CHAPTER 4

RESULTS AND DISCUSSION

This chapter is devoted to experimental results and discussion on density and CO₂ solubility that have been measured in this work. The density is measured at temperature range from 30 to 80 °C for a binary systems of PZ-H₂O, DEA- H₂O, PZ-DEA and the tertiary system PZ-DEA- H₂O. The excess molar volume is calculated using the Redlich-Kister equation. Based on the experimental density data, a generalized set of pair interaction parameters for density calculation of binary systems are determined. The calculated density value is compared with the experimental density data. The solubility CO₂ study is conducted for CO₂-PZ-H₂O and CO₂-PZ-DEA-H₂O systems. The effect of CO₂ partial pressure, amine concentration and temperature on the CO₂ solubility values is investigated. The behavior of the CO₂-amine system studied is compared with other amine systems.

4.1 Volumetric Properties

4.1.1 Density

The raw experimental data on density and excess molar volumes of binary aqueous solution of piperazine, DEA, DEA + PZ and tertiary mixtures of DEA + PZ + H₂O at temperature range from 30 to 80 °C are listed in appendix A. To check the consistency of the equipment, a comparison of density data from this work for 20 % mass DEA solution at 40, 60 and 80 °C with those reported in the literature is
shown in Table 4.1. The results obtained from the measurement are in good agreement with the data of Rinker et al., (1994) and Hsu et al., (1997). The maximum deviation of density measurement between this work and the literature values is about 0.3 %. This is may be due to the purity of the DEA used.

**Table 4.1**: Comparison of densities of aqueous DEA solutions measured with literature values.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (ρ/g.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 mass % DEA</td>
</tr>
<tr>
<td></td>
<td>Rinker et al. (1994)</td>
</tr>
<tr>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>40</td>
<td>1.0142</td>
</tr>
<tr>
<td>60</td>
<td>1.0052</td>
</tr>
<tr>
<td>80</td>
<td>0.9931</td>
</tr>
</tbody>
</table>

4.1.1.1 **Density of binary systems**

Figure 4.1 to 4.3 show the variation of density with amine concentration for PZ-H₂O, DEA-H₂O and DEA-PZ systems. For the binary DEA-PZ system the density is plotted against the PZ mol fraction. In the case of binary system of DEA-H₂O and PZ-H₂O the density increases with the amine concentration. The trend in DEA-H₂O
system is in good agreement with other studies reported in the literature (Rinker et al., 1994, Hsu et al., 1997). However, a different result is observed in DEA + PZ mixtures, where increasing the piperazine concentration results in a decrease in density (Figure 4.3). The density curves indicate that the interaction forces between the DEA and piperazine molecules are very weak. Thus, introducing more piperazine molecules in the mixture will have a disperse effect on the DEA-PZ molecules. This effect will expand the volume and reduce the density value of the mixtures.
Figure 4.1: Densities of aqueous piperazine solutions at different temperatures.
Figure 4.2: Densities of aqueous DEA solutions at different temperatures.
Figure 4.3: Densities of aqueous DEA + PZ mixtures at different temperatures
4.1.1.2 Density of ternary system

Figure 4.4 and 4.5 depicted the density measurement with piperazine concentration for the DEA-PZ-H$_2$O system. Results similar to DEA + PZ mixtures were observed in the mixtures of DEA + PZ + H$_2$O solutions with total concentration of 2M, where increasing the piperazine concentration will decrease the density value. This observation reveals that the interaction forces between the piperazine-DEA molecules is very small, which is in agreement with the results in DEA + PZ mixtures. In the total amine concentration of 4 M of the DEA + PZ + H$_2$O, the density behavior shows an interesting trend where it can be divided into two zones with a separation line at $x_1 = 0.0025$. At lower piperazine concentrations ($x_1 < 0.0025$), the density increases with increase of piperazine concentration, then it passes through a maximum value at $x_1 = 0.0025$ and then decreases gradually with increase in piperazine concentration. This phenomenon may be due to differences in molecular arrangements and interactions in the system. At low piperazine concentrations, the interaction of DEA and water molecules are more dominant thus increasing the clustering effect which was indicated by an increase in the density values. When more piperazine molecules exist in the mixture, the interactions between the DEA and water molecules are broken down. The mixture will experience a dispersion effect which leads to lower density values. The maximum density value corresponds to the highest interactions and clustering effect between the DEA, H$_2$O and PZ molecules.

