

CHAPTER 5

SOLUBILITY AND SPECIATION MODELING

This chapter presents a mathematical modeling of CO₂-PZ-H₂O system using the Kent and Eisenberg approach. The unknown equilibrium constants for the piperazine carbamates, K₂, K₃ and K₄ were determined by fitting the experimental data of the system. This nonlinear data fitting was done by using Isqcurvefit function from the optimization toolbox of MATLAB software. The model was tested by comparing the correlated and the experimental values of CO₂ solubility in the aqueous piperazine solution at 20, 30, 40 and 50 °C. This model is also applied to the CO₂-PZ-DEA-H₂O system. Speciation concentrations in the solution were calculated based on several assumptions.

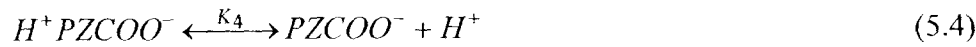
5.1 Modeling for the CO₂-PZ-H₂O system

There are various models available to predict the equilibrium CO₂ loading in aqueous solutions of alkanolamines. These models are essential for the design and simulation of absorbers and strippers in gas treating units. In this work a mathematical model based on Kent and Eisenberg approach was applied to the CO₂-PZ-H₂O system due to its simplicity. Solubility based on this model assume that all the activity coefficients and fugacity coefficients are unity and the non-idealities that are present in the system are combined with some of the K values. This relatively simple model

correlates with the experimental data fairly well, but precludes accurate calculation of the species existing in the solution

5.2 Solubility model development.

The chemical reaction equilibria in the liquid phase of the CO₂-PZ-H₂O system is governed by the following ionic reactions.



The equilibrium constants for the reactions (5.1) – (5.7) can be represented as follows:

$$K_1 = \frac{[PZ][H^+]}{[PZH^+]} \quad (5.8)$$

$$K_2 = \frac{[PZCOO^-][H^+]}{[PZ][CO_2]} \quad (5.9)$$

$$K_3 = \frac{[^-OOC PZCOO^-][H^+]}{[PZCOO^-][CO_2]} \quad (5.10)$$

$$K_4 = \frac{[PZCOO^-][H^+]}{[H^+PZCOO^-]} \quad (5.11)$$

$$K_5 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad (5.12)$$

$$K_6 = \frac{[HCO_3^-][H^+]}{[CO_2]} \quad (5.13)$$

$$K_7 = [OH^-][H^+] \quad (5.14)$$

The mass balance equations governing the reacting species in this system are as follows:

Piperazine mass balance:

$$[PZ]_T = [PZ] + [PZH^+] + [PZCOO^-] + [H^+PZCOO^-] + [^-OOC PZCOO^-] \quad (5.15)$$

Carbon dioxide mass balance:

$$[CO_2]_T = [CO_2] + [PZCOO^-] + 2[^-OOC PZCOO^-] + [H^+PZCOO^-] + [CO_3^{2-}] + [HCO_3^-] \quad (5.16)$$

The electroneutrality balance for the system can be written as:

$$[PZH^+] + [H^+] = [PZCOO^-] + 2[^-OOC PZCOO^-] + 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \quad (5.17)$$

The dissolved free CO₂ concentration in the aqueous piperazine solution can be related to CO₂ partial pressure in the gas phase by the Henry's Law as below.

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (5.18)$$

From equation (5.8) – (5.17), a single polynomial expression in terms of hydrogen ion [H⁺] can be derived as :

$$A[H^+]^6 + B[H^+]^5 + C[H^+]^4 + D[H^+]^3 + E[H^+]^2 + F[H^+] + G = 0 \quad (5.19)$$

where ;

$$A = K_4$$

$$B = K_1 K_4 + K_4 [PZ]_t + K_1 K_2 [CO_2]$$

$$C = K_1 K_2 K_4 [CO_2] - K_4 K_6 [CO_2] - K_4 K_7$$

$$D = -(K_1 K_2 K_4 [CO_2] [PZ]_t + 2 K_4 K_5 K_6 [CO_2] + K_1 K_4 K_7 + K_1 K_2 K_7 [CO_2] + K_1 K_4 K_6 [CO_2] + K_1 K_2 K_6 [CO_2]^2 - K_1 K_2 K_3 K_4 [CO_2]^2)$$

$$E = -(2 K_1 K_2 K_3 K_4 [CO_2]^2 [PZ]_t + 2 K_1 K_4 K_5 K_6 [CO_2] + 2 K_1 K_2 K_5 K_6 [CO_2]^2 + K_1 K_2 K_4 K_7 [CO_2] + K_1 K_2 K_4 K_6 [CO_2]^2)$$

$$F = -(2 K_1 K_2 K_4 K_5 K_6 [CO_2]^2 + K_1 K_2 K_3 K_4 K_7 [CO_2]^2 + K_1 K_2 K_3 K_4 K_6 [CO_2]^3)$$

$$G = -2 K_1 K_2 K_3 K_4 K_5 K_6 [CO_2]^3$$

Even though there is more than one root for the polynomial equation, only one root is chosen based on the assumption that the range of $[H^+]$ is between $10^{-6} - 10^{-9}$ mol/L because the pH of the loaded piperazine solution was in the range from pH 6 to 9.

The total CO_2 loading was calculated using the equation below which was derived from equations (5.8) – (5.17).

$$[CO_2]_T = P + \frac{(KP + K_4[H^+])[H^+]^2[PZ]_T}{K[H^+]([H^+] + K_4P + [H^+]P) + K_4([H^+]^3P + KK_3P)} \quad (5.20)$$

where $P = \frac{P_{CO_2}}{H}$ and $K = K_1 K_2$

Only the equilibrium constants for the piperazine carbamates K_2 , K_3 , and K_4 in equation (5.9) – (5.11) are fitted to the experimental data of the CO_2 -PZ- H_2O

system. In order to solve the non-linear data fitting, Iscurvefit function from the optimization toolbox of Matlab was used to adjust the equilibrium constant values by finding the coefficients x , that best fit the $F(x, xdata)$,

$$\min \frac{1}{2} \|F(x, xdata) - ydata\|_2^2 = \frac{1}{2} \sum_i (F(x_i, xdata_i) - ydata_i)^2 \quad (5.21)$$

The $xdata$ are the given input data and $ydata$ are the observed output data, where $xdata$ and $ydata$ are vectors and $F(x, xdata)$ is a vector valued function (The mathwork, 2001).

The values of K_2 , K_3 , and K_4 were adjusted at each temperature until the measurement experimental loading values were in a good agreement with the model loading. In this way the variation of the piperazine concentrations and CO_2 partial pressures were taken into account in the model. The block diagram representing the process of non-linear data fitting for the adjusted equilibrium constants of the piperazine carbamates is shown in figure 5.1 and the program is in the appendix F.

Once the equilibrium constant values of each of the piperazine carbamates had been determined, they were assumed to be temperature dependent and further correlated according to the following equation.

$$\ln K = A + B/T + C \ln T \quad (5.22)$$

In this work the equilibrium constant values of K_1 , K_5 , K_6 , and K_7 are taken from the open literature. The K values are related to the temperature as shown in Table 5.1. The Henry's constant for CO_2 in pure water is used in this work. The concentration

of the amine in the gas phase is neglected due to the low volatility of piperazine

.Table 5.1 summarizes the literature expression used in this work.

Table 5.1 : Expressions used for the modeling

Expression	Reference
$\ln K_1 = -11.91 - 4351/T$	Pagano et.al., 1961.
$\ln K_5 = 216 - 12,432/T - 35.48 \ln T$	Posey et.al., 1996.
$\ln K_6 = 241.4 - 12092/T - 36.78 \ln T$	Posey et.al., 1996.
$\ln K_7 = 132.9 - 13,446/T - 22.48 \ln T$	Posey et.al., 1996.
$\ln H = 94.4914 - 6789.04/T - 11.4519 \ln T - 0.010454T$	Edwards et. al. 1978.

