous solute is brought in contact with a pre-determined quantity of solvent at a 'constant temperature' in an equilibrium cell of known volume. The attainment of maximum gas solubility in liquid is indicated by the constant pressure above the liquid solution. The solubility of CO₂, methane, ethane and other gases in [C₄mim][BF₄] was determined by Jacquemin et al. (2006b) using isochoric saturation technique at temperature range of 283 K to 343 K at close to atmospheric pressure. However, the main disadvantage of using this technique is the regular calibration of the temperature sensors and equilibrium cell before every measurement and also the limitation of measuring gases solubility at low to moderate pressures.

In synthetic method, the high pressure view cell is partially filled with a known amount of the solvent and gas, followed by the stepwise addition of more solvent in the cell until the gas completely dissolves into the liquid phase. The vessel pressure is then decreased by withdrawing the liquid mixture stepwise until the first small stable bubble appears. The synthetic method allows for the determination of the total pressure required to

dissolve a known amount of gas in a known amount of liquid at given temperature and liquid-phase composition. Kumelan et al. (2005) and Ermatchkov et al. (2006) performed the CO₂ solubility measurements in aqueous MDEA solutions and ILs at low to moderate pressures using high pressure view cell technique with sapphire windows. Shariati and Peters (2004) conducted experiments in order to gain insight for the phase behavior of CO₂ in [C₄mim][PF₆] using two VLE equipments at very high pressures. They suggested that the static method of using VLE apparatus provides high precision for the determination of gas solubility data in various types of solvents with a wide range of temperature and pressure conditions.

The gravimetric microbalance technique works on the principle of measuring weight change of absorbent before and after its interaction with gas. The gas sorption isotherms are then obtained through the information on the measured weight change, pressure and temperature of system. The use of gravimetric approach offers several merits such as requirement of small amount of sample, easy determination of equilibrium time and easy drying/degassing of the sample. However, gravimetric method also has some serious concerns on the critical impact of buoyancy factor on the gas solubility. The solubility of gases is also affected at high pressures due to the introduction of changes in the buoyant forces, aerodynamic drag forces, balance sensitivity and volumetric expansion of samples.

2.4 Solubility of CO₂ in alknolamines

2.4.1 Introduction

The removal of acid gas impurities such as CO₂ and H₂S from gas mixtures is very important in natural gas processing, hydrogen purification, gas synthesis for ammonia manufacture and treatment for refinery-off gases. The technology which has been frequently used to remove undesired components from a gas mixture is absorption-desorption process using physical or chemical solvents. During this process, sour gas stream enters at bottom of the absorber where it is contacted with a solvent which flows

counter currently. The solvent gradually takes up more and more CO₂ and leaves the absorber at the bottom as so-called 'rich solvent' whereas the purified gas leaves the absorber at the top. The rich solvent enters at the top of desorber, where CO₂ is stripped from the solvent at high temperature. Subsequently, the regenerated solvent is fed back to the top of the absorber column, while the stripped CO₂ obtained from desorber can be further processed to make it useful for other appropriate purposes. The gas absorption takes place at low temperature and often at elevated pressure whereas the gas desorption occurs at elevated temperature and low pressure. Therefore, the equilibrium solubility measurements for the target gases need to be explored within relatively wide ranges of temperature, pressure and concentrations of solvents and gases.

The most widely chemical absorbents for CO₂ absorption are aqueous solutions of primary, secondary and tertiary alkanolamines i.e., MEA, DEA and MDEA. The use of primary and secondary amines is restricted due to the limitations for CO₂ absorption capacity i.e., maximum 0.5 mol of CO₂ per mol of amine, even though these amines offer high rate of gas absorption. Moreover, the cost of recovering these solvents is high as they form stable carbamates (reaction by products) due to their direct interaction with carbon dioxide. The tertiary amines lack the N-H bond in their structure and do not react directly with CO₂ without the formation of carbamates. The reaction of CO₂ with tertiary alkanolamines (R₃N) was initially proposed by Donaldson and Nguyen (1980) as following:



The above reaction is essentially a base-catalyzed hydration of CO₂, and the mechanism implies that tertiary amines do not react directly with CO₂. Versteeg and van Swaaij (1988) have studied the absorption of CO₂ into non-aqueous (ethanol) solutions of MDEA and found that only physical absorption occurs in non-aqueous tertiary alkanolamine systems. Their results uphold the validity of the reaction mechanism as shown in equation (2.1). The advantages of MDEA, a tertiary amine, over primary or secondary amine include its high equilibrium loading capacity i.e., 1.0 mol of CO₂ per

mole of amine and its low heat of reaction with CO₂, which leads to lower energy requirement for regeneration. Recently, the blends of primary or secondary amines (Sidi-Boumedine et al., 2004) and PZ (Samanta et al., 2007) have been introduced with tertiary amines (MDEA) as activators for the CO₂ removal from gas mixtures. These ‘activated’ amine solutions are advantageous, since they combine the high absorptive capacity of the tertiary amines with the high absorption rates achievable with primary or secondary amines.

2.4.2 Solubility of CO₂ in aqueous MDEA solutions

The solubility of CO₂ in aqueous solutions of MDEA with a wide concentration range of 10 to 50 (wt.%) at pressure close to atmosphere has been investigated by various researchers (Austgen et al., 1991; Jou et al., 1993; Xu et al., 1998; Lemoine et al., 2000; Park and Sandall, 2001; Ermatchkov et al., 2006; Benamor and Aroua, 2007). The experiments for gas liquid interactions were carried out with rate based approach to investigate system kinetics, mass transfer coefficients and reaction mechanism. The conventional alkanolamines have been frequently used for low pressure for lean-CO₂ gas streams through the chemical absorption and desorption process. However, the degree of absorption of CO₂ is limited by the fixed stoichiometry of the chemical reaction. As a consequence, the use of the chemical absorbents at low pressures for CO₂-rich gas streams lead to high solvent circulation flow rates and high energy requirements (Addicks et al., 2002).

2.4.3 Solubility of CO₂ in aqueous MDEA/PZ solutions

The addition of a primary or secondary alkanolamines such as MEA and DEA to an aqueous MDEA solution has found widespread application in the removal and absorption of carbon dioxide. The principle of such an aqueous blend of a so-called ‘activator’ with MDEA is based on attaining relatively high reaction rate combined with low heat of CO₂ absorption. However, the high volatility of MEA and DEA and formation of permanent by products such as carbamates limit their use blended with other alkanolamines.

Recently, another important effective activator i.e., PZ which is a cyclic diamine has been introduced for industrial CO₂ removal processes.

Xu et al. (1992) used a disk column to investigate the kinetics of absorption of carbon dioxide into PZ activated MDEA solutions. Further studies within the same research group included the equilibrium solubility of CO₂ (Xu et al., 1998; Liu et al., 1999) and absorption rates (Zhang et al., 2001 and 2003) into PZ activated MDEA solutions. Their experimental solubility studies were usually carried out at conditions where the molar ratio between CO₂ and PZ in solution was well over unity. Bishnoi and Rochelle (2000, 2002a, b) performed a more fundamental study in which they firstly reported the individual kinetics of CO₂ with PZ and reported CO₂ equilibrium data in aqueous PZ solutions. Besides the literature mentioned above, there are also some studies which are reported on the kinetics between piperazine and CO₂ (Seo and Hong, 2000; Sun et al., 2005) and on the equilibrium solubility of CO₂ in PZ activated MDEA solutions (Ali and Aroua, 2004; Jenab et al., 2005). Most of the information available in the literature on CO₂ absorption in PZ activated MDEA has been carried out at atmospheric or moderate pressure conditions. However, the CO₂ equilibrium solubility data in these solvents is still scarce at high pressure conditions for pure CO₂ as well as for binary mixtures of CO₂ and methane.

