CHAPTER IV
RESULTS AND DISCUSSION

4.1 Validation of Experimental Set-up

The experimental set-up as described in Chapter III was validated using conventional alkanolamines, 30 wt% MEA, 30 wt% DEA, and 3 M AMP (Shen and Li, 1992; Seo and Hong, 1996; Roberts and Mather, 1988). This procedure was to confirm the reliability of the experimental set-up for analyzing CO_2 solubility in amines. The validation results are shown graphically in Figure 4.1.

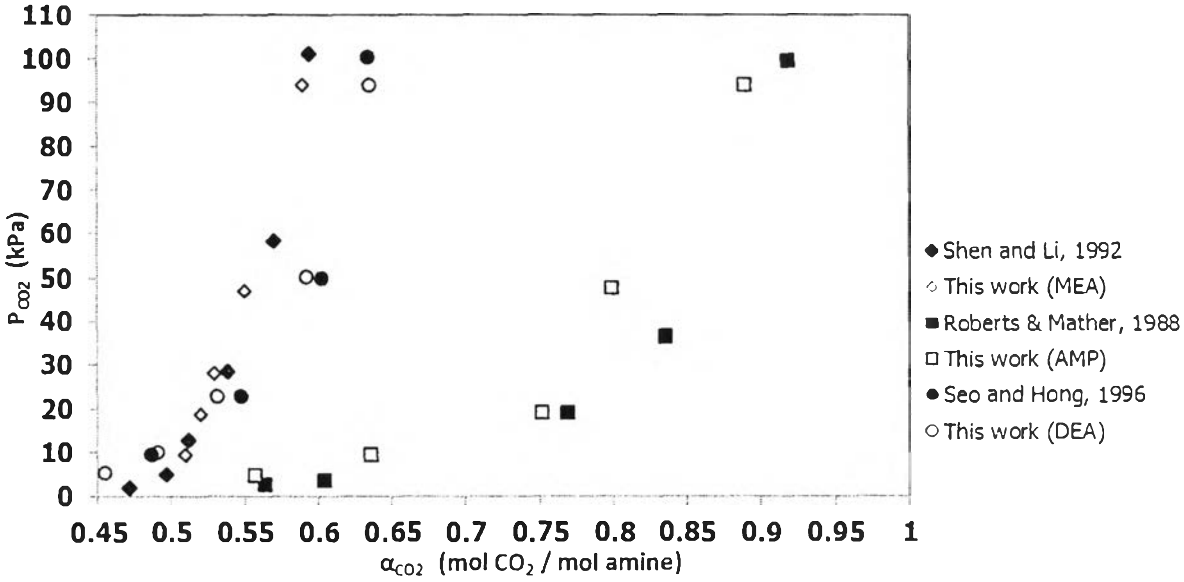

Figure 4.1 Results of validation using 30 wt% MEA vs Shen & Li, 1992; 30 wt% DEA vs Seo & Hong, 1996; and 3 M AMP vs Roberts & Mather, 1988 at 40 °C.

$$\%AAD = \frac{1}{n}\sum\left(\frac{X_{exp} - Y_{lit}}{Y_{lit}}\right) \times 100\% \qquad 4.1$$

The Equation 4.1 above was used to calculate the absolute average deviation (%AAD) of the experimental results with those of literature datas, where 'n' is the number of data points, X_{exp} the measured CO_2 loading from the experiment and Y_{lit} is the CO_2 loading from literature. The calculated %AAD for the analyzed solvents was 3 %. This confirms that the experimental set-up and procedure accurately used to analyze CO_2 solubility in amine solutions used in this research study. The calculated %AAD was compared with similar CO_2 partial pressures of the experiment and literature data.

4.2 CO_2 Solubility and Absorption Working Capacity of Single Solvents

The solubility of CO_2 in potential single solvents (in this case AMP, PZ and MEA) where analyzed to better access their potentials (CO_2 absorption capacity) and limitations (mostly precipitation) at absorption temperature of 40 °C and 100 % CO_2 at atmospheric pressure (93.93 kPa CO_2 partial pressure). These two conditions were chosen because 40 °C is the conventional absorption temperature for CO_2 capture plants and pure CO_2 will guarantee the highest possible loading for the amine solvents. At this temperature and pressure, high concentration of viscous solvents will precipitate. The main solvent experimentally analyzed is AMP which precipitates at high concentrations (Bruder and Svendsen, 2012; Bruder *et al.*, 2011). For PZ which crystallizes and has limited solubility in water, extensive research have been carried out by Freeman (2011) and inferred that PZ concentration in blended amine solutions should be limited to 1.5 M. Freeman (2011) did not actually specify if this PZ concentration is applicable to high concentrations of viscous solvents. Therefore, it's important to note that this 1.5 M PZ in blended amine solutions should be applied when promoting non-viscous solvents. For viscous solvents PZ will have to be used below 1.5 M. In addition, AMP promoted by PZ (AMP – PZ) blends is currently under research and pilot tested by several researchers (Tong *et al.*, 2013; Yang *et al.*, 2010; Dash *et al.*, 2014; Bruder *et al.*, 2011).

The absorption working capacity (aWC) of solvents is a more relevant parameter compared to the CO_2 loading. It represents the amount of CO_2 the amine solution can carry in the absorption section. This can be calculated by multiplying the equilibrium CO_2 loading of the amine solution (αCO_2) by its molar concentration (Equation 4.2).

$$\text{aWC} = \alpha CO_2 \left(\frac{mol\ CO_2}{mol\ amine}\right) \times Amine\ Conc \left(\frac{mol\ amine}{L\ of\ solution}\right) \quad 4.2$$

This is translates to at a given CO_2 loading, the amine solution with the higher concentration will carry more CO_2. For instance, at 0.5 mol CO_2/ mole amine, the amine solution with 5 M will carry more CO_2 than that of 4 M. This have prompted several researchers to investigate high concentration of amine solutions (Freeman *et al.*, 2010b; Bruder and Svendsen, 2012; Aboudheira *et al.*, 2003; Dugas and Rochelle, 2009; Yang *et al.*, 2010).

4.2.1 CO_2 Solubility in AMP

CO_2 solubility was conducted on 2 - 4 M concentrations of AMP at 40 °C and 93.93 kPa CO_2 partial pressure (100 % CO_2). Figure 4.3 shows the different equilibrium CO_2 loading. It was noticed that 5 M AMP precipitated and clogged the apparatus during the CO_2 loading analysis, but the solutions of 2 – 4 M did not form any precipitate, though 4 M AMP was very viscous and later formed some precipitate after it was cooled to 20 °C for over 200 hours (Figure 4.2).

Figure 4.2 Precipitation of rich solution of 4 M AMP after it was cooled to 20 °C for over 200 hours.

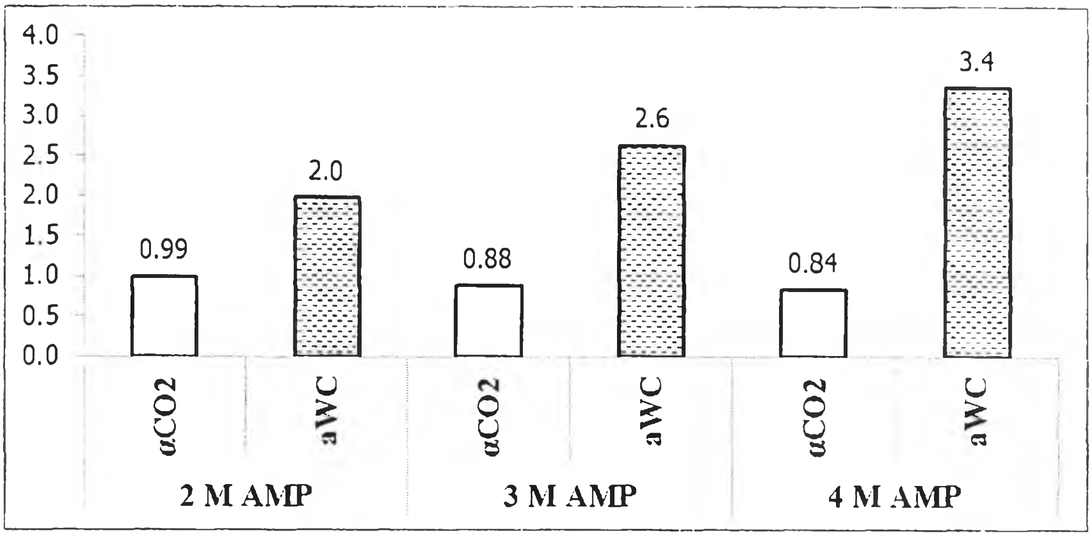

Figure 4.3 CO_2 Solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of 2 – 4 M AMP at 40 °C and 93.93 kPa CO_2 partial pressure.

