CHAPTER SIX

VLE MODELING RESULTS AND DISCUSSION

6.1 INTRODUCTION

In order to perform a complete process simulation for the design of gas treating units, it is essential to develop an accurate model that predicts the vapour-liquid equilibrium behavior of this amine at various operating conditions. The chemical reactions which occur in CO_2-MAE-water system are discussed in Chapter three, together with a survey of a number of models developed for different amines.

This chapter illustrates the results of the proposed technique for predicting the solubility of CO_2 in MAE based on the correlation proposed by Haji-Sulaiman *et al.* (1996). As explained in Chapter 3 of this thesis, this technique involves calculating K_2 which represents the hydrolysis of carbamate ions, by fitting the experimental data of carbamate ion concentrations to a correlation which includes temperature, CO_2 partial pressure and amine concentration. The parameters of the correlation are determined by a least squares fit to the experimental data using non-linear regression. The predicted results are compared with experimental results to assess the accuracy of the model.

6.2 THEORETICAL SOLUBILITY OF CO_2 IN MAE

The carbamate ions concentration was determined experimentally by titrating a sample of the carbonated amine with aqueous NaOH and using equations (4.9) and

(4.10). The results were used to correlate K_2 with temperature, pressure and amine concentration in the form of equation (3.24).

Values of K_2 obtained from this method were fitted to the form of equation (3.24) by non-linear regression by which the parameters of the correlation were determined, as follows;

$$lnK_2 = 1.301 - 4.23/T + 0.0025.P_{CO2} - 0.0334.M + 0.00035.M^2 \qquad (6.1)$$

where K_2 is the equilibrium constant of carbamate ion dissociation, T is the temperature in K, P_{CO2} is CO_2 partial pressure in kPa and M is the amine concentration in mol.dm^{-3}. The correlation was used together with equations (3.12) – (3.20) to find the theoretical (or predicted) values of the loading α in mol.CO_2/mol.MAE, as well as the concentrations of all other species in equilibrium. Figure 6.1 is a flowchart showing the steps adopted in this work to determine the theoretical values of the loading, α, in mol.CO_2/mol.MAE.
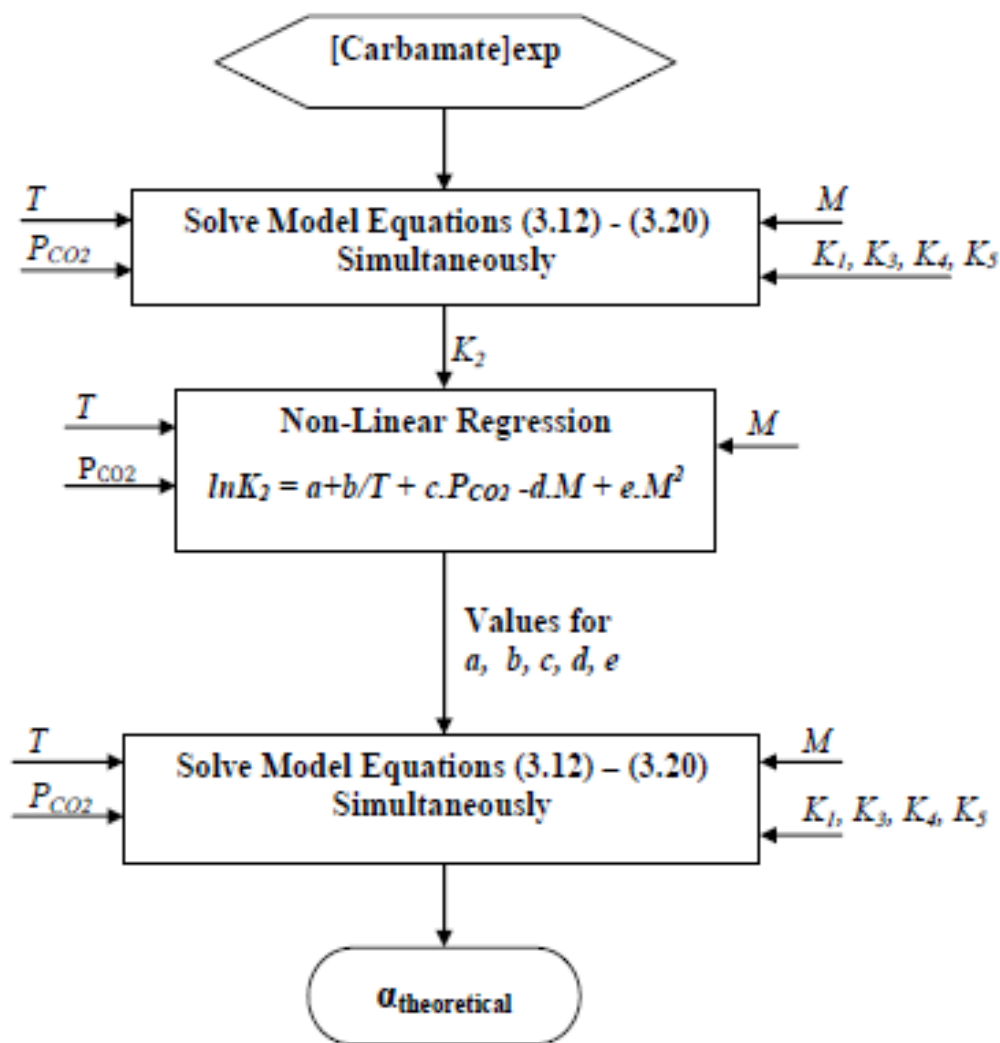
Figure 6.1: Flowchart of the steps adopted to calculate theoretical loading

Tables 6.1 and 6.2 show the experimental and theoretical loadings of carbon dioxide in 1.0 M, 2.0 M and 4.0 M MAE at 30, 40 and 60 $^{\circ}$C and at various CO_2 partial pressures, together with the % error. These results were obtained from the mathematical model explained earlier.

