

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 INTRODUCTION

This chapter presents the results of the absorption of CO₂ in 1.0 M, 2.0 M and 4.0 M aqueous 2-(methylamino) ethanol (MAE) at 30, 40 and 60 °C and at different CO₂ partial pressures using the methods and procedures described in Chapter 4.

In order to assess the performance of this amine, the experimental solubility data of CO₂ in MAE are compared with those of other well known amines; monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino, 2-methylpropanediol (AMPD), 2-amino,2-methylpropanol (AMP) and triisopropanolamine (TIPA)

5.2 VALIDATION OF EXPERIMENTAL DATA

In order to assess the reliability of the data obtained in this work, the CO₂ loading in 2.5 M aqueous monoethanolamine (MEA) was determined experimentally at different CO₂ partial pressures at 40 °C. The results are compared with data available in the literature, as shown in Figure 5.1. The comparison shows a good agreement between the results of this work and the other sources of data which proves that the experimental set-up and procedures used in this work are valid and reliable.

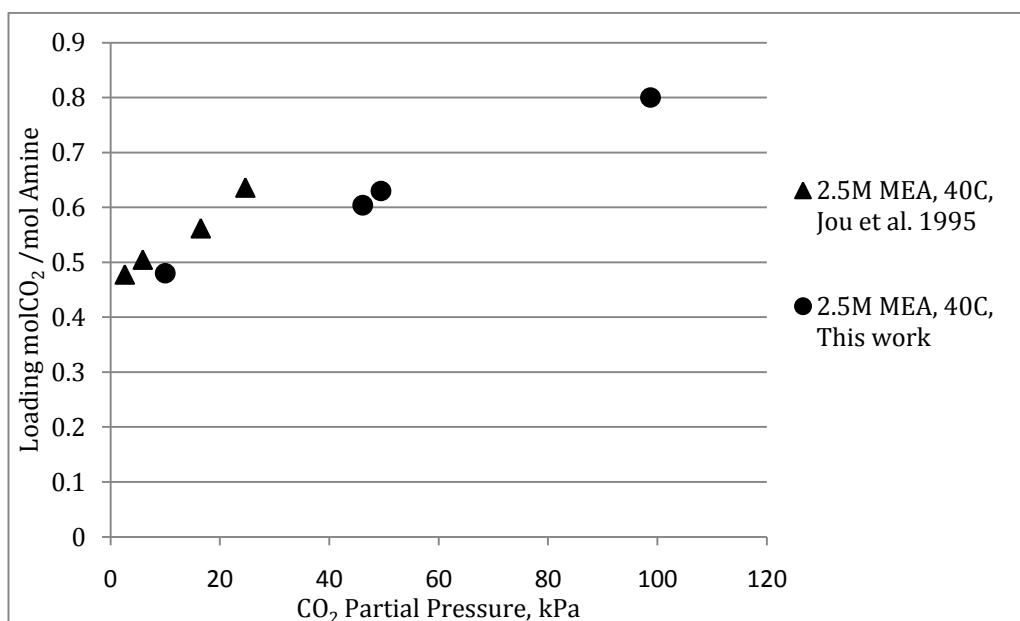


Figure 5.1: Variation of CO₂ loading with CO₂ partial pressure for 2.5 M MEA at 40 °C; Jou et al. (1995) and this work

5.3 ERROR ANALYSIS AND ACCURACY

The accuracy of the experimental results is affected by several factors including volume measurement, amine concentration, vapour phase mole fraction of CO₂ and the total pressure of the system. To ensure the reliability of the results, it is important that the total amine concentration remains constant throughout each run. Therefore, the concentration of the amine is analyzed at the beginning and at the end of each run. The variation in most cases was between 2% and 5%. However, in a few cases, where the CO₂ partial pressure is low, slightly higher differences are obtained. This is attributed to the long time required for equilibrium to be reached and hence evaporation is likely to occur, especially at high operating temperatures. The measured variations also included errors in the analysis, which is estimated to be around 2%. Therefore, without introducing any significant errors, it can be concluded that total amine concentration in the solution remained constant throughout each run.

Since the gas is assumed to be saturated with water vapour, the CO₂ partial pressure at equilibrium was calculated by subtracting the water vapour pressure from the total pressure of the system. The CO₂ solubility data are the averages of three determinations of CO₂ solubility in MAE solution with standard deviation of less than 5% in all cases.

5.4 SOLUBILITY OF CO₂ IN 2-METHYLAMINOETHANOL

The solubility of CO₂ in 1.0 M, 2.0 M and 4.0 M MAE was measured at three different temperatures; 30, 40 and 60 °C and at CO₂ partial pressures ranging from around 1 to 100 kPa. Table 5.1 shows the experimental results of the solubility of carbon dioxide in MAE, expressed in terms of loading, α , (mole CO₂/ mole MAE). These data are plotted in Figures 5.2 - 5.7 which illustrate the effect of variation of temperature, CO₂ partial pressure and amine concentration on CO₂ loading in MAE.

Table 5.1: Experimental carbon dioxide loading in 1.0 M MAE at 30 °C, 40 °C, and 60 °C and at various CO₂ partial pressures.

Concentration ^a (mol.dm ⁻³)	Temperature ^b (°C)	P_{CO_2} ^c (kPa)	Experimental Loading ^d (mole CO ₂ /mole MAE)
1M MAE	30	99.08	0.989
		49.37	0.941
		24.69	0.863
		9.84	0.795
		4.95	0.786
		0.98	0.566
1M MAE	40	98.91	0.982
		49.37	0.912
		24.64	0.808
1M MAE	60	98.41	0.996
		49.37	0.803
		24.64	0.683

^aAccuracy ±0.002 mol.dm⁻³

^bAccuracy ±0.1°C

^cAccuracy ±0.1 kPa

Accuracy ±0.001

Table 5.2: Experimental carbon dioxide loading in 2.0 M and 4.0 M MAE at 30 °C, 40 °C, and 60 °C and at various CO₂ partial pressures.