In all cases, increasing the temperature will decrease the density value. This is expected due to the thermal agitation effect which causes volume expansion and this in turn will reduce the density value.
Figure 4.4: Densities of 2 M mixture of PZ + DEA + H₂O solutions at different temperatures.
Figure 4.5: Densities of 4 M mixture of PZ + DEA + H₂O solutions at different temperatures.
4.1.2 Excess Molar Volumes

The excess molar volumes for the binary mixture of PZ + H₂O, DEA + H₂O, DEA + PZ, tertiary mixtures of DEA + PZ + H₂O with total concentration of 2 M and 4 M are calculated using equation 2.2.4. Figure 4.6 – 4.9 show the trend of excess molar volume versus the mole fraction of the amine. The aqueous piperazine and DEA + PZ systems show a peculiar behavior compared with other amine systems studied in this work. It has positive and negative values of excess molar volumes at temperature less than 60 °C which means there is a volume expansion and contraction occurring. This behavior may be attributed to the physical interactions which involve mainly dispersion forces giving the positive contribution to the excess molar volume especially at low temperature. While the negative values of excess molar volume correspond to the significant contribution of greater interaction forces between the molecules involved in the mixtures and geometrical fitting of one component to another which are more pronounced at high temperature due to the thermal agitation effect.

4.1.2.1 PZ-H₂O system

In the PZ-H₂O systems solutions, a positive excess molar volume is obtained for piperazine concentration greater than 0.0037 and 0.011 mole fraction at temperature 30 and 40 °C respectively. In this region the excess molar volume increases with increase in piperazine concentration. At 50, 60, 70 and 80 °C, the excess molar volume values are negative, an increase in piperazine concentration results in a decrease in the excess molar volume. This indicates that there is both volume expansion and contraction in the range of the mole fraction of piperazine studied
(\(x_1 < 0.02\) mole fraction). The extent of expansion and contraction depends on the temperature and concentration of piperazine. The explanation of this volumetric behavior may be due to the existence of intermolecular attraction forces between the piperazine and water. The piperazine molecules occupy the space between the bulk of water molecules decreasing the volume. This is consistent with the Lumry’s model where at low mole fractions of the cosolvent, typically less than 0.1, the cosolvent (in this case PZ) molecules occupy the space between the bulk of water molecules and disturbs the cooperation fluctuations of the liquid water (Zhang and Hawrylak, 2002). These interactions intensified with an increase in temperature which may be due to the thermal agitation resulted in disrupting the extensive hydrogen-bonding between water molecules; thus a more compact aggregation between the water and piperazine molecules is formed. As the temperature decreases the non-random distribution of water and piperazine molecules is less attractive to each other. The movement of the molecules is less compared to the movement at high temperatures and with the increase of piperazine concentration at low temperature (< 40 °C) the space packing between the piperazine and water molecules becomes larger where the piperazine and water molecules do not cluster together, which in turn will lead to volume expansion. At temperatures greater than 40 °C the physical interaction between the unlike molecules is more dominant due to the disruption of water molecules. Thus increasing the piperazine concentration will reduce the excess volume. Figure 4.6 shows the trend of excess molar volume plotted against the concentration of piperazine.
Figure 4.6: Excess molar volume of aqueous piperazine solutions at different temperatures.
4.1.2.2 DEA-H₂O system

In the case of binary mixture of DEA + H₂O, the excess molar volume increases with an increase in temperature but decreases with an increase of DEA concentration (figure 4.7). This is due to the dominant role of geometrical fitting between unlike molecules. At low temperatures the DEA molecules will occupy the space between the water molecules, causing a local collapse of the ice like structure of water to form more compact arrangement (Maham et al., 1994). However, the interactions between these molecules are weak. Consequently, increasing the temperature will generate greater motion to the molecules. The vigorous motion will cause destruction of the weak DEA-water bonding in the mixture creating larger interspace between these molecules which will increase the excess molar volume.