Table 6.1: Experimental and theoretical carbon dioxide loading in 1.0 M MAE at 30 °C, 40 °C, and 60 °C and at various CO_2 partial pressures with % error

Concentration (mol.dm^{-3})	Temperature (°C)	P_{CO_2} (kPa)	Loading (mol.CO_2/mol.MAE)		% Error
			Experimental	Theoretical	
1M MAE	30	99.08	0.989	1.007	1.82
		49.37	0.941	0.976	3.72
		24.69	0.863	0.928	7.53
		9.84	0.795	0.844	6.16
		4.95	0.786	0.763	2.93
		0.98	0.566	0.513	9.36
1M MAE	40	98.91	0.982	0.982	0.00
		49.37	0.912	0.933	2.30
		24.64	0.808	0.868	7.43
1M MAE	60	98.41	0.996	0.926	7.03
		49.37	0.803	0.836	4.11
		24.64	0.683	0.727	5.36

Table 6.2: Experimental and theoretical carbon dioxide loading in 2.0 M and 4.0 M MAE at 30 °C, 40 °C, and 60 °C and at various CO_2 partial pressures with % error

Concentration (mol.dm^{-3})	Temperature (°C)	P_{CO_2} (kPa)	Loading (mol.CO_2/mol.MAE)		% Error
			Experimental	Theoretical	
2M MAE	30	98.75	0.902	0.956	5.99
		49.04	0.804	0.908	12.94
		24.64	0.759	0.845	11.33
		9.87	0.706	0.735	4.11
		4.95	0.662	0.639	3.47
		0.99	0.548	0.418	23.72
2M MAE	40	98.58	0.853	0.925	8.44
		49.12	0.743	0.857	15.34
		24.64	0.721	0.769	6.66
2M MAE	60	98.57	0.751	0.828	10.25
		49.29	0.679	0.726	6.92
		24.81	0.669	0.613	8.37
4M MAE	30	24.64	0.573	0.794	38.57
		9.89	0.549	0.652	18.76
		4.95	0.521	0.542	4.03
		0.99	0.474	0.313	33.97

Figures 6.2 – 6.8 show the variation of theoretical and experimental CO_2 loadings with partial pressure for 1.0 M, 2.0 M and 4.0 M MAE at 30 ^{o}C, 40 ^{o}C, and 60 ^{o}C, respectively. It is clear that at low amine concentrations the model results are in good agreement with the experimental results, however the disagreement is more pronounced at high amine concentrations. Although the model takes into account amine concentration in the correlation, it seems that the solution behavior approaches ideality only at low amine concentration (1.0 or 2.0 M). However, at high amine concentration the assumption of ideal solution of infinite dilution, where both activity and fugacity coefficients are both assumed to be unity is not valid.

Higher deviations were also observed at very low CO_2 partial pressures. This is expected as the model assumes that free amine in solution is negligible. This assumption can be considered valid at high CO_2 partial pressures where all species are ionized. However, at low CO_2 partial pressure, the concentration of free amine and other molecular species can have considerable affect on the loading. Similar results were obtained by Benamor and Aroua (2005). To get more accurate results at high concentrations and low partial pressures, activity and fugacity coefficients should be determined.
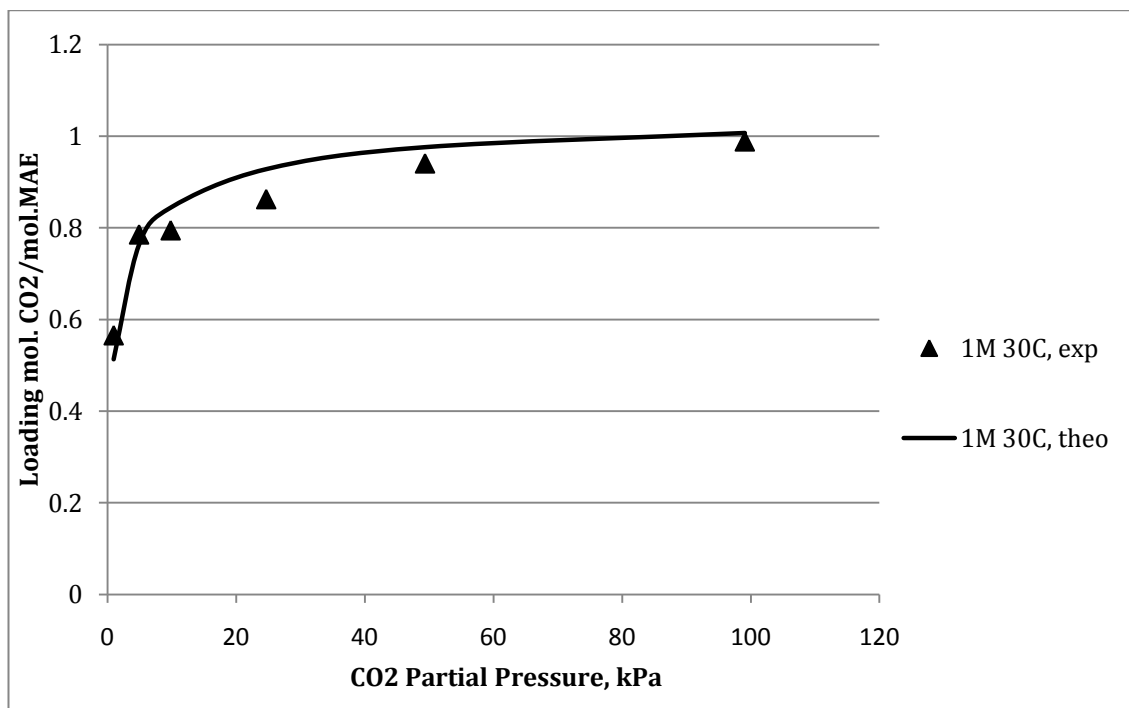
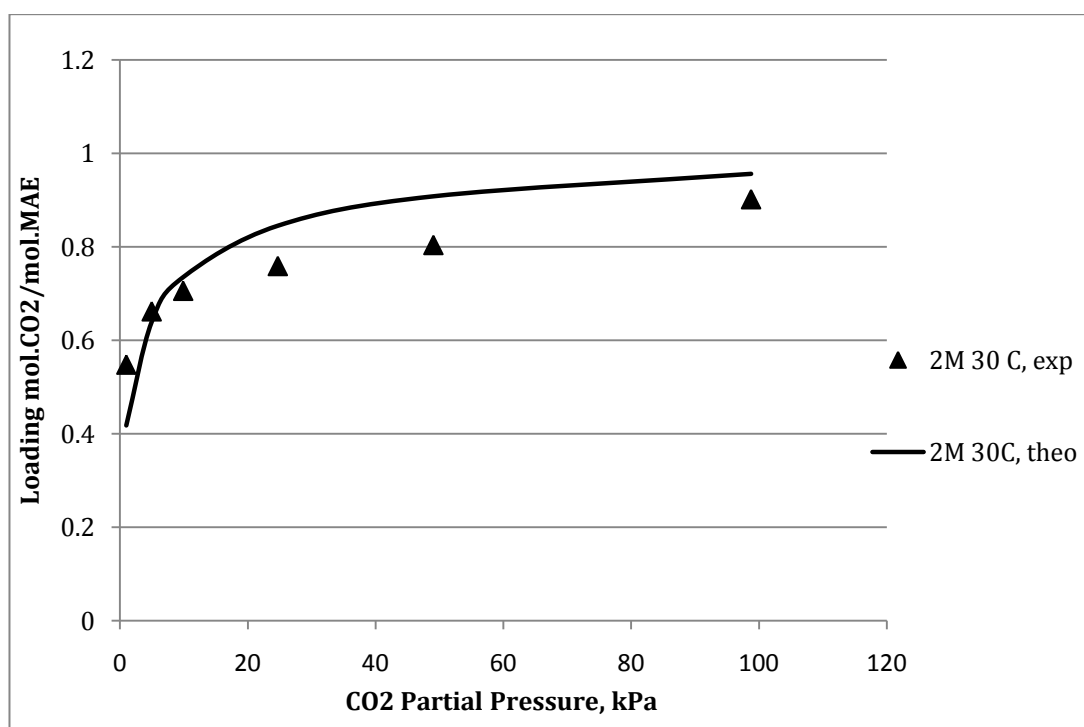Figure 6.2: Experimental and theoretical loading of CO_2 in 1.0 M MAE at 30 °C