2.4.4 Solubility of CO₂ in aqueous MDEA solutions using binary mixtures of CO₂/CH₄

The removal of CO₂ from natural gas using alkanolamines has been the most widely used method on commercial scale. However, in the available literature, the CO₂ solubility data studied as its binary mixtures with CH₄ solubility is very scarce. Addicts et al. (2002) determined the vapor-liquid equilibrium data for binary gas system (CO₂ + CH₄) in 35 and 50 wt.% of aqueous MDEA solutions at pressures up to 200 bar at temperatures of 313.15 K and 353.15 K. The phase equilibrium of the studied system was measured using a variable-volume static cell. The vapor phase was analyzed for CO₂ and CH₄ contents with an assumption that negligible amount of MDEA present in vapor phase. However, the presented CO₂ solubility data is restricted to maximum 20 mol% concentration of

CO₂ and only three solubility data points were measured at equilibrium pressures of 100, 150 and 200 bar.

Recently, Huttenhuis et al. (2007) presented the experimental solubility data for CO₂ in aqueous MDEA solutions with concentrations of 35 and 50 (wt.%). They used the binary mixture of CO₂ and methane and kept the total system pressures of 6.9, 34.5 and 69 bar. They performed the CO₂ solubility experiments in a stirred tank reactor and observed that the solubility of CO₂ is substantially affected with an increase in methane partial pressure. However, their reported solubility data for CO₂ is limited to only two temperatures i.e., 283 K and 298 K. Although they measured the solubility of CO₂ using its binary mixtures with methane, however, their study is restricted to low partial pressures of CO₂ whereas the high system pressure was obtained by the addition of CH₄ as make up gas.

2.5 Solubility of gases in ILs

2.5.1 Introduction

Ionic liquids (ILs) are the novel class of designer solvents which have great potential to replace the conventional organic (physical and chemical) solvents due to their unique and interesting properties. Some of the unique properties of ILs are: negligible vapor pressure, non-toxicity, non-flammability, and high chemical and thermal stability. Ionic liquids are mainly composed of organic cations (imidazolium, pyridinium, tetraalkylphosphonium, pyrrolidinium quaternary ammonium etc.) and organic/inorganic anions (halide, nitrate, acetate, trifluoroacetate, triflate, alkylsulfate, tetrafluoroborate, hexafluorophosphate). The number of estimated ILs could be raised as high as 10¹⁸ (one quintillion) with various combinations of cations and anions which makes them one of the largest known compounds in chemistry (Brennecke and Maginn, 2001).

The interest in the study of ILs has exponentially increased in the recent past due to their wide potential applications (Joglekar et al., 2007; Keskin et al., 2007; Meindersma et al.,

2007). The room temperature ionic liquids (RTILs) are getting significant attention for a large variety of applications in many areas that span from pure sciences to industry, because of their below room temperature melting points (Kim and Kim, 2003). In most of the separation processes, the highly volatile conventional organic solvents contribute significant losses and contamination to the environment. However, these negative impacts caused by the loss of reaction products in to the environment could be easily prevented using ILs which are nonvolatile solvents. Moreover, the ILs can also be recycled without vapor contamination. This is the main reason why ILs are considered as an environmental friendly alternative to the harmful organic solvents.

The imidazolium based ILs have generated a great deal of interest over the past few years as most of them are used as solvents in organic synthesis (Welton, 1999) and separations of gases (Holbrey and Seddon, 1999) as well as liquid-liquid extractions (Huddleston et al., 1998). A large number of ILs can be synthesized through the combinations of various cations and anions. It has been noted that many substrates are less or insoluble, and some reactions of solutes give poor results or do not take place at all, in certain cation-anion combinations of ILs. The difference in the affinity of ILs for selective solutes solely depends on their nature of cation-anion interactions and polarity. A significant barrier to the use of ILs is the absence of understanding on how the structure of the IL affects its physical properties and solvent strength. Since polarity and polarizability are the simplest indicators of solvent strength, organic solvents are frequently classified on their ability to dissolve and stabilize dipolar or charged species.

The solvent strength and polarity of four imidazolium and pyridinium based ILs have been measured using two different fluorescent probes which indicate that these liquids are more polar than acetonitrile but less polar than methanol (Aki et al., 2001). Later, Muldoon et al. (2001) studied the polarity and nucleophilicity for a range of ILs using two solvatochromic dyes and found that the polarity of ILs appeared to be largely cation controlled, while the donor strength is entirely anion dependent. Moreover, Dong et al. (2006) found that the cations and anions are connected with each other to form a

hydrogen-bonded network when they were investigating the cation-anion ion-pairs of some imidazolium based ILs with anions [Cl], [Br], [BF₄], and [PF₆].

