

CHAPTER 5

SOLUBILITY OF GASES IN SOLVENTS

5.1 Introduction

The solubility of pure carbon dioxide (CO_2) in two types of solvents was experimentally measured at three different temperatures of 303.15 K, 318.15 K and 333.15 K at pressures up to 60 bar. The two types of solvents used in present research work are: (i) Aqueous solutions of alkanolamines i.e., *N*-Methyldiethanolamine (MDEA) and Piperazine (PZ) as chemical solvents, and (ii) Imidazolium based ionic liquids (ILs) as physical solvents. Moreover, the solubility of CO_2 and methane (CH_4) using their binary mixtures i.e., CO_2/CH_4 : 60/40 (B_{64}) and 40/60 (B_{46}) by volume percent was also measured in the above mentioned solvents at different temperatures and pressures up to 90 bar. The experimental solubility of gases in all the studied solvents was measured using a high pressure gas solubility cell with an equilibrium based approach. For this purpose, the gases were brought in contact with solvents in the solubility cell and allowed to attain an equilibrium saturation pressure at a given temperature. The analysis of gaseous mixture phase was performed using a gas chromatograph before and after each set of absorption measurement. The process was repeated to determine gases solubility data for different temperatures at high pressure. The effect of MDEA concentrations and the type of IL on the extent of gases solubility in the studied solvents has also been evaluated. The effect of operating parameters such as temperature and pressure on the solubility of CO_2 and CH_4 in all the solvents has also been analyzed. In addition, the effect of adding PZ as an activator in aqueous MDEA solutions on the CO_2 solubility has been investigated at the studied range of temperature and pressure conditions. The performance of all the studied solvents has been examined with perspective to their CO_2

removal tendency at the exploration conditions of natural gas fields i.e., low temperature and high pressures (LTHP).

5.2 Solubility of CO₂ in solvents

The solubility of CO₂ in aqueous MDEA solutions i.e., MDEA + water, PZ activated aqueous MDEA solutions i.e., MDEA + PZ + water and imidazolium based ILs was experimentally determined using a static high pressure equilibrium apparatus. The operating parameters for CO₂ solubility in all the studied solvents were maintained keeping in view of exploration conditions of natural gas at upstream i.e., low temperature and high pressures. The effect of MDEA and PZ concentrations in their aqueous solutions, and the type of IL anion on the solubility of CO₂ has also been one of the key issues considered in the present work.

5.2.1 MDEA + water

The solubility of CO₂ has been experimentally measured in aqueous solutions of alkanolamines i.e., MDEA + water at temperatures 303.15 K, 318.15 K and 333.15 K and pressures up to 60 bar. For this purpose, two concentrations of aqueous MDEA solutions i.e., 32.28 wt.% or 4 molal (moles.kg⁻¹) and 48.80 wt.% or 8 molal (moles.kg⁻¹) have been used. The experimental CO₂ solubility data for both concentrations of aqueous MDEA solutions are presented in Tables B-1 and B-2 of Appendix B respectively.

5.2.1.1 Pressure and temperature effects on CO₂ solubility

The effect of pressure on the solubility of CO₂ in 4 and 8 (molal) aqueous MDEA solutions is presented in Figures 5.1 and 5.2 respectively as solubility isotherms at temperatures of 303.15 K, 318.15 K and 333.15 K. It was found that the equilibrium solubility of CO₂ in both aqueous MDEA solutions increased with an increase in the gas partial pressure for all the investigated temperatures. The overall solubility behavior at high pressures reveals that the total amount of CO₂ dissolved in aqueous MDEA

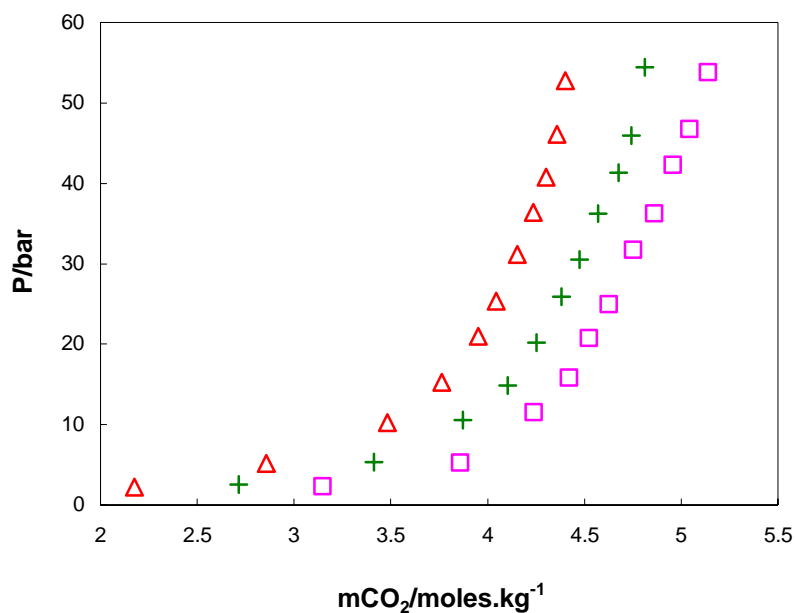


Figure 5.1: Effect of pressure on CO_2 solubility in aqueous MDEA solution.
[for 4 molal at temperatures of 303.15 K (\square), 318.15 K (+) and 333.15 K (Δ)]

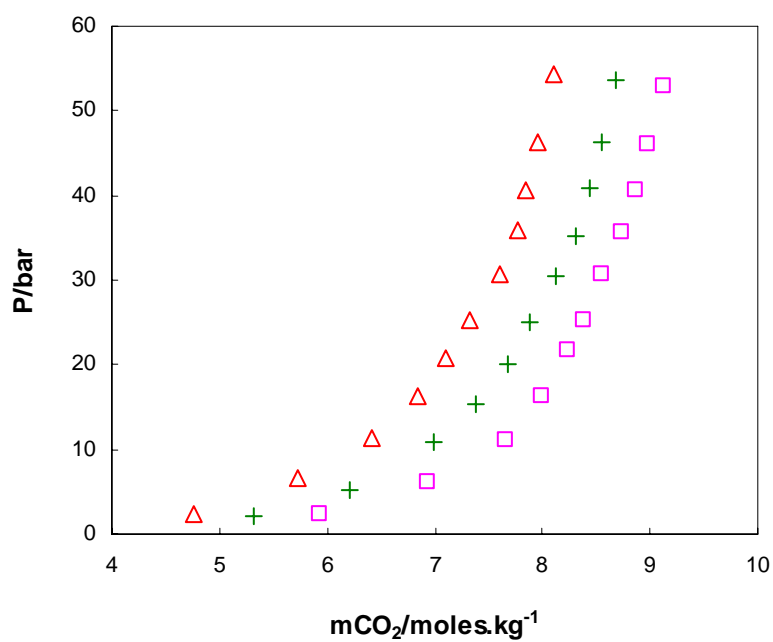


Figure 5.2: Effect of pressure on CO_2 solubility in aqueous MDEA solution.
[for 8 molal at temperatures of 303.15 K (\square), 318.15 K (+) and 333.15 K (Δ)]

solutions is the combination of chemical and physical absorption. However, the solubility of CO₂ in both concentrations of aqueous MDEA solutions take place predominantly by chemical reactions at low to moderate pressure regions and physically at high pressure gas loadings.

It is interesting to note that the amount of CO₂ dissolved in both aqueous MDEA solutions is almost equal to their molal (moles.kg⁻¹) concentrations at low to moderate pressures. For example, the amount of CO₂ dissolved in 4 molal aqueous MDEA solution reaches to 3.858 moles.kg⁻¹ at P = 5.24 bar and the amount of CO₂ dissolved in 8 molal aqueous MDEA solution reaches to 7.986 moles.kg⁻¹ at P = 16.37 bar. Thus it is believed that the high amount of CO₂ solubility attained in aqueous MDEA solutions at low to moderate pressures could be due to the dissolution of CO₂ in nonvolatile ionic form of solvents such as hydroxide (OH⁻), hydronium (H₃O⁺) and protonized MDEA (MDEAH⁺), through chemical reactions (Silkenbäumer et al., 1998). However, as soon as the amount of CO₂ dissolved in both concentrations of solvents surmounts the overall molality of amine solution, the CO₂ solubility curve increases steeply which was indicated for system pressure beyond 10 bar. This shows that CO₂ is no more chemically absorbed in the solvents but is dissolved through physical means i.e., as a neutral CO₂ molecule in aqueous amine solution. Later, the solubility curve straightens out which is an indication of the maximum loading capacity of the gas in respective solvents. Similar behavior of CO₂ solubility (qualitatively) has been observed in both aqueous MDEA solutions for the other two investigated isotherms i.e., 318.15 K and 333.15 K.

The effect of temperature on the solubility of CO₂ in both concentrations of aqueous MDEA solutions i.e., 4 and 8 (molal) is presented in Figure 5.3. For this purpose, the CO₂ solubility data for both concentrations of aqueous MDEA solutions on molality scale obtained at low (10 bar), medium (25 bar) and high (50 bar) pressure regions, is plotted versus the whole range of studied temperature. It was observed that the CO₂ solubility in both concentrations of aqueous MDEA solutions decrease linearly with an increase in temperature for the whole range of studied system pressure.

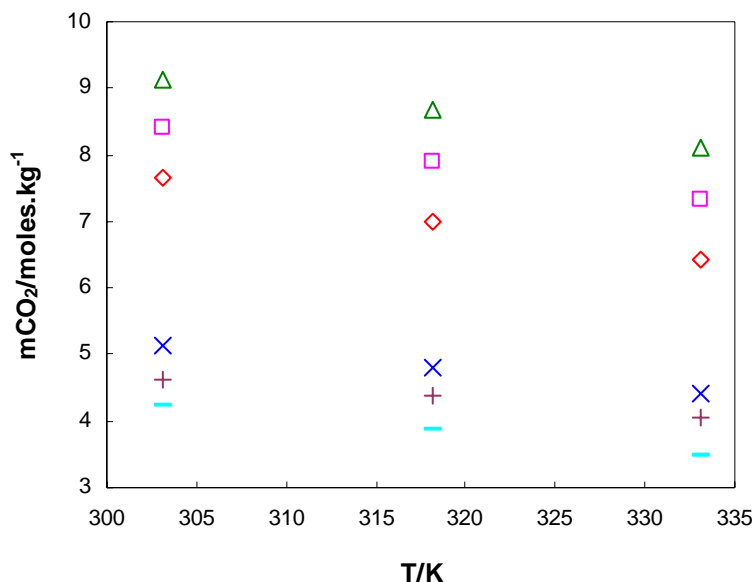


Figure 5.3: Effect of temperature on CO₂ solubility in aqueous MDEA solutions.