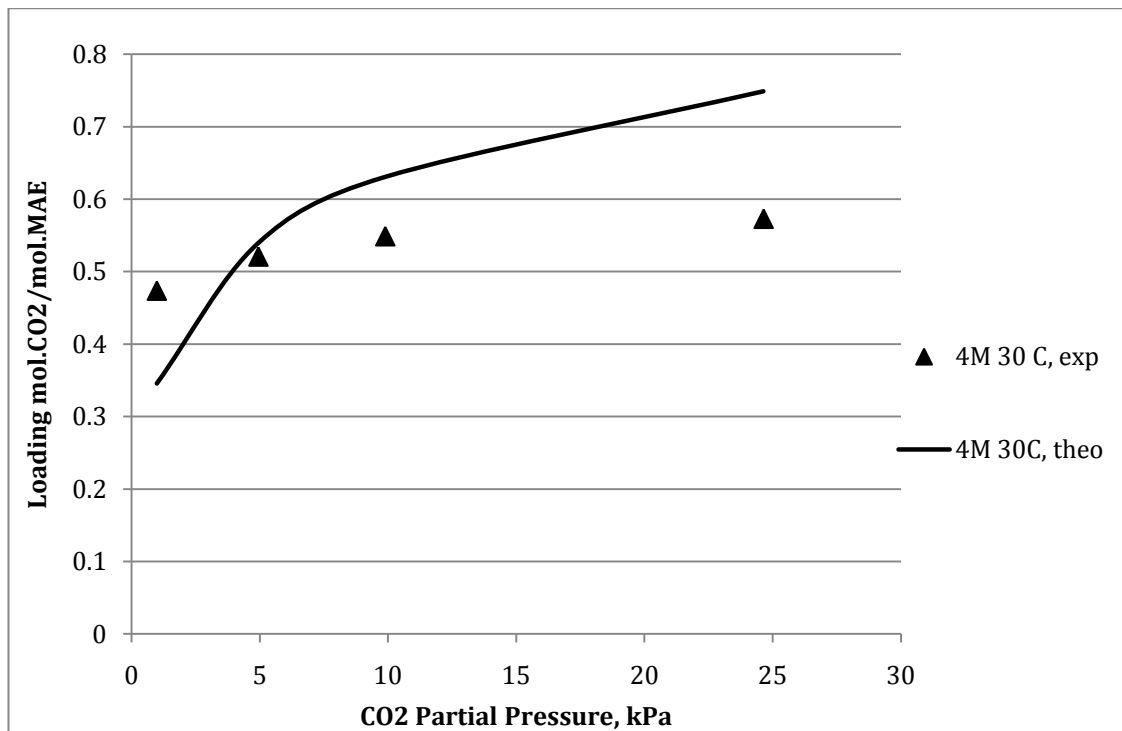Figure 6.3: Experimental and theoretical loading of CO_2 in 2.0 M MAE at 30 °C

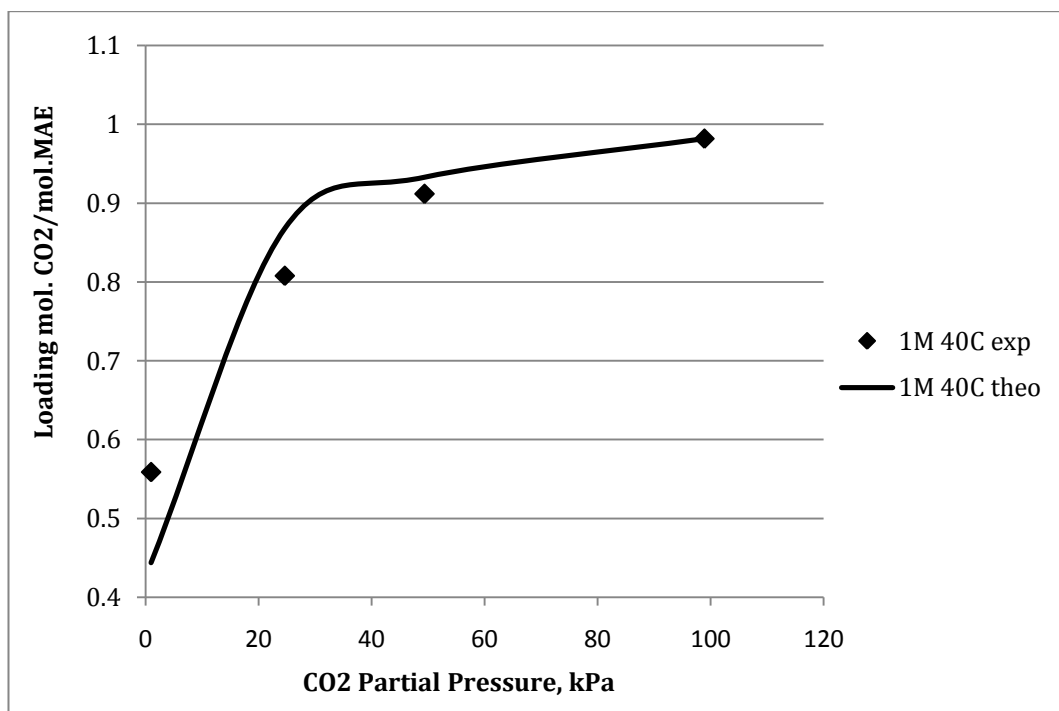Figure 6.4: Experimental and theoretical loading of CO_2 in 4.0 M MAE at 30 °C