Concentration ^a (mol.dm ⁻³)	Temperature ^b (°C)	P_{CO_2} ^c (kPa)	Experimental Loading ^d (mole CO ₂ /mole MAE)
2M MAE	30	98.75	0.902
		49.04	0.804
		24.64	0.759
		9.87	0.706
		4.95	0.662
		0.99	0.548
2M MAE	40	98.58	0.853
		49.12	0.743
		24.64	0.721
2M MAE	60	98.58	0.751
		49.29	0.679
		24.81	0.669
4M MAE	30	98.41	0.598
		49.37	0.588
		24.64	0.573
		9.89	0.549
		4.95	0.521
		0.99	0.474

^aAccuracy ±0.002 mol.dm⁻³

^bAccuracy ±0.1°C

^cAccuracy ±0.1 kPa

Accuracy ±0.001

5.4.1 Effect of Temperature and CO₂ Partial Pressure on CO₂ Loading

Figures 5.2, 5.3 and 5.4 show the effect of temperature and CO₂ partial pressure on the equilibrium CO₂ loading in 1.0 M, 2.0 M and 4.0 M MAE, respectively. It can be observed that CO₂ loading decreases with increasing temperature of the solution. The observed variation with temperature is expected as the reaction of CO₂ with amine solution is exothermic. It is also known that the solubility of gases in liquids decreases with increasing temperature. Both factors result in decrease of loading with increasing temperature. Results also showed that CO₂ loading increased with increasing CO₂ partial pressure. The observed trend of the variation of loading with CO₂ partial pressure agrees with that of other alkanolamine solutions published in the literature, Benamor (1998), Si Ali (2007), Hosseini (2009) and many others. According to Le Chatelier's principal, increasing CO₂ partial pressure causes more CO₂ diffusion to the liquid phase which increases the chemical potential of the liquid phase ions resulting in higher CO₂ loading.

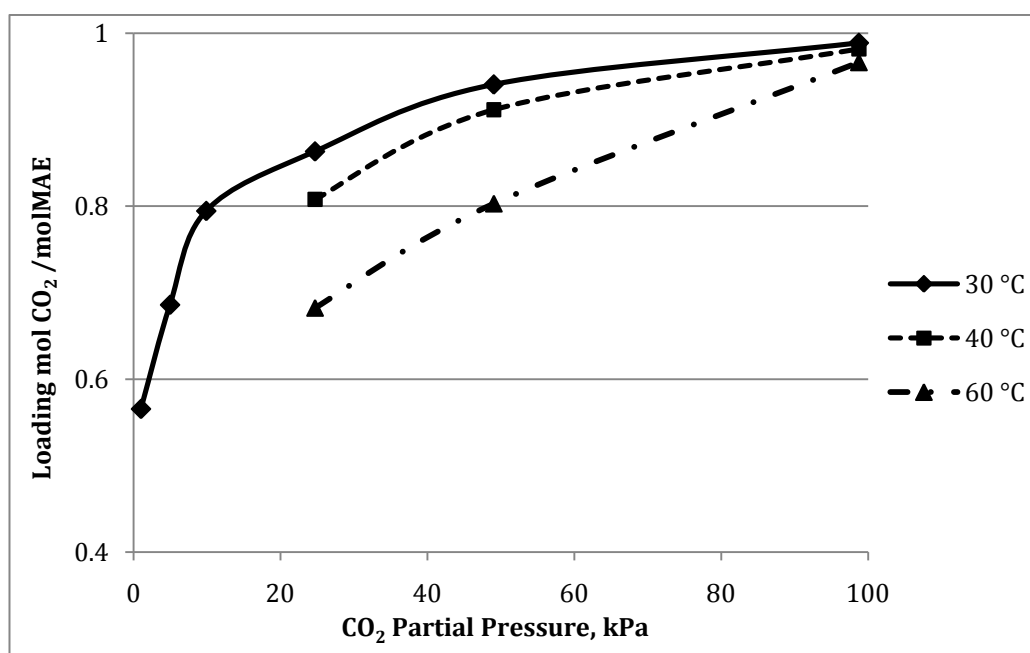


Figure 5.2: Variation of CO₂ loading in 1.0 M MAE with partial pressure at 30 °C, 40 °C and 60 °C

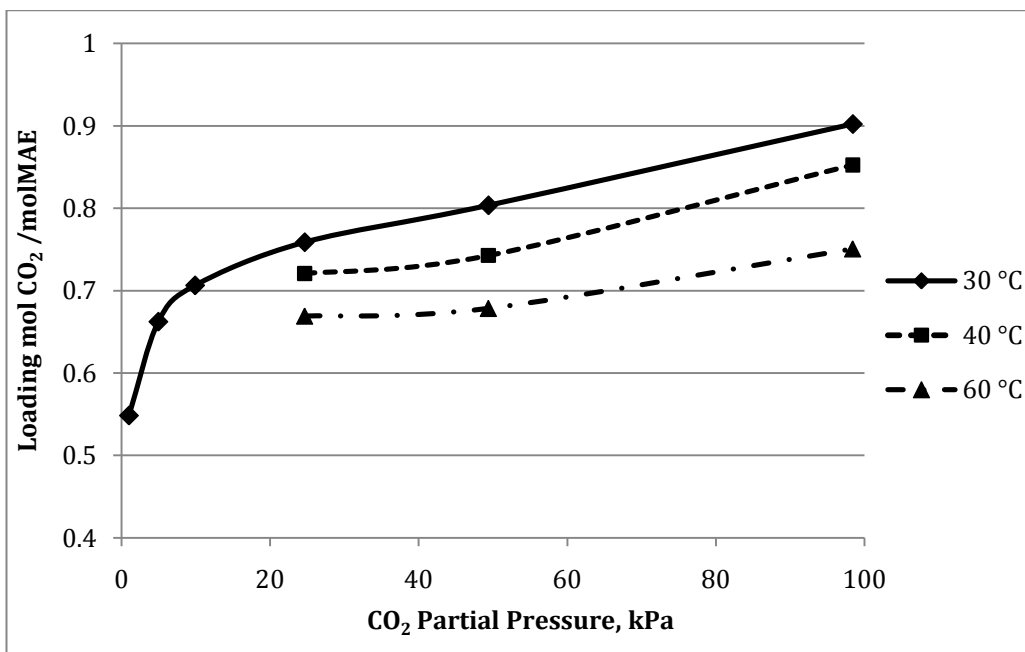


Figure 5.3: Variation of CO₂ loading in 2.0 M MAE with partial pressure at 30 °C, 40 °C and 60 °C