[for 4 molal at pressures of 10 bar (—), 25 bar (+), 53 bar (×); for 8 molal at pressures of 10 bar (◇), 25 bar (□) and 53 bar (△)]

5.2.1.2 Effect of MDEA concentration on CO₂ solubility

The solubility of CO₂ was measured in two different concentrations of aqueous MDEA solutions i.e., 4 and 8 (molal) to investigate the effect of amine concentration on gas solubility. A comparison for CO₂ solubility data in both concentrations of aqueous MDEA is shown in Figure 5.4 at different temperatures and pressures. It can be observed from Figure 5.4 that the solubility of CO₂ in aqueous MDEA solutions is highly dependent on their concentrations. For example, the solubility of CO₂ in 8 molal aqueous MDEA solution appeared to be 44% higher than its solubility in 4 molal solution at T = 303.15 K and P = 54 bar. The maximum CO₂ removal using 4 and 8 molal aqueous MDEA solutions was found to be 5.138 and 9.132 (moles.kg⁻¹) respectively at temperature of 303.15 K and for the whole pressure range studied in the present work.

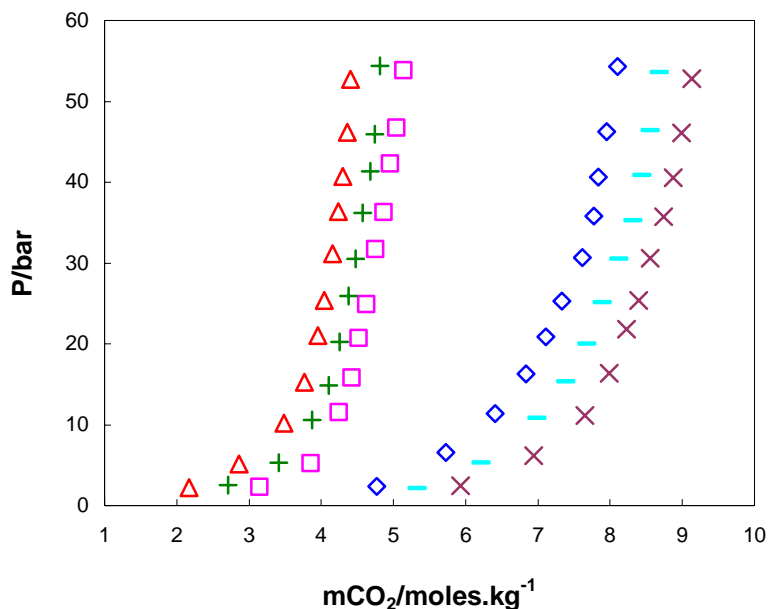


Figure 5.4: Comparison of CO₂ solubility in two different concentrations of aqueous MDEA solutions at pressures up to 60 bar.

[for 4 molal at temperatures 303.15 K (+), 318.15 K (□) and 333.15 K (Δ); for 8 molal at temperatures 303.15 K (×), 318.15 K (—) and 333.15 K (◇)]

5.2.2 MDEA + PZ + water

The solubility of CO₂ in PZ activated aqueous solutions of MDEA has been experimentally measured at temperatures 303.15 K, 318.15 K and 333.15 K and pressures up to 60 bar. All the samples of PZ activated aqueous MDEA solutions were prepared by adding PZ at concentrations of 1.74, 5.14 and 10.35 (wt.%) in each aqueous MDEA solutions with concentrations 4 and 8 (molal) respectively. The experimental CO₂ solubility data for all concentrations of PZ activated aqueous MDEA solutions is presented in Tables B-3, B-4, B-5, B-6, B-7 and B-8 of Appendix B.

5.2.2.1 Pressure and temperature effects on CO₂ solubility

The CO₂ solubility isotherms in aqueous MDEA/PZ solutions with concentrations 32.28/1.74 and 48.80/1.74 (wt.%) at temperatures of 303.15 K, 318.15 K and 333.15 K,

and pressures up to 60 bar are illustrated in Figures 5.5 and 5.6 respectively. The CO₂ solubility isotherms for other concentrations of aqueous MDEA/PZ solutions i.e., 32.28/5.16, 32.28/10.35, 48.80/5.16 and 48.80/10.35 (wt.%) are shown in Figures B-1, B-2, B-3 and B-4 of Appendix B respectively. The trends for the solubility behavior of CO₂ in all concentrations of PZ activated aqueous MDEA solutions have been found to be very much similar to that of aqueous MDEA solutions. In general, it can be said that the major amount of total CO₂ solubility is achieved within 20 bar of the system pressure. For example, the amount of CO₂ dissolved in aqueous MDEA/PZ solution with concentration 48.80/1.74 (wt.%) at 20.21 bar is 4.741 moles.kg⁻¹ which is 90% of the total amount of gas absorbed up to 53 bar. It could be due to the fact that solubility of CO₂ in PZ activated aqueous MDEA solutions is dominated by chemical absorption.

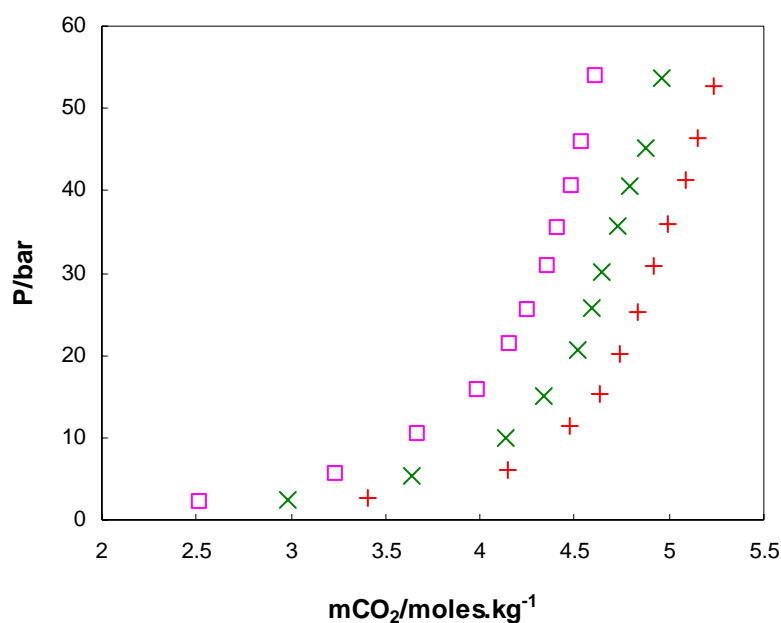


Figure 5.5: Effect of pressure on CO₂ solubility in aqueous MDEA + PZ solution.
[for 32.28/1.74 (wt.%) at temperatures 303.15 K (+), 318.15 K (x) and 333.15 K (□)]

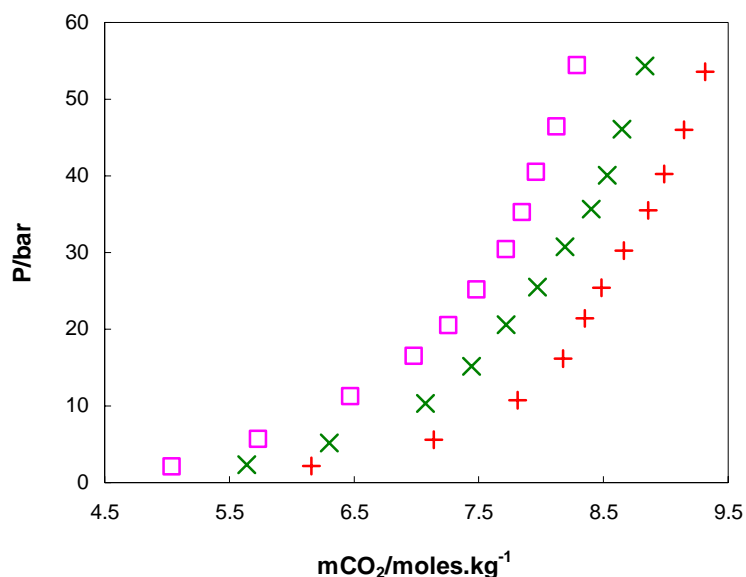


Figure 5.6: Effect of pressure on CO₂ solubility in aqueous MDEA + PZ solution.
[for 48.80/1.74 (wt.%) at temperatures 303.15 K (+), 318.15 K (x) and 333.15 K (□)]

5.2.2.2 Effect of adding PZ in aqueous MDEA solutions on CO₂ solubility

The experimental results for the overall amount of CO₂ dissolved in samples which were prepared by PZ addition with concentrations 1.74, 5.16 and 10.35 (wt.%) in aqueous MDEA solutions of 32.28 and 48.80 (wt.%), versus the total CO₂ pressure have been plotted in Figures 5.7 and 5.8 respectively at temperature 303.15K and pressures up to 60 bar. The effect of PZ addition on CO₂ solubility for both concentrations of MDEA solutions has been analyzed with a comparison of their result outcomes. The solubility of CO₂ is found to increase in both concentrations of aqueous MDEA solutions with an increase in the concentration of PZ addition. The extent of increase for CO₂ solubility by PZ addition is found to be higher in case of 32.28 wt.% of aqueous MDEA solution than in 48.80 wt.%, which means that the effectiveness of adding PZ was also found to be dependent on the MDEA concentrations. A significant increase in CO₂ solubility has been observed when PZ concentration was increased from 1.74 to 5.16 (wt.%) in aqueous MDEA solution with 32.28 wt.% concentration. Moreover, with further increase in PZ concentration to 10.35 wt.%, the extent of increase in CO₂ solubility was insignificant which could be explained due to the limiting effect of PZ concentration.

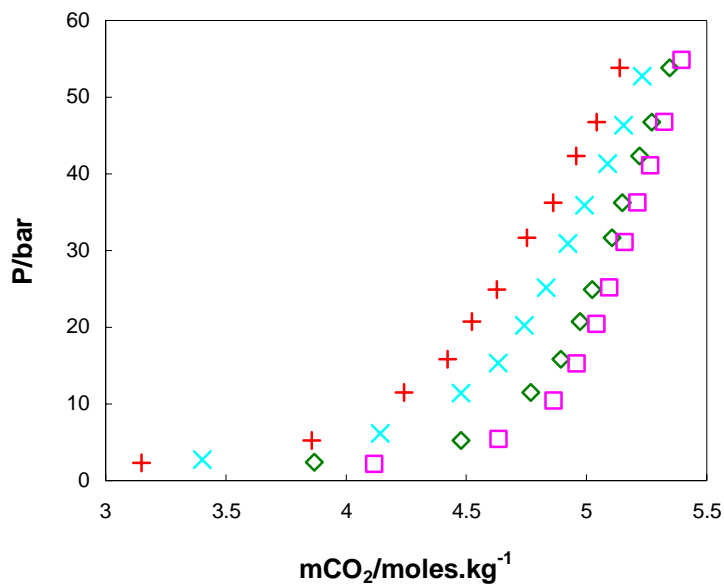


Figure 5.7: Effect of PZ addition on CO₂ solubility in aqueous MDEA solution.