T = Kelvin K = mol dm⁻³ H = kg atm/mole

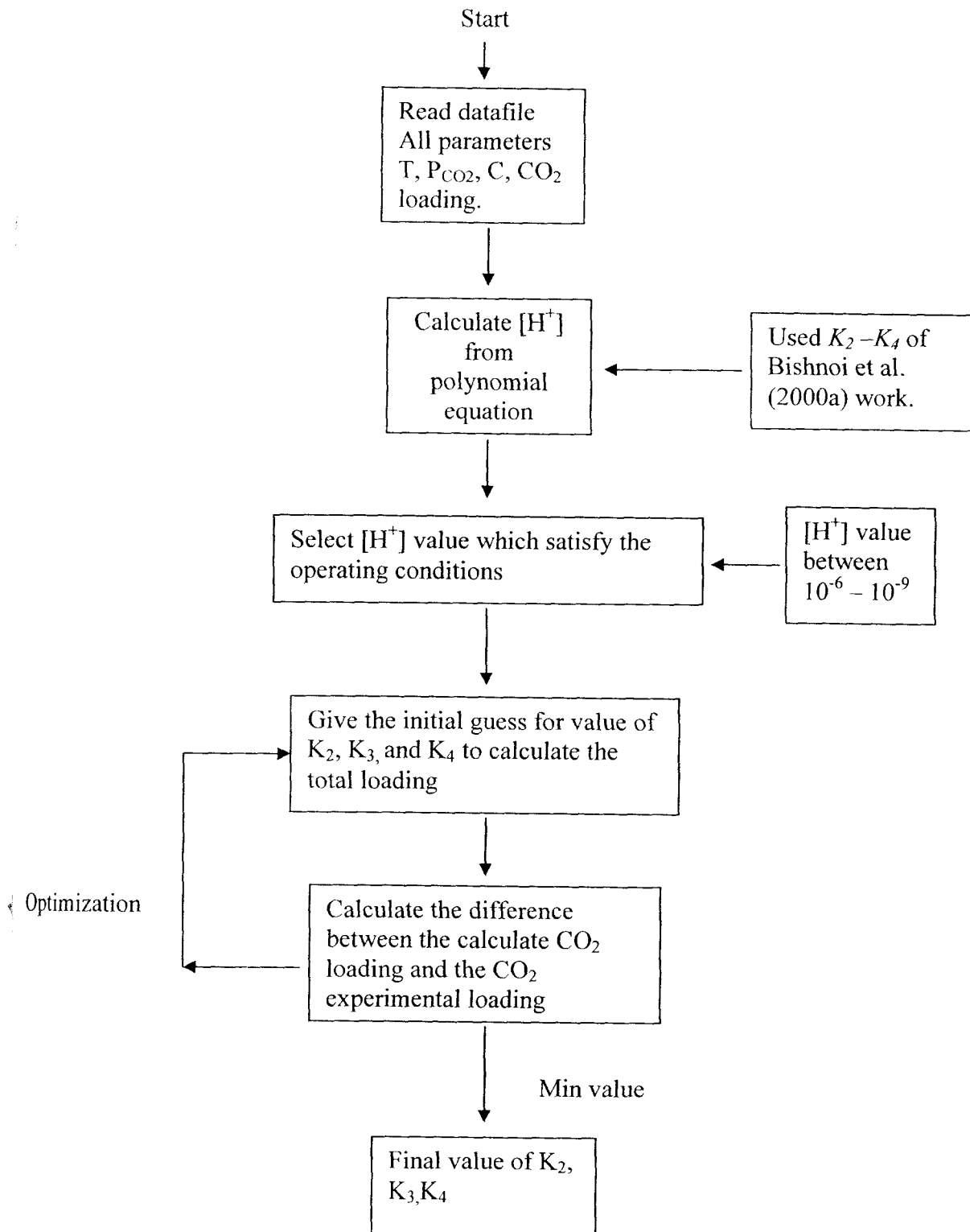


Figure 5.1: Block diagram for the process of fitting the adjusted K's value of the piperazine carbamates.

5.3 Results and discussion

The coefficients A, B and C generated for the equilibrium constants of the various piperazine carbamates as given in equation (5.21) are tabulated in Table 5.2. These values were obtained based on the non-linear regression performed on the 140 experimental CO₂ solubility data points of the CO₂-PZ-H₂O system. The model equilibrium constant values K₂ and K₃ of the piperazine carbamates at 40 °C are consistent with those determined by Bishnoi and Rochelle (2000) (Table 5.3) except for the value of K₄ which is smaller in this work. This may be due to the value of K₄ itself which is very small. Introduction of a small error will have a great impact on the value. As a result of the low K₄ value and knowing that the pH of the carbonated piperazine is between 6 and 9, one can predict the reaction (5.4) lies to the left and piperazine monocarbamate is a minor compound in the system. As such, reaction (5.4) can be considered negligible under the investigated condition of this work

Table 5.2 : The coefficient of the equilibrium constant for the piperazine carbamates.

	A	B	C
ln K ₂	3969.201	- 155702	- 606.042
ln K ₃	61332.28	- 2825780	- 9104.68
ln K ₄	- 72620.6	3270627	10814.06

Table 5.3 : Comparison of the piperazine carbamates equilibrium constant with literature value.

K value at 40 °C		
	This work	Bishnoi and Rochelle (2000)
ln K ₂	2.28E-05	1.144E-05
ln K ₃	2.02E-06	2.62E-06
ln K ₄	2.03E-14	1.267E-11

Figure 5.2 - 5.5 show the comparison between the calculated CO₂ total loading using the model and the experimental values at the respective temperature as indicated in each figure. The percentage deviations were calculated and are listed in appendix G. The model values agree fairly well with the experimental data at low to moderate CO₂ partial pressure with piperazine concentrations greater than 0.4 M. However, large discrepancies were observed at high partial pressure as well as in the low piperazine concentrations (< 0.4 M). This is due to the strong influence of the physical absorption of CO₂ in the solution. It was calculated that at a CO₂ partial pressure of 95 kPa with a piperazine concentration of 0.1 M and 0.2 M, the contribution of CO₂ absorption is about 14.8 % and 11.6 % of the total CO₂ loading respectively. The Henry's constant value that was assumed to be in pure water was also expected to introduce a significant error at high CO₂ partial pressures. While in the lower piperazine concentration region, the deviation may also due to the degree of accuracy of CO₂ loading measurement in the liquid phase since the amount of measured CO₂ loading was very small. Therefore, a small difference between the

experimental data and the model value will cause large deviation. Obviously, a greater error is generated at both, high CO₂ partial pressure and low piperazine concentration conditions where the contribution of the physical absorption of CO₂ into the solution relative to the chemical absorption is higher.

The overall average deviation between the experimental and predicted CO₂ loading is about 16.65 %. A closer agreement is observed as the temperature increased. It would be well worth effort to apply other models which include the ionic interaction parameters in model in order to produce higher accuracy.