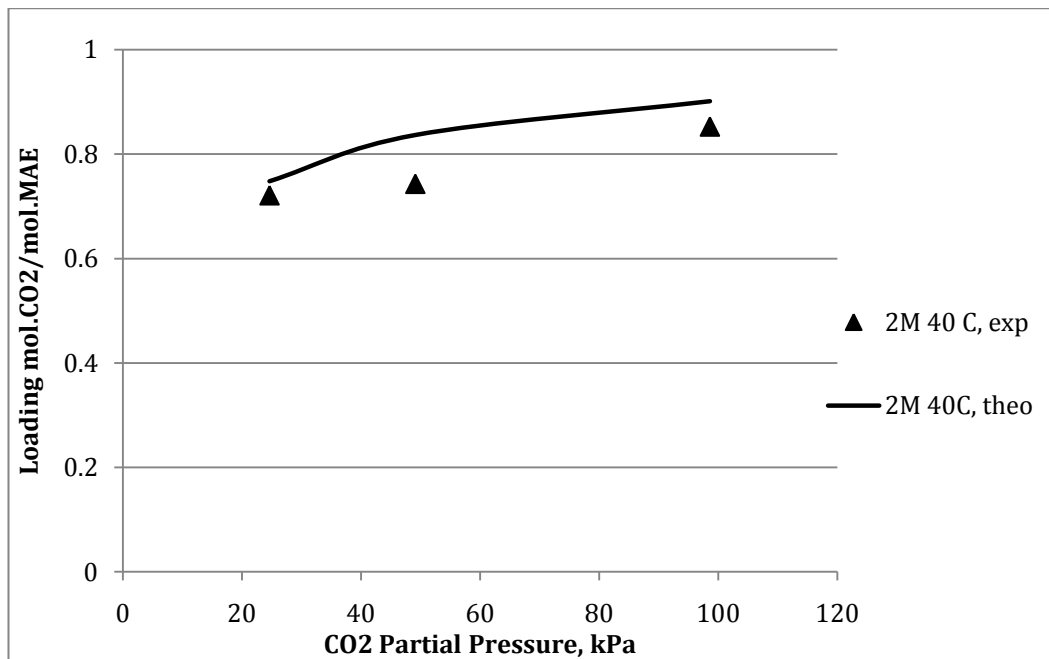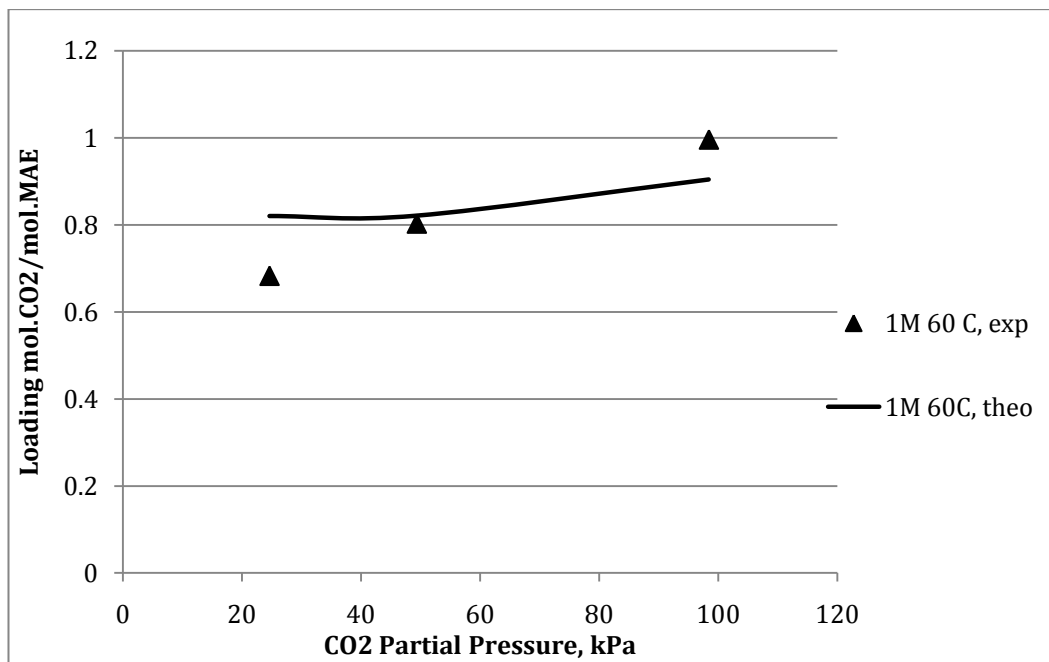Figure 6.5: Experimental and theoretical loading of CO_2 in 1.0 M MAE at 40 °C

Figure 6.6: Experimental and theoretical loading of CO_2 in 2.0 M MAE at 40 °C

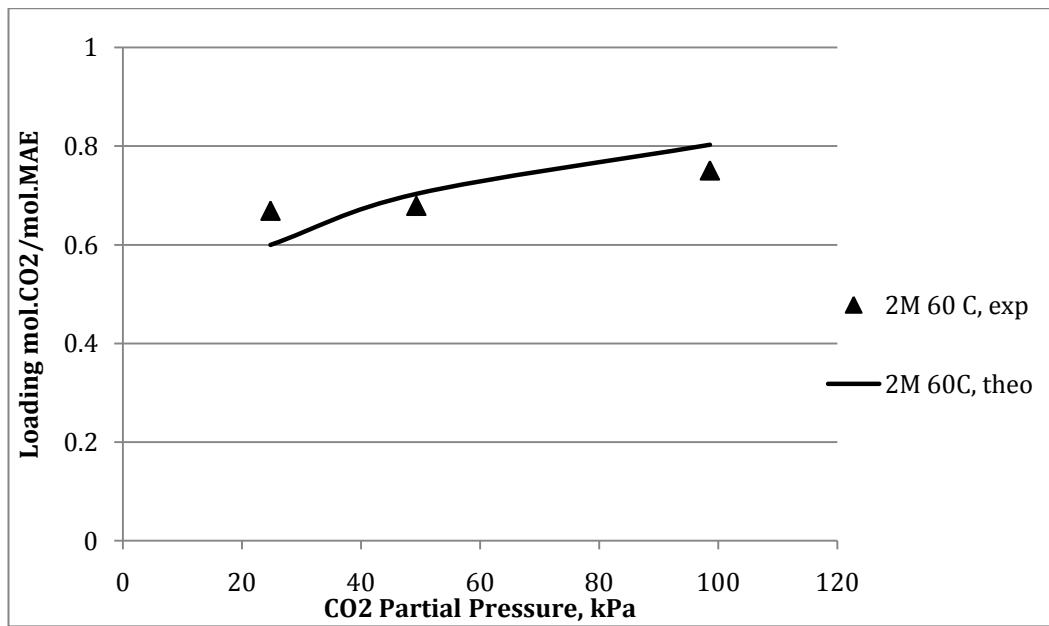Figure 6.7: Experimental and theoretical loading of CO_2 in 1.0 M MAE at 60 °C