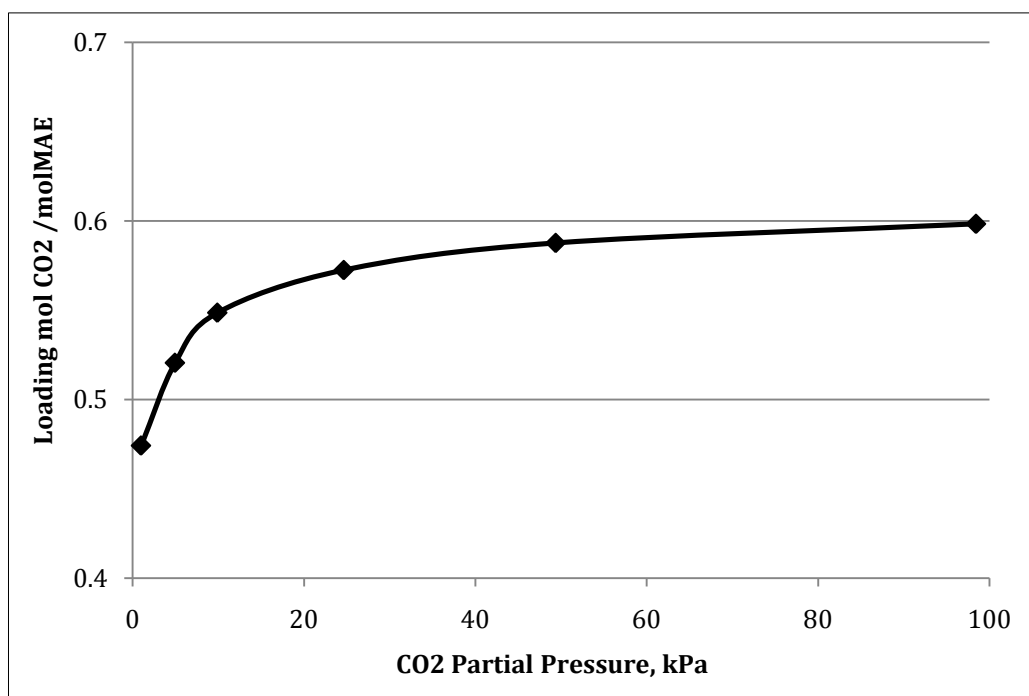


Figure 5.4: Variation of CO₂ loading with partial pressure of 4.0 M MAE at 30 °C

5.4.2 Effect of Amine Concentration on CO₂ Loading

Figures 5.5, 5.6 and 5.7 show the variation of equilibrium CO₂ solubility in aqueous 1.0 M, 2.0 M and 4.0 M MAE at temperatures of 30 °C, 40 °C and 60 °C, respectively. The results illustrate that the CO₂ loading decreases with increase of MAE concentration. This trend is similar to that of other primary and secondary amines published in the literature, Aroua et al. (2002), Baek & Yoon (1998), Benamor (1998), and many others.

Since the relation between solubility and concentration is generally non-linear, and since the solubility is expressed in mole CO₂ per mole amine, therefore, the solubility associated with increasing amine concentration is divided by the amine molarity to get the loading. This will result in a slight decrease in the loading at higher amine concentrations.

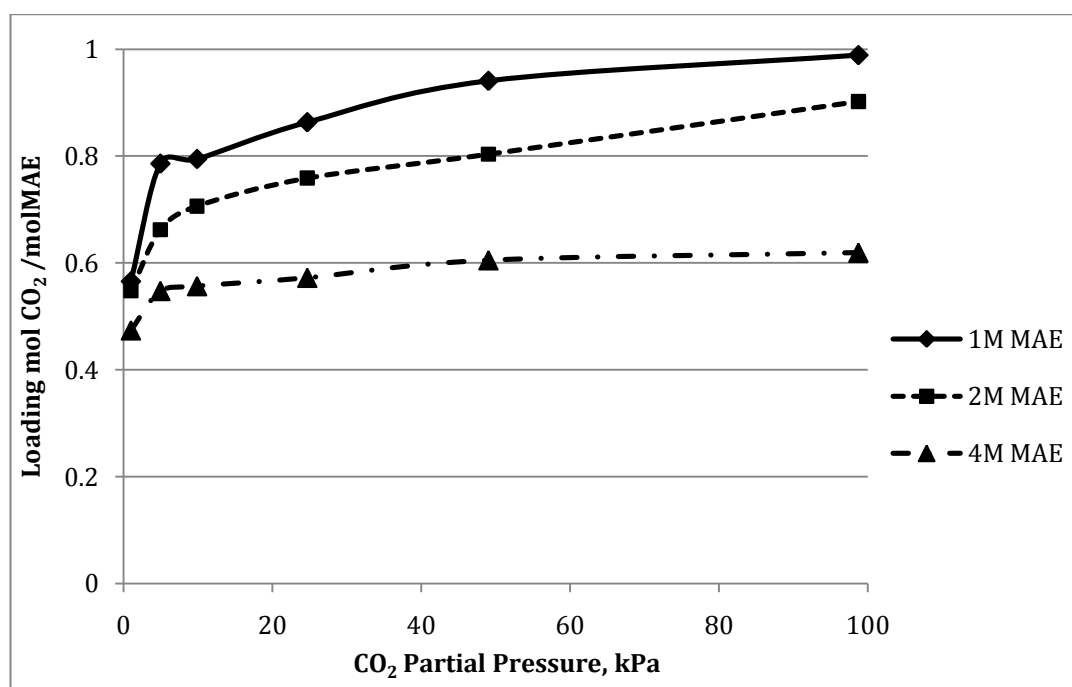


Figure 5.5: Variation of CO₂ loading with CO₂ partial pressure of 1.0 M MAE, 2.0 M MAE and 4.0 M MAE at 30 °C

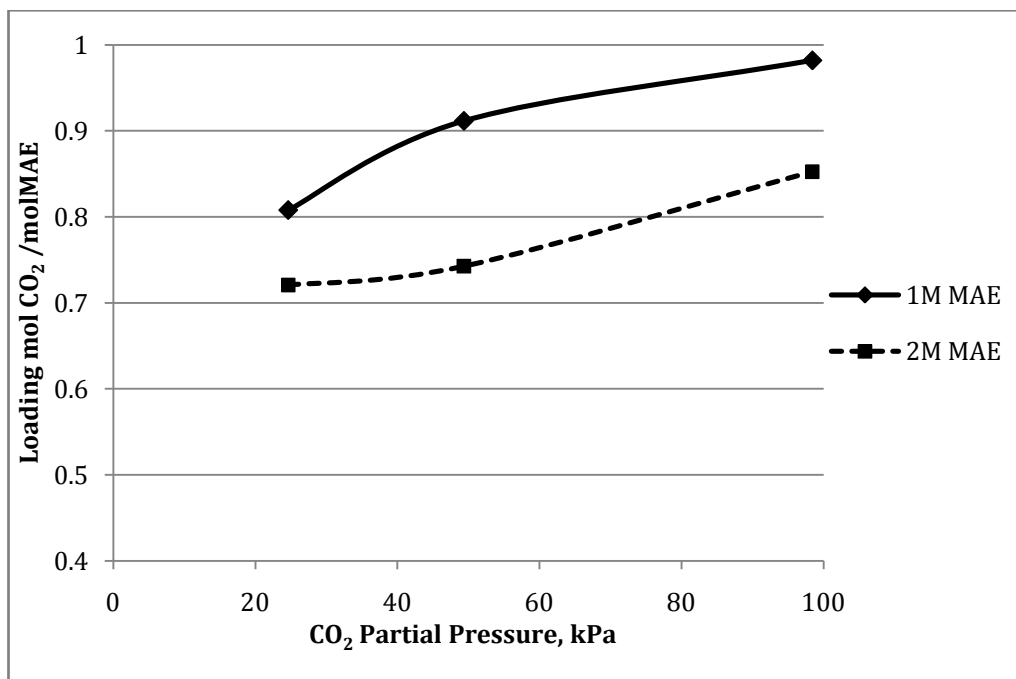


Figure 5.6 : Variation of CO₂ loading with CO₂ partial pressure of 1.0 M MAE and 2.0 M MAE, at 30 °C