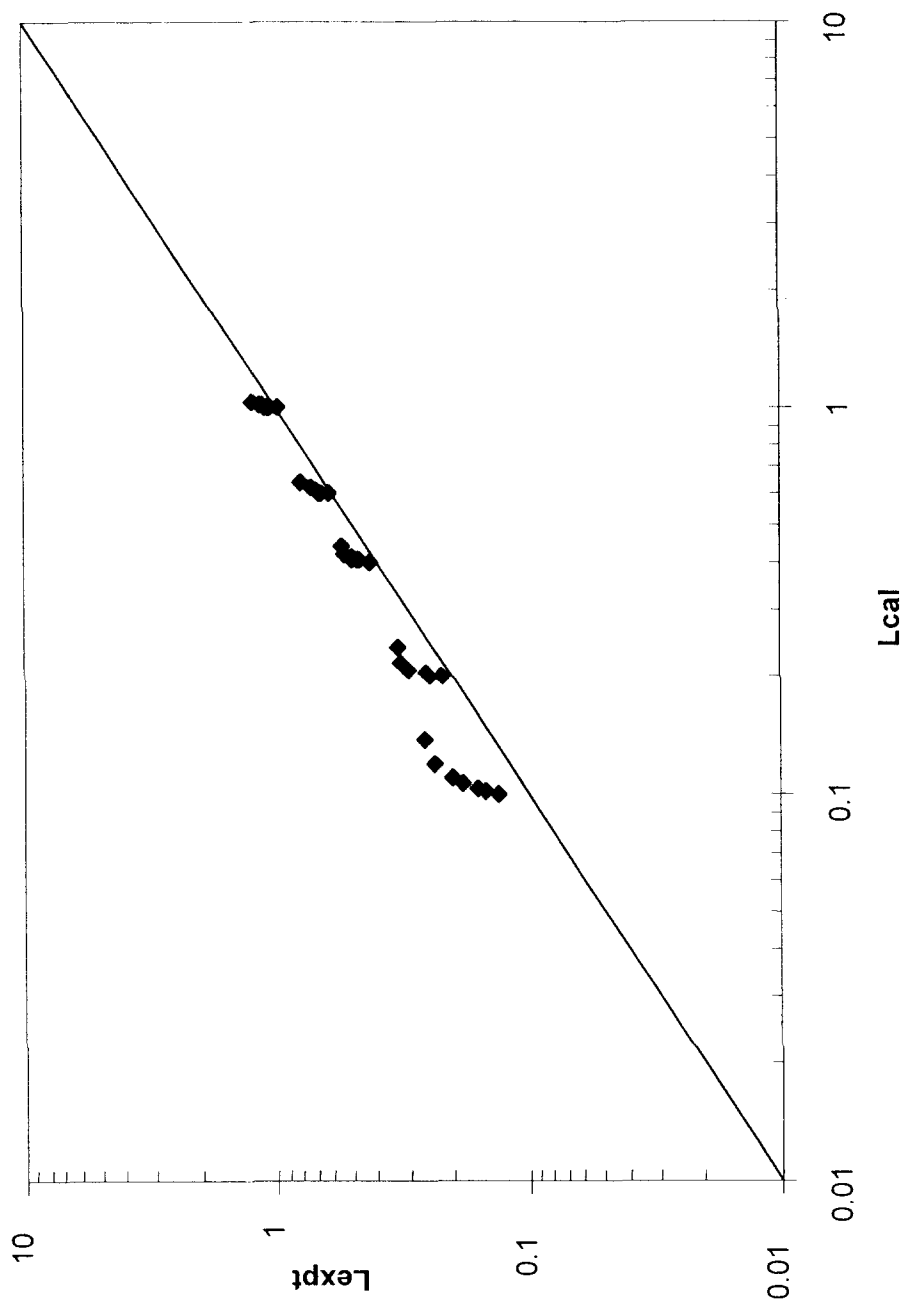


Figure 5.2 : The total CO₂ loading calculated from the model and the experimental loading at 20 °C.

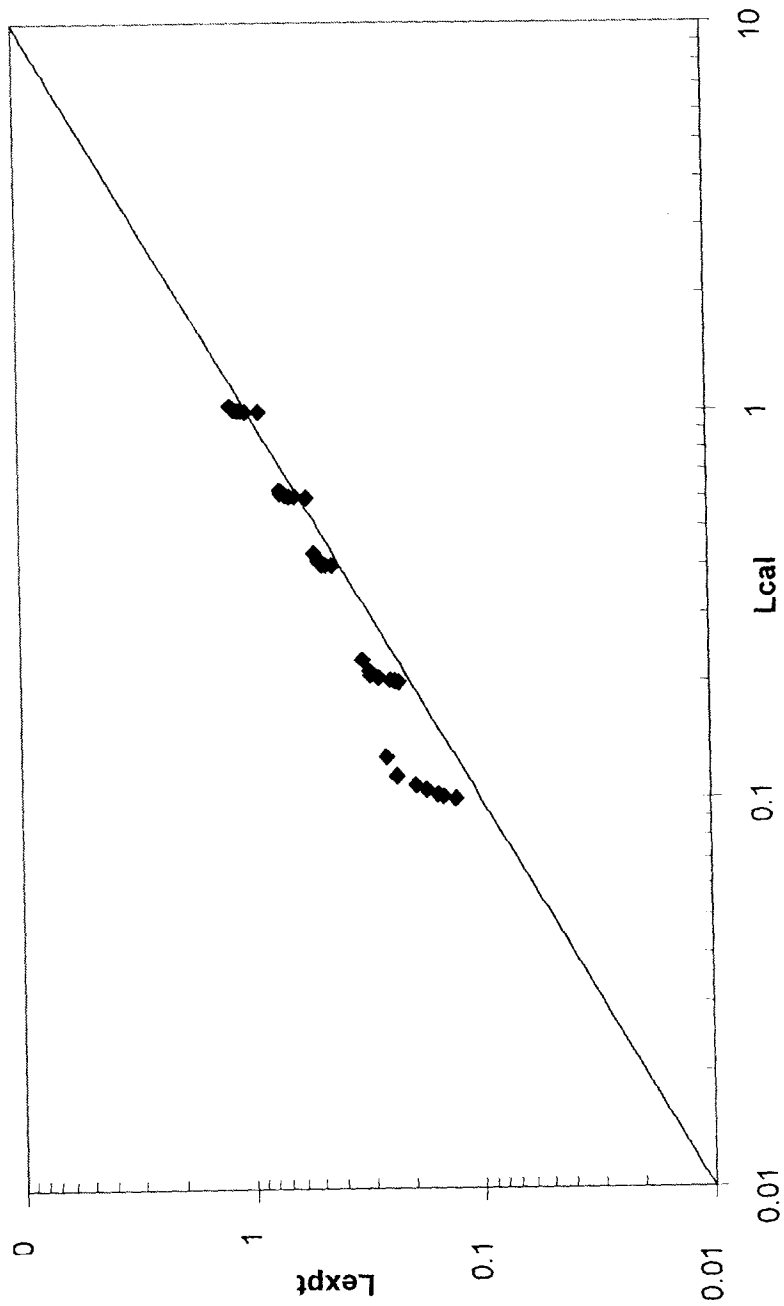


Figure 5.3 : The total CO₂ loading calculated from the model and the experimental loading at 30 °C.

