

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

The separation of carbon dioxide ( $\text{CO}_2$ ) from natural gas is of great importance as the presence of  $\text{CO}_2$  in natural gas not only lowers its fuel value but also promotes corrosion problems in pipelines during transmission and processing equipments. The commercially available absorption method for  $\text{CO}_2$  removal from natural gas uses chemical solvents such as aqueous alkanolamines solutions. The development of an absorption process through introducing new potential solvents for bulk  $\text{CO}_2$  removal from natural gas at upstream conditions of high pressures is currently a key research issue. Therefore, in the present work, a fundamental and systematic investigation on the potential application of imidazolium based ionic liquids (ILs) for bulk removal of  $\text{CO}_2$  from natural gas at high pressures i.e., up to 90 bar has been presented in comparison to aqueous MDEA/PZ solutions.

For this purpose, initially several important thermophysical properties including density, isobaric coefficients of thermal expansion, viscosity, surface tension, refractive index and thermal stability of all the studied solvents was measured and correlated followed by the solubility measurements of pure  $\text{CO}_2$  in all the solvents were performed using a static high pressure gas solubility cell with equilibrium based approach of the total system pressure. The solubility measurements for  $\text{CO}_2$  in recycled ILs were made through an absorption-desorption cycles to shows their pure physical solubility behavior and a potential alternate of alkanolamine solvents. Finally, the solubility measurements for

binary mixtures of CO<sub>2</sub> and Methane with rich CO<sub>2</sub> contents were made using aqueous MDEA solutions and ionic liquids. All the solubility measurements were performed at exploration conditions of natural gas at upstream i.e., low temperature and high pressure.

The density of aqueous MDEA solutions, aqueous PZ solutions, PZ activated MDEA solutions and ILs were investigated using a highly precise densitometer (DMA 5000, Anton Paar) for a wide temperature range of 298.15 K to 338.15 K at a regular interval of 5 K. The densities of MDEA + water were found to be higher than PZ + water for all the studied amine concentrations. The measured densities for aqueous MDEA solution with concentration 48.80 wt.% were found to be higher than its 32.28 wt.% solutions for the whole range of studied temperature. However, the effect of PZ concentration increasing from 1.74 to 10.35 (wt.%) on the density of their studied solutions appeared to be insignificant. With the addition of PZ in both concentrations of aqueous MDEA solutions, their densities were found to slightly decrease. The density values for all the studied ILs were found to be higher than all the studied aqueous alkanolamine solutions. In general, the density of all the studied solvents decreases linearly with an increase in temperature. From the constant values of isobaric thermal expansion coefficients which were calculated through density data, it can be concluded that the variation of volume expansion for all the studied solvents is independent of temperature.

The viscosity of MDEA + water was found to be slightly higher as compared to PZ + water for all the studied concentrations. The effect of amine concentrations was insignificant on the viscosities of all the studied alkanolamine solutions. The ILs appeared to be highly viscosity than aqueous alkanolamine solutions. The viscosities of all the solvents decreased exponentially with an increase in temperature. The surface tension of solvents was found to be in decreasing order of PZ + water, MDEA + PZ + water, MDEA + water and ionic liquids. The refractive index of ILs appeared to be slightly higher as compared to aqueous alkanolamine solutions. The surface tension and refractive index of all the solvents decreased linearly with an increase in temperature. The imidazolium based ILs showed very high thermal stability with their onset temperature values reaches three times higher than all the studied aqueous alkanolamine solutions.

The solubility of CO<sub>2</sub> in aqueous MDEA/PZ solutions increased with an increase in total system pressure and decreased with increase in temperature. The solubility of CO<sub>2</sub> in aqueous MDEA solutions with concentrations 32.28 wt.% or 4 molal reached to 5.138 moles.kg<sup>-1</sup> and 48.80 wt.% or 8 molal reached to 9.132 moles.kg<sup>-1</sup> at pressure of approximately 54 bar and at temperature of 303.15 K. However, the amount of CO<sub>2</sub> dissolved in both concentrations of MDEA solutions became equal to the solution molality within 20 bar of system pressure. Later, the CO<sub>2</sub> solubility curve increased steeply and tended to straighten out at high pressures. The solubility behavior of CO<sub>2</sub> in aqueous MDEA solutions demonstrate that the dissolution of CO<sub>2</sub> at low to moderate pressure is dominated by chemisorption and at high pressure it is dissolved more through physical absorption. The addition of PZ with concentrations 1.74 and 5.16 (wt.%) in both concentrations of aqueous MDEA solutions significantly increased the CO<sub>2</sub> solubility. However, the extent of CO<sub>2</sub> solubility increase was insignificant with further increase in PZ concentration to 10.35 wt.% which favors the use of PZ as low concentrations in aqueous MDEA solutions. Moreover, the extent of CO<sub>2</sub> solubility increase with PZ addition is found to be higher in case of 32.28 wt.% of aqueous MDEA solution than in 48.80 wt.%.