4.1.2.3 DEA-PZ system

For DEA-PZ mixtures, positive excess molar volume values were observed at piperazine concentrations greater than 0.057 mole fraction at 30 and 40 °C (Figure 4.8). Positive excess molar volumes were also observed at temperature of 50 and 60 °C and at piperazine concentrations greater than 0.077 and 0.192 mole fraction respectively. These observations suggest that the interaction forces between the unlike molecules (DEA-PZ) is weak. But at high temperature the impact of the agitation will break down the bonds between the DEA and piperazine molecules in the mixtures thus allowing geometrical fitting of one component into another.
Figure 4.7: Excess molar volumes of aqueous DEA solutions at different temperatures
Figure 4.8: Excess molar volumes of DEA + PZ mixtures solutions at different temperatures.
4.1.2.4 DEA-PZ-H$_2$O system

In the ternary system of DEA + PZ + H$_2$O, all the excess molar volume values are negative. The total amine concentrations of 2 M and 4 M exhibit different trends of excess molar volume. This is due to the different composition of DEA and water molecules in the mixtures, even though the piperazine composition is the same. In the total amine concentration of 2 M, the excess molar volume value increases as the piperazine concentration increases. A cross over in the excess molar volume curves was observed at 0.002 mole fraction of piperazine. This result could be related to the point where strongest bonding of interaction occurred between the DEA, piperazine and water molecules. At this point, it will not be affected by the heat applied. At piperazine concentrations greater than 0.002 mole fraction, the interaction forces between the three molecules (DEA, PZ, H$_2$O) begin to loose, thus increasing the temperature will increase the excess molar volume.

The system with total amine concentration of 4 M exhibits a peculiar excess molar volume behavior. The excess molar volume as a function of piperazine concentration can be divided into three regions. The first region is where the excess molar volume decreases as the piperazine concentration is increased until to a point where a minimum excess molar volume value is reached at a piperazine concentration of 0.0025 mole fraction. The second region lies between 0.0025 $< x_1 < 0.008$ where the excess molar volume increases gradually as piperazine concentration increases and the excess molar volume curved intercept at $x_1 = 0.008$, where the strongest bonding between the three unlike molecules exists. Finally, the third region where $x_1 > 0.008$, the excess molar volumes continue to increase as the piperazine concentration
increases. This phenomena may be due to the dominant role of DEA-H₂O molecules geometrical fitting for the first region, then followed by the role of interaction forces between the DEA-PZ-H₂O molecules in the second region and finally the third region is due to the dominant role of piperazine molecules indicated by the increase of excess molar volume values.

The effect of temperature on the excess molar volume can be divided into two zones. This separation line occurs at \( x_1 < 0.002 \) for 2 M DEA-PZ-H₂O and \( x_1 < 0.008 \) for 4 M DEA-PZ-H₂O mixtures. As shown in figure 4.9 and 4.10, at \( x_1 < 0.002 \) and \( x_1 = 0.008 \) respectively, the excess molar volumes decrease as the temperatures decrease; however, at \( x_1 > 0.002 \) in 2 M DEA-PZ-H₂O and at \( x_1 > 0.008 \) in 4 M DEA-PZ-H₂O, the excess molar volumes increase as the temperatures increase. This suggest that at lower piperazine concentration (\( x_1 < 0.002 \) in 2 M DEA-PZ-H₂O and at \( x_1 < 0.008 \) in 4 M DEA-PZ-H₂O), the interaction forces between the three unlike molecules are stronger as the temperature increases, whereas at higher piperazine concentration (\( x_1 > 0.002 \) in 2 M DEA-PZ-H₂O and at \( x_1 > 0.008 \) in 4 M DEA-PZ-H₂O) the interaction forces between the DEA-PZ-H₂O molecules increase as the temperatures decrease.
Figure 4.9: Excess molar volumes of 2 M of PZ + DEA + H₂O mixtures solutions at different temperatures.
Figure 4.10: Excess molar volumes of 4 M PZ + DEA + H₂O mixtures solutions at various temperatures.
4.1.3 Comparison of volumetric properties in various amines studied

Densities values of different mixture of amine system studied in this work at 40 °C are presented in figure 4.11. The DEA + PZ mixtures densities appeared to be the highest among all the amine mixtures studied. This is primarily due to high molecular weight of DEA and piperazine. The density of activated DEA (DEA + PZ + H₂O) decreases as the piperazine concentration increases shows that density of mixtures is dominated by the DEA, whereby increasing the piperazine concentration will reduce the DEA component in the mixtures resulting in a lower density value. This feature is supported by the density curve of aqueous DEA where increasing the DEA concentration will increase the density value. The similar trend of density curves were observed in the different amine mixtures studied at other temperatures.

