

CHAPTER THREE

MODELING OF CO₂ SOLUBILITY DATA

3.1 INTRODUCTION

A mathematical model is a simple description of a process. It can help to analyze the chemical and physiological processes or mechanisms, enabling better design of experiments that can make sense of the results.

Aqueous alkanolamine solutions have been widely used for the capture and removal of CO₂ from acid gases. The relationship between the concentration of acid gas in an amine solution and its pressure in the gas phase at equilibrium is probably the most important item of data for the design of treating plants. This relationship may be referred to as gas solubility or vapor-liquid equilibrium (VLE). Charts and tables of experimental data are useful for preliminary studies. However, correlations are needed for interpolating and extrapolating data to specific conditions.

In this chapter, several mathematical techniques for alkanolamine absorption calculations will be discussed in terms of simplicity, applicability and accuracy for different types of alkanolamine systems. The methods adopted for calculating the CO₂ absorption in MAE will be illustrated and discussed while results and comparisons will be shown in Chapter 6.

3.2 VAPOUR-LIQUID EQUILIBRIUM

Numerous studies have been conducted and reported in the literature to develop mathematical models for predicting vapour liquid equilibria, (VLE) relationships corresponding to different amine solutions. Most of these studies are concerned with the most commonly used amines like monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). The first practical, and widely used model was proposed by Kent & Eisenberg (1976). This model assumes that all activity coefficients and fugacity coefficients to be unity (i.e. ideal solutions and ideal gases) and forces a fit between experimental and predicted values by treating two of the equilibrium constants (K_1 and K_2) as variables. Like all subsequent models, the Kent-Eisenberg correlation is based on defining the chemical reaction equilibria in the liquid phase. Weiland *et al.* (1993) indicated that the Kent-Eisenberg model was found to provide a good fit between experimental and predicted values for CO₂ loading in a wide range of conditions. This model has the important advantage of computational simplicity and has been incorporated into several computer models used for treating plant design.

A more rigorous model was proposed by Deshmukh & Mather (1981). It uses the same chemical reactions in solution but estimates values for activity and fugacity coefficients that are used in the calculation of liquid phase equilibrium constants and in the application of Henry's law to the VLE. Although this model gives more accurate results than the Kent-Eisenberg's model, but it is known to be rather complicated.

A simpler technique was proposed by Chakravarty *et al.* (1985). This technique was used for estimating VLE data in a simulation model developed by Sardar & Weiland (1984) and by Weiland *et al.* (1993) for estimating VLE data for the most important commercial amines over a wide range of conditions. In a related study, Li &

Mather (1994) used Pitzer's excess Gibbs energy equations, Pitzer (1991), to predict VLE data for some common amine mixtures. Hu & Chakma (1990) suggested that, in spite of the complexity of the calculations, the results of these rigorous models were not better than those of the Kent-Eisenberg model.

One of the most accurate models available at this time was proposed by Austgen *et al.* (1991). This model is based on the Electrolyte-NRTL model of Chen & Evans (1986). It was used successfully to correlate experimental VLE data for a number of amines and mixed amine solutions over a wide range of conditions and proved to produce highly accurate results.

3.3 REACTION MECHANISM

It is well known that absorption of CO₂ by alkanolamine solutions is basically a combination of both physical absorption and chemical reaction. As such, both thermodynamic and kinetics equilibria are considered important parameters in determining the achievable gas loading (mole CO₂/mole amine) of a particular CO₂ absorption system. The mechanisms for absorption reactions have been proposed by many researchers. Dankwerts & McNeil (1967) provided important illustrations of the rates of chemical reactions and equilibria involved in absorption of CO₂ into aqueous amine solutions.

Absorption of CO₂ by amine solutions involves the formation of carbamate and/or bicarbonate. The relative ratio of these ions depends on the nature of the alkanolamine and the process conditions such as temperature, CO₂ partial pressure and CO₂ loading (mole CO₂ absorbed /mole amine). The amine reacts with CO₂ in solution to form protonated amine (AmH⁺), and carbamate (AmCOO⁻) as follows;

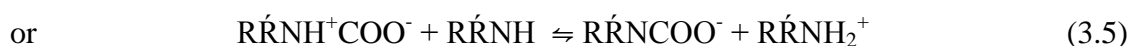
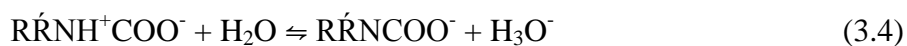
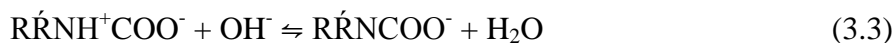


where R is an alkyl group and R' is hydrogen for primary amines or another alkyl group for secondary amines.