Figure 6.8: Experimental and theoretical loading of CO_2 in 2.0 M MAE at 60 °C

Figure 6.9 shows a comparison between theoretical and experimental results of CO_2 loading in 1.0 M, 2.0 M and 4.0 M MAE at 30 °C, 40 °C, and 60 °C. It is clear that the proposed technique provide a good prediction for CO_2 loading, as the plotted values remain close to the curve of experimental loading = theoretical loading.
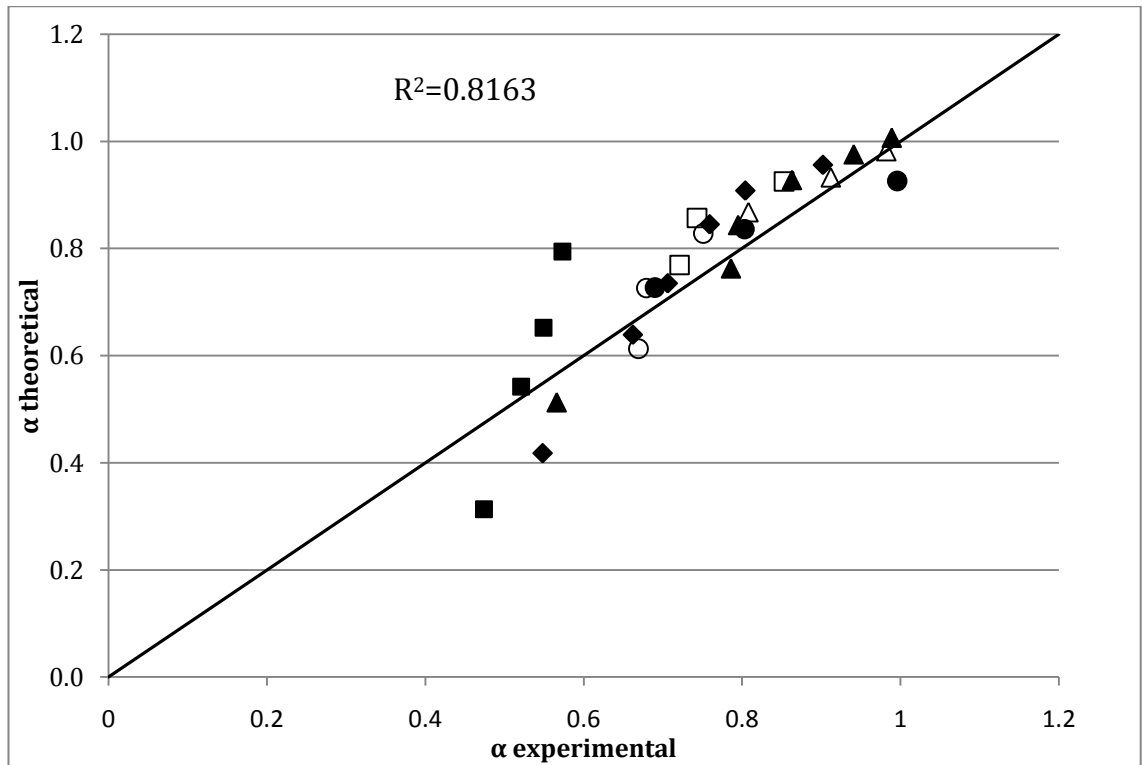
Figure 6.9: Comparison experimental and predicted CO_2 loading in MAE
▲ 1.0 M 30 ^{o}C, ♦ 2.0 M 30 ^{o}C, ■ 4.0 M 30 ^{o}C, Δ 1.0 M 40 ^{o}C,
□ 2.0 M 40 ^{o}C, ● 1.0 M 60 ^{o}C and ○ 2.0M 60 ^{o}C

The coefficient of determination, R^2 determines how well the model represents the observed data. It can be calculated as follows;

$$R^2 = 1 - \frac{\text{SSerr}}{\text{SStot}} \tag{6.2}$$

where *SSerr* is the sum of the squares of errors, $SSerr = \sum_{1}^{n}(\alpha_{iexp.} - \alpha_{itheo.})^2$ and *SStot* is the total sum of the squares (relative to the sample mean, $\bar{\alpha}$); $SStot = \sum_{1}^{n}(\alpha_{iexp.} - \bar{\alpha})^2$. According to this relation, R^2 was found to be 0.82. This means that 82% of the data is explained by the model.

The accuracy of this model was further quantified by determining the absolute mean percentage error (*MPE*) as follows;

$$MPE = \frac{1}{n} \sum_{1}^{n} \frac{|(CO_2 \, loading)_{experimental} - (CO_2 \, loading)_{theretical}|}{(CO_2 \, loading)_{experimental}} \, x \, 100\% \qquad (6.3)$$

where n is the total number of data points. The overall mean percentage error was found to be 10.4%. This means that the model can provide good results for predicting CO_2 loadings in this range of temperatures, pressures and amine concentrations.

The deviations of the predicted results from the proposed model are mainly at high amine concentrations. These deviations are attributed to the assumption of ideal conditions where the activity and fugacity coefficients were both assumed to be unity. Results reveal that at low amine concentrations the solution behavior approaches ideality while at low amine concentrations the assumption of ideal solution is not valid.