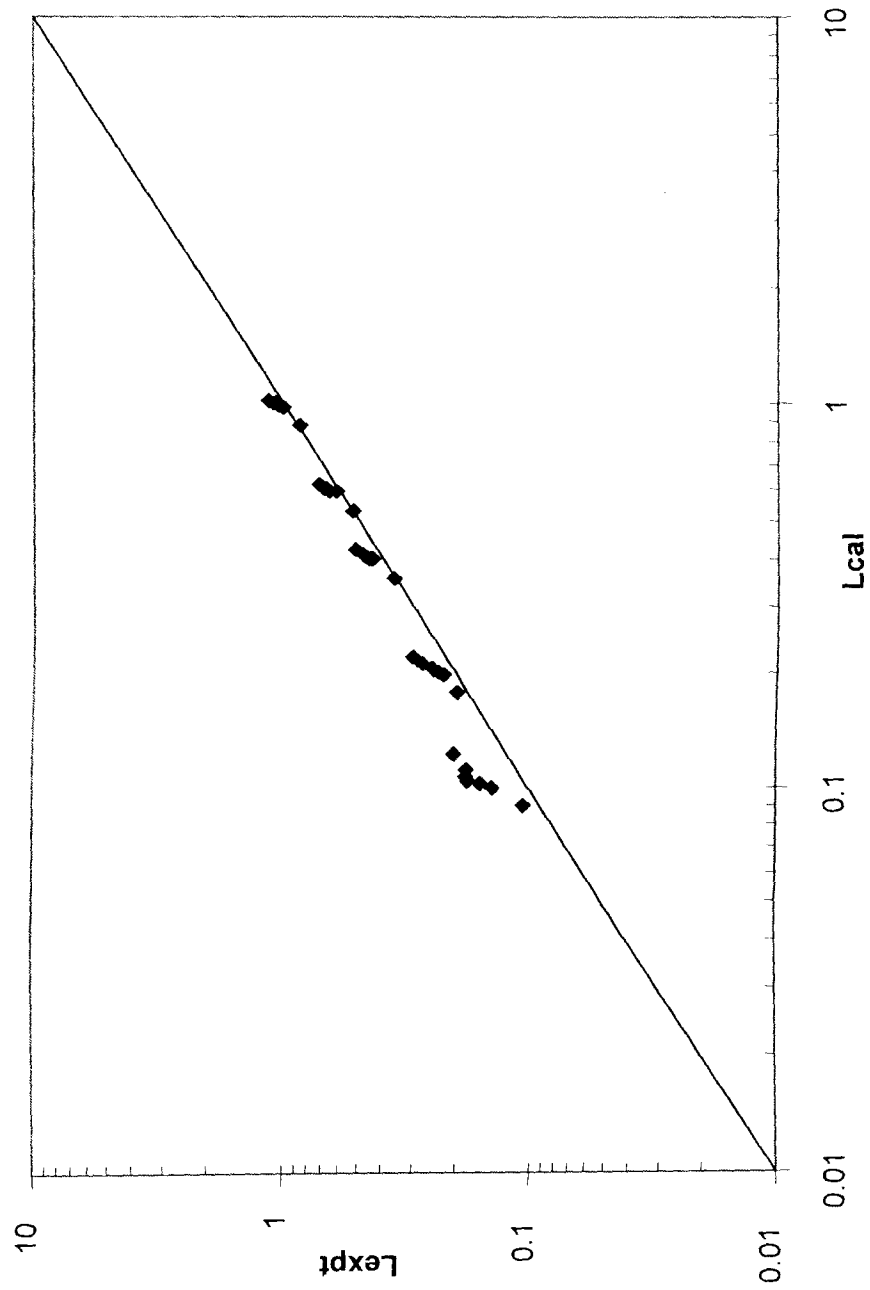


Figure 5.4 : The total CO₂ loading calculated from the model and the experimental loading at 40 °C.

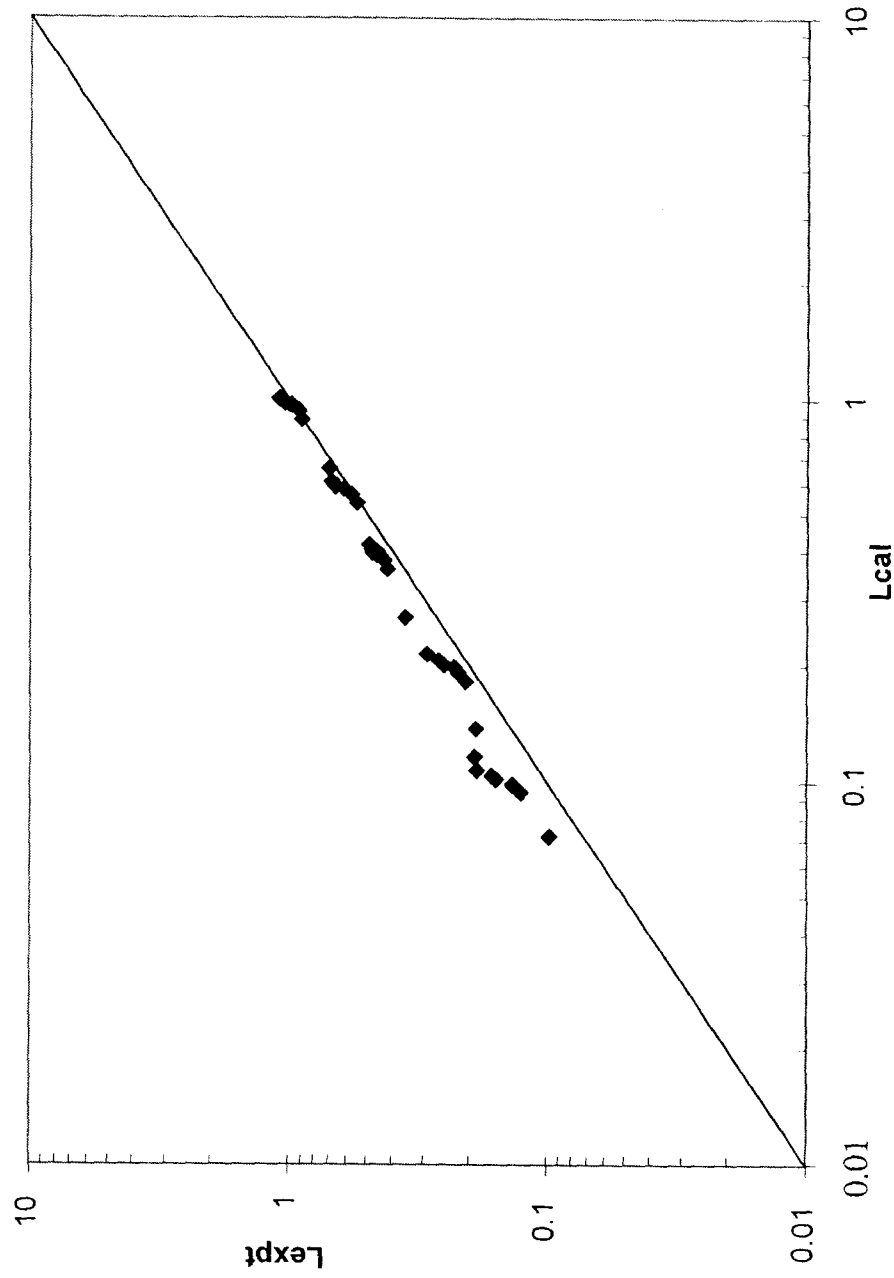


Figure 5.5 : The total CO₂ loading calculated from the model and the experimental loading at 50 °C.

5.4 Speciation in CO₂-PZ-H₂O systems

In this section we are proposing a simple model for the concentration profile of the main species present at equilibrium in CO₂-PZ-H₂O systems.

5.4.1. Speciation model assumptions.

Based on thermodynamical predictions and experimental results, one can deduce the following assumptions:

- 1) The concentration of OH⁻ and H⁺ are very low and could be assumed negligible since at equilibrium the pH of the solution was between 6 – 9.
- 2) Since the pK₁ value in reaction 5.1 is about 12, while the pH of the carbonated piperazine solution at equilibrium is between 6 and 9, reaction 5.1 lies to the left and the concentration of free PZ can be neglected.
- 3) The concentration of CO₃²⁻ is neglected since its equilibrium constant is generally 3 to 4 orders of magnitude smaller than the formation of HCO₃⁻. For example at 40 °C, the value of K₅ is estimated to be 1.037 x 10⁻¹² compared to K₆ which is 1.882 x 10⁻⁴.
- 4) The concentration of PZCOO⁻ is neglected since the the equilibrium pH is in the range of 6 to 9, while the pK₄ in reaction 5.4 is more than 11, which indicates that reaction 5.4 lies to the left and the piperazine monocarbamate is only a minor compound in the solution.
- 5) PZCOO⁻ species is required in order to form ⁻OOC PZCOO⁻. Since the concentration of PZCOO⁻ in the solution is very small, therefore the formation of ⁻OOC PZCOO⁻ will be negligible.