It can be noticed from Figure 4.3 that as the AMP concentration increases the CO_2 loading decreases. This is because the equilibrium solubility of CO_2 in solvents is limited in the liquid phase, and as such CO_2 loading decreases as concentration increases. On the contrary, an increase in solvent concentration can be of huge advantage (higher absorption working capacity) if the solvent viscosity does not increase drastically and trigger precipitation. This will lead to safe handling during industrial applications. Taking reference from Figure 4.3, as the AMP concentration increased from 2 – 4 M the CO_2 loading decreased while the absorption working capacity increased. In other words, to its advantage the absorption working capacity increases as concentration is increased.

4.2.2 CO_2 Solubility in PZ

Experimental analysis of CO_2 solubility was carried out on PZ at 0.5 – 1.5 M. Figure 4.4 shows the equilibrium CO_2 loading and absorption working capacity of the analyzed concentrations. This further confirms the theoretical CO_2 loading of PZ at low concentrations which is equivalent to 1 mol CO_2/ mol PZ. The reason for the decrease in CO_2 loading and increase in the absorption working capacity as concentration increases is described in Section 4.2.1.

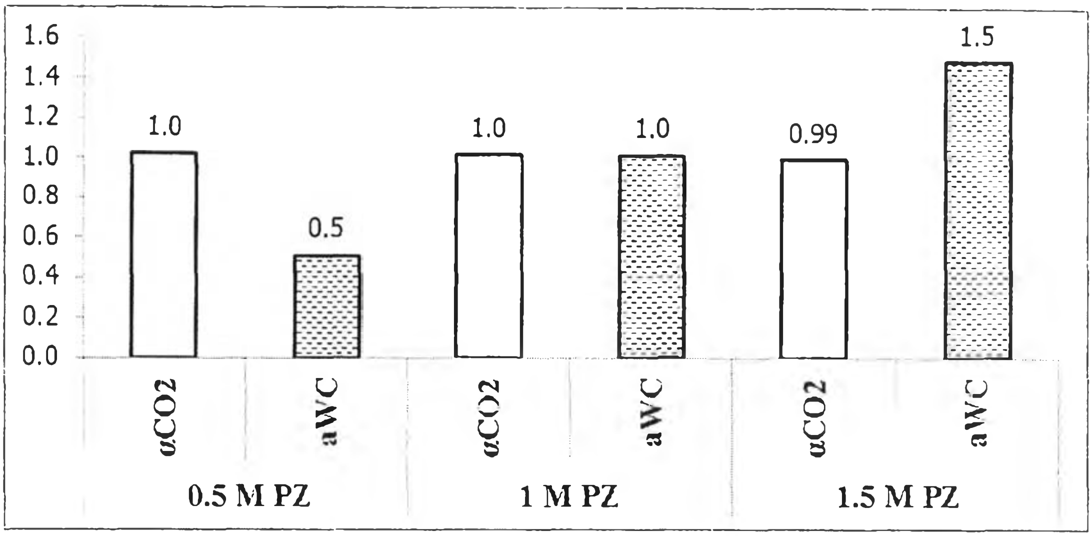

Figure 4.4 Solubility of CO_2 (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) in different concentrations of PZ at temperature and CO_2 partial pressure of 40 °C and 93.93 kPa respectively.

4.2.3 CO_2 Solubility in MEA

The solubility of CO_2 in MEA was carried out during the validation of the experimental set up. Therefore, possible precipitation of MEA at high concentration was studied. It was observed experimentally that pure MEA (99 wt%) which is about 16.5 M did not form any precipitate at 40 °C and 93.93 kPa CO_2 partial pressure (100 % CO_2). The rich 16.5 M MEA was also cooled to 20 °C for 480 hours without any solid precipitate formation but was viscous (Figure 4.5). This is a unique potential of MEA compared to AMP which forms solid precipitates at a concentration of 5 M and PZ which have limited solubility is water. The reason for this non-precipitation of MEA can be attributed to the liquid form of MEA carbamate. Pure MEA was also studied by Bruder and Svendsen (2012) without identifying any formation of precipitate. Figure 4.6 indicates that 16.5 M MEA still maintains MEA theoretical capacity of 0.5 mol CO_2/mol MEA and with a very high absorption working capacity. This high concentration of MEA cannot be applied in the industry because of excessive corrosion and very high viscosity.

Figure 4.5 Non-precipitation of rich solution of 16.5 M MEA (99 wt %) after it was cooled at 20 °C for over 480 hours.

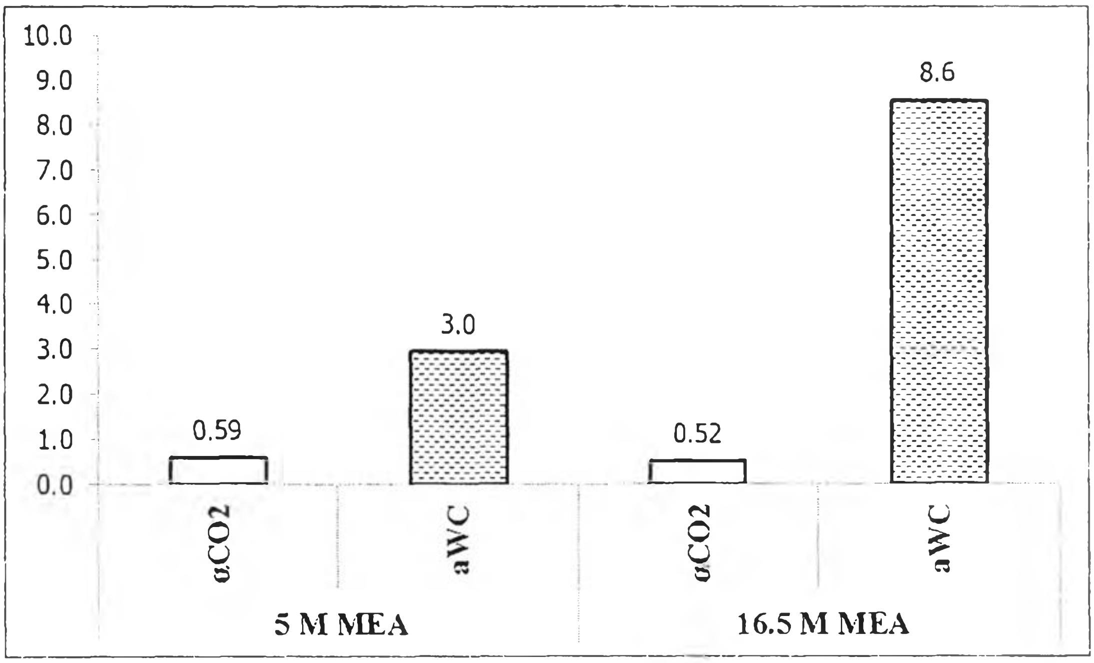

Figure 4.6 Solubility of CO_2 (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) in different MEA concentrations at temperature and CO_2 partial pressure of 40 °C and 93.93 kPa respectively.

4.3 CO_2 Solubility in AMP-PZ Binary Blends

The experimental results from the single solvents (AMP, PZ and MEA) led to the analysis of AMP-PZ binary blends. This binary blend was chosen ahead of AMP-MEA because from the results presented in Figures 4.3-4.4 and 4.6, both the CO_2 loading and absorption working capacity of AMP and PZ are higher than that of MEA. This can be attributed to the high theoretical capacity (1 mol CO_2/mol amine) of both AMP and PZ compared to that of MEA (0.5 mol CO_2/mol MEA). This infers that the binary blend of AMP - PZ will have higher CO_2 loading and absorption working capacity than AMP - MEA or PZ - MEA binary blends. Figure 4.7 depicts the CO_2 loading and absorption working capacity of different AMP – PZ concentrations. The focus was to analyze at low concentrations where precipitation would not occur. The concentration of AMP was kept at 2 M while that of PZ was varied between 0.5 – 1 M. The low concentration of PZ was to avoid crystallization and precipitation prior, during and after the CO_2 loading analysis. For binary blends, the maximum PZ concentration of 1.5 M was suggested by Freeman (2011) as this allows all the PZ crystals to completely dissolve in the solution. Crystallization will occur if all the PZ crystals do not completely dissolve in the solution. The concentration of 3 M AMP – 1.5 M PZ was then analyzed because it was inferred as the optimal concentration of AMP - PZ binary blend that will not form solid precipitate (Bruder *et al.*, 2011). This higher concentration was investigated by both Yang *et al.* (2010); Bruder *et al.* (2011) as a potential alternative to the conventional 5 M MEA for CO_2 capture. It's important to note that all the PZ crystals completely dissolved in the different blends. All the rich solutions of the studied AMP - PZ concentrations were cooled at 20 °C for 480 hours to monitor any possible formation of precipitation. It was observed that none of the binary blends formed a solid precipitate, though 3 M AMP – 1.5 M PZ was slightly viscous (Figure 4.8).