The activated DEA with total amine concentration of 4 M has the most negative excess volume value compared with other amine mixtures studied (Figure 4.12). This corresponds to a structure breaking solute where the alkanolamine molecules which have different shape and size may fit into the empty spaces between the water molecules, causing a local collapse to the structure of water forming a more compact arrangement. Even though the concentration of piperazine in the activated DEA with total amine concentrations of 2 M and 4 M is the same, the excess volume values of these mixtures are different. This is due to the different concentration of DEA in these two mixtures. The composition of DEA corresponds to a point plotted at the same piperazine concentration in total amine of 4 M is higher than in 2 M. This provide good evidence that in 4 M of activated DEA, there are more DEA molecules which can be fitted into the empty spaces of the water molecules resulting in
volumetric contraction. The strong interaction forces between the DEA and water molecules will also reduce the volume which will give more negative excess values. The highest excess molar volume values in aqueous piperazine solutions indicate that the clustering effect in this mixture is very small compared with other amine mixtures. Therefore, the interaction forces between the piperazine molecules and other component molecules are very weak. Consequently, increasing the piperazine concentration will increase the excess molar volume of the mixtures. This can be confirmed by the density curve of DEA + PZ mixtures and activated DEA where the excess molar volume increase as the concentration of piperazine increase, indicating a volume expansion.
Figure 4.11: Comparison of densities in various systems studied at 40 °C.
Figure 4.12: Comparison of excess molar volumes in various systems studied at 40°.
4.1.4 Density Correlation

In this work a Redlich-Kister equation of the excess molar volume was used to correlate the density of the amine liquid mixtures. Based on the experimental density data collected, a generalised set of pair interaction parameters for density calculation of binary amine systems was determined and presented in Table 4.2.

**Table 4.2**: The binary interaction parameters using the Redlich-Kister equation of excess volume.

<table>
<thead>
<tr>
<th></th>
<th>PZ + H2O</th>
<th>DEA + H2O</th>
<th>PZ + DEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_0$</td>
<td>$A_1$</td>
<td>$A_0$</td>
</tr>
<tr>
<td>b</td>
<td>3.4151</td>
<td>-3.8596</td>
<td>0.1538</td>
</tr>
<tr>
<td>c</td>
<td>-0.0359</td>
<td>0.0386</td>
<td>-0.0010</td>
</tr>
</tbody>
</table>

The binary interaction parameters for the amine density are calculated using Microsoft Excel. First, with the measured density value of the amine mixture, the molar volume of the liquid mixture is calculated using equation (2.2.5). Then the binary excess molar volume of the liquid mixture can be determined using equation (2.2.4) where the density of pure fluid of each component is calculated based on expression 2.2.6. With a set of known values of binary excess molar volume at each level of temperature, the pair parameter ($A_i$) can be generated from equation (2.2.1) by data regression using the Excel. Once the pair parameters have been successfully determined at each level of temperature, the binary interaction parameter of the amine system can be determined by the correlation of equation (2.2.2).
The detailed descriptions on the development of the density correlation have been described in section (2.2.1). The density of the pure fluid which is required to calculate the excess molar volume was calculated using equation (2.2.6). The parameters as shown in Table 4.3 were extracted from the available literature data except for piperazine, where the parameters were generated based on few data published by manufacturers (BASF and Chemical Limited Company) as described in appendix B. Note, the temperature unit used in this work is in degree Celsius. The densities of the pure fluids at various temperature are presented in Table 4.4. The calculated density results and the deviation between the calculated and measured density values are listed in appendix C. The average deviation for the PZ + H₂O, DEA + H₂O, DEA + PZ, DEA + PZ + H₂O (2 M) and DEA + PZ + H₂O (4M) systems is 0.02 %, 0.04 %, 0.06 %, 0.24 % and 0.37 % respectively.