2.5.2 Solubility of CO₂ in ILs at low pressure

The solubility study of gases in ILs at low pressure conditions of gas has received the least focus from researchers as most of the ILs undergo physical solubility. However, to predict the efficient use of ILs in an industrial process, it would also be useful to first determine their ability for gases solubility at low pressures. The experimental solubility of CO₂ and hydrocarbon gases such as ethane, ethane, propane, propene and butane in [C₂mim][EtSO₄] and [C₄mim] based ILs with anions [BF₄], [PF₆], [NO₃] at close to atmospheric pressure was studied by Camper et al. (2004) and Camper et al. (2005). They reported a small increase in CO₂ solubility with an increase in alkyl chain length. However, they found that the type of anion has significant effect on the solubility of gases. They also found that the solubility of CO₂ in all the studied ILs is much higher than hydrocarbon gases. Jacquemin et al. (2006a,b) has reported the experimental solubility of various gases such as carbon dioxide, methane, ethane, oxygen, nitrogen, hydrogen, argon and carbon monoxide in two ILs i.e., [C₄mim][BF₄] and [C₄mim][PF₆] at temperatures between 283 K and 343 K and close to atmospheric pressures. They also found that the CO₂ solubility is the most soluble gas with mole fraction solubilities of the order of 10⁻² as compared to other gases. Their results for gases solubility in imidazolium based ILs were found to be in good agreement with that of Camper et al. (2004) and Camper et al. (2005).

2.5.3 Solubility of CO₂ in ILs at high pressure

The solubility of CO₂ in imidazolium based ILs at pressures higher than atmospheric has been investigated by Liu et al. (2003), Kamps et al. (2003), Kim et al. (2005), Kumelan et al. (2006) and Chen et al. (2006). In many cases, the experiments conducted uses the IL ([C₄mim][PF₆]) since it is one of the initial ILs which were synthesized with an objective of air and water stable compounds. All the researchers observed that the CO₂ solubility in

ILs increases almost linearly with an increase in gas pressure, which is a practically typical behavior reflecting physical solubility. They also found a decrease in CO₂ solubility in ILs with an increase in temperature, which is similar to that obtained for common organic solvents. Marsh et al. (2004) reported that a reasonable agreement in the Henry's constant values for CO₂ solubility in various ILs exists at low temperatures of the published work, however, a significant difference in solubility values still occur at higher temperatures.

2.5.4 Effect of cation and anion of ILs on CO₂ solubility

The influence of alkyl chain length of cation on the solubility of CO₂ in imidazolium ILs with anion [BF₄] was determined by Chen et al., 2006, for cations: 1-butyl-3-methyl imidazolium tetrafluoroborate ([C₄mim]), 1-hexyl-3-methyl imidazolium tetrafluoroborate ([C₆mim]) and 1-octyl-3-methyl imidazolium tetrafluoroborate ([C₈mim]) at temperatures (307 to 322) K and at high pressures. They found that the CO₂ solubility increases slightly with an increase in alkyl chain length of cations from butyl to octyl. Moreover, a decrease in the density of ILs was observed with an increase in alkyl chain length for a given type of IL cation (imidazolium). Therefore, it can be concluded that the marginal increase in CO₂ solubility with increase in alkyl chain length may be due to the availability of more free volume within ionic liquids.

Aki et al. (2004) presented the experimental measurements for the solubility of CO₂ in seven ILs with common cation; 1-butyl-3-methylimidazolium ([C₄mim]) and different anions; nitrate ([NO₃]), tetrafluoroborate ([BF₄]), hexafluorophosphate ([PF₆]), trifluoromethanesulfonate ([TfO]) and tris(trifluoromethylsulfonyl)methide ([methide]) at temperatures 298 K, 313 K and 333 K and pressures to 150 bar. The CO₂ solubility was found to increase linearly with an increase in pressure and decreased with an increase in temperature for all the ionic liquids investigated. However, from the CO₂ solubility results it was found that the extent of gas solubility was highly dependent on the type of anion for all the ILs. The solubility of CO₂ in [C₄mim] based ILs with different anions was found to be in increasing order of [TfO], [BF₄], [PF₆] and [methide] at all

temperatures. Therefore, it may be believed that the amount type of anions for imidazolium based ILs, is one of the contributing factors for the difference in their CO₂ loading capacity. The solubility measurements for CO₂ in various ILs with different anions has also been reported from other leading groups in this field which further supports the key role of anions in determining the CO₂ solubility in ionic liquids (Cadena et al., 2004; Shiflett and Yokozeki, 2005; Kumelan et al., 2006; Muldoon et al., 2007).