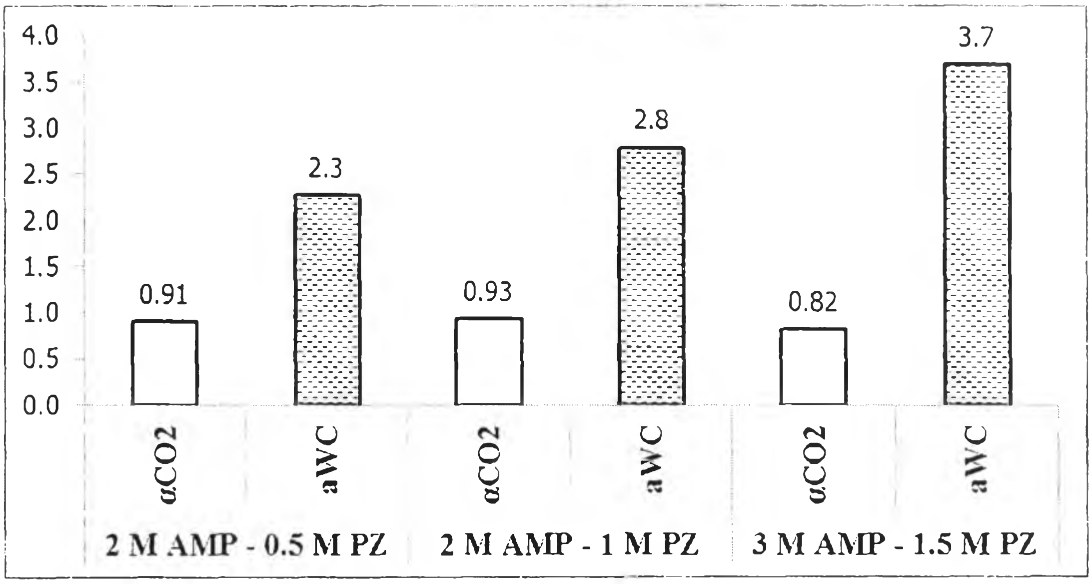

Figure 4.7 CO_2 Solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of AMP – PZ blends at 40 °C and 93.93 kPa CO_2 partial pressure.

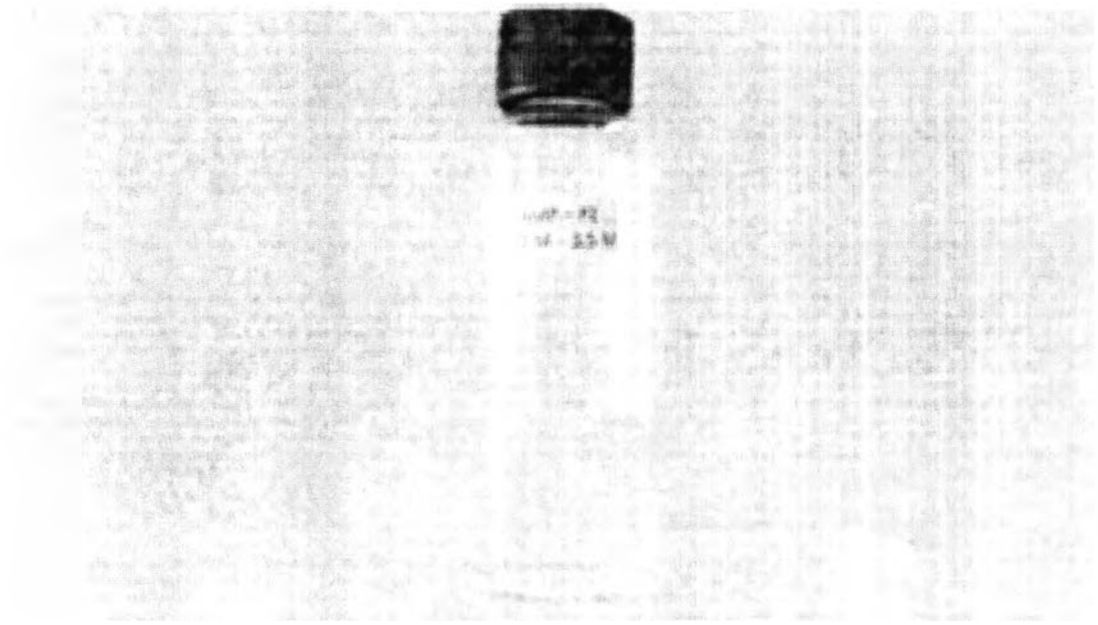

Figure 4.8 Rich solution of 3 M AMP – 1.5 M PZ it was cooled at 20 °C for over 480 hours.

From the results in Figure 4.7, it can be seen that at constant AMP concentration and increase in PZ concentration increases the equilibrium CO_2 loading and hence higher absorption working capacity. This increase in CO_2 loading as a result of increase in PZ concentration outlines the promoting effect (high absorption rate) of PZ which have been detailed by several researchers (Bishnoi and Rochelle, 2000; Ibrahim *et al.*, 2014; Dash and Bandyopadhyay, 2013 ; Optimized Gas Treating Inc., 2008; Bruder *et al.*, 2011; Samanta and Bandyopadhyay, 2009).

4.4 AMP-PZ-MEA Ternary Blends

The individual solvents in this novel ternary blend was chosen considering their individual high absorption capacity (AMP and PZ) and high reaction kinetics (PZ and MEA), and non-precipitation of MEA at high concentrations. These potentials were confirmed experimentally as discussed Section 4.2 and were also stated by several researchers (Satori and Savage, 1983; Tontiwachwuthikul *et al.*, 1991; Freeman *et al.*, 2011; Derks *et al.*, 2006; Bishnoi and Rochelle, 2000; Brúder and Svendsen, 2012). In addition, the individual solvent limitations like, precipitation (AMP, PZ), crystallization (PZ), were all considered as it served as a guide towards choosing a safe solvent concentration.

4.4.1 Chemical Equilibria of AMP-PZ-MEA

The solubility of CO_2 into aqueous solutions of single and blended amines is similar to an acid– base buffer reaction, which involves several complex reversible reactions in the liquid phase. For this novel AMP-PZ-MEA system, the main reaction mechanism with CO_2 can be described as (Tontiwachwuthikul *et al.*, 1991; Bishnoi and Rochelle, 2000; Derks *et al.*, 2006; Samanta and Bandyopadhyay, 2007; Plaza and Rochelle, 2011; Sartori, G., Savage, 1983; Gupta *et al.*, 2013);

$$2H_2O \overset{k1}{\leftrightarrow} H_3O^+ + OH^- \qquad 4.3$$

$$CO_2 + 2H_2O \overset{k2}{\leftrightarrow} H_3O^+ + HCO_3^- \qquad 4.4$$

$$HCO_3^- + H_2O \overset{k3}{\leftrightarrow} H_3O^+ + CO_3^{2-} \qquad 4.5$$

$$AMPH^{+} + H_2O \overset{k4}{\leftrightarrow} AMP + H_3O^{+} \tag{4.6}$$

$$PZH_2^{2+} + H_2O \overset{k5}{\leftrightarrow} PZH^{+} + H_3O^{+} \tag{4.7}$$

$$PZH^{+} + H_2O \overset{k6}{\leftrightarrow} PZ + H_3O^{+} \tag{4.8}$$

$$MEAH^{+} + H_2O \overset{k7}{\leftrightarrow} MEA + H_3O^{+} \tag{4.9}$$

$$AMPCOO^{-} + H_2O \overset{k8}{\leftrightarrow} AMPH^{+} + HCO_3^{-} \tag{4.10}$$

$$\mathrm{PZ} + CO_2 + H_2O \overset{k9}{\leftrightarrow} PZCOO^{-} + H_3O^{+} \tag{4.11}$$

$$PZCOO^{-} + CO_2 + H_2O \overset{k10}{\leftrightarrow} H^{+}PZCOO^{-} + HCO_3^{-} \tag{4.12}$$

$$H^{+}PZCOO^{-} + H_2O \overset{k11}{\leftrightarrow} PZCOO^{-} + H_3O^{+} \tag{4.13}$$

$$PZCOO^{-} + CO_2 + H_2O \overset{k12}{\leftrightarrow} PZ(COO^{-})_2 + H_3O^{+} \tag{4.14}$$

$$MEA + CO_2 + H_2O \overset{k13}{\leftrightarrow} MEACOO^{-} + H_3O^{+} \tag{4.15}$$

$$MEACOO^{-} + H_2O \overset{k14}{\leftrightarrow} MEAH^{+} + HCO_3^{-} \tag{4.16}$$

The Equations 4.3 to 4.5 are ionization reactions typical of aqueous systems that contain CO_2. Equations 4.6 and 4.10 which represent AMP protonation and the AMP carbamate hydrolysis respectively was proposed by Tontiwachwuthikul *et al.* (1991). Sartori and Savage (1983) previously studied the formation of AMP carbamate which they stated as being unstable and was attributed to the steric hindrance caused by the substitution on the α-carbon adjacent to the amino group. Therefore, the important reaction between CO_2 and AMP is the hydrolysis of AMP carbamate (Equation 4.10). The concentration of the AMP carbamate was investigated by Xu *et al.* (1992) and found it to be only of the order of 10^{-4} of the CO_2 loaded AMP concentration. This verification means that the carbamate of sterically hindered amines (like AMP) may quickly undergo hydrolysis, thereby leading to the formation of bicarbonates and free amine molecules. This quick hydrolysis of AMP carbamate increases the theoretical loading up to 1 mol CO_2/mol AMP (Sartori and Savage, 1983). Considering the low stability of AMP carbamate, its reaction was neglected (Dash and Bandyopadhyay, 2013).