The concentrations of the different species in the system were evaluated using the model. Figures 6.10 - 6.16 show, respectively, the variation of the concentrations of different species at equilibrium with CO_2 loading for 1.0 M MAE at 30 ^{o}C, 2.0 M MAE at 30 ^{o}C, 4.0 M MAE at 30 ^{o}C, 1.0 M MAE at 40 ^{o}C, 2.0 M MAE at 40 ^{o}C, 1.0 M MAE at 60 ^{o}C and 2.0 M MAE at 60 ^{o}C. It is clear that the most significant ions present at equilibrium are the protonated amine and the bicarbonate. This behavior is in agreement with the findings of Huang *et al.* (2000) who concluded that for MAE most of the carbamate undergoes hydrolysis to bicarbonate. It is also clear that the hydrolysis is more pronounced at higher temperatures. This behavior is somehow different from that of DEA which was determined by Benamor & Aroua (2005) in which they found that at low partial pressure and therefore at low loading, most of the CO_2 absorbed into the solution is in the form of carbamate with a small amount in the form of bicarbonate (or hydrogen carbonate).
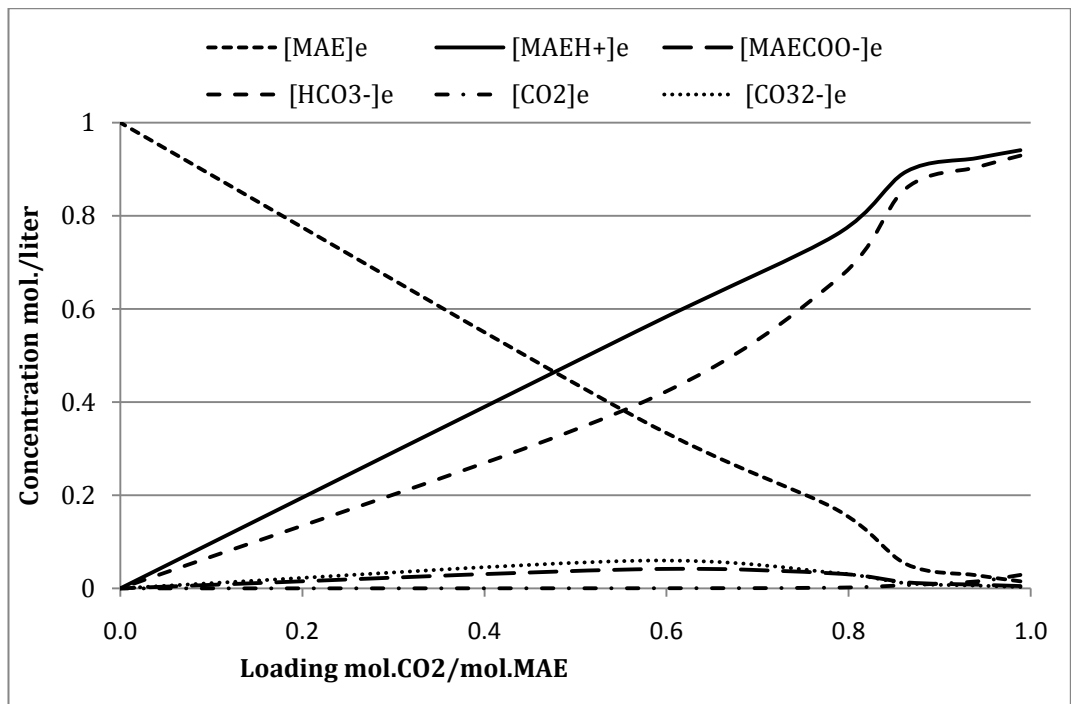
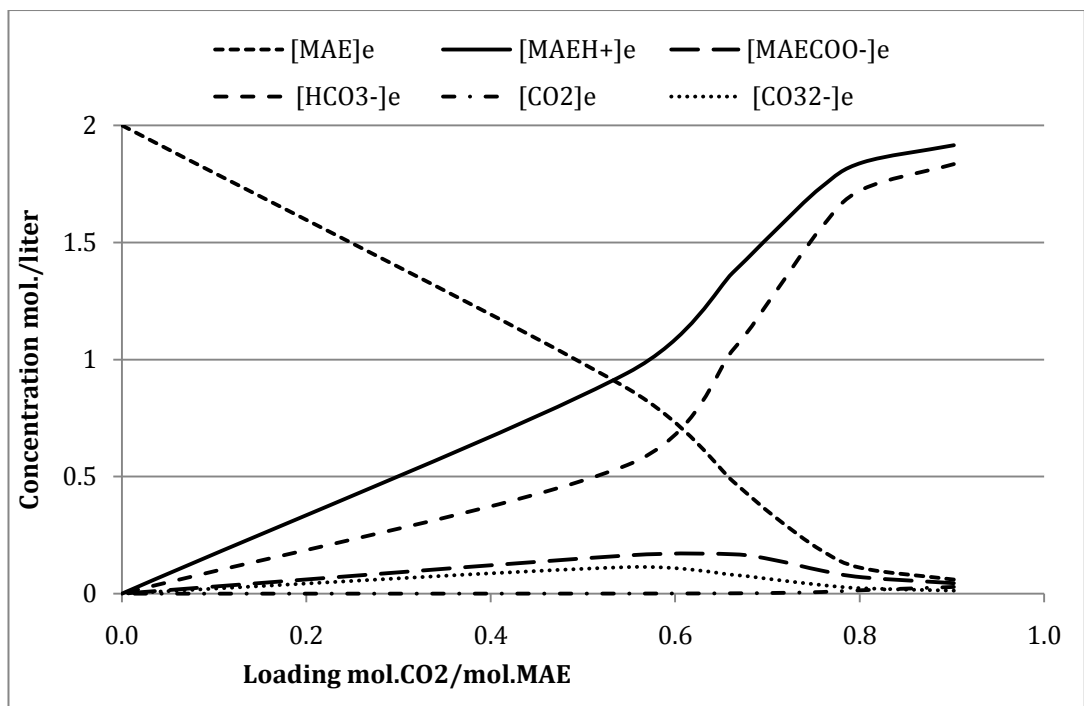Figure 6.10: Liquid phase concentration profile in carbonated solution
of 1.0 M MAE at 30 ^{o}C