[for (MDEA + water); 32.28 wt.% (+), (MDEA + PZ + water); 32.28/1.74 wt.% (x), 32.28/5.16 wt.% (◇), 32.28/10.35 wt.% (□), at T = 303.15 K and pressure up to 60 bar]

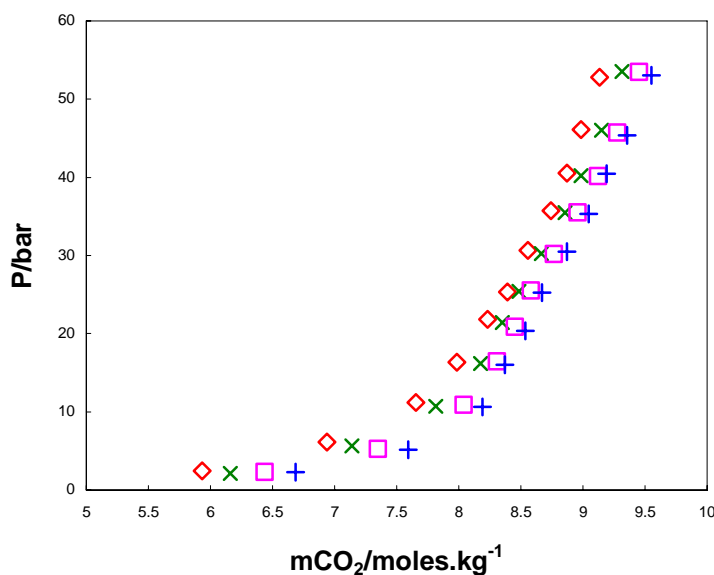


Figure 5.8: Effect of PZ addition on CO₂ solubility in aqueous MDEA and aqueous MDEA/PZ solutions.

[for (MDEA + water); 48.80 wt.% (◇), (MDEA + PZ + water); 48.80/1.74 wt.% (x), 48.80/5.16 wt.% (□), 48.80/10.35 wt.% (+), at T = 303.15 K and pressure up to 60 bar]

5.2.3 Ionic liquids (ILs)

The solubility of CO₂ was investigated in three ILs: 1-hexyl-3-methyl imidazolium tetrafluoroborate; [C₆mim][BF₄], 1-hexyl-3-methyl imidazolium hexafluorophosphate; [C₆mim][PF₆] and 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide; [C₆mim][Tf₄N] at three different temperatures i.e., 303.15 K, 318.15 K, 333.15 K and pressures up to 60 bar.

5.2.3.1 [C₆mim][BF₄]

The experimental solubility data for CO₂ in [C₆mim][BF₄] is presented in Table B-9 of Appendix B. The effect of pressure on the solubility of CO₂ in [C₆mim][BF₄] is shown in Figure 5.9 at three different temperatures i.e., 303.15 K, 318.15 K and 333.15 K. An increase in the solubility of CO₂ was observed in [C₆mim][BF₄] with an increase in gas partial pressure. As expected, the CO₂ solubility in the IL decreased with an increase in temperature. The difference in the CO₂ solubility between all the temperatures was found to be low at pressures up to 10 bar. However, the difference in CO₂ solubility between temperatures 303.15 K and 333.15 K increases up to 42% as the pressures were increased to 57 bar.

5.2.3.2 [C₆mim][PF₆]

The experimental solubility data for CO₂ in [C₆mim][PF₆] is presented in Table B-10 of Appendix B. The effect of pressure on the solubility of CO₂ in [C₆mim][PF₆] is shown in Figure 5.10 at three different temperatures i.e., 303.15K, 318.15K and 333.15K. The solubility of CO₂ in [C₆mim][PF₆] was found to increase with an increase in gas partial pressure whereas with an increase in temperature, a decrease in CO₂ solubility was observed. The CO₂ solubility difference between all the studied temperatures was found to be small at low pressures of up to 10 bar. However, the difference in CO₂ solubility between temperatures 303.15 K and 333.15 K increases up to 44% as the pressures were increased to 57 bar.

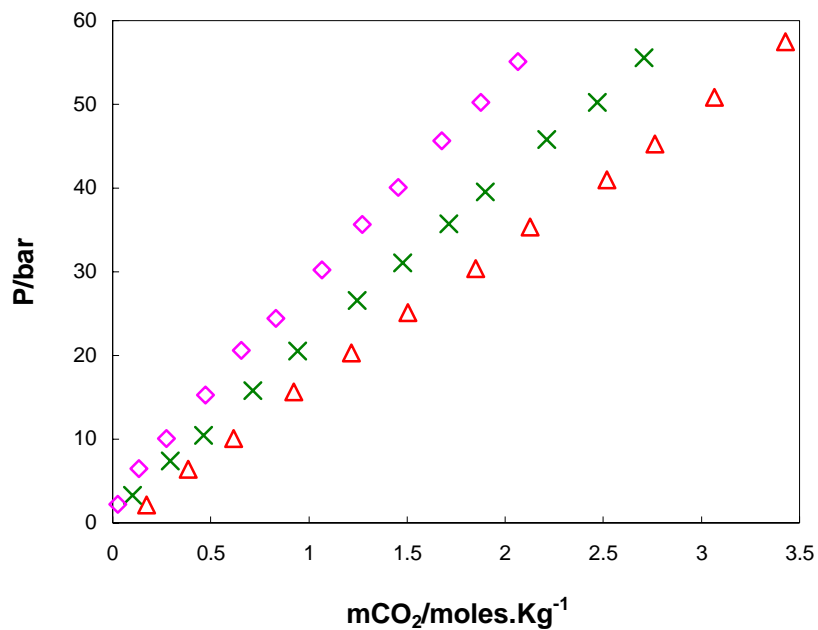


Figure 5.9: Solubility of CO₂ in [C₆mim][BF₄].

[at temperatures; 303.15 K (Δ), 318.15 K (×), 333.15 K (◇) and pressure up to 60 bar]

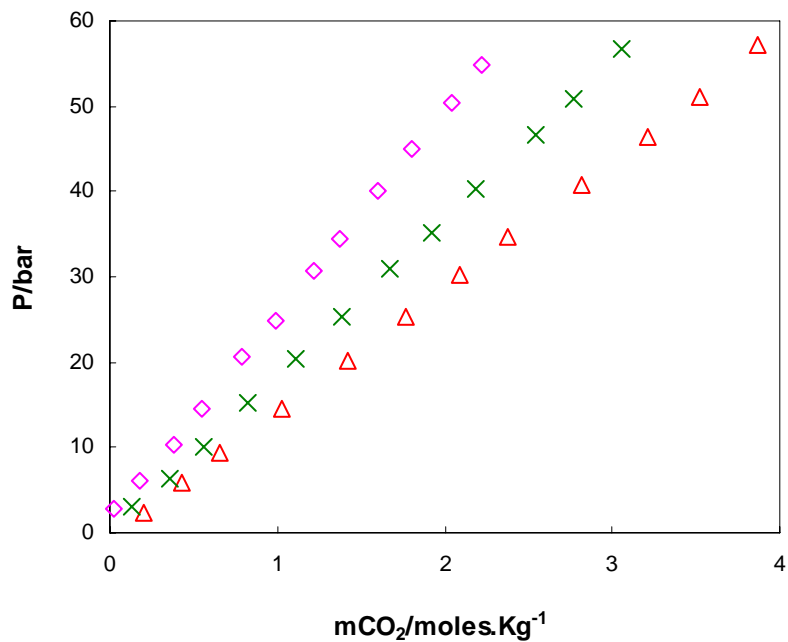


Figure 5.10: Solubility of CO₂ in [C₆mim][PF₆].

[at temperatures; 303.15 K (Δ), 318.15 K (×), 333.15 K (◇) and pressure up to 60 bar]

5.2.3.3 [C₆mim][Tf₂N]

The experimental solubility data for CO₂ in [C₆mim][Tf₂N] is presented in Table B-11 of Appendix B. The effect of pressure on the solubility of CO₂ in [C₆mim][Tf₂N] is shown in Figure 5.11 at three different temperatures i.e., 303.15 K, 318.15 K and 333.15 K. The solubility of CO₂ in [C₆mim][Tf₂N] has been found to increase with an increase in gas partial pressure whereas a decrease in CO₂ solubility was observed with an increase in temperature. The CO₂ solubility difference between all the studied temperatures is found to be small at pressures up to 5 bar. However, the difference in CO₂ solubility between temperatures 303.15 K and 333.15 K increases up to 52% as the pressures were increased to 57 bar.

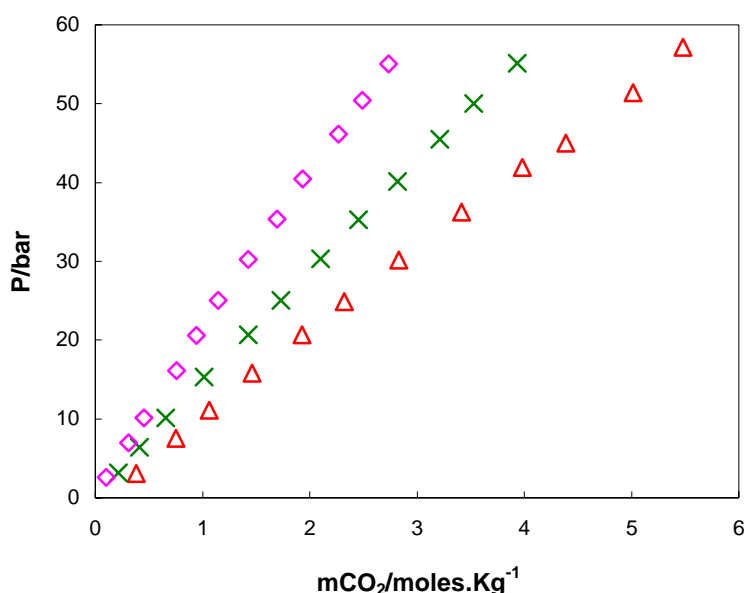


Figure 5.11: Solubility of CO₂ in [C₆mim][Tf₂N].

[At temperatures; 303.15 K (Δ), 318.15K (×), 333.15K (◇) and pressures up to 60 bar]

5.2.3.4 Pressure and temperature effects on CO₂ solubility in ILs

It is apparent from all the Figures 5.9, 5.10 and 5.11 that the solubility behavior of CO₂ in all the ILs appeared to be similar i.e., the solubility of CO₂ in the solvents increased

practically linearly with an increase in partial pressure of CO₂. This typical behavior for any gas absorption in a solvent demonstrates purely a physical solubility (Kamps et al., 2003). As expected, a decrease in the solubility of CO₂ is observed with an increase in temperature for all the three types of ILs. The CO₂ solubility data for the entire ILs exhibit a linear trend with the increase in CO₂ pressure which leads towards the mechanism of physical absorption of gas in the bulk of ILs. However, the slope of CO₂ solubility curve appears to be steeper at pressures beyond 50 bar leading towards the attainment of maximum loading capacity of CO₂ for each corresponding ionic liquid. The effect of temperature on the CO₂ solubility in all the studied ILs has been shown in Figure 5.12 at low (10 bar), medium (25 bar) and high (56 bar) pressures. A linear decrease in the CO₂ solubility in all the ILs has been observed with an increase in temperature for the whole range of studied pressure.