The reaction mechanism between CO_2 and PZ leads to the production of PZ carbamate and hydrogenated PZ carbamate in the presence of a base (Bishnoi and Rochelle, 2000; Derks *et al.*, 2006; Samanta and Bandyopadhyay, 2007; Plaza and Rochelle, 2011; Gupta *et al.*, 2013). The contribution of each base would depend on its concentration (Bishnoi, 2000; Hagewiesche *et al.*, 1995). Hence, in the ternary blend consisting of AMP, PZ and MEA, the PZ carbamate and hydrogenated PZ carbamate formation would likely be caused by the presence of PZ itself, AMP, or MEA and to a lesser extent from H_2O and OH^-. Equations 4.11 to 4.14 shows the chemical reaction between CO_2 and PZ to produce the various carbamates (Bishnoi and Rochelle, 2000; Derks *et al.*, 2006; Samanta and Bandyopadhyay, 2007; Plaza and Rochelle, 2011; Gupta *et al.*, 2013).

The reaction of MEA with CO_2 generates a stable carbamate which is the dominant reaction. According to Sartori and Savage (1983) this stable MEA carbamate limits the theoretical loading to 0.5 mol CO_2/mol MEA (Equation 4.15). Sartori and Savage (1983) also confirmed that the MEA carbamate undergoes slight hydrolysis which allows the CO_2 loading to exceed 0.5 mol CO_2/mol MEA, especially at high pressures (Equation 4.16).

4.4.2 CO_2 Solubility in AMP-PZ-MEA Ternary Blends

The limited solubility of PZ in blended amines (Freeman *et al.*, 2010b; Freeman 2011) and possible precipitation of AMP at concentrations higher than 3 M were all considered. Their individual potentials from high absorption capacity of AMP (Satori and Savage, 1983), higher reaction kinetics of PZ compared to primary amines (Bishnoi and Rochelle, 2000; Rochelle *et al.*, 2011; Xu *et al.*, 1998) as well as the good kinetics of MEA (Mandal *et al.*, 2001; Dey and Aroonwilas, 2009; Choi *et al.*, 2009) were integral in this ternary blend. The non-precipitation of MEA at 16.5 M is a good potential for this novel research. This led to choice of keeping the concentration of AMP at 2 M, while the PZ and MEA concentrations were varied between 0.5 – 1 M and 2 – 4 M respectively for this research study. The total solution concentration was varied in the range of 5 – 7 M. Figure 4.9 depicts the CO_2 loading and absorption working capacity of various AMP-PZ-MEA concentrations at 40 °C and 93.93 kPa CO_2 partial pressure.

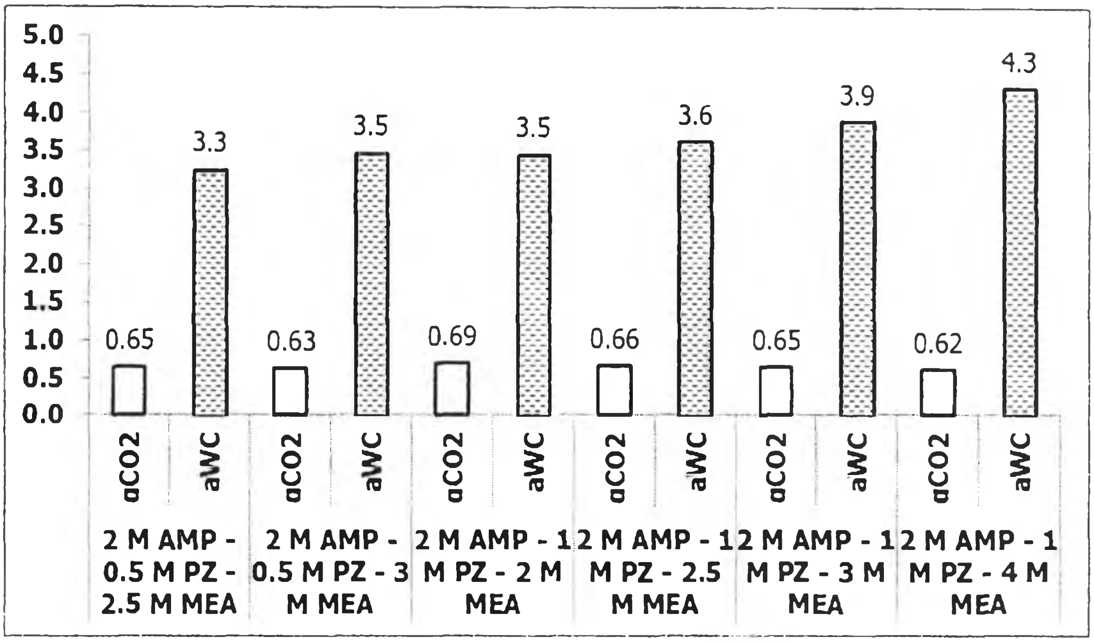

Figure 4.9 CO_2 Solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of different concentrations of ternary AMP-PZ-MEA Blends at 40 °C and 93.93 kPa CO_2 partial pressure.

Table 4.1 Visual and tests observations for the different AMP-PZ-MEA concentrations at 40 °C and 93.93 kPa CO_2 partial pressure before and after CO_2 loading

Concentration (M)			Observations
AMP	PZ	MEA	
2	1	2	At maximum of 4 – 5 hours, PZ crystals completely dissolved at 25 °C. This long time can be attributed to a low H_2O/PZ molar ratio. No precipitation or crystallization was observed before and after loading. After loaded with CO_2, the rich solvent was subjected to 20 °C, and no crystallization formed after 480 hours.
2	1	2.5	Similar to 2 M AMP – 1 M – 2 M MEA.
2	1	3	The same observations as 2 M AMP – 1 M – 2 M MEA, but it took a bit more than 5 hours for the PZ crystals to be completely dissolved. No precipitation was observed after the rich solvent was cooled to 20 °C for 480 hours.
2	1	4	All the PZ crystals dissolved completely after 8 hours. No precipitation was formed after the rich solution was cooled to 20 °C for 480 hours.
2	0.5	2.5	The crystals of PZ dissolved completely within 2 hours at 25 °C , without any form of mixing or heating. Precipitation was not noticed even after it was fully loaded with CO_2 and when subjected to 20 °C for 480 hours.
2	0.5	3	It took a little bit longer than 2 hours for the PZ crystals to completely dissolve, but did not exceed maximum of 3 hours. Other observations were similar to those of 2 M AMP – 0.5 M – 2.5 M MEA.

The experimental absorption temperature of 40 °C was chosen considering it is the conventional absorption temperature (Rao and Rubin, 2002). The CO_2 partial pressure of 93.93 kPa was also chosen knowing fully well that high concentration of amine solutions, especially those containing both AMP and PZ precipitates at high CO_2 loading (which is proportional to high CO_2 partial pressure). Comparing the results from Figures 4.6 and 4.8, it can be discovered that the entire ternary blends of AMP-PZ-MEA had both superior CO_2 loading (6.9 – 19 %) and absorption working capacity (from 13.8 % to 48.3 %) than the conventional 5 M MEA. The ternary blends analyzed also showed their competitive with the optimal blend of AMP – PZ (3 M AMP – 1.5 M PZ) as indicated in Figures 4.7 and 4.9. The very high concentrations (6 – 7 M) of the ternary AMP-PZ-MEA blend show higher absorption working capacity (5.4 – 16.2 %) than the 3 M AMP – 1.5 M PZ. Precipitation and crystallization was also monitored before and after CO_2 loading analysis for the different AMP-PZ-MEA concentrations. It was confirmed that none of the analyzed AMP-PZ-MEA formed any precipitate when their rich solutions were cooled to 20 °C for 480 hours (Figure 4.10). Table 4.1 shows a list of the qualitative observations of the visually monitored concentrated solutions.