**Table 4.3**: Pure fluid parameters for the density equation.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>a₁</th>
<th>a₂</th>
<th>a₃</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZ</td>
<td>1.18</td>
<td>-0.0037</td>
<td>1 X 10⁻⁵</td>
<td>This work</td>
</tr>
<tr>
<td>DEA</td>
<td>1.20715</td>
<td>-1.512 x 10⁻⁴</td>
<td>-7.6653 x 10⁻⁷</td>
<td>Hsu and Li, (1997)</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.863559</td>
<td>1.21494 x 10⁻¹</td>
<td>2.5708 x 10⁻⁶</td>
<td>Hsu and Li, (1997)</td>
</tr>
</tbody>
</table>
Table 4.4: The density of the pure fluid at various temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g. cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PZ</td>
</tr>
<tr>
<td>30</td>
<td>1.078</td>
</tr>
<tr>
<td>40</td>
<td>1.048</td>
</tr>
<tr>
<td>50</td>
<td>1.020</td>
</tr>
<tr>
<td>60</td>
<td>0.994</td>
</tr>
<tr>
<td>70</td>
<td>0.970</td>
</tr>
<tr>
<td>80</td>
<td>0.948</td>
</tr>
</tbody>
</table>

Comparisons between the calculated and experimental measured densities are shown graphically in Figure 4.13 – 4.16. The ratios of experimental density to calculated density are very close to unity. In fact, the maximum deviation between the experimental and calculated density is only about 0.67% found in the activated DEA mixtures. This shows that the results of the calculated density were in a good agreement with the experimental density data. Therefore, a density calculation using the general set of binary interaction parameters for the systems tested can be used, whenever immediate density data are required.
Figure 4.13: Comparison between experimental and calculated density values in aqueous piperazine solutions.
Figure 4.14: Comparison between experimental and calculated density values in aqueous DEA solutions.
Figure 4.15: Comparison between experimental and calculated density values in DEA + PZ mixtures.
Figure 4.16: Comparison between experimental and calculated density values in aqueous activated DEA solutions.
4.2 Solubility studies

4.2.1 Solubility of CO$_2$ in aqueous piperazine solutions

A systematic investigation on equilibrium solubility of CO$_2$ in aqueous piperazine solutions has been conducted in a double-jacketed stirred cell reactor. The solubility of CO$_2$ in the solution has been measured at 20, 30, 40 and 50 °C with CO$_2$ partial pressures varying from 0.4 to 95 kPa. The concentration of the piperazine in the solution was varied from 0.1 to 1.0 M. The overall reproducibility of the data is less than 5 %; however, for CO$_2$ partial pressures less than 1 kPa, the deviation achieved is as high as 10 %. The CO$_2$ partial pressure at equilibrium was calculated by subtracting the vapor pressure of water from the total pressure of the system. The raw data on the solubility of CO$_2$ in aqueous piperazine solutions are given in appendix D.

4.2.1.1 Effect of partial pressure and concentration

The effects of CO$_2$ partial pressure and concentration on the CO$_2$ loading at 20, 30, 40 and 50 °C are shown in figure 4.17 – 4.20. The CO$_2$ loading is expressed as mol of CO$_2$/mol of piperazine. In all cases, the same trend was observed where the CO$_2$ loading increases with the increase of partial pressure but decreases with increasing concentrations. The increase of loading with partial pressure is more rapid at high concentration (> 0.2 M) which is indicated by the steep slope of the solubility curve. However, the effect of partial pressure is more prominent at low piperazine concentrations. For example, an increase of partial pressure from 1 to 96 kPa in 0.1 M of piperazine solution at 30 °C, results in a 100 % increase in CO$_2$ loading,
whereas in 1 M of piperazine, the increase of loading is only about 20%. This characteristic is also observed at all temperatures investigated.

It can also be seen that from these figures (4.17 – 4.20) the solubility of CO₂ increases remarkably at low piperazine concentration, particularly at high partial pressures. Decreasing the concentration of piperazine from 0.2 to 0.1 M at a partial pressure of 95 kPa at 20 °C, results in an increase of 100% of the CO₂ loading. Theoretically, the maximum loading that can be achieved in the aqueous piperazine solution is 2.0 in the absence of carbamate formation. However, as clearly shown in this figures (4.17 and 4.18) at CO₂ partial pressures greater than 46 kPa in the solution of 0.1 M piperazine the loading exceeded the theoretical value. The excess of this CO₂ absorbed is due to the effect of physical absorption. This can be explained, whereby at 97 kPa and 30 °C, the concentration of the physical absorbed CO₂ that is calculated using the Henry’s Law is 0.03 M which is not far away from the excess CO₂ observed in this work. At other concentrations and conditions the ultimate loading achieved is well below 2 which confirm the presence and stability of piperazine carbamates in the liquid phase.
Figure 4.17: Solubility of CO$_2$ into aqueous piperazine solution at 20 °C.
Figure 4.18: Solubility of CO₂ into aqueous piperazine solution at 30 °C
Figure 4.19: Solubility of CO\(_2\) into aqueous piperazine solution at 40 °C.
Figure 4.20: Solubility of CO₂ into aqueous piperazine solution at 50 °C.
4.2.1.2 **Effect of temperature**