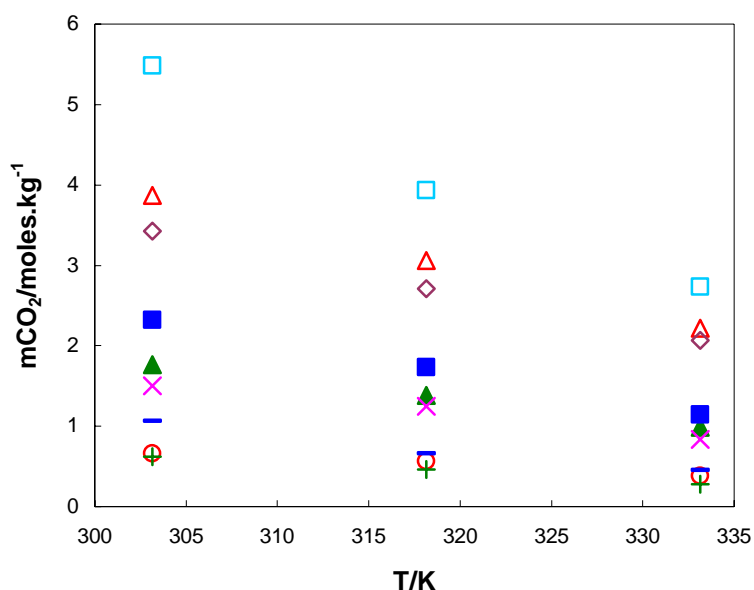


Figure 5.12: Effect of temperature on CO₂ solubility in ILs.

{for [C₆mim][BF₄] at pressures 10 bar (+), 25 bar (×), 53 bar (◇), [C₆mim][PF₆] at pressures of 10 bar (○), 25 bar (▲), 53 bar (△), and [C₆mim][Tf₂N] at pressures of 10 bar (—), 25 bar (■) and 53 bar (□)}

5.2.3.5 Effect of anions on CO₂ solubility in [C₆mim] based ILs

The effect of the type of anion on the solubility of CO₂ was investigated by comparing three fluorinated anions: [BF₄], [PF₆] and [Tf₂N] attached with 1-hexyl-3-methyl imidazolium cation of IL. The amount of CO₂ solubility in the studied ILs with different anions was found to be in decreasing order of [Tf₂N], [PF₆] and [BF₄] for all the investigated temperatures as shown in Figures 5.13, 5.14 and 5.15. In other words, it could be said that the IL with [Tf₂N] anion has a considerably higher affinity for CO₂ than ILs with anions [BF₄] and [PF₆]. For example, at T = 303.15K and P ≈ 60 bar, the solubility of CO₂ in IL with [Tf₂N] anion is 5.483 moles.kg⁻¹ or 71 mole%, which is 34% more than its solubility in [BF₄] based IL i.e., 3.428 moles.kg⁻¹ or 47 mol%. The ILs; [C₆mim][BF₄] and [C₆mim][PF₆] have shown almost same extent of solubility at low CO₂ pressures at all the investigated temperatures. However, at high partial pressures of CO₂ beyond 20 bar, the gap in the intensity of solubility trend widens between both ILs for the whole range of studied temperature. In Figure 5.13 shows that the difference in amount of CO₂ absorbed in [C₆mim][PF₆] and [C₆mim][BF₄] is higher i.e., 0.49 moles.kg⁻¹ at gas pressure of 57 bar as compared to its value i.e., 0.04 moles.kg⁻¹ at 10 bar.

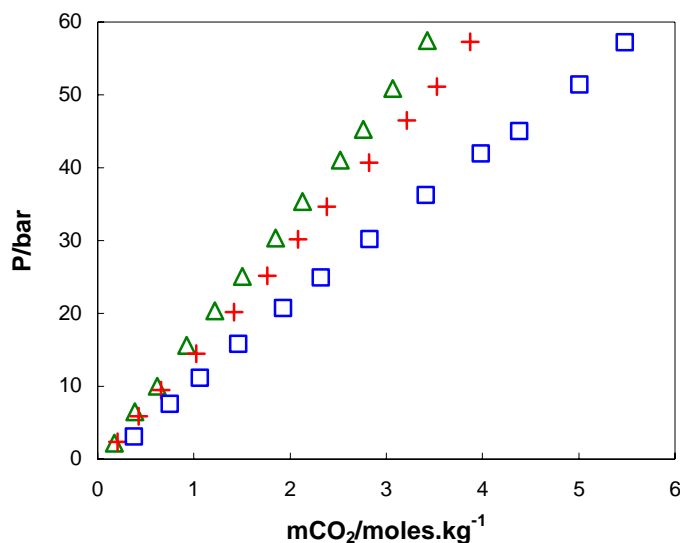


Figure 5.13: Comparison of CO₂ solubility in all ILs.

{for [C₆mim] based ILs with anions [BF₄] (Δ), [PF₆] (+), [Tf₂N] (□)] at T = 303.15 K and pressures up to 60 bar}

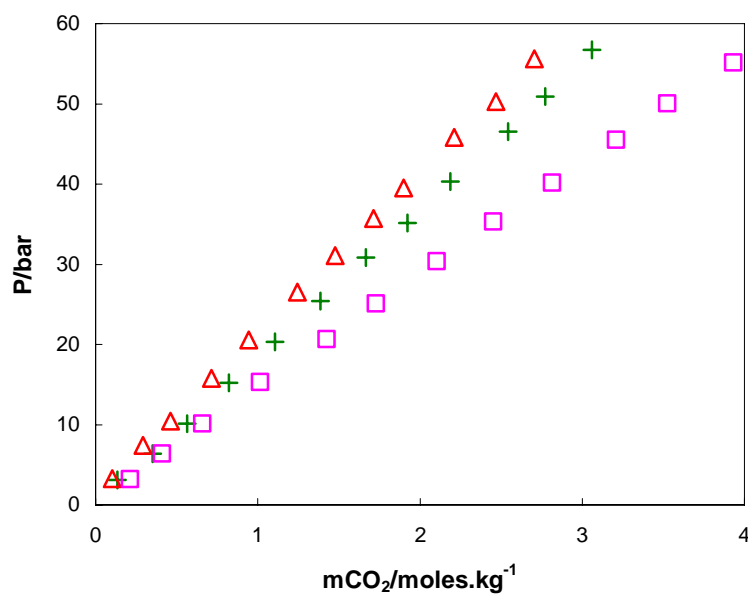


Figure 5.14: Comparison of CO₂ solubility in all ILs.

{for [C₆mim] based ILs with anions [BF₄] (+), [PF₆] (Δ), [Tf₂N] (□) at T = 318.15 K and pressures up to 60 bar}

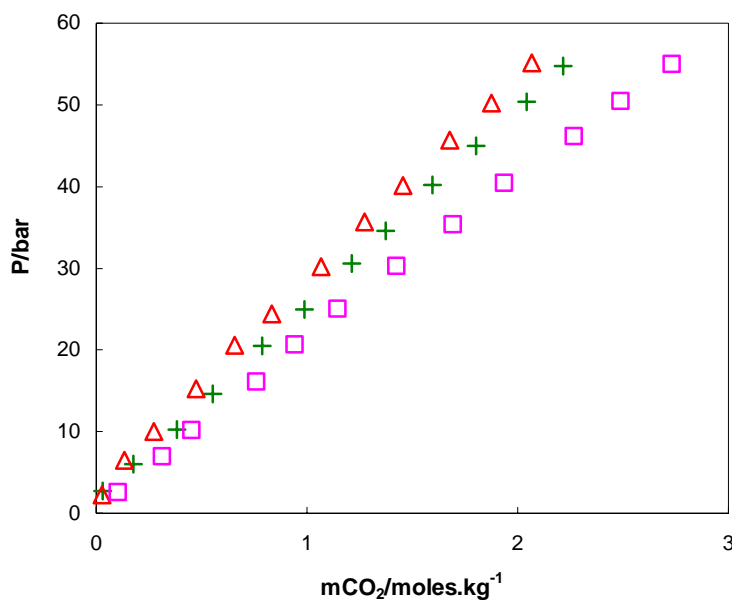


Figure 5.15: Comparison of CO₂ solubility in all ILs.

{for [C₆mim] based ILs with anions [BF₄] (Δ), [PF₆] (+), [Tf₂N] (□) at T = 333.15 K and pressures up to 60 bar}

The difference for the solubility of CO₂ among all the studied imidazolium based ILs with different types of anions can be further explained in the following sub-sections:

a) Fluorination of IL anion

In the present work, the effect of anion on the solubility of CO₂ in ILs was found to be in decreasing order of [Tf₂N], [PF₆] and [BF₄] which is in line with the increase in strength of fluorination for these anions. This observation leads to the fact that the amount of anion fluorination for imidazolium based ILs is one of the contributing factors for obtaining different extent of CO₂ loading capacity in each IL. The research work of Pringle et al. (2003) also supports the prominent effect of fluorinated anions on CO₂ solubility. They found low Henry's constant value i.e., 47 ± 6 atm for CO₂ solubility in [C₂mim] based IL with fluorinated anion ([Tf₂N]) as compared to 76 ± 8 atm with non fluorinated anion i.e., bis(methanesulfonyl)imide; [Nmes₂] at 293 K. The above mentioned postulate is further strengthened with the research work of Aki et al. (2004). They showed that the CO₂ solubility for [C₄mim] based ILs increased with an increase in anion fluorination such as [PF₆] > [BF₄] at temperature 298 K.

b) Size or molar volume of IL anion

The ILs, and more specifically room temperature ionic liquids (RTILs) i.e., ILs which are liquids at room temperature, have weak inter-ion interaction force due to large anion size. On the other hand ordinary inorganic salts have strong inter-ion coulombic force due to small size of ionic species. The low strength of cation-anion interactions of ILs contribute in providing larger 'free volume' between their ions which play a significant role in getting high values of CO₂ solubility in the ILs (Blanchard et al., 2001). Thus the anions with large sizes or molar volumes would result in obtaining high solubility of CO₂ as compared to small sized anions for a common cation based IL. The results presented in this work are in good agreement with above mentioned hypothesis i.e., the affinity for CO₂ solubility increased with an increase in anion size of imidazolium based ILs i.e., [BF₄] < [PF₆] < [Tf₂N]. Kazarian et al. (2000) analyzed the CO₂ absorbed IL samples

through ATR (attenuated total reflectance)-IR spectroscopy and concluded that the CO₂-anion interactions facilitate the IL swelling by further decreasing the anion-cation interactions. Therefore, a linear increase for CO₂ solubility in all the studied ILs on pressurization could be believed due to the swelling of ionic liquids.