Two mechanisms have been proposed for this reaction; The first one is the zwitterion mechanism originally proposed by Caplow (1968). In this mechanism, the reaction takes place in two steps. The first step is the formation of an intermediate zwitterion, (locally ionic, neutral molecule), and the second step is the deprotonation of the zwitterion using a base to produce carbamate, as follows;

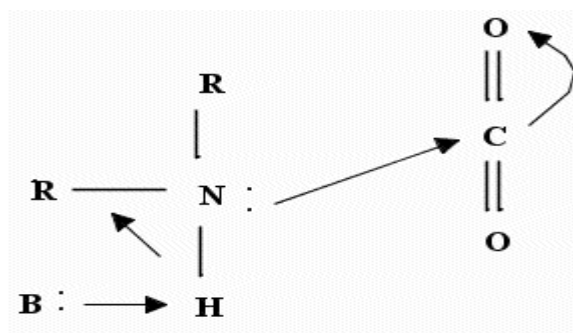


Theoretically, any base present in solution can deprotonate the zwitterion such as hydroxide, water or amine, as shown;



Due to the stable nature of the carbamate formed in the primary carbonated amine solutions, the equilibrium loading capacity of CO₂ is limited to 0.5 mole of CO₂ per mole of amine. Dankwerts (1979) introduced this mechanism into the literature, and Blauwhoff *et al.* (1984) showed that this mechanism explained much of the data in literature, especially those for DEA and other secondary amines.

The second model of the reaction mechanism is a single step mechanism proposed by Crooks & Donnellan, as follows, (da Silva, 2005);



(3.6)

where B is a base or a water molecule.

In this mechanism bonding between the amine and CO₂ and the proton transfer take place simultaneously. It has been argued that the rate-expression of the zwitterion-mechanism can be better used to fit experimental data. However, other articles (da Silva & Svendsen, 2004, Si Ali, 2007, & da Silva, 2005) concluded that rate-expressions based on both mechanisms can be fit equally well to the experimental data.

Bishnoi (2000) suggested that, although investigators consider the zwitterion species to be attacked by a base which extracts a proton, they ignored the suggestion that the amine group may be hydrated before forming the zwitterion.

In a CO₂-MAE-H₂O system, Ohno *et al.* (1999) proved that MAE reacts with CO₂ to form a carbamate, (MAECO₂⁻) and a protonated amine (MAEH⁺). The former (carbamate) subsequently reacts with CO₂ and H₂O to form MAEH⁺ and bicarbonate (HCO₃⁻). This article assumes that the zwitterion mechanism is valid, and that this zwitterion species is instantaneous and unstable. Mathematically however, it has been proven that these two mechanisms result in the same expression.

As these reactions occur, more CO₂ is driven from the gaseous phase into the solution due to the lower chemical potential of the liquid phase compounds at ambient temperature.

3.4 EQUILIBRIUM CONSTANTS K_i

The equations describing the equilibrium of carbon dioxide with aqueous secondary alkanolamines, are assumed by Kohl & Nielsen (1997), Haji-Sulaiman *et al.* (1996), Baek *et al.* (2000) and many others, as follows;

- Dissociation of protonated amine



- Hydrolysis of carbamate



- Hydrolysis of carbon dioxide



- Dissociation of water



- Dissociation of bicarbonate ion



where K_i , $i=1,2,3,4,5$, represent the equilibrium constants of reactions (3.7), (3.8), (3.9), (3.10) and (3.11) respectively.

For these reactions, the equilibrium constants are expressed as follows;

$$K_1 = \frac{[\text{H}^+][\text{RRNH}]}{[\text{RRNH}_2^+]} \quad (3.12)$$

$$K_2 = \frac{[\text{RRNH}][\text{HCO}_3^-]}{[\text{RRNCOO}^-]} \quad (3.13)$$

$$K_3 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (3.14)$$

$$K_4 = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (3.15)$$

$$K_5 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3.16)$$

The concentration of carbon dioxide can be estimated from Henry's law;

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (3.17)$$

where P_{CO_2} represents CO_2 partial pressure in kPa and H_{CO_2} represents Henry's constant in $kPa \cdot m^3/kmol$.