Figure 4.21 and 4.22 show the effect of temperature on the equilibrium loading. It was observed that the solubility of CO₂ increases with decrease in temperature. This can be explained based on the Le Chatelier principle where a change in conditions of any system at equilibrium will produce a reaction to offset the change. In this process, the reaction is exothermic; therefore, when external heat is applied to the system, the amount of material corresponding to the product will be decreased, consequently reducing the amount of CO₂ loading. This characteristic is in agreement with other types of aqueous amine solutions reported in the open literature. The same trend is observed at all piperazine concentrations.

4.2.1.3 **Comparison with published data**

A comparison between the work of Bishnoi and Rochelle (2000) and the values obtained in this study on the solubility of CO₂ in 0.6 M of aqueous piperazine solution at 40 °C are shown in figure 4.23. The CO₂ solubility data in this work is higher by 17% compared with those of Bishnoi and Rochelle (2000) work. This is due to the different method used to determine the CO₂ solubility in the aqueous piperazine. Bishnoi and Rochelle measured the solubility CO₂ in aqueous piperazine by bracketing equilibrium with both absorption and desorption measurements. Then they constructed a plot of CO₂ flux as a function of CO₂ interfacial partial pressure at constant loading. The equilibrium partial pressure was determined by interpolation to a value of flux equal to zero. The accuracy of such technique is questionable since only three data points were used in the interpolation process, whereas in this study, a wet chemistry titration method was used. This is the most common method...
employed by many investigators to determine the CO₂ solubility in the aqueous alkanolamine.

In order to identify the unique characteristics of piperazine, the aqueous piperazine behavior was compared with those of conventional alkanolamine. The CO₂ loading in 1.0 M of piperazine solution at 30 °C was expressed in terms of mol CO₂/mol total amine and plotted along with CO₂ loading in 2.0 M solutions of conventional alkanolamine as shown in figure 4.24. It can be seen that at low partial pressures the CO₂ absorption capability in the aqueous piperazine solution is higher compared to MDEA and DEA but very close to that of AMP. However, at high CO₂ partial pressure it has the lowest CO₂ loading value compared with all the other amines.
Figure 4.21: Solubility of CO₂ in 1 M aqueous piperazine solution at various temperatures.
Figure 4.22: Solubility of CO₂ in 0.6 M of aqueous piperazine solution at various temperatures.
Figure 4.23: Comparison of the CO₂ solubility in 0.6 M aqueous piperazine at 40 °C of the present work with that of Bishnoi and Rochelle (2000).
Figure 4.24: Solubility of CO₂ in different types of amine solution at 30 °C with a total amine concentration of 2 M.
4.2.2 Solubility of CO₂ in aqueous activated DEA solutions

In order to investigate further the role of piperazine in CO₂ absorption process, the solubility of CO₂ in activated DEA was studied at temperatures of 30, 40 and 50 °C with partial pressures ranging from 95 kPa to 0.4 kPa. The activated DEA was prepared from aqueous DEA solution doped with a small amount of piperazine. The concentration of piperazine varies from 0.1 M to 1.0 M. A total concentration of 2 M and 4 M of amine were used in the experiment. The raw data on the solubility of CO₂ into the activated DEA are presented in appendix E.

4.2.2.1 Effect of piperazine composition in activated DEA

The effect of piperazine composition on CO₂ loading can be seen graphically in figures 4.25 and 4.26 with total amine concentration of 2 M and 4 M respectively. Increasing the ratio of piperazine to DEA concentration does not improve the loading capacity significantly. In fact, in the higher CO₂ partial pressure region, increasing the piperazine concentration in the activated DEA will decrease the loading. The CO₂ loading in 1.8 M DEA + 0.1 M PZ appears to be higher than those in 0.1 M DEA + 0.95 M PZ. This is expected due to the formation of stable piperazine carbamates which will reduce the free piperazine molecules to absorb more CO₂ thus decreasing the CO₂ loading. Only a slight increase of loading was observed at low partial pressures (<10 kPa). As clearly seen from figure 4.25, at higher total amine concentrations, the change of piperazine composition does affect the CO₂ loading very much. For example, at 30 °C, an increase of piperazine concentration from 0.1 M to 1 M in total amine concentration of 4 M with CO₂
partial pressure of 93.6 kPa will decrease the loading by 4% only. Similarly, the same trend was observed at other temperature investigated in this work.