5.2.3.6 CO₂ solubility comparison with available literature

The most widely studied ILs for the experimental solubility determination of various gases including CO₂ are, 1-butyl-3-methyl imidazolium; [C₄mim] based ILs with anions [PF₆] and [BF₄]. The solubility data of CO₂ in the above mentioned ILs is available in literature by different research groups at specific temperature and pressure conditions. However, the systematic investigations for the solubility data with the motive of IL potential to capture CO₂ from natural gas at high pressure and low temperature are still lacking. The solubility behavior for CO₂ in the studied ILs is compared with the available published work of different research groups in Figure 5.16 irrespective of the methodology and solubility measuring approach.

Shariati and Peters (2004) studied phase behavior of [C₆mim][PF₆] + CO₂ mixtures using an autoclave apparatus at high pressures. A good agreement in the CO₂ solubility twelve data points of this work at 303.15 K and three data points of Shariati and Peters (2004) at temperatures between 303.34 K to 303.48 K can be observed from Figure 5.16 at pressures up to 60 bar. The solubility of CO₂ in ILs investigated in the present work is in qualitative agreement with the literature. The measurement of CO₂ solubility in [C₆mim][BF₄] was done by Chen et al. (2006) using high pressure cell with gravimetric approach. They calculated the amount of CO₂ dissolved in the IL by the difference in the mass of gas cylinder after achieving equilibrium. The CO₂ solubility results of this work at 303.15 K are found to be in good agreement with the five data points of Chen et al. (2006) at 317.45 K and at pressures up to 60 bar, with maximum percent deviations of $\pm 8\%$.

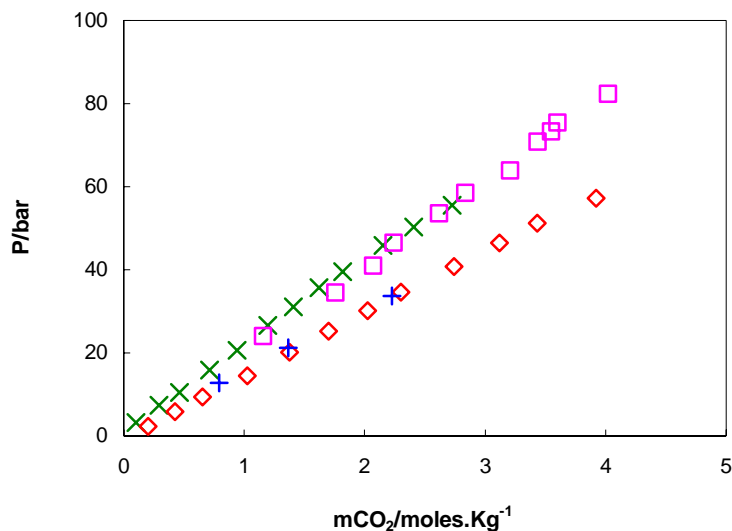


Figure 5.16: Comparison for CO₂ solubility in ILs of this work and literature at high pressures.

{for [C₆mim][BF₄]; this work (×) at 318.15 K, Chen et al. (2006) (□) at 317.45 K, For [C₆mim][PF₆]; this work (◇) at 303.15 K, Shariati and Peter (2004) (+) at (303.34 to 303.48) K}

5.2.4 Recycled ionic liquids (RILs)

The ILs; [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] which were once used for CO₂ solubility measurement, were recycled to investigate their potential capability for another run of CO₂ solubility measurement. The recycling of ILs was carried out by desorption of the CO₂ gas through depressurization followed by the application of vacuum to 0.45 bar to ensure the complete removal of CO₂ from ionic liquid. The recycled solvent samples were kept overnight in vacuum oven to ensure the removal of air bubbles prior to be utilized for their CO₂ solubility measurements.

5.2.4.1 [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N]

The experimental solubility data of CO₂ in recycled ILs: [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] is presented in Tables B-12, B-13 and B-14 respectively of Appendix

B. The effect of pressure on CO₂ solubility in recycled ILs are shown in Figures B-5, B-6 and B-7 of Appendix B at three different temperatures 303.15 K, 318.15 K and 333.15 K. The CO₂ solubility behavior in recycled ILs was found to be very much similar to the one obtained for fresh ILs.

5.2.4.2 Comparison of CO₂ solubility between ILs and recycled ILs

A comparison on the CO₂ solubility measurement between the ILs and recycled ILs is plotted in Figures 5.17, 5.18 and 5.19 for [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] respectively. The experiments were conducted at three different temperatures of 303.15 K, 318.15 K and 333.15 K. The comparative analysis of CO₂ solubility in ILs and recycled ILs reveals that there is apparently no significant difference between both sets of solubility data up to CO₂ partial pressure of 20 bar at all the investigated temperatures. However, the difference for CO₂ solubility in recycled ILs as compared to ILs was found to be more at high CO₂ partial pressures practically beyond 20 bar. The maximum decrease for CO₂ in recycled ILs as compared to ILs was found to be in case of IL with [PF₆] anion i.e., 6.8% at P = 57 bar and T = 318.15 K.

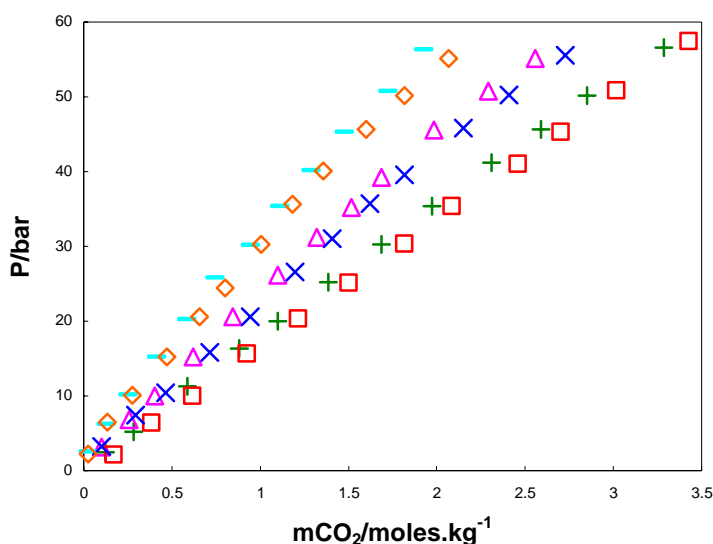


Figure 5.17: Comparison of CO₂ solubility in fresh and recycled IL; {[C₆mim][BF₄]}. [for fresh IL: at T = 303.15 K (□), 318.15 K (×), 333.15 K (◇), for recycled IL: at T = 303.15 K (+), 318.15 K (△), 333.15 K (—), at pressures up to 60 bar]

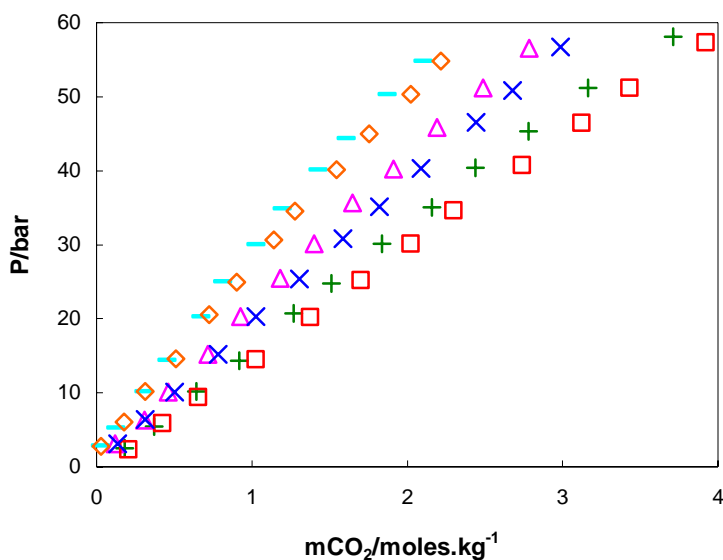


Figure 5.18: Comparison of CO₂ solubility in fresh and recycled IL; {[C₆mim][PF₆]}. [for fresh IL: at T = 303.15 K (□), 318.15 K (×), 333.15 K (◇) and recycled IL: at T = 303.15 K (+), 318.15 K (△), 333.15 K (—), at pressures up to 60 bar]

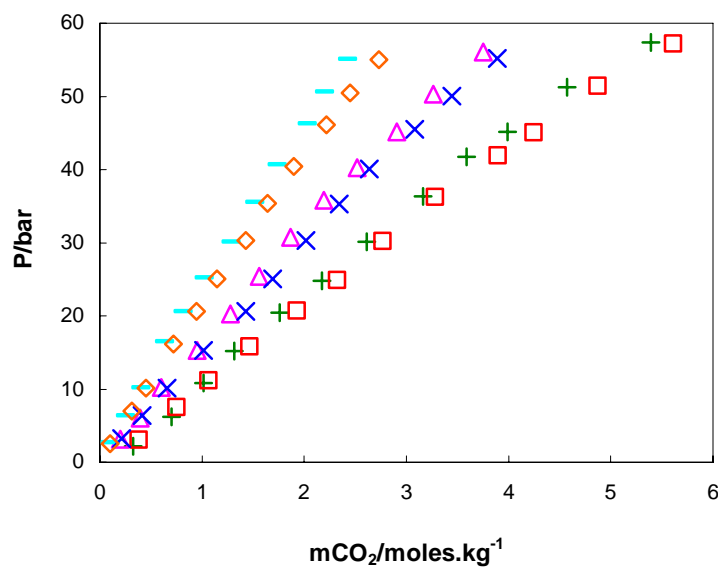


Figure 5.19: Comparison of CO₂ solubility in fresh and recycled IL {[C₆mim][Tf₂N]}. [for fresh IL; at T = 303.15 K (□), 318.15 K (×), 333.15 K (◇) and recycled IL; at T = 303.15 K (+), 318.15 K (△), 333.15 K (—), at pressures up to 60 bar]

5.3 Solubility of CO₂ and CH₄ in solvents using binary mixtures of CO₂/CH₄

The solubility of CO₂ and CH₄ in aqueous MDEA solutions with concentrations of 4 and 8 (mola), and in ILs; [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] is determined experimentally using a high pressure static equilibrium apparatus. For this purpose, two binary mixtures of CO₂/CH₄ i.e., 60/40 (B₆₄) and 40/60 (B₄₆) by volume percent were used to explore the effect of CH₄ presence on the extent of CO₂ solubility in all solvents at temperatures 303.15 K, 318.15 K, and 333.15 K and pressures up to 90 bar. The effect of temperature, pressure, amine concentration and the type of ILs on gases solubility behavior has also been analyzed from the result outcomes of experimental measurements.