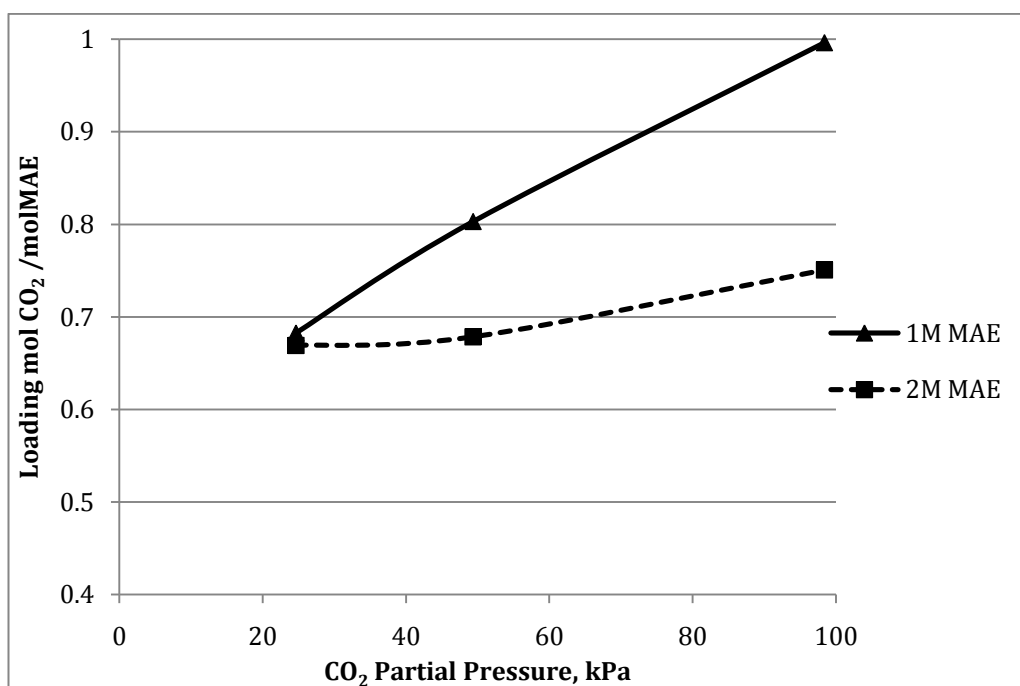


Figure 5.7: Variation of CO₂ loading with CO₂ partial pressure at 60 °C of 1.0 M MAE and 2.0 M MAE

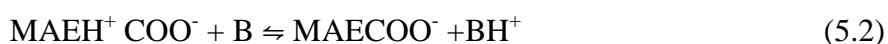
5.4.3 Carbamate Ion Concentration

The reaction mechanism of aqueous solutions of MAE with CO₂ is expected to follow the same pattern as the secondary amine DEA which was described by Benamor *et al.* (2007). They suggested that the accepted mechanism is the one originally proposed by Caplow (1968), which involves the formation of an intermediate zwitterion followed by the removal of a proton by a base, B. As a result a carbamate ion is formed, as follows;

- Formation of zwitterion



- Removal of the proton by a base



where the base B could be a water molecule, a hydroxide ion or another amine molecule.

The carbamate ion concentration can be determined using the same technique adopted by Benamor & Aroua (2005) and Benamor *et al.* (2007) who investigated the significance of carbamate formation in the mechanism of the reaction of CO₂ with DEA.

In this work, the concentration of carbamate ion in the loaded amine solution was determined by reacting it with standard NaOH solution using the same titration technique used by Haji-Sulaiman *et al.* (1996). In this case, only the bicarbonate, the protonated amine and the free CO₂ will react with the hydroxide ions. Thus, the concentration of carbamate, [MAECO⁻] can be related to the CO₂ loading, α , and the concentration of NaOH, B , by equations (4.10) and (4.11).

Experimental results of carbamate ion contribution to the overall absorbed CO₂ at 30, 40 and 60 °C are shown in Table 5.3. These results are plotted in Figures 5.8 and 5.9. It is clear that the total contribution of carbamate ion to the overall absorbed CO₂

has an average of 26.4% with a standard deviation of 12.2 which is much lower than that for DEA which was determined by Benamor *et al.* (2007). This result confirms the assumption made by Huang *et al.* (2000) that much of the carbamate will undergo hydrolysis to bicarbonate. Hence, the high loading capacity of MAE can be attributed to this behavior.

Results also show that the equilibrium carbamate ion concentration decreases with increasing CO₂ partial pressure, and increases with increasing amine concentration. The same trend has been established for DEA by Benamor *et al.* (2007). At high CO₂ partial pressure more hydrolysis of carbamate is expected leading to lower carbamate ion concentration, while at higher amine concentration greater number of carbamate ions will be present at equilibrium.

Table 5.3 Contribution of carbamate ion to the overall absorbed CO₂ in MAE

M (mol.dm⁻³)	Temp. (°C)	P_{CO2} (kPa)	[MAECOO⁻] (mol.dm⁻³)	Carb. (mol/mol)	Carb./Loading (%)
1M MAE	30	49.37	0.210	0.208	22.12
		24.69	0.289	0.301	34.85
2M MAE	30	24.69	0.554	0.274	36.15
		9.87	0.438	0.217	30.67
4M MAE	30	4.96	0.119	0.029	5.72
		0.99	0.112	0.028	5.88
1M MAE	40	98.91	0.141	0.146	14.92
		24.64	0.318	0.331	40.98
2M MAE	40	24.64	0.533	0.264	36.62
		0.986	0.325	0.164	29.91
1M MAE	60	98.41	0.148	0.154	15.46
		24.64	0.249	0.246	36.11
2M MAE	60	24.81	0.464	0.229	34.31
Average (%)					26.44