4.2.2.2 Effect of partial pressure and temperature.

The influence of partial pressure and temperature on solubilities of CO$_2$ in activated DEA was similar as in the other general amine solutions. The CO$_2$ loading increases with increase in CO$_2$ partial pressure but decreases with temperature. Figure 4.27 and 4.28 illustrated this behavior at 40 °C with a total amine concentration of 2 M and 4 M respectively.
Figure 4.25: Solubility of CO₂ in an activated DEA at 30 °C with different composition of piperazine in total amine concentration of 2 M.
Figure 4.26: Solubility of CO₂ in an activated DEA at 30 °C with different composition of piperazine in total amine concentration of 4 M.
Figure 4.27: Solubility of CO$_2$ in a 0.2 M DEA + 0.9 M PZ solution at different temperatures.
Figure 4.28: Solubility of CO₂ in a 3.98 M DEA + 0.01 M PZ solution at different temperatures.
4.2.2.3 **Comparison between activated DEA and its single amine**

A comparison of CO₂ solubility in activated DEA and in a single amine at 40 °C with a total concentration of 2 M is shown in figure 4.29. Apparently, the experimental data show that the activated DEA which contains small amount of piperazine (< 0.1 M) showed better CO₂ absorption capacity compared to its own single amine or activated DEA which contain high piperazine concentration at high partial pressure. For example, the addition of 0.1 M of piperazine into 1.8 M of aqueous DEA solution at 40 °C will increase the amount of CO₂ loading about 12 % compared to a 2 M of aqueous DEA solution alone at 93.6 kPa. This denotes that only small amount is required to improve the CO₂ loading capacity at this condition. Thus, increasing the concentration of piperazine in the activated DEA is not a viable option at high partial pressures. However, at low partial pressures, the aqueous piperazine solution shows better absorption performance compared to aqueous DEA or activated DEA. Therefore, this confirms that increasing the piperazine concentration is only beneficial at low partial pressures (< 1 kPa), while at high partial pressures only a small amount is needed to enhance the absorption capacity.

The same trend was observed in activated DEA with total amine concentration of 4 M where the loading in activated DEA which contains 0.05 M of piperazine was 30 % greater than the loading in 4 M of DEA aqueous solution. This indicates that the presence of piperazine in small amounts does not only improve the CO₂ loading at low partial pressure but also increases the absorption capacity significantly at high concentrations of activated DEA solution. Thus, on the basis of this observation, it is
clear that the presence of small amount of piperazine in the higher total amine concentration is beneficial to improve the loading capacity.
Figure 4.29: Solubility of CO₂ in aqueous single amine and its mixtures at 40 °C with total amine concentration of 2 M.
4.2.2.4 *Comparison between activated DEA and other amine mixtures*

A comparison on the performance of CO\textsubscript{2} loading was evaluated between activated DEA and other amine mixtures. Due to the inconsistency of total amine concentrations and units used in this work and those of other investigators, only few data are available to be compared with. Figure 4.30 shows the loading as a function of partial pressure for activated DEA, MEA + MDEA and DEA + MDEA mixtures at the same total amine concentration of 4 M. It was observed that the activated DEA has a higher loading capacity at low to moderate CO\textsubscript{2} partial pressures compared with the other two amine mixtures (MEA + MDEA, DEA + MDEA). At 0.9 kPa CO\textsubscript{2} partial pressure, the loading capacity of 2 M DEA + 1 M PZ mixture is about 2.0 and 1.18 times greater than 2 M DEA + 2 M MDEA and 2 M MEA + 2 M MDEA, respectively. This feature indicates that the aqueous activated DEA solution is another potential amine solvent to be employed in the gas treatment unit, particularly at low CO\textsubscript{2} partial pressures.
Figure 4.30: Solubility of CO₂ in various types of amine mixtures at 30 °C with total concentration of 2 M.
Figure 4.31: Solubility of CO₂ in various types of amine mixtures at 30 °C with total concentration of 4 M.