Appendix H shows that only small amount of the species mentioned above are present in the carbonated piperazine solution at equilibrium condition.

Based on the above assumptions, one can predict that at equilibrium the major species are HCO_3^- , PZH^+ , H^+PZCOO^- and free CO_2

Therefore, the CO_2 balance, the electroneutrality and the carbamate balance equations are given by,

$$[\text{CO}_2]_T = [\text{CO}_2] + [\text{H}^+\text{PZCOO}^-] + [\text{HCO}_3^-] \quad (5.23)$$

$$[\text{PZH}^+] = [\text{HCO}_3^-] \quad (5.24)$$

$$[\text{CAR}]_T = [\text{H}^+\text{PZCOO}^-] \quad (5.25)$$

The system of the equation (5.23) – (5.25), can be solved to calculate the different species concentrations, providing the CO_2 Henry's Constant, $[\text{CO}_2]_T$ and $[\text{CAR}]_T$ are known. In this simplified model, the experimental values of $[\text{CO}_2]_T$ and $[\text{CAR}]_T$ determined in chapter 4, and the CO_2 Henry's Constant in pure water were used.

5.4.2. Species profile

Typical profiles of species concentration as function of CO_2 loading are given in Figure 5.6 – 5.10 at 50 °C and total piperazine concentration varying from 0.1 to 1.0 M. The protonated piperazine carbamate is the dominant species in the aqueous piperazine solution. In most cases, H^+PZCOO^- accounts for more than 70 % of the total CO_2 loading capacity in the absorption process. This shows that CO_2 is being absorbed mainly in the form of H^+PZCOO^- . Furthermore, the variation of H^+PZCOO^-

species concentration as a function of total CO₂ loading is very small which indicates that it is a very stable species.

The concentration of free CO₂ increases with increase in CO₂ loading. This is expected since free CO₂ corresponds to the physical absorption. Only a small increase of HCO₃⁻ and PZH⁺ was observed as the total CO₂ loading increased except at 0.1 M of piperazine solution concentration where the concentration of these species decreased as the CO₂ loading increased. This may be due to the reversion of HCO₃⁻ to CO₂ since the pH at the equilibrium is low (less than 7). This will reduce the amount of HCO₃⁻ in the liquid phase.

5.4.3. Validation of the speciation model

In order to assess the performance of this simple model, the total piperazine mass balance equation is used. For this purpose, the value of total piperazine predicted by the model is compared with the actual concentration of piperazine used in the experiments. Table 5.4 summarizes the distribution of the relative deviation among all the experimental data used. The relative deviation is expressed as :

$$\frac{[PZ]_{\text{expt}} - [PZ]_{\text{model}}}{[PZ]_{\text{expt}}} \times 100$$

Table 5.4 : Deviation between the experimental and calculated total piperazine values.

Deviation (%)	0 - 10	11 – 20	21 – 30	31 – 49	> 50
No. of data	39	46	21	15	19
Data (%)	27.9	32.9	15.0	10.7	13.6

As shown in Table 5.1, 60.8 % of the overall data analyzed for the speciation model deviate less than 21 % from the experimental total piperazine concentration value. Another 13.6 % of the data deviate more than 50 %, all these data are the low piperazine concentration region (less than 0.4 M). The significant deviation may be due to the titration method used to determine the total carbamate which is not suitable to be used at low piperazine concentrations since the total carbamate value is very small. A slight error in the titration reading may give a great impact on the total carbamate value. Therefore, this simple speciation model is more reliable for the piperazine concentrations greater than 0.4 M.

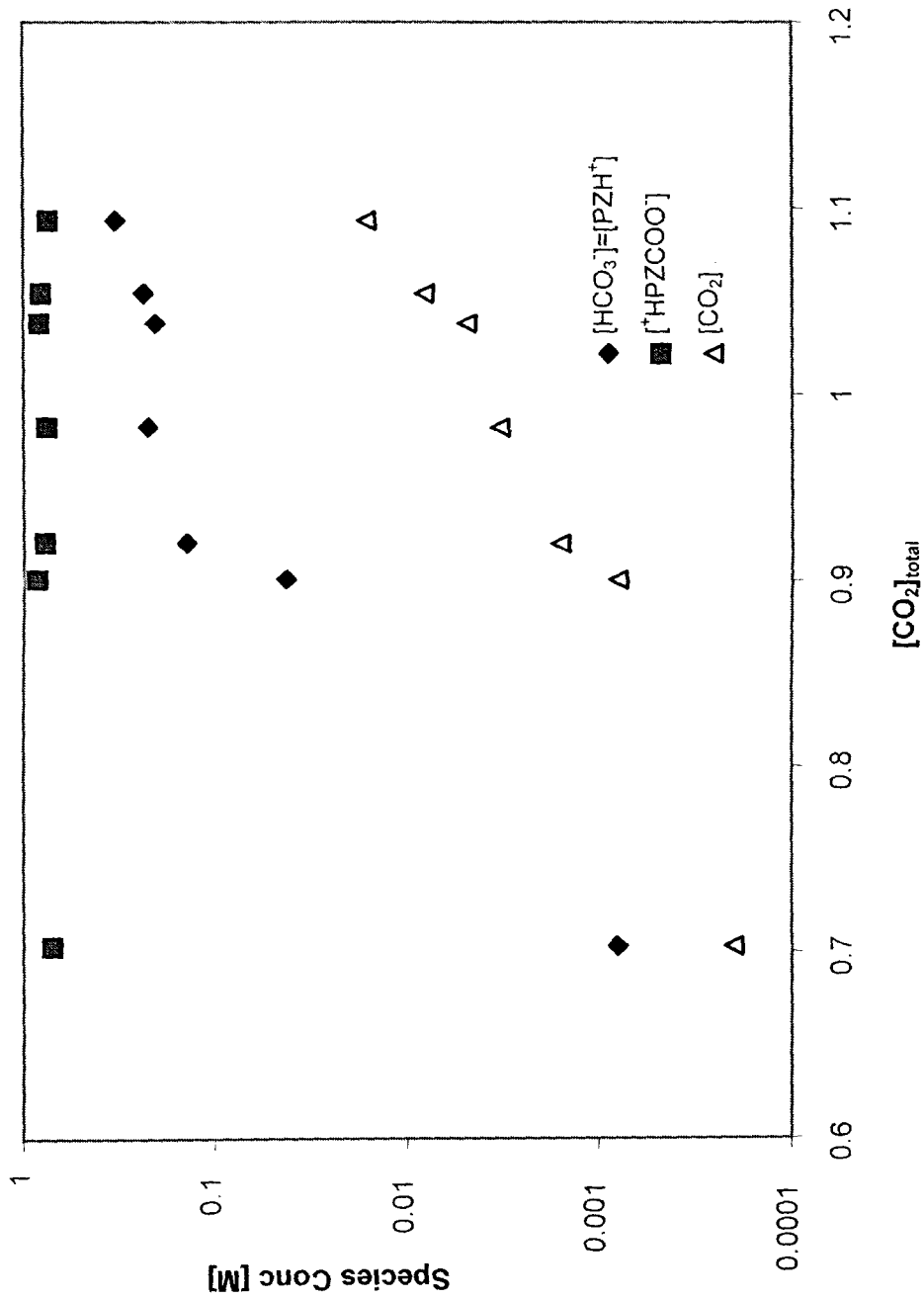


Figure 5.6: Species concentration profile in 1.0 M of aqueous piperazine solution at 50 °C.