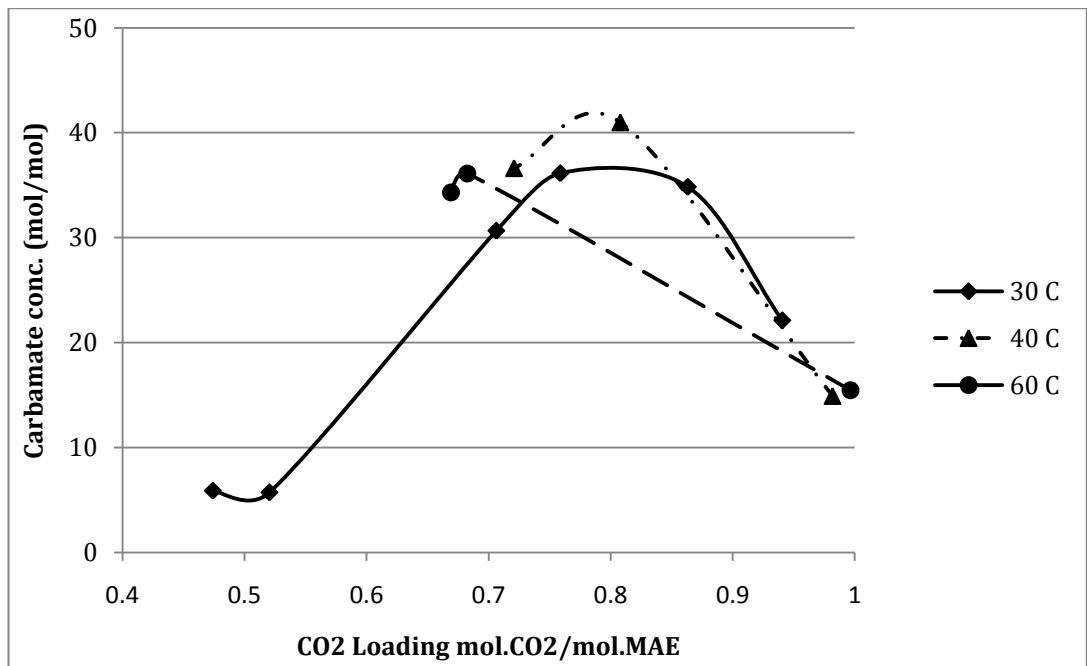


Figure 5.8: Variation of carbamate ion concentration with CO₂ loading at 30, 40 and 60 °C

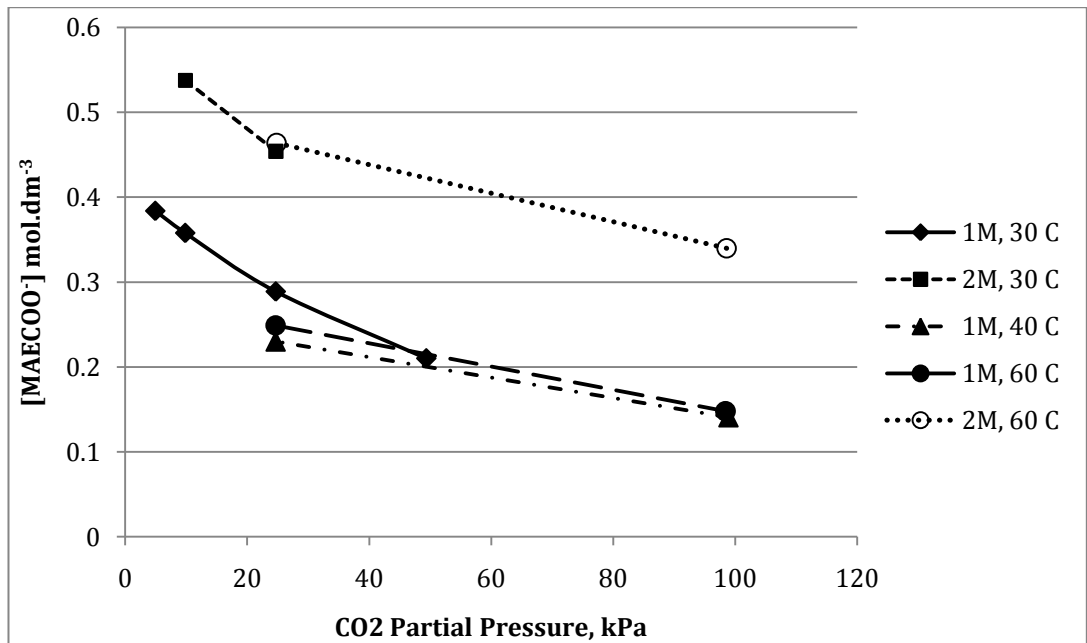


Figure 5.9: Variation of carbamate ions concentration with CO₂ partial pressure of 1.0 M MAE at 30 °C, 2.0 M MAE at 30 °C, 1.0 M MAE at 40 °C, 1.0 M MAE at 60 °C and 2.0 M MAE at 60 °C.

5.4.4 Equilibrium Time

Appendix B.2 lists the time to reach equilibrium of MAE at different operating conditions of temperature CO_2 partial pressure and amine concentration. It is clear that MAE demonstrated a fast reaction with CO_2 illustrated by the short time to reach equilibrium particularly at high temperature, low amine concentration and high CO_2 partial pressure. Ma'mun (2003) concluded that MAE had the highest reaction rate with CO_2 when compared with MEA, EMEA, MDEA, BEA and AEEA. However, more elaborate kinetics studies are required to confirm their findings.

5.5 PERFORMANCE COMPARISON BETWEEN MAE AND OTHER ALKANOLAMINES

5.5.1 Comparison with Monoethanolamine (MEA)

It is well known that primary amines like MEA form stable carbamate that limit the total loading capacity, while secondary amines like DEA and MAE and sterically hindered amines like AMP form unstable carbamate that will eventually undergo hydrolysis to bicarbonate and free amine which will be available to absorb more CO_2 . This results in almost doubling the loading capacity of these amines.

Figure 5.10 shows a comparison between the variation of the solubility of CO_2 in 2.0 M MAE with that in 2.0 M MEA with CO_2 partial pressure at 30 °C. The figure shows that MAE has higher loading at these partial pressures.