5.3.1 MDEA + water

The experimental solubility data of CO₂ and CH₄ in aqueous MDEA solutions with concentrations of 4 and 8 (molal) using binary mixtures of CO₂/CH₄ i.e., B₆₄ and B₄₆, is presented in Tables B-15, B-16, B-17 and B-18 respectively of Appendix B. All the solubility measurements were performed at temperatures 303.15 K, 318.15 K, 333.15 K and pressures up to 90 bar. The solubility isotherms of CO₂ and CH₄ in both aqueous MDEA solutions for B₆₄ and B₄₆ gas mixtures are illustrated in Figures B-8, B-9, B-10 and B-11 respectively of Appendix B at temperatures of 303.15 K, 318.15 K and 333.15 K.

The equilibrium solubility of CO₂ and CH₄ in both aqueous MDEA solutions i.e., 4 and 8 (molal) increased with an increase in total pressure at all the investigated temperatures. The solubility of CO₂ and CH₄ in both aqueous MDEA solutions decreased with an increase in the temperature. In general, the CO₂ solubility trends obtained for both aqueous MDEA solutions using binary gas mixtures of CO₂/CH₄ i.e., (B₆₄ and B₄₆) as shown in Figures B-8 and B-9 of Appendix B, are similar to those which were obtained for pure carbon dioxide. The solubility of CH₄ in both aqueous MDEA solutions has shown a linear increase with an increase in total pressure of gases mixtures (B₆₄ and B₄₆).

The amount of CH_4 solubility is also found to be dependent on amine concentration as well as the partial pressure of CH_4 in gaseous mixtures as shown in Figure 5.20.

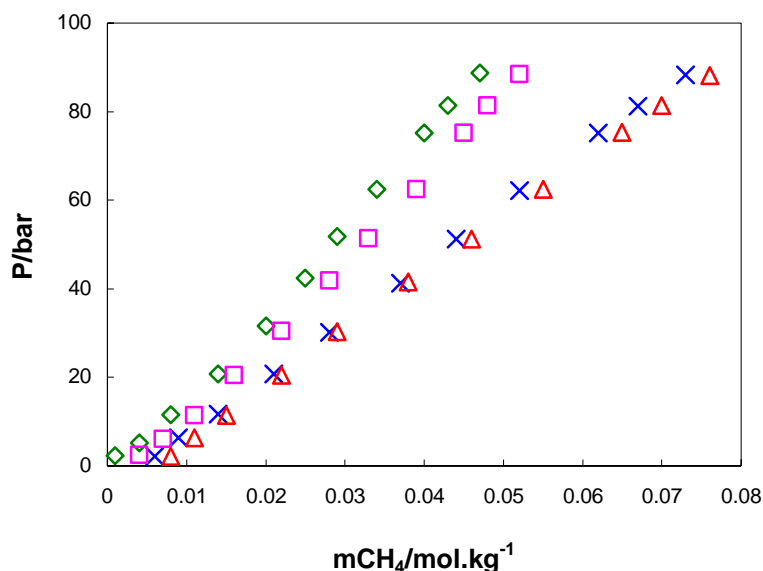


Figure 5.20: Solubility of CH_4 in aqueous MDEA solutions using binary mixtures of CO_2/CH_4 .

[for B₆₄; 4 molal (◇), 8 molal (×), for B₄₆; 4 molal (□), 8 molal (△), at T = 303.15 K pressure up to 90 bar]

5.3.1.1 Effect of CH_4 presence on CO_2 solubility

The solubility isotherm of CO_2 as pure gas and its binary mixtures with methane i.e., CO_2/CH_4 (B₆₄ and B₄₆) in aqueous MDEA solutions with concentrations 4 and 8 (molal) is shown in Figure 5.18 at temperature of 303.15 K and pressures up to 90 bar. A significant decrease for the solubility of CO_2 was observed if its binary mixtures with CH_4 were used i.e., B₆₄ and B₄₆ as compared to its solubility as pure carbon dioxide in both concentrations of aqueous MDEA solutions. However, the effect of CH_4 presence on the reduction of CO_2 solubility in aqueous MDEA solutions appears to be more in 8 molal than 4 molal. For instance, in the presence of CH_4 , the amount of decrease i.e., 2.4 moles.kg⁻¹ for CO_2 solubility in 8 molal aqueous MDEA solution, is higher than its value in 4 molal aqueous MDEA solution which is 1.7 moles.kg⁻¹ at T = 303.15 K and at

pressure of approximately 52 bar. It was also observed from that the solubility of CO₂ is further decreased with an increase in partial pressure of CH₄ i.e., CO₂ solubility in aqueous MDEA solutions using B₄₆ is lower than B₆₄. Thus it can be concluded that the solubility of CO₂ is substantially affected by the CH₄ presence in gas mixture.

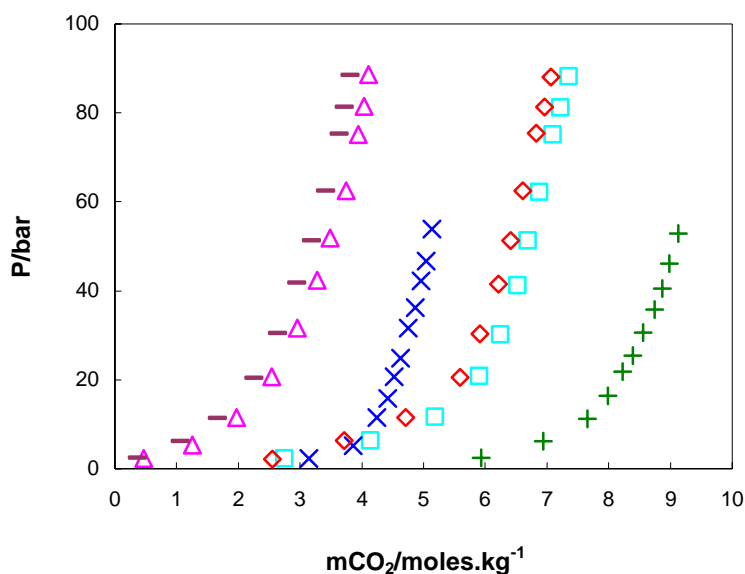


Figure 5.21: Effect of CH₄ presence on CO₂ solubility in aqueous MDEA solutions. [for pure CO₂; 4 molal (×), 8 molal (+), for binary mixtures of CO₂/CH₄ (B₆₄); 4 molal (Δ), 8 molal (□), for binary mixtures of CO₂/CH₄ (B₄₆); 4 molal (—), 8 molal (◇) at 303.15 K]

5.3.2 [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N]

The experimental solubility data of CO₂ and CH₄ in [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] using B₆₄ is presented in Tables B-19, B-20 and B-21, and for B₄₆ presented in Tables B-22, B-23 and B-24 of Appendix B respectively. The experiments were conducted at temperatures of 303.15 K, 318.15 K, 333.15 K and pressures up to 90 bar. The solubility isotherms of CO₂ and CH₄ using B₆₄ and B₄₆ are illustrated in Figures B-12 and B-13 for [C₆mim][BF₄], B-14 and B-15 for [C₆mim][PF₆], B-16 and B-17 for [C₆mim][Tf₂N] in Appendix B at temperatures of 303.15 K, 318.15 K and 333.15 K. The solubility of CO₂ and CH₄ in all ILs was observed to increase almost linearly with an

increase in total pressure of both gaseous mixtures for the whole range of investigated temperature. With an increase in system temperature, a decrease in the solubility of CO₂ and CH₄ for all ILs is observed for both types of mixed gas systems. The effect of temperature on the gases solubility in ILs is more substantial at pressures beyond 20 bar. The solubility results for gases demonstrate that CH₄ solubility is less temperature dependent as compared to the CO₂ solubility for all types of studied ionic liquids. For instance at pressure of approximately 88 bar and raising temperature from 303.15 K to 333.15 K, causes the CH₄ solubility in [Tf₂N] based IL to decrease by 15% (on molality scale) compared to the decrease of CO₂ solubility which is 34%. The overall CO₂ solubility trends obtained for both types of gaseous mixtures of CO₂/CH₄ are similar to those observed for CO₂ solubility as pure gas in all the respective ionic liquids.

The solubility of CO₂ and CH₄ in [C₆mim] based ILs with [Tf₂N] anion is higher than [BF₄] and [PF₆] for all the studied temperatures. The effect of IL anion type on the solubility of both gases could be further described with respect to the fluorination and size of anion. In other words, the solubility of both gases increases with an increase in fluorination and size of anion attached to the corresponding IL. For example, using B₆₄ gaseous mixture, the solubility of CO₂ in [Tf₂N] based IL is found to be 5.932 moles.kg⁻¹ or 73 mole% at T = 303.15K and pressure of approximately 88 bar which is 22% and 30% more than its solubility in [PF₆] and [BF₄] based ILs respectively. Similarly the solubility of CH₄ in [Tf₂N] based IL is found to be 0.358 moles.kg⁻¹ or 13 mole%, which is 54% and 31% more than its solubility in [PF₆] and [BF₄] based ILs respectively.

The solubility of CH₄ in all the studied ILs using binary mixtures of CO₂/CH₄ i.e., 60/40 (B₆₄) and 40/60 (B₄₆) by volume percent is shown in Figure 5.22 at pressures up to 90 bar and temperature of 303.15 K. It was found that solubility of CH₄ in ILs is slightly higher in B₆₄ gas mixture as compared to B₄₆ as shown in Figure 5.22. Although the composition of CH₄ in B₄₆ is higher compared to B₆₄ gas mixture, the CH₄ solubility in all ILs is relatively more in later case which could be due to the preferential absorption of CO₂ in ionic liquids.

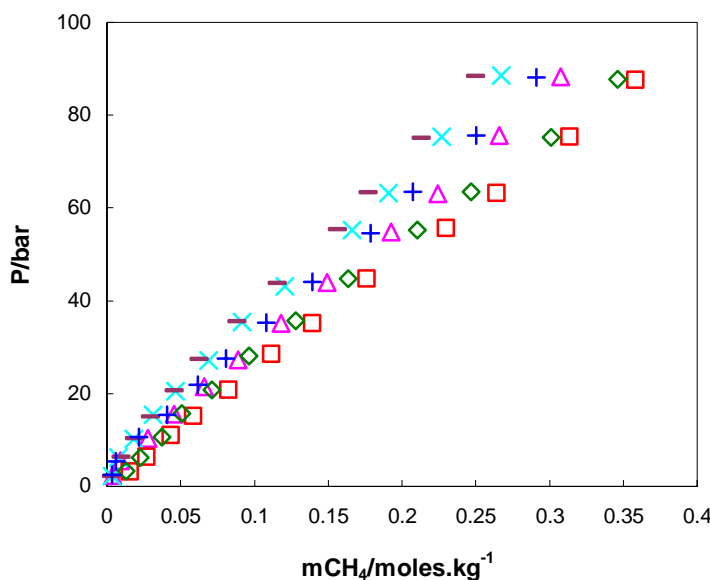


Figure 5.22: Solubility of CH₄ in ILs using binary mixtures of CO₂/CH₄.