Figure 6.11: Liquid phase concentration profile in carbonated solution
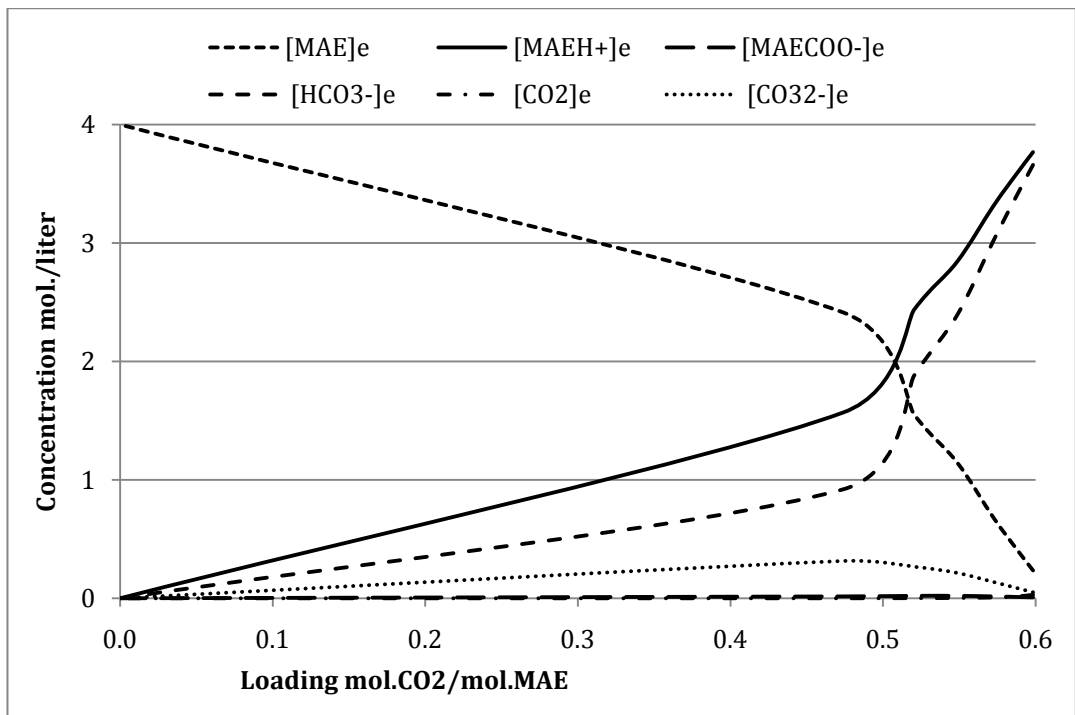of 2.0 M MAE at 30 ^{o}C

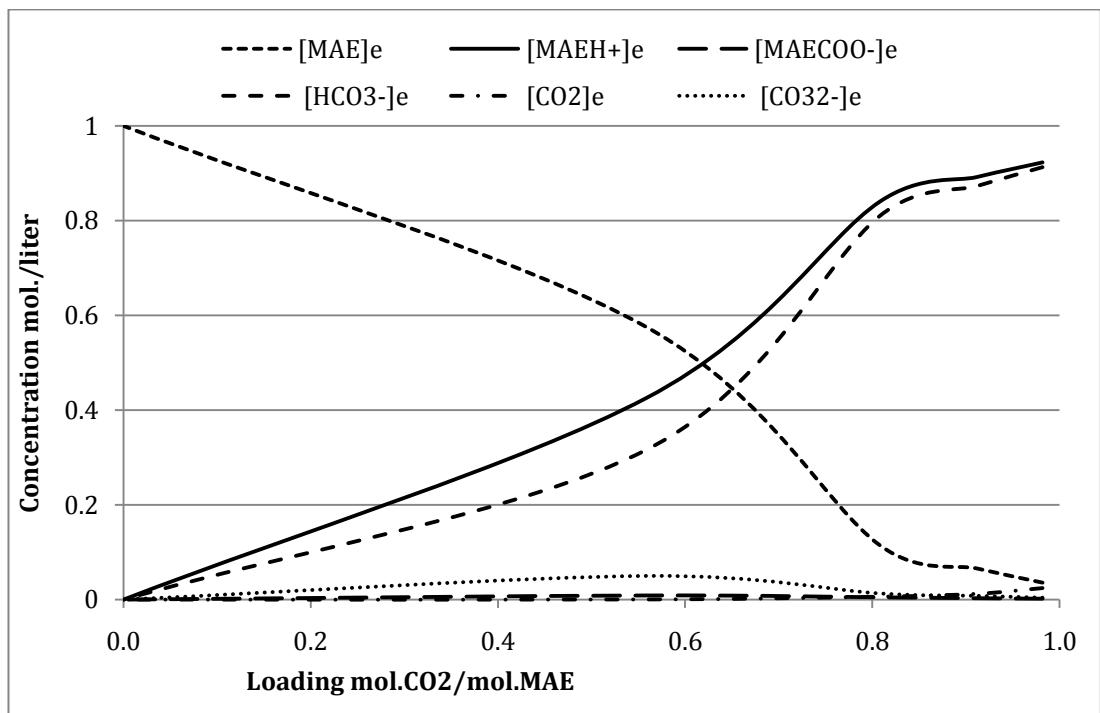Figure 6.12: Liquid phase concentration profile in carbonated solution of 4.0 M MAE at 30 ^{o}C

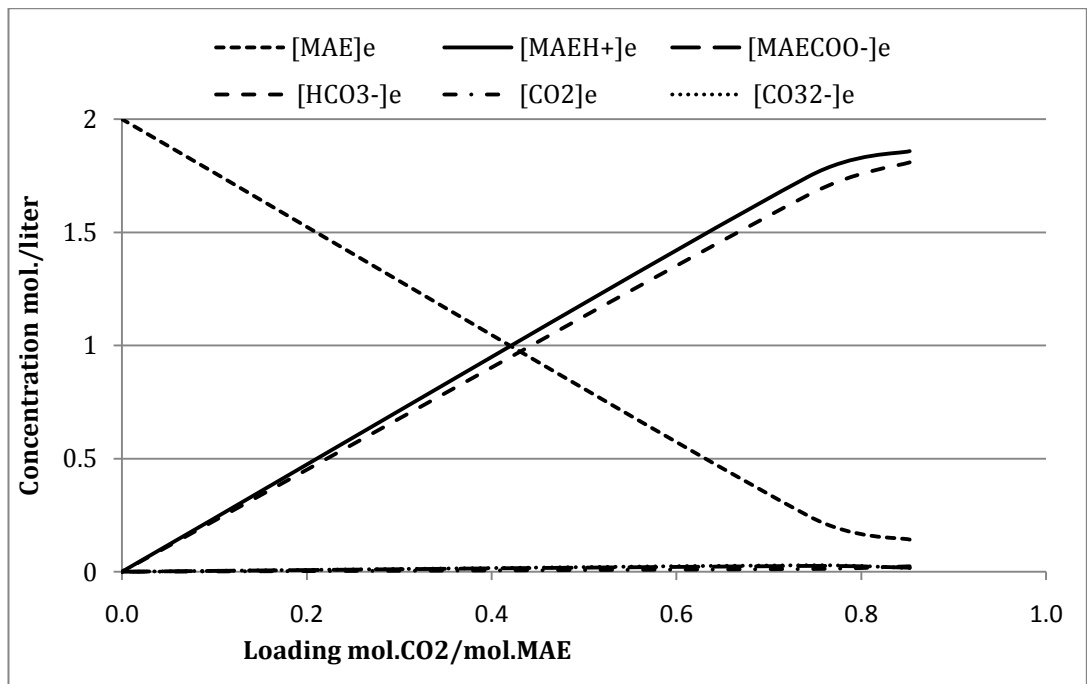Figure 6.13: Liquid phase concentration profile in carbonated solution of 1.0 M MAE at 40 ^{o}C