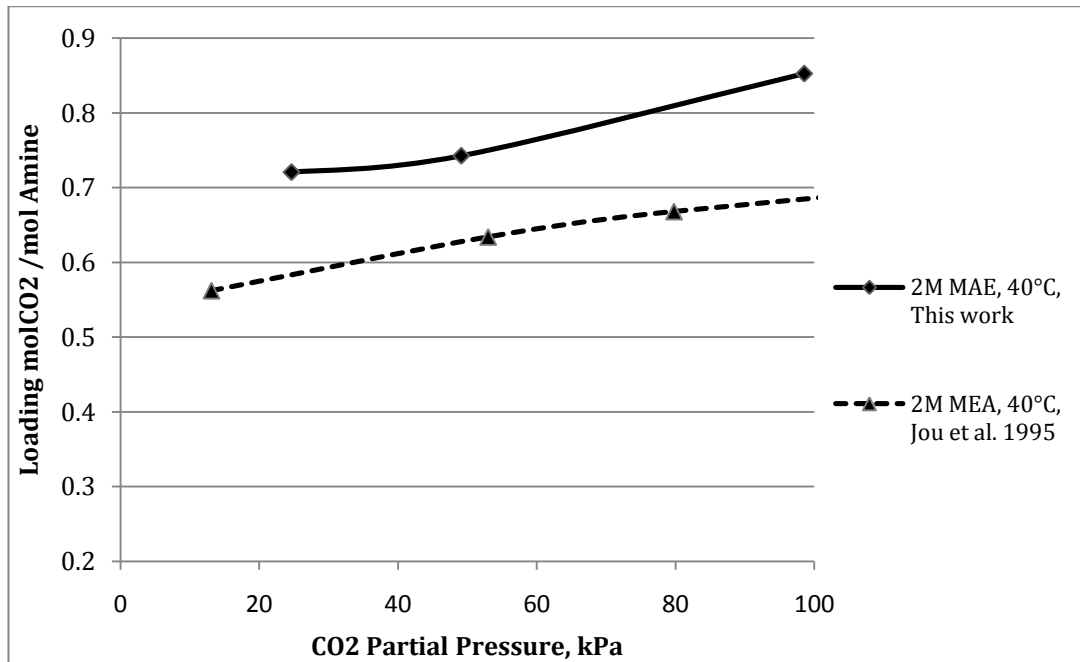


Figure 5.10: Variation of CO₂ loading with CO₂ partial pressure at 40 °C, 2.0 M MAE and 2.0 M MEA

5.5.2 Comparison with Diethanolamine (DEA)

DEA is a secondary alkanolamine with two hydroxyl groups. It is widely used for CO₂ absorption due to its relatively high absorption capacity and moderate reactivity with CO₂. Si Ali (2007) indicated that the principal reaction that occurs when CO₂ is reacted with aqueous DEA is as follows;



The carbamate is unstable and thus it will hydrolyze to bicarbonate and generates a free amine molecule which will be available for more CO₂ absorption.

Figure 5.11 shows a comparison between the solubility of CO₂ in 2.0 M MAE with that in 2.0 M of DEA at 40 and 60 °C and at different CO₂ partial pressures. The data for DEA are obtained from Si Ali (2007). The figure shows that MAE has slightly higher loading capacity than DEA. The similarity in the solubility behavior can be attributed to the similarity in the structure of the two alkanolamines. It can be observed

that higher loading capacity is in line with the lower carbamate stability of MAE as compared to that of DEA.

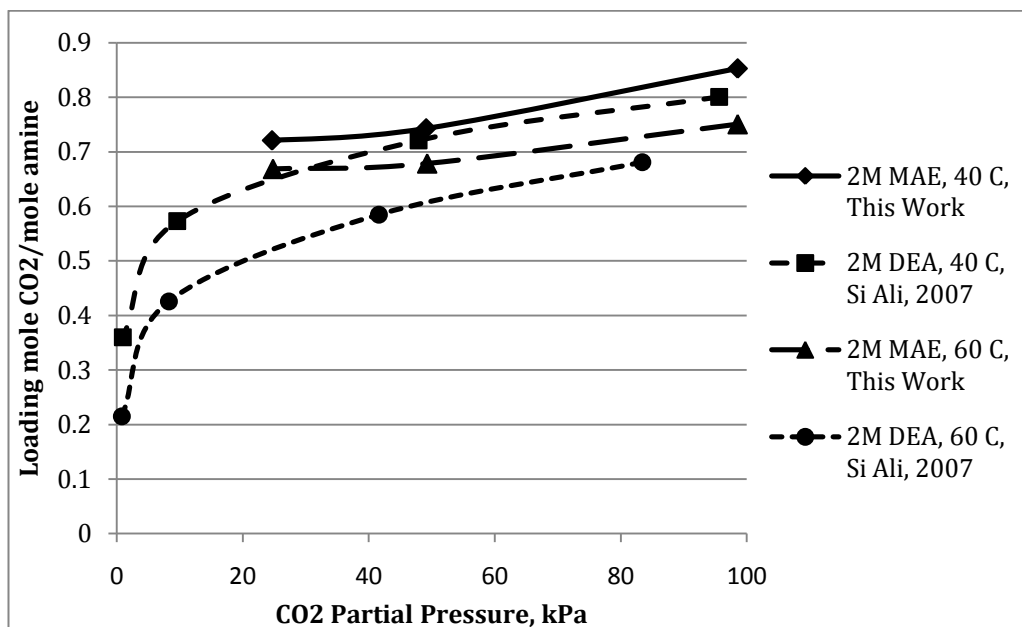


Figure 5.11: Variation of CO₂ loading with CO₂ partial pressure of 2.0 M MAE and 2.0 M DEA at 40 °C and 60 °C

5.5.3 Comparison with 2-Amino-2-methylpropanol (AMP)

AMP is a primary sterically hindered amine due to the presence of a bulky carbon atom attached to the amine group. According to Bishnoi (2000), AMP is considered a moderately hindered amine which can be used for bulk non-selective removal of CO₂ and H₂S from flue gas. Due to this moderate steric hindrance, the reaction of AMP with CO₂ will form very unstable carbamate which will hydrolyze to bicarbonate according to the following equation;



This will enhance its absorption capacity to almost double of its non-steric counterparts.

Figure 5.12 shows a comparison between the solubility of CO₂ in 2.0 M MAE with that in 2.0 M of AMP at 30 °C and at different CO₂ partial pressures. The data for AMP are obtained from Hosseini (2009). The figure shows that MAE has lower loading capacity than AMP. This can be attributed to the steric hindrance of the carbon atom attached to the amine group. Although MAE has a lower loading capacity than that of AMP it has the advantage of low molecular mass which will shift the preference to its side when the comparison in absorption capacity is based on mass% and not mol/mol.