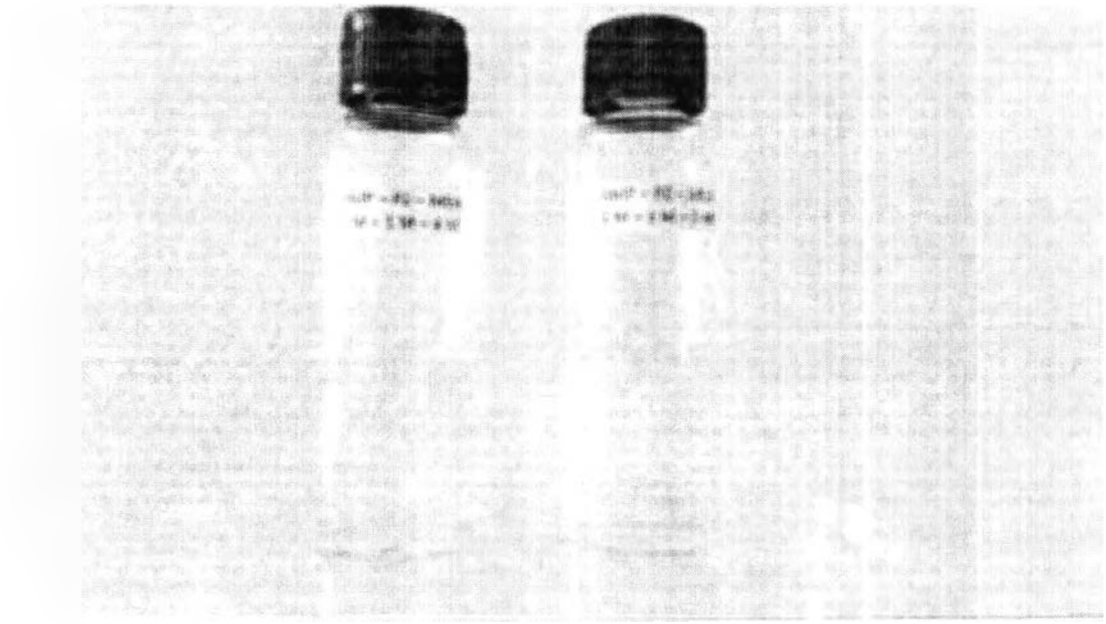

Figure 4.10 Non-precipitation of rich solution of the highly concentrated (6 – 7 M) ternary blends after they were cooled at 20 °C for over 480 hours.

4.4.2.1 Effect of Water – Amine Molar Ratio

The water molar concentration in any aqueous amine solution is very important because it helps to drive the CO_2 into the amine solution. A low water-amine molar ratio will cause solvation issues both for the amines themselves and for the ionic species formed during the amine-H_2O-CO_2 reaction (Aronu *et al.*, 2011).

For amine solutions involving AMP, water concentration becomes very important since the AMP carbamate hydrolysis (Equation 4.10) can only occur in the presence of water (sufficient water concentration). In the absence of sufficient water, the AMP carbamate will not completely hydrolyze to bicarbonate as seen in Equation 4.10. In such situation, the AMP carbamate will then accumulate and form solid precipitate common with high concentrations of AMP (i.e. 4 – 5 M). For solutions containing PZ or the PZ in amine blended solutions, sufficient water remediates the solvation problems related with PZ. High concentrations of aqueous PZ solutions form solid precipitates because there is not enough water in the solution to completely dissolve all the PZ crystals. From research results of Ma *et al.* (2011); Freeman *et al.* (2010); Hilliard (2008) they stated that the PZ species (Equations 4.11 – 4.14) formed due to PZ-H_2O-CO_2 reactions are more soluble in water than the crystals of PZ. Ma *et al.* (2011) further confirmed that precipitation of PZ will also arise if the concentration of the lean PZ (in CO_2 capture plant) is sufficiently high. This also mean that precipitation can also occur in the regeneration process when the lean PZ solution returning from the reboiler is cooled down to the temperature of the absorption process. Freeman (2011) suggested that the concentration of PZ in blended amine solution should be limited to 1.5 M to prevent solvation issues. This further verifies that the water concentration in an aqueous amine solution (containing PZ) is very essential because it will lead to the complete dissolution of all the crystals of PZ without additional effort (heating and stirring). For the MEA-H_2O-CO_2 reactions, the formed MEA carbamate is liquid and also soluble, thereby not leading to solid precipitates. Bruder and Svendsen (2012) successfully studied the absorption capacity of 100 % MEA, and they did not report any precipitation issues. This was also experimentally investigated in-house, and we also confirmed that at 40 ^{o}C and 93.93 kPa CO_2 partial pressure, 16.5 kmol/m^3 MEA (99 wt% MEA) did not form any precipitate (though it was very sticky). No precipitation was noticed when the rich MEA solution was cooled to 20 ^{o}C for 480 hours.

Therefore, for the purpose of this research study, which involves the ternary blend of AMP-PZ-MEA, we will investigate the water-amine molar ratio in terms of a H_2O/PZ molar ratio. The higher the H_2O/PZ molar ratio the reduced possibility of PZ solvation issues.

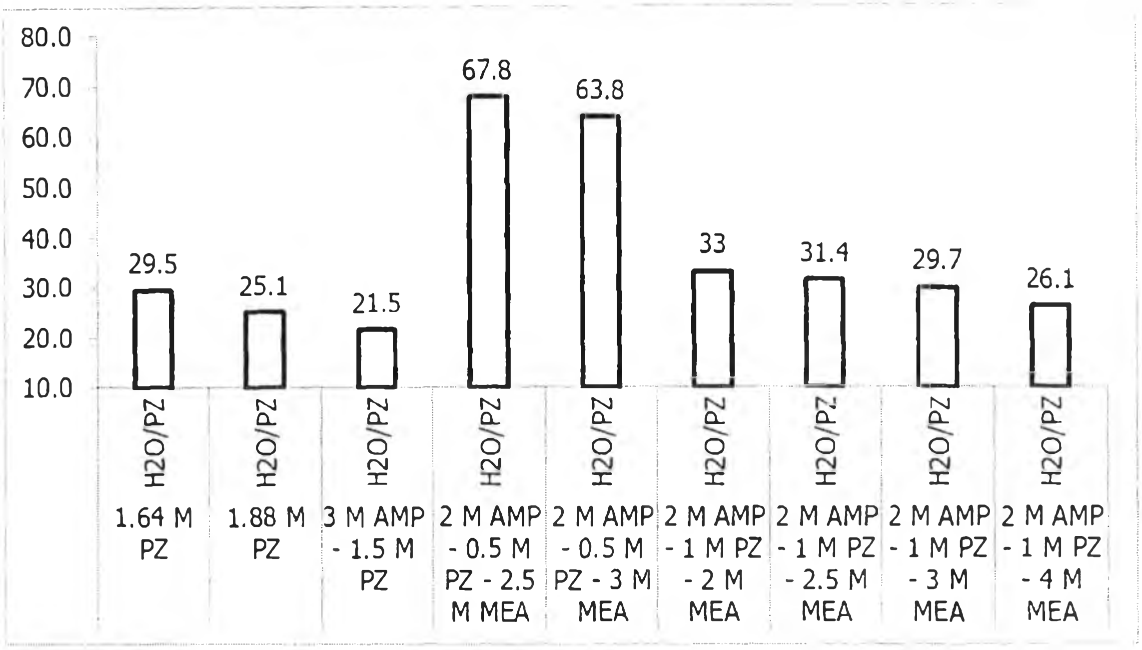

Figure 4.11 Water – Amine molar ratio in terms of H_2O/PZ.

4.4.2.1.1 H_2O/PZ Molar Ratio

In 2000, Bishnoi studied the solid-liquid equilibrium (SLE) of unloaded PZ by adding a certain amount of water to anhydrous PZ and observed when PZ crystallization occurred at a particular temperature. The analysis confirmed that at 20 °C and 25 °C, PZ solubility in water was 1.64 M and 1.88 M respectively. In another research work, Freeman *et al.* (2009) also stated that due to the nature and magnitude of the absorption/stripping systems, PZ concentrations above its room temperature (20 °C) solubility that corresponds to 14 wt% (about 1.64 M) should not be applied. Based on the reports from previous studies regarding the limitation of PZ concentration, the parameter H_2O/PZ molar ratio was determined and also used to predict the solubility of PZ in the aqueous amine solutions. The H_2O/PZ molar ratio is determined by first calculating the H_2O concentration in the unloaded aqueous amine solution (containing PZ), which is then followed by dividing the H_2O concentration by the concentration of the PZ. Appendix F further discussed the calculation of H_2O/PZ molar ratios of the studied aqueous amine solutions containing PZ. For 1.64 M PZ and 1.88 M PZ (single solvents), their corresponding H_2O/PZ molar ratios is 29.5 and 25.1 respectively as shown in Figure 4.11. These two H_2O/PZ molar ratios (at 20 °C and 25 °C) will be used as a benchmark for all the studied binary and ternary solvent blends in this research.

From Figure 4.11 it is seen that all the investigated ternary solvent blends have higher H_2O/PZ molar ratios than then the benchmark of 25.1 (25 °C). This confirms that all the investigated ternary solvent blends have less possibility to experience PZ solvation issues at 25 °C (Table 4.1). For the H_2O/PZ molar ratio at 20 °C (29.5), it is observed that only 2 M AMP – 1 M PZ – 4 M MEA (H_2O/PZ molar ratio of 26.1) will likely have PZ solvation issues. Applying the same benchmark to the binary blend of 3 M AMP – 1.5 M PZ, it can be seen (Figure 4.11) that it's H_2O/PZ molar ratio (21.5) is lower than both benchmarks of 29.5 and 25.1 (20 °C and 25 °C). This means that the crystals of 1.5 M PZ in the binary AMP-PZ blend will not completely dissolve at both 20 °C and 25 °C except with additional effort like heating or stirring. Therefore, the binary blend of 3 M AMP – 1.5 M PZ is more susceptible to solvation problems than all the ternary solvent blends.