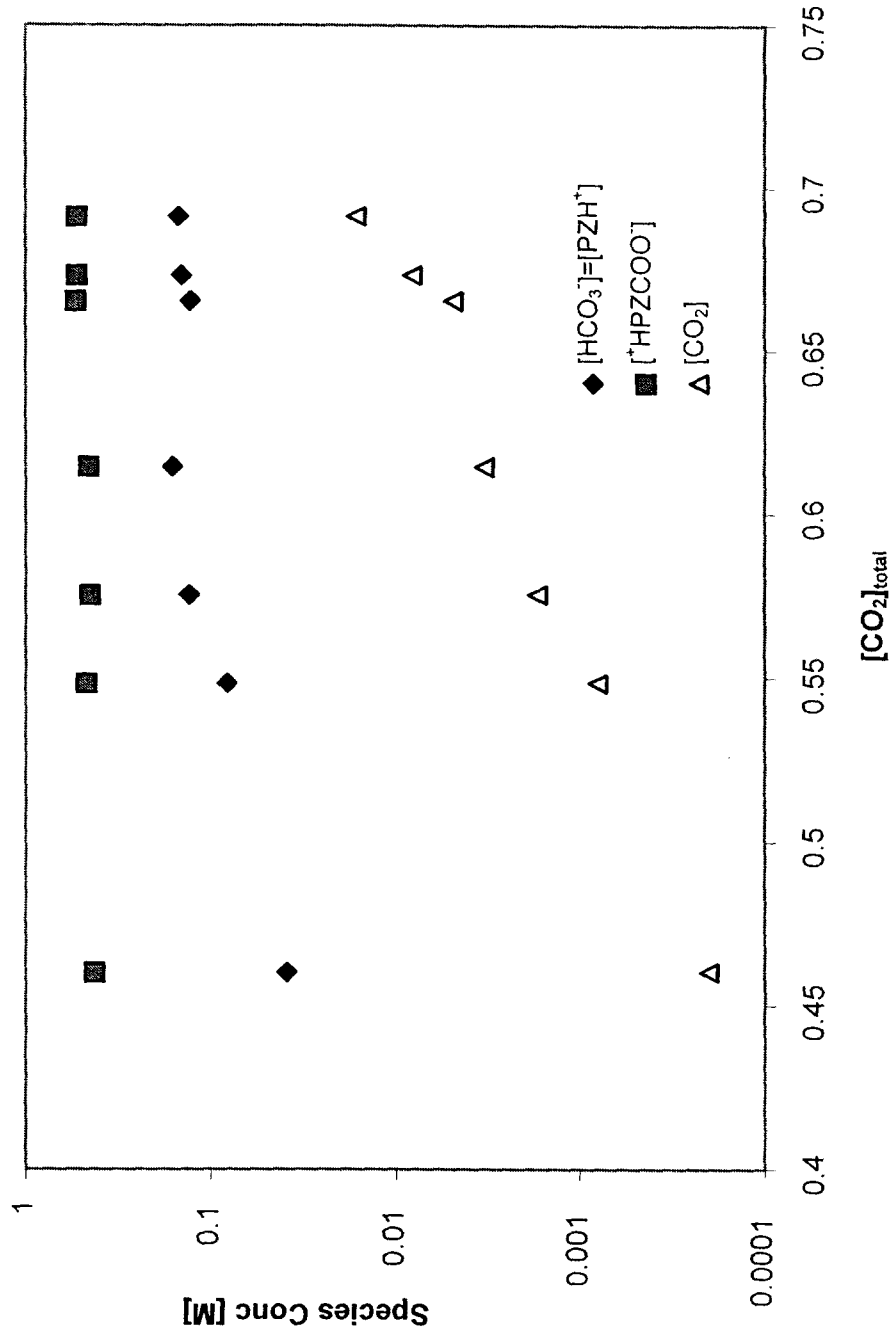


Figure 5.7: Species concentration profile in 0.6 M of aqueous piperazine solution at 50 °C.

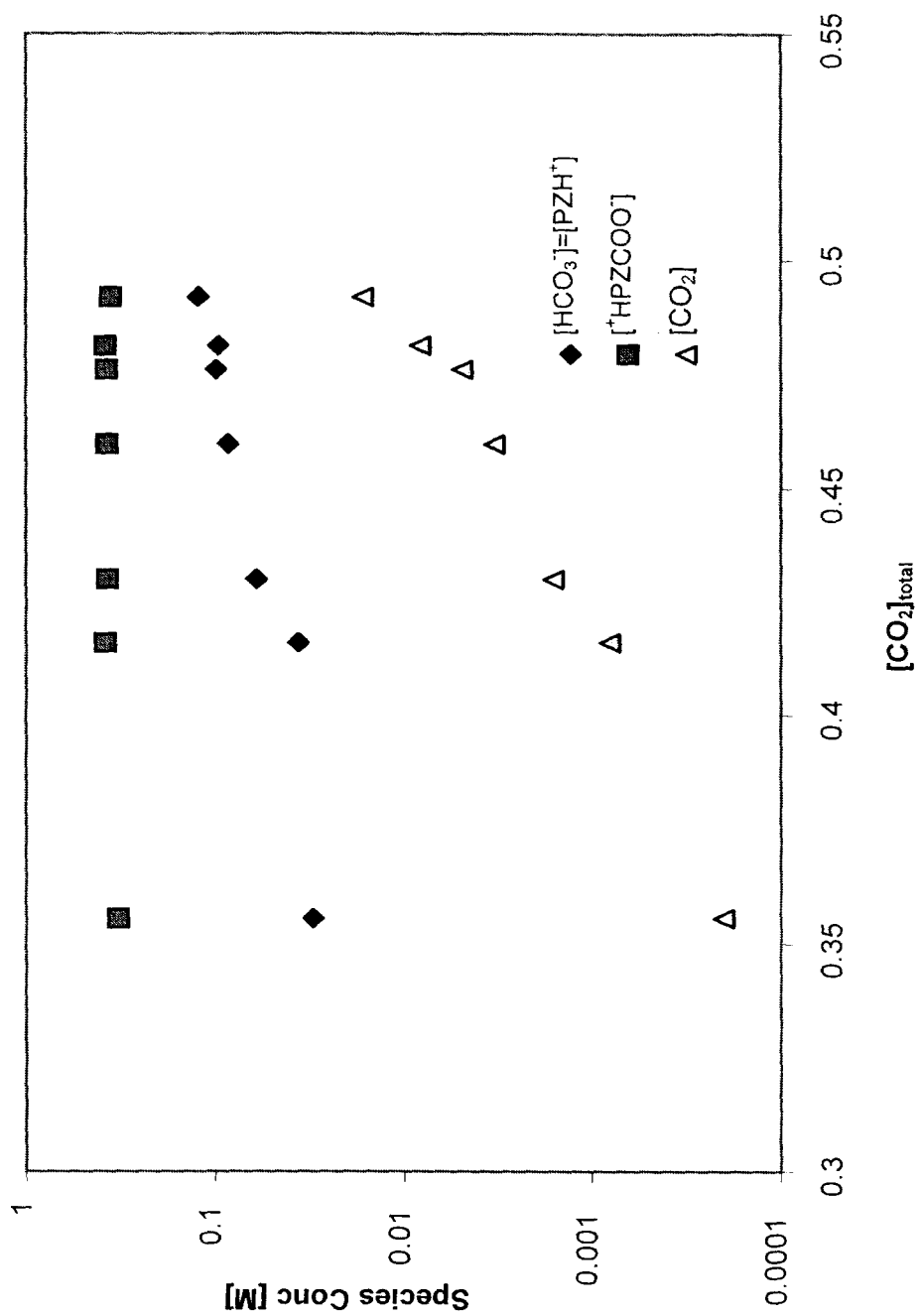


Figure 5.8: Species concentration profile in 0.4 M of aqueous piperazine solution at 50 °C.