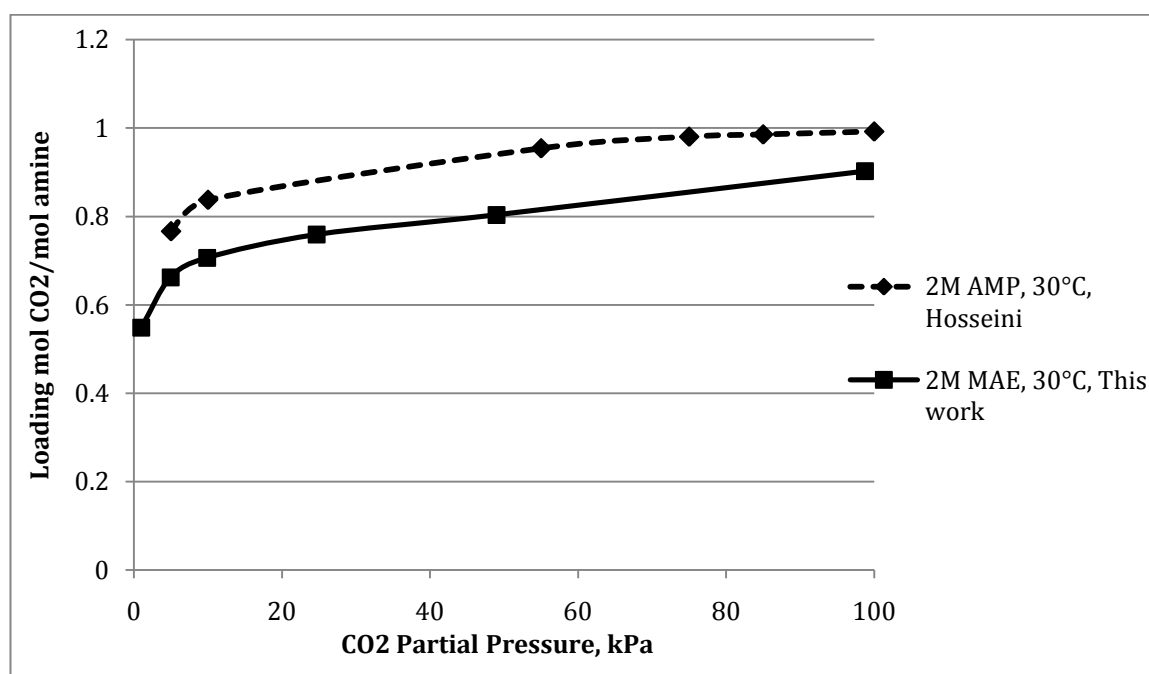


Figure 5.12: Variation of CO₂ loading with CO₂ partial pressure at 30 °C of 2.0 M MAE and 2.0 M AMP

5.5.4 Comparison with 2-Amino-2-methylpropanediol (AMPD)

Baek and Yoon (1998) and Baek et al. (2000) studied the equilibrium solubility of CO₂ in 10% (about 1 M) and 30% (about 4 M) aqueous solutions of AMPD at various temperatures and CO₂ partial pressures. AMPD is a primary sterically hindered amine with two hydroxyl groups. It reacts with CO₂ producing unstable carbamate which will

eventually undergo hydrolysis to bicarbonate which leads to doubling its absorption capacity. Baek & Yoon (1998) concluded that, at 40 °C, the tendency of the solubility of CO₂ in 30% AMPD is similar to that in 30% MDEA.

Figure 5.13 shows a comparison between the solubility of CO₂ in 1.0 M MAE with that in 1.0 M AMPD at 40 °C and at different CO₂ partial pressures. The data for AMPD were obtained from Baek et al. (2000). It is clear from this figure, that at higher CO₂ partial pressure, the loading approaches 1.0 mol/mol while the difference is much more pronounced at lower partial pressures.

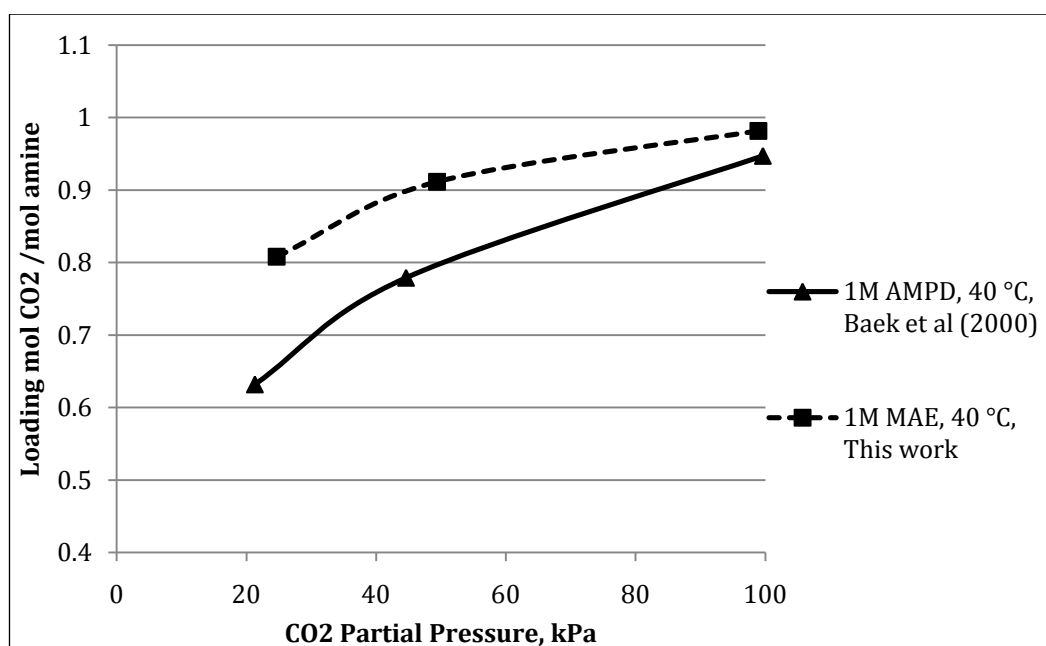


Figure 5.13: Variation of CO₂ loading with CO₂ partial pressure at 40 °C of 1.0 M MAE and 1.0 M AMPD

5.5.5 Comparison with Methyldiethanolamine (MDEA)

While primary amines are characterized by low loading capacity and high rate of reaction with CO₂, tertiary amines like MDEA are known for their high loading capacity and slow reaction with CO₂. They do not form carbamate ion due to the lack of extra hydrogen.

The most distinct advantage of MDEA is that it is readily selective towards H₂S in the presence of CO₂. Other advantages include low vapour pressure, low heat of reaction, low corrosivity and resistance to degradation, Austgen *et al.* (1991). The reaction of CO₂ with MDEA is as follows;



Figure 5.14 shows a comparison between the solubility of CO₂ in 2.0 M MAE with that in 2.0 M MDEA at 30 °C and at different CO₂ partial pressures. The data for MDEA were obtained from Si Ali (2007). The figure shows that at high partial pressure the profile is almost similar, however, MAE has much higher loading capacity at low partial pressures. This is due to the formation of carbamate ion that enhances the loading at low pressure. Thus, MAE combines the advantages of primary and secondary amines at low pressure and the advantages of tertiary amines at high pressure.