Figure 6.14: Liquid phase concentration profile in carbonated solution
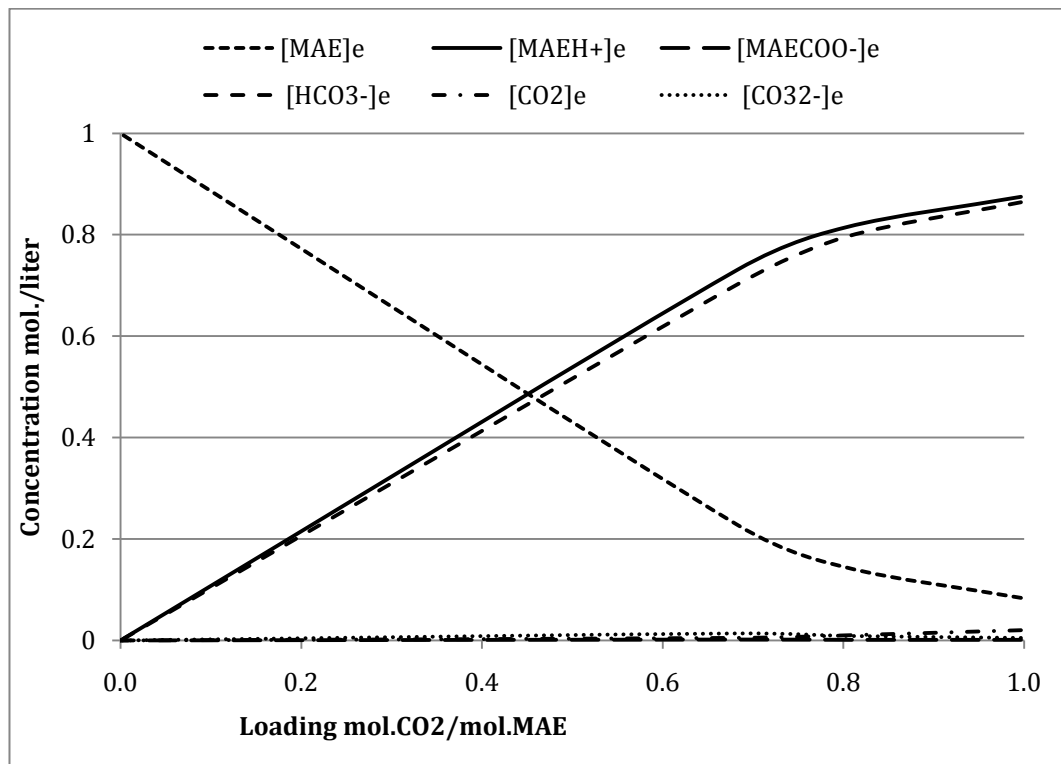of 2.0 M MAE at 40 $^{\circ}$C

Figure 6.15: Liquid phase concentration profile in carbonated solution
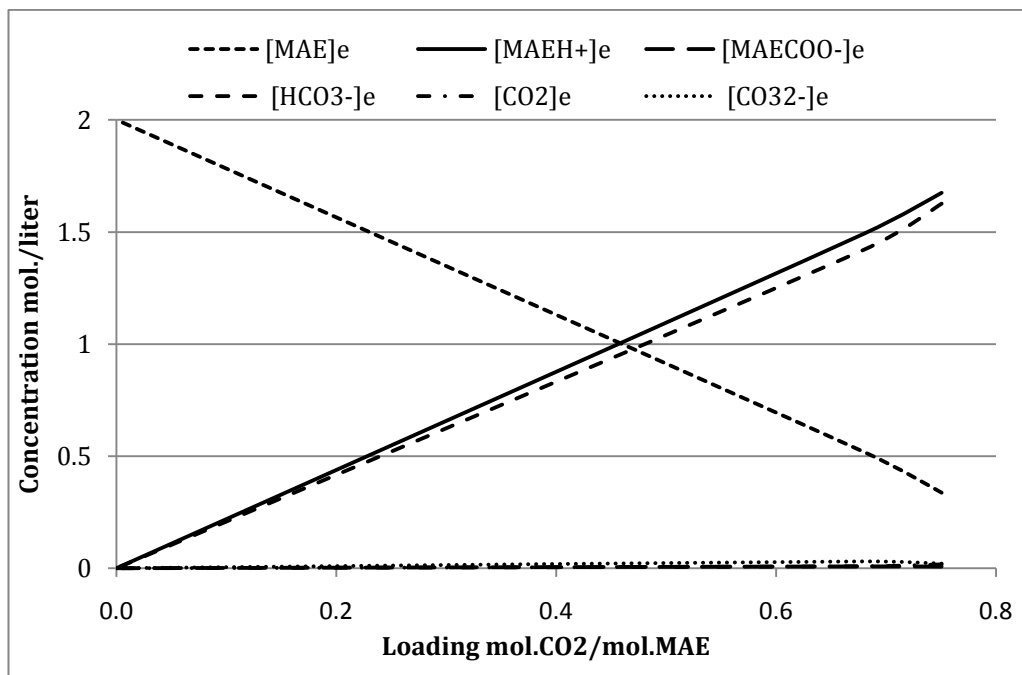of 1.0 M MAE at 60 $^{\circ}$C

Figure 6.16: Liquid phase concentration profile in carbonated solution
of 2.0 M MAE at 60 $^{\circ}$C

6.3   SUMMARY

The equilibrium constant representing hydrolysis of carbamate ions is correlated by non-linear regression with pressure, temperature and amine concentration using experimental equilibrium carbamate ions concentration. Theoretical (or predicted) solubility data of CO_2 in MAE were then calculated by solving equations (3.12) – (3.20) simultaneously. The experimental and theoretical results of CO_2 loading in MAE at various temperatures, CO_2 partial pressures and amine concentrations are listed in Tables 6.1 and 6.2. These results are plotted in Figures 6.2–6.8. Figure 6.9 shows a comparison between experimental and theoretical CO_2 loading in MAE.

The results show good agreement between experimental and theoretical results especially at low amine concentrations. The coefficient of determination was found to be 0.82 and the overall mean percentage error was 10.4%. This proves that the proposed

model is suitable for predicting the solubility of CO_2 in MAE.

Figures 6.10-6.16 show the concentrations of different species at equilibrium as calculated by the proposed model. These figures show that the most significant ions present at equilibrium are the protonated amine and the bicarbonate, indicating hydrolysis of carbamate ions to bicarbonate.