2.5.5 Solubility of CO₂ in ILs using binary mixtures of CO₂/CH₄

Ionic liquids (ILs) have received growing attention as alternate solvents for gas separation processes due to their reasonable affinity for selective gases. The experimental solubility data for most of the gases in ILs has been determined using pure gases, which could not be directly used for the design and development processes to separate undesired gas from a gas mixture. Kim et al. (2007) measured the solubility of pure CO₂ as well as its mixtures with nitrogen in 1-hexyl-3-methylimidazolium tri(bisfluoromethylsulfonyl) imide at temperature 298.15 K and pressure up to 10 bar. The solubility of CO₂ using its binary mixture with N₂ in the studied IL was found to be lower (0.141) mole fraction than its solubility as pure gas (0.205) mole fraction at 298.15 K and 8.2 bar. Thus it can be fairly concluded that the solubility of a target gas in solvents is significantly affected due to the presence of a second component of a gas mixture. Therefore, the use of experimental solubility data for pure gases could have detrimental effects for the design and development of a gas separation process treating gaseous mixtures.

2.6 Summary

From the foregoing brief literature survey, it can be observed that the knowledge of thermophysical properties of solvents is extremely important for recognizing their nature which further helps to develop an understanding about their potential applications in gas separation processes. The physical properties of aqueous MDEA solutions, aqueous PZ solutions and PZ activated MDEA solutions have been measured by various researchers for a wide temperature ranges, however, most of these measurements are limited in terms

of solvent purity, equipments with low precision, and specific amine concentrations. A few researchers have attempted to measure physical properties of recently introduced imidazolium based ILs. However, the [C₄mim] based ILs with [BF₄] and [PF₆] anions are widely studied among all ionic liquids. Most of the reported data for properties of ILs lacks the information of impurities associated with these ILs and also large discrepancies exist specially in their viscosity and surface tension values. Although much attention has been paid to density and viscosity measurements of solvents, however, the reported data is widely scattered. Moreover, the data for other important properties of solvents such as surface tension, isobaric coefficients of thermal expansions, refractive index and thermal stability is quite scarce.

The aqueous MDEA/PZ solutions find their widespread applications for CO₂ removal from natural gas and other refinery off gases through chemical absorption/regeneration process at low pressures. However, for the CO₂ removal from upstream natural gas, a large amount of energy is consumed for its recompression before sent to downstream. Moreover, the available CO₂ solubility data in alkanolamine solvents is widely scattered and also restricted to low pressure conditions. Most of the researchers have performed the CO₂ solubility measurements using pure CO₂ and the solubility data for its binary mixtures with CH₄ are very much limited. Therefore, the CO₂ solubility data obtained using pure carbon dioxide at low pressures can not be directly applied for the development of an absorption process for bulk removal of CO₂ from natural gas at its exploration pressure i.e., 100 bar.

Most recently, a novel class of solvents such as ILs has attracted various researchers in the field of selective separation of gases due to having negligible vapor pressure. The unique properties of ILs would lead them to be utilized as potential solvents in CO₂ separation processes to replace the conventional alkanolamine solvents. In the present research work, a fundamental and systematic study has been carried out to investigate the potential application of imidazolium based ILs for CO₂ removal from natural gas in comparison to aqueous MDEA/PZ solutions. For this purpose initially the thermophysical properties of both kinds of the studied solvents were experimentally measured and

correlated. The performance of these solvents for CO₂ solubility using pure CO₂ and its binary mixtures with CH₄ has been studied using a static equilibrium solubility cell at temperature ranging from 303.15 K to 333.15 K and at pressures up to 90 bar.