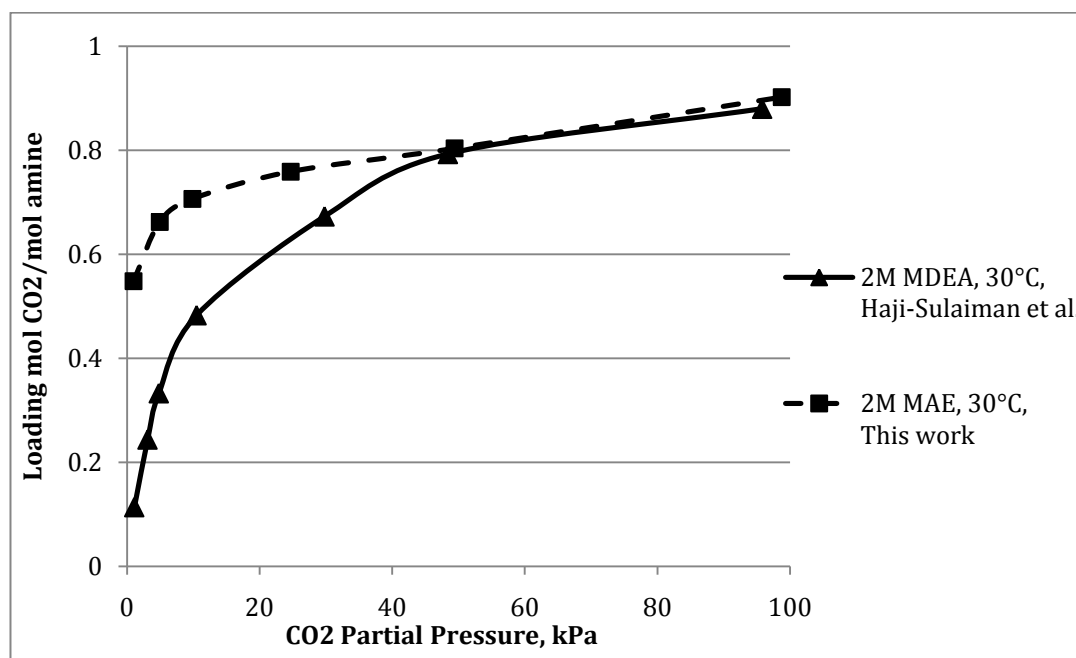


Figure 5.14: Variation of CO₂ loading with CO₂ partial pressure at 30 °C of 2.0 M MAE and 2.0 M MDEA

5.5.6 Comparison with Triisopropylamine (TIPA)

TIPA is a tertiary, severely hindered alkanolamine. It has been investigated by Danneshvar *et al.* (2003) together with MEA, PZ and their blends as a potential CO₂ absorber due to its relative low cost and high absorption capacity with CO₂ compared to other tertiary amines like MDEA. Since TIPA is a tertiary, severely hindered amine, its reaction with CO₂ is through acid-base reaction mechanism and thus, the carbamate ion concentration is zero. TIPA also has a low heat of reaction with CO₂ and therefore, it is expected to be regenerated with lower energy consumption. For the same reason, it is expected that TIPA is more resistant to degradation.

Figure 5.15 shows a comparison between the solubility of CO₂ in 2.0 M MAE with that in 2.0 M TIPA at 30 °C, and 40 °C and at different CO₂ partial pressures. The figure shows that MAE has higher loading through the entire range of partial pressures.

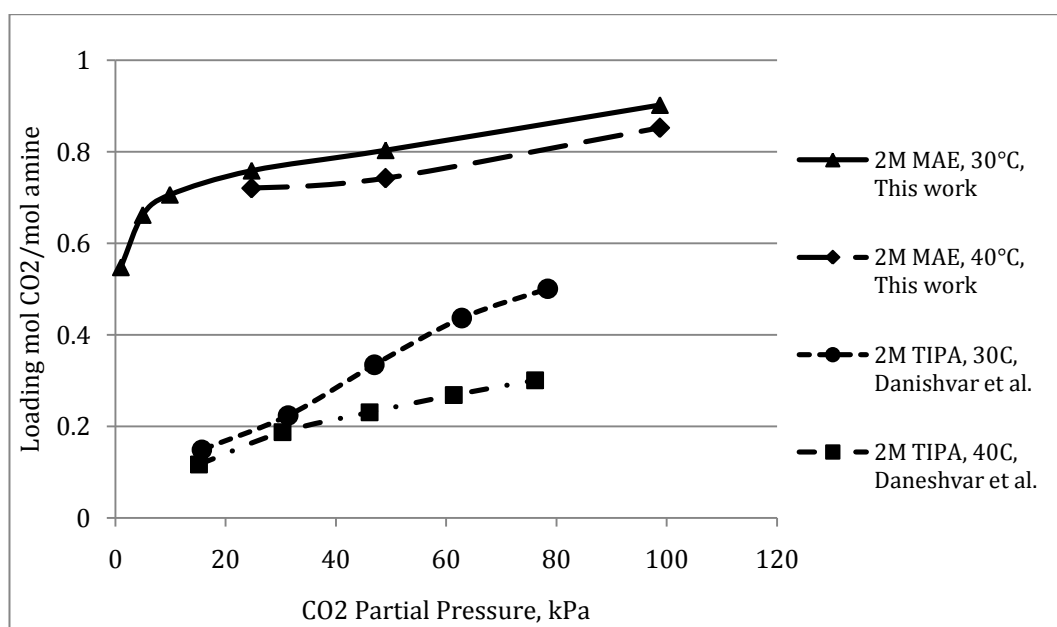


Figure 5.15: Variation of CO₂ loading with CO₂ partial pressure of 2.0 M MAE, at 30 °C, 2.0 M MAE at 40 °C, 2.0 M TIPA at 30 °C and 2.0 M TIPA at 40 °C

5.6 SUMMARY

The absorption of 1.0 M, 2.0 M, and 4.0 MAE was investigated at temperatures of 30 °C, 40 °C and 60 °C and CO₂ partial pressures from 0.9 to 100 kPa. The data generated in this experimental procedure was validated with published data using 2.0 M and 2.5 M MEA at 40 °C. The results were in good agreement with various sources of data.

The absorption of CO₂ by MAE was found to increase with increasing CO₂ partial pressure but decreases with increasing temperature. The amine concentration was found to have a slight negative effect on the value of loading (α) in mol. CO₂/mol.MAE. The carbamate ion concentration was found to have a similar profile to that of DEA.

The performance of MAE was compared with other well-known alkanolamines (MEA, DEA, AMP, AMPD, MDEA and TIPA). The results show that the loading of MAE is higher than all other amines except for AMP which showed higher loading due to its steric hindrance and its higher alkalinity.