The ternary amine blend of 2 M AMP – 0.5 M PZ – 3 M MEA was further analyzed considering its very high H_2O/PZ molar ratio of 63.8 (Figure 4.11). In addition, it also possess a higher absorption working capacity than 2 M AMP – 0.5 M PZ – 2.5 M MEA (Figures 4.9) and 5 M MEA (Figure 4.9).

4.4.2.2 Effect of PZ Concentration

The promoter effect of PZ is well documented in several literatures, which confirms that PZ facilitates the hydration of CO_2 and/or carbamate hydrolysis when used as a promoter in blended amine solution (Bishnoi and Rochelle, 2000; Ibrahim *et al.*, 2014; Dash and Bandyopadhyay, 2013 ; Optimized Gas Treating Inc., 2008; Bruder *et al.*, 2011; Samanta and Bandyopadhyay, 2009). As shown from Figure 4.10, equilibrium loading of CO_2 increases as the concentration of PZ increases. Comparing the ternary blend solutions of 2 M AMP – 0.5 M PZ – 2.5 M MEA and 2 M AMP – 1 M PZ – 2.5 M MEA, an increase in the PZ concentration from 0.5 – 1 M increased the CO_2 loading and absorption working capacity by 1.5 and 9.1 % respectively. This increase as a result PZ concentration increase was also observed for the solutions containing 3 M MEA, which the CO_2 loading and absorption working capacity increased by 3.2 % and 11.4 %

respectively. For the amine solutions containing the same concentration of PZ it was also observed that the promoter effect of PZ was more evident in the amine solutions with lower concentration (Figure 4.9). This effect is believed to be caused by an increased viscosity of the amine solution (which is proportional to an increase in amine solution concentration) which resulted in low diffusivities and hence reduced CO_2 loading. More importantly, the absorption working capacity which is a more relevant parameter increases as solution concentration increases. It can also be noticed from Table 4.1 that the rich solutions of the two highest concentrations of AMP-PZ-MEA at 6 M and 7 M (containing 1 M PZ) did not form precipitate even after they were was cooled to 20 °C for 480 hours. The non-precipitation can be related to the fact that PZ can dissolve in moderately high non-viscous MEA (in the presence of low concentration of viscous AMP). In addition, these high concentrations possess high H_2O/PZ molar ratio which limits possibility of precipitation.

The equilibrium CO_2 loading of 2 M AMP – 0.5 M PZ – 3 M MEA was further analyzed considering that it possess both higher CO_2 loading and absorption working capacity than the conventional 5 M MEA. This ternary solution also contains very high H_2O/PZ molar ratio showing that all the PZ crystals will dissolve without stirring or heating.

4.4.2.3 Effect of MEA Concentration

An increase in MEA concentration decreases the equilibrium CO_2 loading (unlike PZ where CO_2 loading increases with increasing PZ concentration), although the absorption working capacity increased due to increased amine solution concentration (Figure 4.9). For the ternary solutions of 2 M AMP – 1 M PZ – MEA which the concentration of MEA increased from 2 to 4 M, their CO_2 loading decreased between 4.3 % and 10.1 %, while their absorption working capacity increased in the range of 2.9 % and 22.9 %. For the 2 M AMP – 0.5 M PZ – MEA solutions, increasing the MEA concentration from 2.5 M to 3 M decreased CO_2 loading by 3.1 % while the absorption working capacity increased by 6.1 %. It is believed that the major reason why the equilibrium CO_2 loading of the solution decreases as MEA concentration increases is directly related to the limited stoichiometric CO_2 loading of MEA. This situation is different in the case of PZ, because due to the high absorption capacity of PZ an increase in the concentration of PZ increases the equilibrium CO_2 loading of the solution (Figure 4.8). The huge advantage with increasing the concentration of MEA is that it triggers an increase in the absorption working capacity of the amine solution. Satori and Savage (1983) in their previous research stated that the lower theoretical CO_2 loading of MEA (compared to AMP with lower carbamate stability) is due to the high stability of the MEA carbamate, which limits the theoretical CO_2 loading to 0.5 mol CO_2/mol MEA. In addition, the liquid state of the MEA carbamate will not trigger precipitation formation. This is also supported by the in-house CO_2 solubility analysis of 16.5 M MEA (pure MEA). It was observed that 16.5 M MEA did not form any precipitate after it was loaded with CO_2 and also when it was cooled to 20 °C for 480 hours. This confirms the benefit of utilizing a secondary promoter (3^{rd} solvent) which should also be non-viscous and non-precipitating. Therefore, from the precipitation and reactive standpoint, it will be more advantageous to increase the concentration of MEA than that of AMP. Also comparing MEA and PZ, it will be more beneficial to increase the concentration of MEA than that of PZ to avoid possibilities of crystallization and precipitation. Henni *et al.* (2003) studied the viscosity of MEA and AMP, and they found that the viscosity of 1 M AMP is higher than that of 5 M MEA. Also Weiland *et al.* (1998); Dey and Aroonwilas (2009) indicated that at 25 °C the viscosity of 5 M MEA is 2.52 mPa.s compared to 67.7 mPa.s of an equivalent AMP. The detailed explanation prompted the selection of 2 M AMP – 0.5 M PZ – 3 M MEA for further CO_2 loading analysis.

4.5 CO_2 Solubility in Novel 2 M AMP - 0.5 M PZ – 3 M MEA

From the results of the CO_2 loading analysis investigated in the AMP-PZ-MEA ternary blend, 2 M AMP – 0.5 M PZ – 3 M MEA was selected for further solubility tests at temperature and CO_2 partial pressure of 25 – 40 °C and 2 – 100 kPa respectively. This solution concentration was also chosen citing its very high H_2O/PZ molar ratio which translates to less probability of forming precipitates. Though 2 M AMP – 0.5 M PZ – 2.5 M MEA possess higher H_2O/PZ molar ratio, 2 M AMP – 0.5 M PZ – 3 M MEA have higher absorption working capacity. More importantly, its absorption working capacity and equilibrium CO_2 loading is higher than that of 5 M MEA (Figures 4.6 and 4.9).

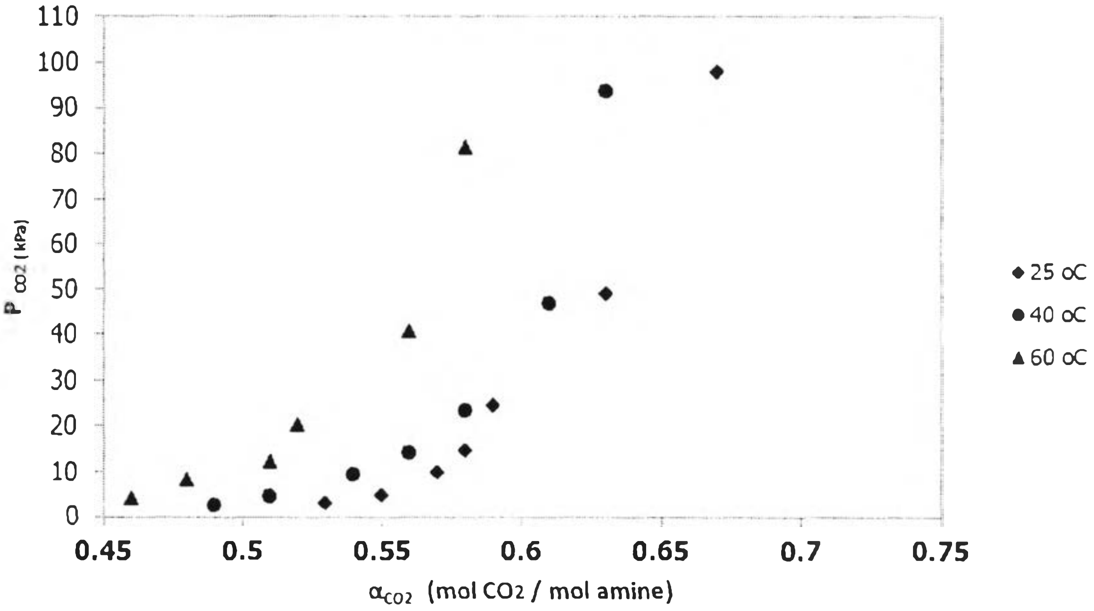

Figure 4.12 Equilibrium CO_2 loading in 2 M AMP – 0.5 M PZ – 3 M MEA.

Figure 4.12 illustrates the temperature effect on the CO_2 loading. As expected, the equilibrium CO_2 loading decreases as temperature increases. It's also noticed that this blend have a bit high CO_2 loading at 60 °C. This signifies that it can be possibly utilized at slightly higher temperature and yet retains a significant absorption working capacity. This is an important advantage because the effect of absorption and regeneration temperatures is integral because a decrease in the delta temperature between the absorption and regeneration section will reduce the energy penalty (Peeters *et al.*, 2007).