The solubility of CO<sub>2</sub> in imidazolium based ILs increased almost linearly with increase in gas pressure which indicates the pure physical absorption and decreased with an increase in temperature. The CO<sub>2</sub> solubility in imidazolium based ILs with different anions was found to be in decreasing order of [C<sub>6</sub>mim][Tf<sub>2</sub>N], [C<sub>6</sub>mim][PF<sub>6</sub>] and [C<sub>6</sub>mim][BF<sub>4</sub>] at pressures up to 60 bar and temperature range from 303.15 K to 333.15 K. The effect of anion of ILs appeared to play the most significant role in determining the CO<sub>2</sub> solubility as the IL with [Tf<sub>2</sub>N] anion has shown highest CO<sub>2</sub> solubility (5.483 moles.kg<sup>-1</sup>) as compared to [PF<sub>6</sub>] and [BF<sub>4</sub>] i.e., 3.428 and 3.872 (moles.kg<sup>-1</sup>) respectively. The solubility CO<sub>2</sub> in recycled ILs was also measured for the same conditions of temperature and pressure as that for ILs. The recycled ILs were obtained after desorption of CO<sub>2</sub> from fresh ILs by depressurizing the gas solubility cell. The amount of CO<sub>2</sub> dissolved in recycled ILs was found to be similar to that obtained for ILs with maximum deviation of 6.8% obtained in case of IL with [PF<sub>6</sub>] anion.

The solubility of CO<sub>2</sub> in aqueous MDEA solutions with concentrations 32.28 and 48.80 (wt.%) and ILs were also measured using binary mixtures of CO<sub>2</sub>/CH<sub>4</sub> i.e., 60/40 (B<sub>64</sub>) and 40/60 (B<sub>46</sub>) by volume percent at temperatures 303.15 K, 318.15 K, and 333.15 K and pressures up to 90 bar. The solubility of CO<sub>2</sub> in all the studied solvents significantly decreased due to presence of methane in gaseous mixtures in comparison to its solubility in case of using pure carbon dioxide. The extent of decrease for CO<sub>2</sub> solubility using binary mixtures of CO<sub>2</sub>/CH<sub>4</sub> was found to be higher in aqueous MDEA solution with concentration 48.80 wt.% than 32.28 wt.%. The solubility of CH<sub>4</sub> in aqueous MDEA solutions and ILs was observed to be very low than carbon dioxide. The reduction for CO<sub>2</sub> solubility using binary mixtures of CO<sub>2</sub>/CH<sub>4</sub> in ILs was lower than aqueous MDEA solutions which shows that ILs have acceptable potential for selective solubility of CO<sub>2</sub> from its gaseous mixtures at high pressure.

In summary, it is demonstrated that ILs have reasonable potential for selective solubility of CO<sub>2</sub> from its binary mixtures with methane at high pressures, however, the solubility of CO<sub>2</sub> in [C<sub>6</sub>mim] based ILs with anions [BF<sub>4</sub>], [PF<sub>6</sub>] and [Tf<sub>2</sub>N] was found to be lower than aqueous MDEA solution at low to moderate pressures. As the solubility of CO<sub>2</sub> in ILs undergoes physical absorption, therefore, the regeneration of ILs can be easily accomplished by reducing the system pressure. Moreover, the amount of CO<sub>2</sub> absorbed in recycled ILs was found to be almost same as that for fresh ILs and negligible vapor pressure of ILs also minimizes the risk of solvent loss during regeneration process. Therefore, the use of ILs such as [C<sub>6</sub>mim][Tf<sub>2</sub>N] is of great interest as an attractive alternate to aqueous MDEA solutions for bulk removal of CO<sub>2</sub> from a gas mixture containing CH<sub>4</sub> at high pressures.

## 6.2 Recommendations

The present work explores the thermophysical properties of conventional and novel solvents and their potential applications for bulk CO<sub>2</sub> removal from upstream natural gas at its exploration high pressures. Based on the observations during this research work, the

following recommendations can be useful to investigate the importance of various solvents for gases separation.

- The experimental measurements for physical properties of solvents can be extended to high pressure conditions along with a wide range of temperatures. The attempts should be made to exploit the opportunity to “tailor” the properties of the solvents especially in case of ILs by changing the cations and anions in order to design specific solvents for a desired gas separation
- The solubility of pure CO<sub>2</sub> and binary mixtures of CO<sub>2</sub> and methane need to be studied for various types of less viscous ILs to improve gases mass transfer/diffusivity and to minimize any associated pumping costs. The solubility of CO<sub>2</sub> mixtures with other light hydrocarbons such as ethane, propane and butane in amine solvents and functionalized or task specific ILs should be measured.
- The mechanism for gases interaction with solvents can be investigated in situ analysis of solvents during absorption through UV-vis/Raman spectrophotometer techniques.
- The combined mixtures of ILs and alkanolamines (MEA, DEA and MDEA) can also be demonstrated for the solubility measurements of CO<sub>2</sub> from natural gas. In this way, the increase in CO<sub>2</sub> solubility might be obtained due to the presence of amine, while still taking advantage of the non-volatile and wide liquidus range of the ionic liquids.