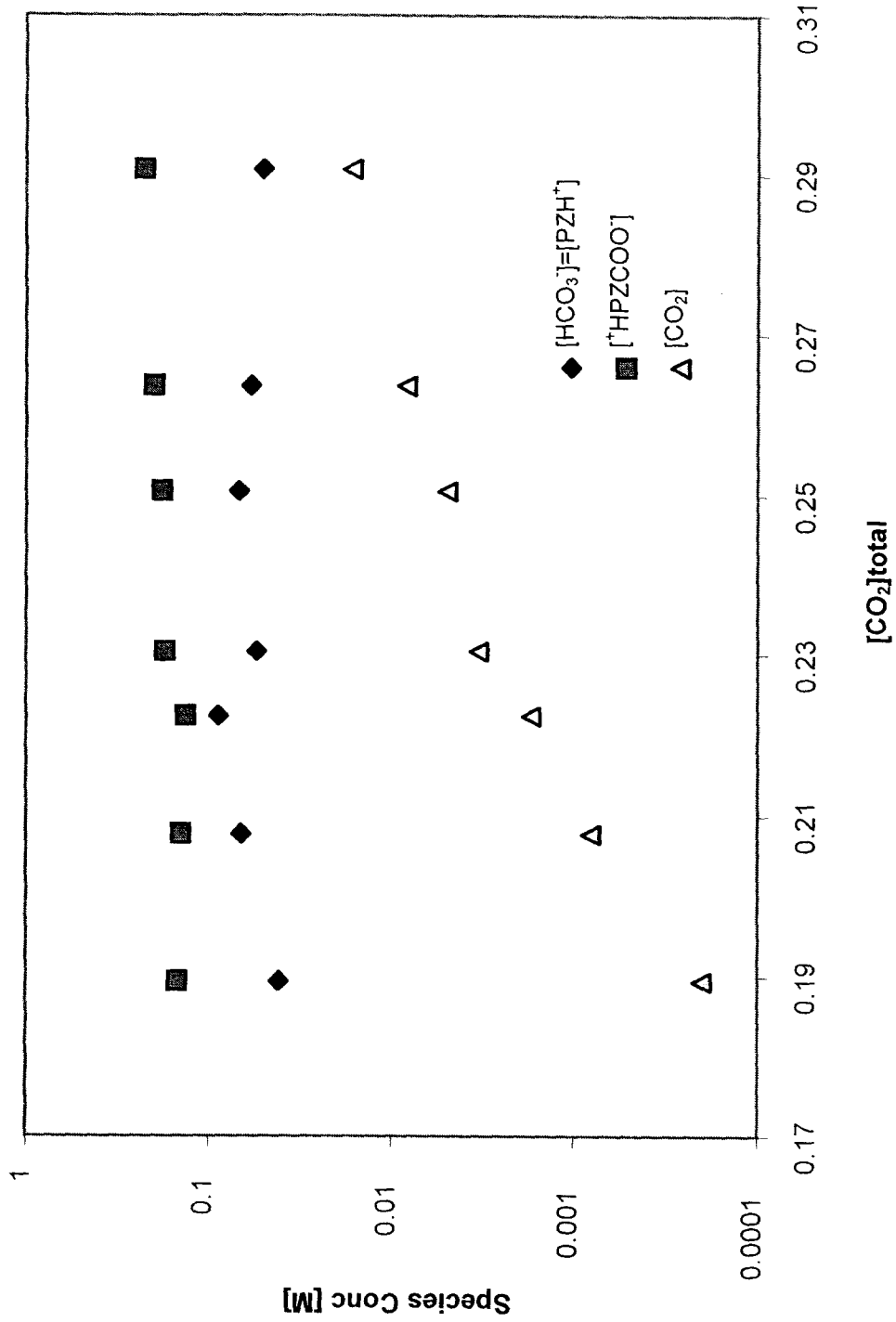


Figure 5.9: Species concentration profile in 0.2 M of aqueous piperazine solution at 50 °C.

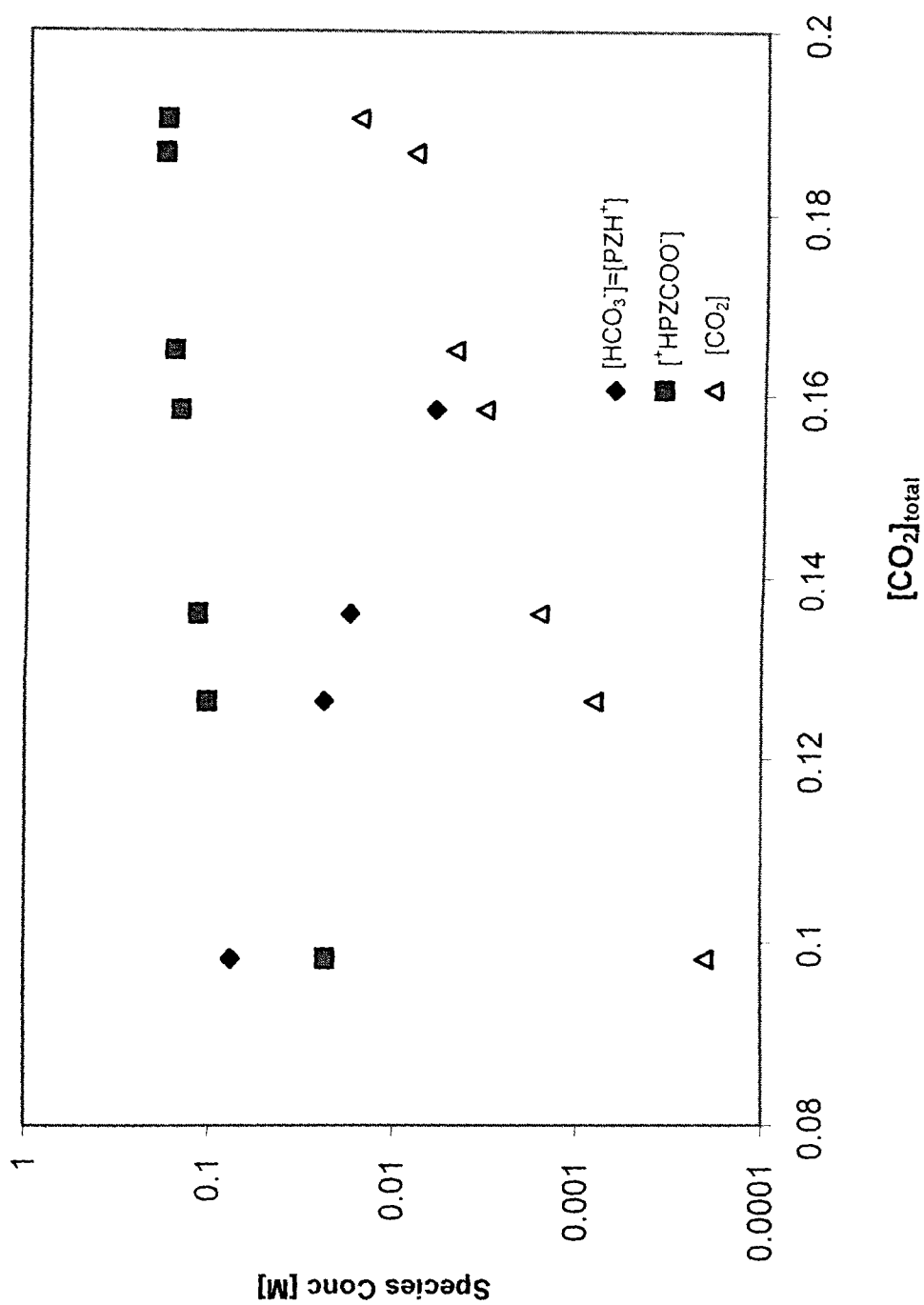


Figure 5.10: Species concentration profile in 0.1 M of aqueous piperazine solution at 50 °C