{for B₆₄; [C₆mim][BF₄] (×), [C₆mim][PF₆] (Δ), [C₆mim][Tf₂N] (□), and B₄₆; [C₆mim][BF₄] (—), [C₆mim][PF₆] (+), [C₆mim][Tf₂N] (◇), at T = 303.15 K pressures up to 90 bar.}

As a general note, the amount of CO₂ solubility in [C₆mim][Tf₂N] is found to be much higher as compared to the solubility of CH₄ at all investigated temperatures irrespective of the composition of binary gas mixtures. The solubility data obtained at temperature of 303.15 K and pressure of approximately 88 bar shows that the CO₂ solubility in [Tf₂N] based IL is found to be 5.5 times higher than the solubility of methane. The solubility results for gases in the investigated imidazolium based ILs demonstrate that these ILs have great potential for bulk separation of CO₂ from its binary mixtures with CH₄ at relatively high pressures.

5.3.2.1 Effect of CH₄ presence on CO₂ solubility

The solubility of CO₂ in all the studied ILs was measured using binary mixtures of CO₂ and CH₄ to investigate the effect of presence of CH₄ on the selective solubility of CO₂ at high pressures and temperatures ranging from 303.15 to 333.15 K. To observe the effect

of CH₄ presence on CO₂ solubility, the solubility data of CO₂ in ILs is plotted versus total system pressure using binary mixtures of CO₂/CH₄ and pure CO₂, which is shown in Figure 5.23 at temperature 303.15 K. The solubility of CO₂ as pure gas and its binary mixture with CH₄ (B₆₄) in all the ILs was increased with an increase in gas pressure. However, it was observed that the presence of CH₄ significantly affected in the reduction of CO₂ solubility in all the studied ILs as compared to its solubility as pure gas. For instance, when a gas mixture B₆₄ i.e., 60/40 volume percent of CO₂/CH₄ is used instead of pure CO₂, the CO₂ solubility in [C₆mim][Tf₂N] is decreased by 25% on molality scale at temperature of 303.15 K and pressure of approximately 56 bar. The effect of CH₄ presence on the reduction of CO₂ solubility in [C₆mim][Tf₂N] increases further for B₄₆ i.e., 40/60 volume percent of CO₂/CH₄ than B₆₄ due to the increase in CH₄ partial pressure in the former gaseous mixture.

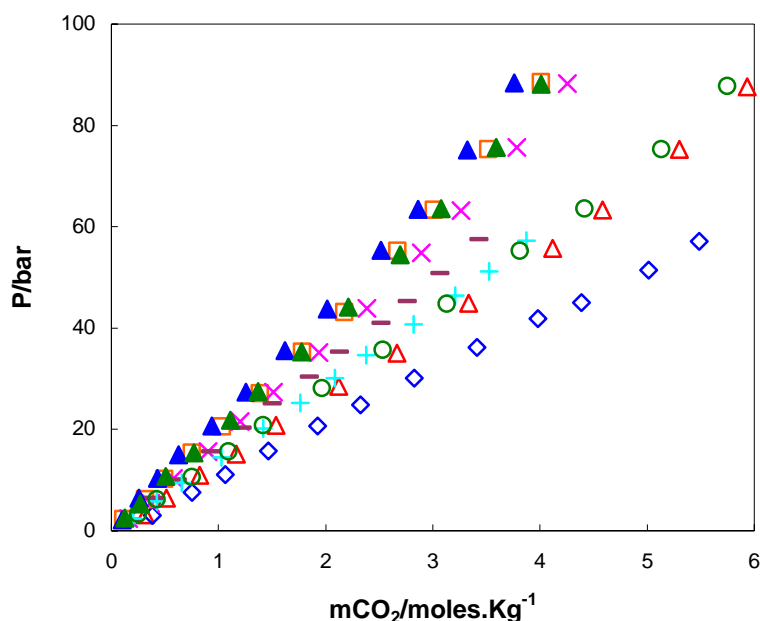


Figure 5.23: Effect of CH₄ presence on solubility of CO₂ in ILs.

[for CO₂ (pure gas); [C₆mim][BF₄] (–), [C₆mim][PF₆] (+), [C₆mim][Tf₂N] (◇), for binary mixtures of CO₂/CH₄ i.e., B₆₄; [C₆mim][BF₄] (□), [C₆mim][PF₆] (×), [C₆mim][Tf₂N] (△), and B₄₆; [C₆mim][BF₄] (▲), [C₆mim][PF₆] (▲) [C₆mim][Tf₂N] (○) at T = 303.15 K and pressure up to 90 bar]

5.4 Comparison of CO₂ solubility in aqueous MDEA solutions and ILs

The solubility of CO₂ in aqueous MDEA solutions with 4 and 8 (molal) concentrations, and IL with [Tf₂N] anion is demonstrated in Figures 5.24 for pure CO₂ and Figure 5.25 for binary mixture of CO₂/CH₄ (B₆₄) at T = 303.15 K. As mentioned in Sections 5.2.3.5 and 5.2.2 that high solubility of CO₂ was observed for [C₆mim] based ILs with [Tf₂N] anion compared to the IL with [BF₄] and [PF₆] anions. Therefore, the comparison for CO₂ solubility is made between aqueous MDEA solutions and [C₆mim] based IL with [Tf₂N] anion.

The amount of CO₂ absorbed in both concentrations of aqueous MDEA solutions is more than [C₆mim][Tf₂N] at low and moderate pressures as most of the CO₂ solubility is achieved by chemical absorption. However, it was observed that the amount of pure CO₂ absorbed in [C₆mim][Tf₂N] exceeds than its amount in 4 molal of aqueous MDEA solution at high pressure of 50 bar as shown in Figure 5.24. This can be explained due to the difference in solubility behavior for both kinds of the studied solvents. The major portion of CO₂ solubility in aqueous MDEA solutions is chemically absorbed at low to moderate pressures. The CO₂ solubility curve for aqueous MDEA solutions tends to straighten at high pressures which indicate that gas solubility is approaching to saturation conditions. On the other hand, the CO₂ solubility in ILs was found to increase almost linearly with an increase in gas partial pressure which is purely a physical absorption phenomenon. Therefore, at high pressures the amount of CO₂ absorbed in ILs surmounts as compared to aqueous MDEA solutions.

In case of CO₂/CH₄ mixture (B₆₄), the amount of CO₂ absorbed in [C₆mim][Tf₂N] exceeded the amount absorbed in aqueous MDEA solution (4 molal) at pressure of approximately 40 bar as shown in Figures 5.25. This indicates that the selectivity for CO₂ solubility in IL; {[C₆mim][Tf₂N]} is better than 4 molal aqueous MDEA solution at elevated pressures. The loading capacity of CO₂ in ILs appears to be strongly dependent on the partial pressure of CO₂ in contrast to its chemical reactivity feature in case of aqueous MDEA solutions. Therefore, it can be concluded that the ILs show a great

potential for bulk CO₂ removal when compared with aqueous MDEA solutions at high operating pressures.

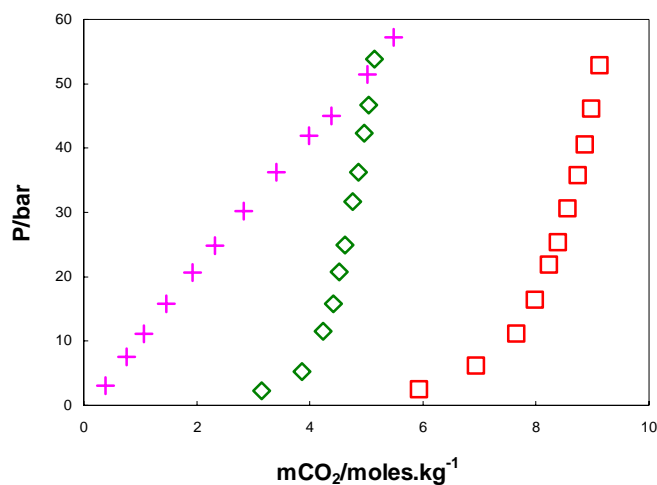


Figure 5.24: Comparison of pure CO₂ solubility in aqueous MDEA solutions and IL. [for (MDEA + water); 4 molal (\diamond), 8 molal (\square), and [C₆mim][Tf₂N] (+), at T = 303.15 K and pressure up to 60 bar]

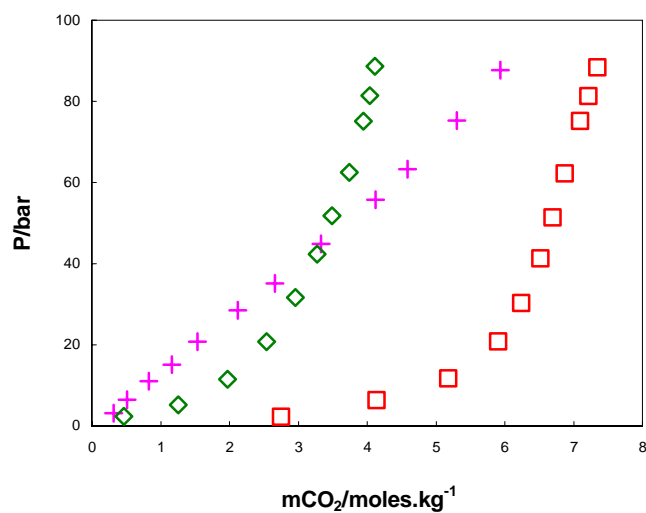


Figure 5.25: Comparison of CO₂ solubility using binary mixture of CO₂/CH₄ (B₆₄) in aqueous MDEA solutions and IL. [for (MDEA + water); 4 molal (\diamond), 8 molal (\square) and IL; [C₆mim][Tf₂N] (+), at T = 303.15 K and pressure up to 90 bar]

The solubility of CH_4 in aqueous MDEA solutions with concentrations 4 and 8 (molal), and $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ for its binary mixture with CO_2 i.e., B_{64} has is shown in Figure 5.26 at temperature of 303.15 K. The CH_4 solubility in IL with $[\text{Tf}_2\text{N}]$ anion was found to be $0.358 \text{ moles.kg}^{-1}$ at $P = 88 \text{ bar}$ and $T = 303.15 \text{ K}$, which is comparatively higher than its solubility in 8 molal aqueous MDEA solution i.e., $0.073 \text{ moles.kg}^{-1}$ at the same conditions. Although the observed CH_4 solubility in ILs is relatively higher than aqueous MDEA solutions, the studied ILs have shown acceptable potential towards the selective solubility of CO_2 at high pressures. The amount of CO_2 absorbed in recycled ILs was found to be almost same as that for pure ILs. Therefore, the use of ILs is of great interest as an attractive alternate to the conventional alkanolamines for CO_2 removal from natural gas at its upstream conditions. As the CO_2 solubility in ILs undergoes physical absorption, therefore, the regeneration of ILs can be easily accomplished by reducing the system pressure. The negligible vapor pressure of ILs also minimizes the solvent loss in the vapor phase during the gases absorption and desorption process. The experimental results for CO_2 solubility in all the studied solvents proposes that the IL; $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ could be potentially used for the bulk removal of CO_2 from a gas mixture containing CH_4 at high pressures.