From the standpoint of CO_2 partial pressure, it can also be observed that the CO_2 solubility increased with increasing CO_2 partial pressure (Figure 4.12). An increase in CO_2 partial pressure increases the interfacial mass transfer thereby facilitating the gas phase mass transfer from the gas bulk phase into the gas-liquid interface.

4.6 CO_2 Capture Plant Simulation

Process simulation have become very important and an integral tool for the study of various chemical processes because of its potential to predict experimental and process plant operating parameter with just adjustments in key variables (Mudhasakul *et al.*, 2013). This helps in parametric sensitivity analysis and to overcome the time consuming and costly experimental tests in the laboratory or pilot plants. Considering the fast pace of development of computer technology, computer-aided simulations have enjoyed great popularity in many aspects of science and engineering (Gao *et al.*, 2014). Previously, Aspen Plus®, Aspen HYSYS®, and ProMax® have been used by some researchers to model and optimize amine-CO_2 absorption process (Desideri and Paolucci, 1999; Erik, 2007; Idem *et al.*, 2011; Plaza and Rochelle, 2011; Kale *et al.*, 2011; Dash *et al.*, 2014; Younas and Banat, 2014; Gao *et al.*, 2014).

4.6.1 Simulation using ProMax 3.2

The simulation package ProMax is flexible and powerful which is used globally by engineers to design and optimize gas processing, refining and chemical facilities. It has a simple user interface, multiple flow sheet capabilities, and covers 50 thermodynamic packages and 2300 pure components (Bryan Research & Engineering, 2013). ProMax®3.2 has been proven over the past 30 years by improving the technology of its predecessors, TSWEET® and PROSIM®. The TSWEET Kinetics Model have now been incorporated into ProMax, and this unification have significantly improved the capabilities of the software particularly in the area of amine sweetening (CO_2 absorption). It's also important to note that the TSWEET Kinetics Model is not applicable to liquid treating. According to Bryan Research & Engineering (2013) ProMax®3.2 successfully models (either individually or as blends) monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), triethanolamine (TEA), and 2-amino-2-methyl-1-propanol (AMP). Also modeled are activated amines using piperazine (PZ).

Electrolytic models account for the dissociation of molecular species in water, and all components are treated as Henry's Law components (Bryan

Research & Engineering, 2013). They are used for systems where compounds dissociation is very important, For example acid gas (CO_2 and H_2S) capture using amine solvents. In ProMax the available electrolytic models mostly used and recommended for CO_2 capture are amine sweetening, electrolytic ELR (Extended Long Range) and electrolytic NRTL (Non Random Two Liquid). Amine sweetening property package which is an improvement of the electrolytic ELR package, accounts for non-ideal ionic interactions except at very high acid gas loadings (> 1 mol/mol), and can be used for most applications. According to Bryan Research & Engineering (2013) the electrolytic ELR is a significant modification of the Pitzer-Debye-Hückel model described in Pitzer and Kim (1974). Whereas, the electrolytic NRTL property package is a Gibbs Excess Energy/ activity coefficient model which calculates liquid phase activity coefficients for predicting multicomponent phase equilibria (Chen and Evans, 1986). For this simulation project, amine sweetening thermodynamic property package was chosen because it is recommended by Bryan Research & Engineering (2013).

4.6.2 The MEA Base Case and Validation

The base case simulation for this research project represents a 400 MWe western Canadian pulverized coal boiler producing (Singh *et al.*, 2003). The key operating conditions are summarized below:

Table 4.2 Flue gas composition and process parameters

CO_2 Capture Plant Specifications	
Net power output (MWe)	400
Flue gas flow rate (kgmol/hr)	54,633
Flue Gas Temp (°C)	40
N_2 (vol. %)	69.95
O_2 (vol. %)	2.85
SO_2 (vol. %)	0.02
Ar (vol. %)	0.9
H_2O (vol. %)	11.68
CO_2 (vol. %)	14.59
MEA (wt. %)	30
CO_2 Capture Efficiency (%)	90
Absorber Pressure (kPa)	120
Stripper Pressure (kPa)	200

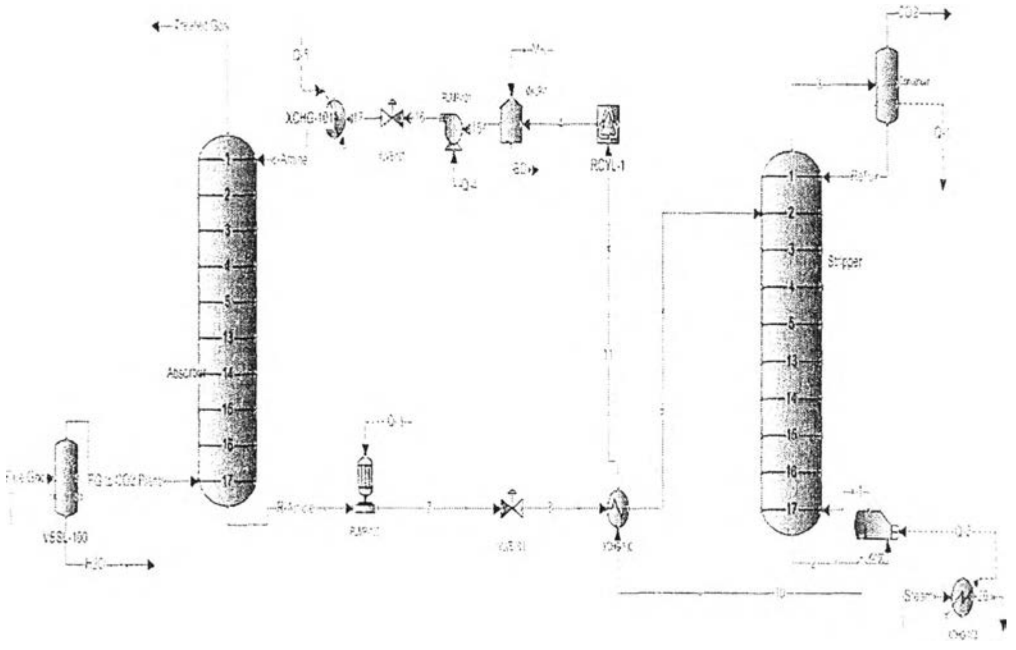

Figure 4.13 A typical CO_2 capture process configuration.

4.6.2.1 Process Flow Sheet Development

Figure 4.13 shows the 30 wt% (5 M) MEA base case simulation flow sheet. The separator upstream of the absorber was used to remove all light liquids in the flue gas which was mainly water. The SO_2 in the flue gas was removed in the simulation because this will form heat stable salts (HSS) and accumulate in the system which will require continuous removal with a reclaimer. Since the simulation is focused on a simple process, the SO_2 was hence removed from the flue gas composition. The absorber parameters were set in the process data tab to let the kinetic effects involving CO_2-amine interactions to take place. As recommended by Bryan Research & Engineering (2013) TSWEET Kinetics Model was set as the absorber type, which calculates approximately the kinetic effects based on residence time on a stage. In the absorber specifications tab, Sulzer Mellapak®250Y metal was chosen as the structured packing type. In the data tab, the pressure drop was set at 10 kPa, while the residence time and flooding was set to 1.5 seconds and 80 % respectively. This helps to calculate the approximate diameter of the absorber and stripper. All the pumps used were set at 75 % efficiency while the temperature approach of the cross exchanger was set at 5 °C to ensure maximum heat transfer efficiency.

In the stripper process tab, TSWEET alternate stripper was selected as recommended by Bryan Research & Engineering (2013). In the data tab, the pressure drop was set at 20 kPa and flooding of 80 %. The Sulzer Mellapak®250Y metal was also used as the stripper packing. The reboiler temperature was specified at 120 °C. The user specified properties used for the base case simulation can be seen in Appendix G (Figures G1 to G7).

4.6.2.2 Base Case Validation Results

The base case simulation results were validated with literature data of Singh *et al.* (2003). Table 4.3 depicts the validation results.

Table 4.3 Base case validation for 30 wt % MEA

	Literature	**Simulation**	**Deviation (%)**
Reboiler Duty (GJ/ton CO_2)	3.8	3.8	0
CO_2 Purity (%)	99.6	99	0.6
Steam Cost (ton steam/ton CO_2 captured)	1.7	1.6	6.25

$$\%AAD = \frac{1}{n}\sum\left(\frac{X_{sim} - Y_{lit}}{Y_{lit}}\right) \times 100\% \qquad 4.17$$

The %AAD for the base case simulation was calculated using Equation 4.1 by replacing X_{exp} with X_{sim} as seen in Equation 4.17. The validated results matched the literature data with 2.3 % absolute average deviation (%AAD) indicating that the simulation might be further used to study other amine solvents.