5.5 Applying the Kent and Eisenberg model to CO₂-PZ-DEA-H₂O system

The application of the Kent and Eisenberg model was extended to the CO₂-PZ-DEA-H₂O system. The equilibrium constants for the piperazine carbamates were taken from this work (Table 5.2), which was generated earlier. Initially, the equilibrium constants for protonated DEA and DEA carbamate (equation (5.26) and (5.27) respectively) developed by Benamor (1998) were used in this model at a total amine concentration of 2 M. However, significant deviation was observed between the predicted and experimental CO₂ loading values. This may be due to the limitation of these equations which are more applicable to DEA concentrations greater than 2 M. Therefore, the equilibrium constants for infinite dilution were used for the protonated DEA (Perrin, 1965) and DEA carbamate (Benamor, 1998). The same Henry's constant (Edwards et al., 1978) as in the work of CO₂-H₂O-PZ system was applied to this system. The equilibrium constant for the protonated DEA (K_8) and DEA carbamate (K_9) are as follow:

$$K_8 = [\exp(-3071.15/T + 6.776904 \ln T - 48.7594)] [\exp(-0.4559 \ln PCO_2 + 0.2584 \ln(AM))] \quad (\text{Benamor, 1998}) \quad (5.26)$$

$$K_9 = [\exp(-17067.2/T - 66.8007 \ln T + 439.709)] [\exp(-0.002386 \ln PCO_2 + 2.88 \ln(AM))] \quad (\text{Benamor, 1998}) \quad (5.27)$$

$$K_8 = [\exp(-3071.15/T + 6.776904 \ln T - 48.7594)] \quad (\text{Perrin, 1965}) \quad (5.28)$$

$$K_9 = [\exp(-17067.2/T - 66.8007 \ln T + 439.709)] \quad (\text{Benamor, 1998}) \quad (5.29)$$

Based on the known correlation of all the equilibrium constants and Henry's constant in the CO₂-PZ-DEA-H₂O system, the CO₂ loading values were calculated using the POLYMATH software. The program and an example of the output are listed in

appendix K. CO₂ loading values calculated based on the Kent and Eisenberg model are listed in appendix L. Figure 5.11 illustrates the deviation between the experimental and calculated model CO₂ loading values at amine concentration of 0.2 M DEA + 0.9 M PZ . It can be clearly seen from this figure that most of the $L_{\text{expt}}/L_{\text{model}}$ ratio values lies in the range of 0.8 to 1. This indicates that the model can give a reasonable prediction of CO₂ solubility values. Generally, a deviation greater than 50 %, with a maximum deviation of 119 % was observed at low CO₂ partial pressure and high temperature. This may be due to the limitation of the equilibrium constants used in the model since they are taken from single amine systems.

The error may also be due to the contribution of Henry's Law constant used in the system. The CO₂ Henry's Law expression of pure water used in the model may not represent the physical absorption of CO₂ accurately in the activated DEA solution. Therefore, Henry's Law constant of CO₂ in the aqueous mixture of DEA with PZ obtained by the N₂O analogy method are necessary to account for the CO₂ physical absorption in the amine solution. However, the CO₂ Henry's Law constant for the aqueous piperazine system is not available in the open literature.

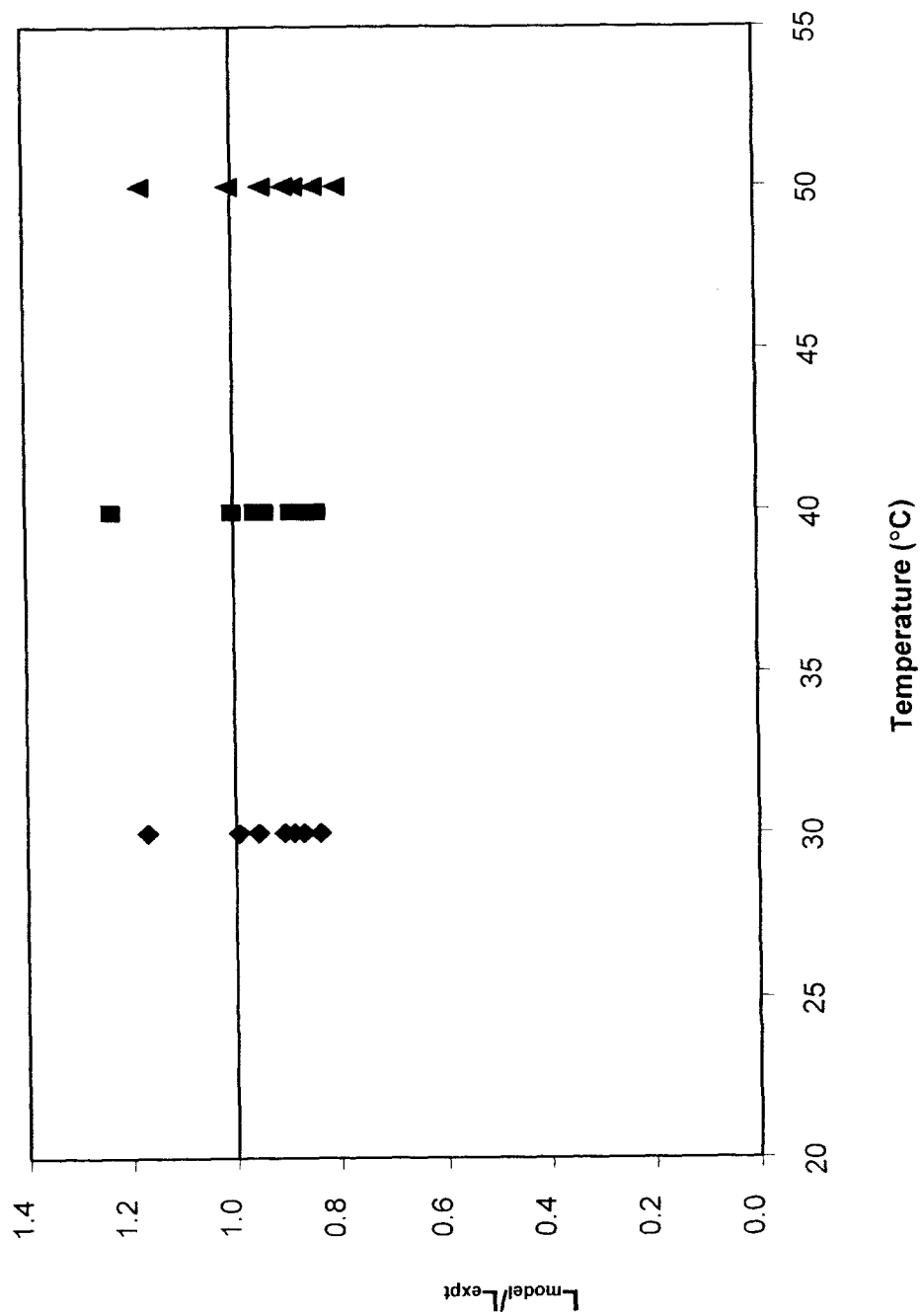


Figure 5.11: Comparison between the experimental and model CO₂ loading values at amine concentration of 0.2 M DEA + 0.9 M PZ.