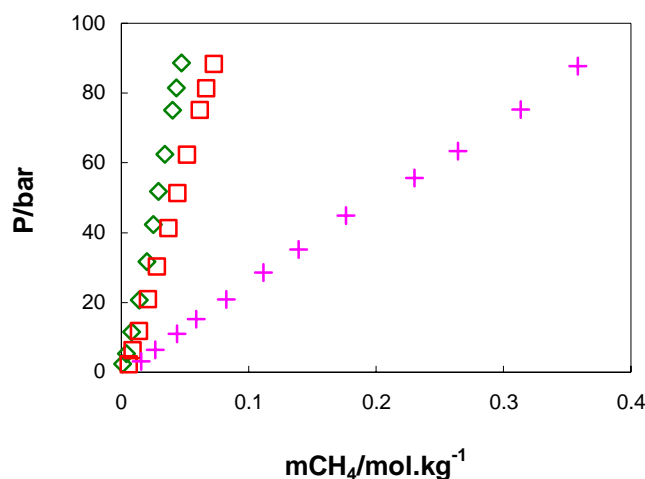


Figure 5.26: Comparison of CH_4 solubility using binary gas mixture of CO_2/CH_4 (B_{64}) in aqueous MDEA solutions and IL.

[for (MDEA + water); 4 molal (\diamond), 8 molal (\square), and IL; $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ ($+$), at $T = 303.15 \text{ K}$ and pressure up to 90 bar]

5.5 Thermodynamic parameters for CO₂ solubility in solvents

In the present work, the solubility of CO₂ in aqueous MDEA solutions and ILs was measured at several temperatures with focus given to high pressure conditions. The purpose is to investigate the potential applications of these solvents for bulk CO₂ removal from natural gas at its exploration conditions i.e., low temperature and high pressure. From the equilibrium gas solubility data obtained from experiments, a few important thermodynamic parameters including Henry's constants, enthalpies, Gibbs free energy and entropies of absorption were determined. An understanding of thermodynamic properties for any new or existing solvents and their equilibrium solubility behavior with gases is important for the design, development and optimization of separation processes.

5.5.1 Henry's Constant

The solubility of a gas in liquid is frequently presented using the Henry's law constant. In literature, one can find several conventional ways to define Henry's constants. However, in general, Henry's constant is defined as a proportionality constant which relates the partial pressure of a gas to its solubility in a liquid at infinitely dilute conditions (Prausnitz et al., 1999). In the present work, the solubility of CO₂ in aqueous MDEA solutions and ILs has been studied on the molality scale therefore the values of Henry's constant are determined using the following equation (Kamps et al., 2003):

$$k_{H,CO_2}(T) = \lim_{P \rightarrow P^s} \left(\frac{f_{CO_2}(T, P)}{(m_{CO_2} / m^o)} \right) \quad (5.1)$$

where, $k_{H,CO_2}(T)$ is the Henry's law constant, $f_{CO_2}(T, P)$ is the fugacity of CO₂ at equilibrium temperature and pressure, m_{CO_2} is the solubility of CO₂ in solvents (on molality scale) and $m^o = 1 \text{ mole.kg}^{-1}$.

The condition for the phase equilibrium is mostly satisfied when the fugacities of the gas component have equal values in both phases at constant temperature and pressure as follows:

$$f_1^g = f_1^L \quad (5.2)$$

Where, f_1^g and f_1^L are the fugacity of a component in the gas and liquid phase respectively. In this work, two different types of solvents namely, aqueous MDEA solutions and ILs are used to investigate their potential applications for CO₂ solubility measurements. The calculations for CO₂ fugacity in case of aqueous MDEA solvents were made based on assumption that the amount of MDEA in the vapor phase is negligible. This assumption is based on small vapor pressure values at temperature of 313.15 K, for MDEA i.e., 2.6×10^{-5} bar (MSDS, Merck) and Water i.e., 7.4×10^{-2} bar (Addicks et al., 2002). However, in the case of ionic liquids, only CO₂ exists in the gas phase as ILs are regarded as non-volatile solvents due to their almost zero vapor pressure. The fugacity of a gas at equilibrium temperature and pressure is the product of total pressure and the fugacity coefficient as follows:

$$f_{CO_2}(T, P) = P\phi_{CO_2}(T, P) \quad (5.3)$$

where, P is total pressure and $\phi_{CO_2}(T, P)$ is the fugacity coefficient of CO₂ at equilibrium temperature and pressure. The relationship of fugacity with temperature and pressure can be expressed using the Equation of State (EOS). Among the various Equations of States available, the Peng-Robinson Equation of State (PR-EOS) is the most popular with wide practical applications (Twu et al., 1998). In this work, the values for the fugacity coefficients of CO₂ are calculated with PR-EOS as shown in Appendix C, using Thermosolver software (version 1.0) introduced by Barnes and Koretsky (2003).

The Henry's constant values to reflect the CO₂ solubility in all the studied solvents are calculated using equation 5.1 and presented in Table 5.1 for three different temperatures

i.e., 303.15 K, 318.15 K and 333.15 K. A small value of Henry's constant indicates that the gas is more soluble in solvent and vice versa. The effect of temperature on the Henry's constant values is demonstrated in Figure 5.27. The CO₂ solubility in all the studied solvents was found to be highly dependent on temperature. A linear increase in Henry's constant values was obtained with an increase in temperature which indicates that solubility of CO₂ in solvents decreases with an increase in temperature.

Table 5.1: Henry's constants of CO₂ in solvents at different temperatures.

Solvents	K _H /bar		
	T = 303.15 K	T = 318.15 K	T = 333.15 K
MDEA + water (4 molal)	8.00	8.74	9.70
MDEA + water (8 molal)	4.29	4.79	5.39
[C ₆ mim][BF ₄]	12.06	15.77	21.39
[C ₆ mim][PF ₆]	10.66	14.16	19.06
[C ₆ mim][Tf ₂ N]	7.52	10.80	16.16

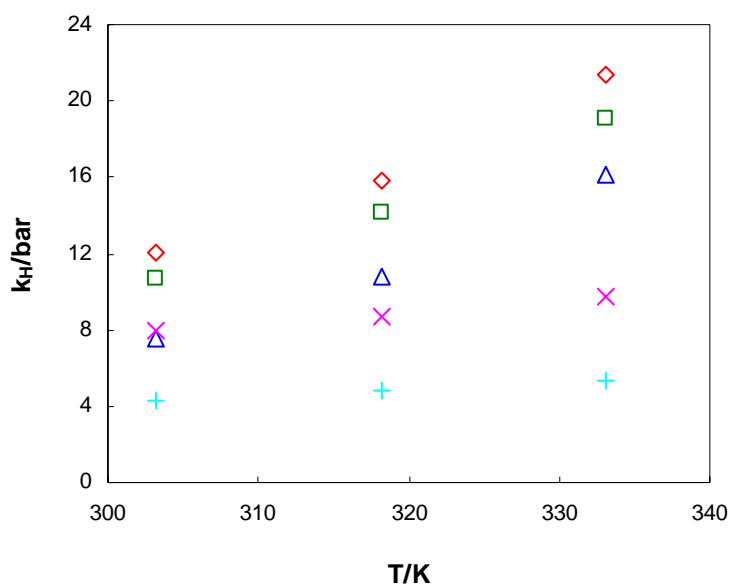


Figure 5.27: Henry's constants of CO₂ solubility in solvents.

[for (MDEA + water); 4 molal (×), 8 molal (+) and for ILs; [C₆mim][BF₄] (◇), [C₆mim][PF₆] (□), [C₆mim][Tf₂N] (△), at temperatures 303.15 K, 318.15 K, 333.15 K]

5.5.2 Enthalpy, Gibbs free energy and Entropy

The knowledge of Henry's constants for solubility of CO₂ in solvents can be used to determine other thermodynamic properties such as enthalpy, Gibbs free energy and entropy of solutions. The enthalpy yields information about the strength of interaction between the liquid and dissolved gas, whereas the entropy indicates the level of ordering that takes place in the liquid/gas mixture (Anthony et al., 2005). These properties for CO₂ absorption in the studied solvents have been calculated after considering the temperature effects on the gas solubility using the following correlations:

$$\Delta H_m (kJ.mol^{-1}) = R \left(\frac{\partial \ln k_H(T, P) / P^o}{\partial (1/T)} \right)_P \quad (5.4)$$

$$\Delta G_m (kJ.mol^{-1}) = RT \ln k_H(T, P) / P^o \quad (5.5)$$

$$\Delta S_m (J.K^{-1}.mol^{-1}) = (\Delta H_m - \Delta G_m) / T \quad (5.6)$$

where, ΔH_m is enthalpy, ΔG_m is Gibbs free energy, ΔS_m is entropy of solutions, T is temperature, R is ideal gas constant, $k_H(T, P)$ is Henry's gas constant and $P^o = 1$ bar. The values for enthalpy, Gibbs free energy and entropy of solutions after CO₂ absorption in solvents were calculated using equations 5.4, 5.5 and 5.6 respectively and presented in Table 5.2.

Table 5.2: Enthalpy, Gibbs free energy and entropy of CO₂ absorption in various solvents for high pressure region.

Solvents	$\Delta H_m (kJ.mol^{-1})$	$\Delta G_m (kJ.mol^{-1})$	$\Delta S_m (J.K^{-1}.mol^{-1})$
Aqueous MDEA solution (4 molal)	-5.43	5.76	-35.16
Aqueous MDEA solution (8 molal)	-6.42	4.16	-33.26
[C ₆ mim][BF ₄]	-16.13	7.35	-73.79
[C ₆ mim][PF ₆]	-16.33	7.05	-72.83
[C ₆ mim][Tf ₂ N]	-21.52	6.36	-70.66

The enthalpy of a solution provides important information for the strength of interactions between the solvent and dissolved gases. As shown in Table 5.2, the high values of enthalpies for CO₂ in ILs show their strong interactions between absorbed CO₂ and solvents. However, the high negative values of entropies in obtained in case of ILs indicate their less degree of disorder for CO₂ dissolution in solvents as compared to aqueous MDEA solutions.