Considering that Singh *et al.* (2003) did not publish all necessary datas for their 30 wt% MEA for complete comparison with this base case simulation results, other available literature datas (400 MW coal-fired power plant) were used for comparison. Razi *et al.* (2013) modeled an MEA process for a 400 MWe coal fired power plant which is same capacity of the base case for this research. According to Razi *et al.* (2013) stated that the CO_2-MEA chemical reaction occur in the liquid phase and due to its exothermicity, the temperature of the amine increases. This causes the temperature of the flue gas to increase from the bottom of the absorber towards the top where the lower temperature lean amine decreases the flue gas temperature. Therefore, temperature bulge can be noticed near the top of absorber and the position depends on the heat of reaction (Razi *et al.*, 2013). Figure 4.14 shows the temperature profile of the absorber for this simulation model.

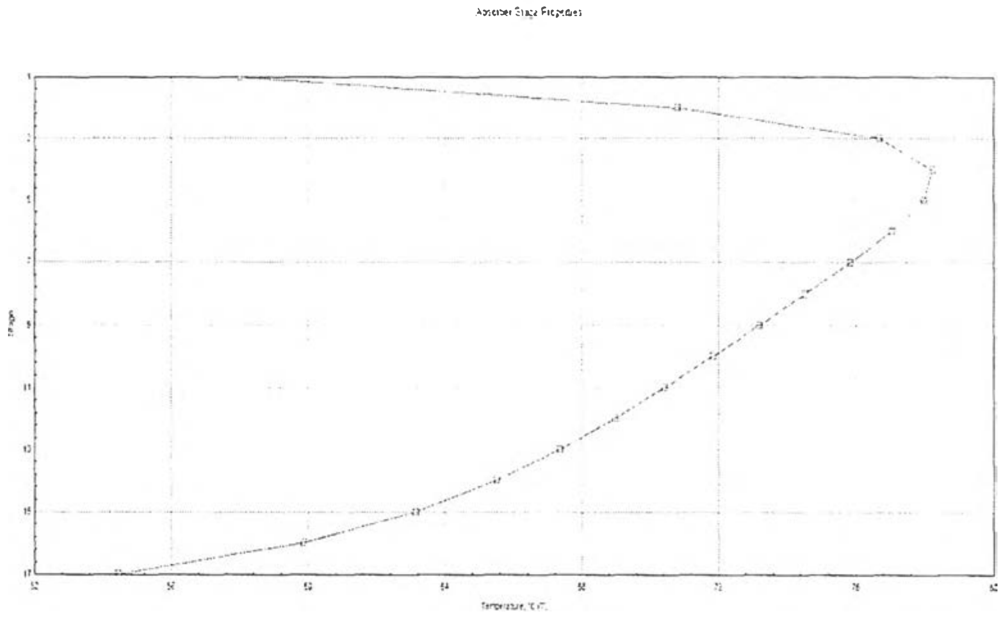

Figure 4.14 Temperature profile of the base case (30 wt% MEA) simulation.

4.6.3 AMP – PZ – MEA vs MEA Simulation

Several parameters were used to check the viability and potential of the various concentrations of the ternary blend through simulation, as compared to the conventional 5 M MEA. This comparison covered the net cyclic capacity and reboiler duty.

4.6.3.1 Cyclic Capacity

Cyclic capacity (CC) of any amine solution is a true indication of the CO_2 absorption capacity of that solution. It provides information on the ability of the amine solution to absorb CO_2 and as well desorb CO_2. CC is the difference between the rich and lean loading multiplied by its concentration as shown in Equation 4.18 (Ma'mun *et al.*, 2007). This is a true indication of the carrying capacity of the amine. Cyclic capacity is sometimes referred to as the working capacity.

$$CC = [\alpha CO_2\ (rich) - \alpha CO_2\ (lean)] \times Amine\ Conc. \qquad 4.18$$

Table 4.4 Cyclic capacity prediction and comparison of the amine solution using ProMax 3.2

Concentration (M)			**αCO_2 (Rich)** (mol CO_2/mol Amine)	**αCO_2 (Lean)** (mol CO_2/mol Amine)	**Cyclic Capacity** (mol CO_2/L Amine Solution)
AMP	PZ	MEA			
-	-	5	0.5	0.3	1
2	0.5	2.5	0.45	0.27	0.9
2	0.5	3	0.48	0.29	1.01
2	1	2	0.49	0.29	1
2	1	2.5	0.52	0.31	1.16
2	1	3	0.55	0.33	1.32
2	1	4	0.71	0.38	2.31

According to Maneeintr *et al.* (2009) higher cyclic capacities (CC) of a chemical solvent (than MEA) will have significantly less thermal energy consumption for CO_2 regeneration. From Table 4.4 the highly concentrated ternary blends indicated higher net cyclic capacity more than the base case 5 M MEA. This indicates lower amine circulation rate and hence reduction in reboiler duty.

4.6.3.2 Reboiler Duty

Reboiler duty for amine based CO_2 capture account for 70 - 80 % of the plant operational cost (Aaron and Tsouris, 2005), and as such have become parasitic to the entire process. Therefore, it needs to be carefully taken into consideration. Figure 4.15 shows the comparison between the reboiler of the base case 5 M MEA and all the ternary blends. It can be confirmed (from the simulation) that the ternary blends (above 5 M) indicated lower reboiler duties between 5.3 – 26.3 % compared to 5 M MEA.

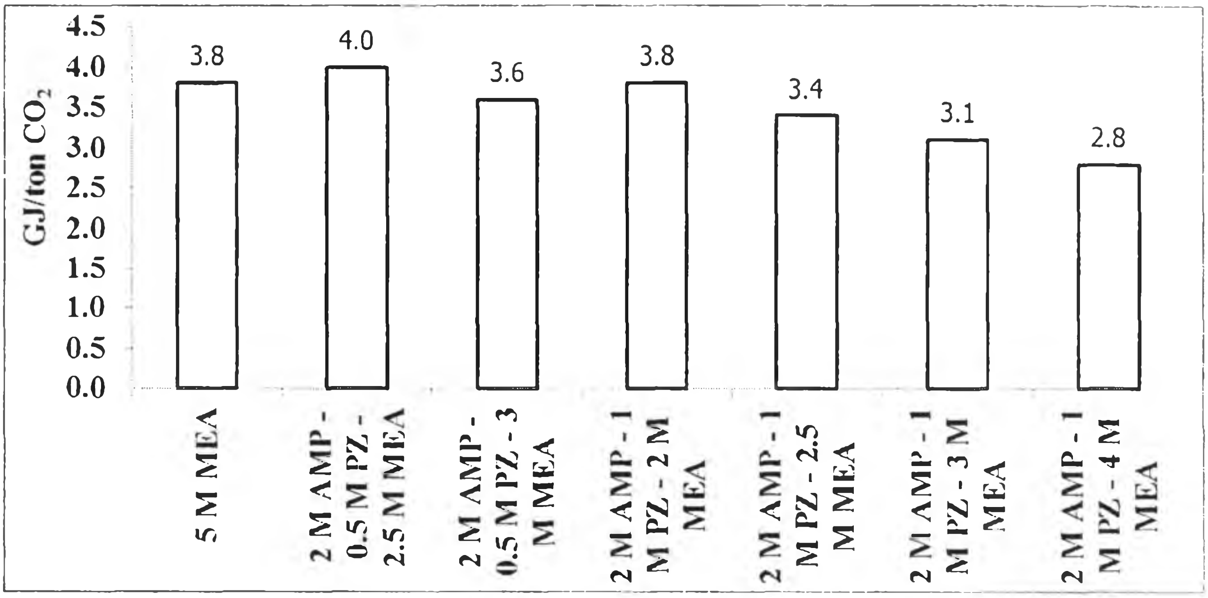

Figure 4.15 Reboiler duty comparisons between the base 5 M MEA, 3 M AMP – 1.5 M PZ and the ternary AMP-PZ-MEA blends.

Taking reference from the amine solutions comparison based on ProMax 3.2 simulation, the ternary solvent blend of concentration above 5 M all indicate good potentials in terms of its lower higher net cyclic capacity and more importantly lower reboiler duty. The shorting comings with the simulation of the ternary blends is that, the ProMax 3.2 simulation was not able to accurately predict their equilibrium loadings compared to experimental results. This can be confirmed while comparing CO_2 loadings from the simulation (15 % CO_2) and experimental results in Figure 4.9 (100 % CO_2). This can be attributed to the novelty of ternary amine blends for CO_2 capture. It also important to note that for adequate parametric analysis of amine solvents through simulation packages, reliable datas from both experimental analysis and pilot plant testing need to be available. This will guarantee a more accurate approach towards predicting plant performance using simulation. In addition, more CO_2 solubility analysis (physical and thermodynamic properties etc.) needs to be done for this ternary solvent blend in order to provide adequate datas required for mathematical modelling. This will help process simulator companies to incorporate the datas into their respective models for easy prediction. Appendix G provides all the simulation results and variables for the base case (MEA) as well as major results for all the ternary solvent blends.