The overall material and charge balance equations can be written as follows;

$$[R\dot{R}NH]_t = [R\dot{R}NH]_e + [R\dot{R}NH_2^+]_e + [R\dot{R}NCOO^-]_e \quad (3.18)$$

$$\alpha[R\dot{R}NH]_t = [HCO_3^-]_e + [R\dot{R}NCOO^-]_e + [CO_3^{2-}]_e + [CO_2] \quad (3.19)$$

$$[R\dot{R}NH_2^+]_e = [HCO_3^-]_e + [R\dot{R}NCOO^-]_e + 2[CO_3^{2-}]_e \quad (3.20)$$

where α represents CO_2 loading (mole CO_2 /mole amine), and subscripts t and e represent total and equilibrium, respectively.

The temperature dependency of the equilibrium constants (or Henry's law constant) can be expressed in the form;

$$\ln K \text{ (or } \ln H) = a + b/T + c \ln T + dT \quad (3.21)$$

Values of the coefficients of equation (3.21) are given by Kent & Eisenberg (1976) and Edwards *et al.* (1978), which can be used to find the values of the equilibrium constants (and Henry's constant) at different temperatures, as given in Table 3.1.

Table 3.1: Values of the coefficients for equation (3.21)

<i>K</i> or <i>H</i>	<i>a</i>	<i>B</i>	<i>c</i>	<i>d</i>	Range of validity	Source
K_3	231.482	-12092.10	-36.7816	0	0-225 °C	Edwards <i>et al.</i> (1978)
K_4	140.932	-13445.9	-22.4773	0	0-225 °C	Edwards <i>et al.</i> (1978)
K_5	216.049	-12431.70	-35.4819	0	0-225 °C	Edwards <i>et al.</i> (1978)
H	170.7126	-8477.71	-21.9574	0.00578	0-100 °C	Kent & Eisenberg (1976)

Benamor & Aroua (2005) used the correlation of equation (3.21) to determine K_1 and K_2 for diethanolamine (DEA) and methyldiethanolamine (MDEA) as functions of temperature only and applied the Deshmukh-Mather model by fitting experimental data to generate interactive parameters and to calculate the activity coefficients in the model.

The equilibrium constant, K , of Equation (3.12) representing MAE protonation was determined experimentally by Littel *et al.* (1990) at four different temperatures, assuming it is a function of temperature, as shown in Table 3.2;

Table 3.2: Values of pK_1 at different temperatures (Littel et al, 1990)

Temperatures, T	293 K	303 K	318 K	333 K
pK_1	9.95	9.64	9.35	8.94

However, equilibrium constants may also be influenced by acid gas partial pressure, acid gas loading and/or amine concentration, (Chakma & Meisen, 1987), (Jou *et al.*, 1982).

Several correlations were proposed in the literature for fitting the experimental data to link K values with other variables. Li & Shen (1992) correlated K_1 of equation (3.7) representing amine protonation and K_2 representing hydrolysis of carbamate ions, with temperature, CO_2 loading and amine concentration, as follows;

$$\ln K_1 \text{ or } \ln K_2 = a_1 + a_2/T + a_3/T^2 + b_1 \cdot \alpha + b_2/\alpha + b_3/\alpha^2 + b_4 \cdot \ln M \quad (3.22)$$

where T is the temperature, in Kelvin, α is the CO_2 loading (mole CO_2 /mole amine), M is the amine concentration in $\text{mol} \cdot \text{dm}^{-3}$ and a_i , b_i are the correlation parameters which are determined by non-linear regression using least-squares fit to the experimental loading data.

The model presented in equation (3.22) was used by Baek *et al.* (2000) to

correlate K_1 of 2-amino-2-methyl-1,3-propanediol (AMPD) and by Tourneux (2007) to correlate K_1 and K_2 of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD). It yielded good performance for the prediction of CO₂ solubility in alkanolamine solutions besides being simple compared to other more complicated models.

Patil *et al.* (2006) presented another correlation for predicting the solubilities of both H₂S and CO₂ in aqueous MDEA solutions. In this correlation the equilibrium constant is expressed as a function of temperature, amine concentration, amine loading and free acid composition, as follows;

$$K_1 = \exp(a + b/T + c.[CO_2] + d.\ln M + e.\ln \alpha_{CO_2} + f.\ln([CO_2]) + g(\alpha_{CO_2} + \alpha_{H_2S}) + h.\ln([CO_2] + [H_2S])) \quad (3.23)$$

Haji-Sulaiman *et al.* (1996) expressed the equilibrium constant for AMP and DEA as a function of temperature, CO₂ partial pressure and amine concentration, as follows;

$$pK' = a + b/T + c.P_{CO_2} + d.M + e.M^2 \quad (3.24)$$

where pK' is the apparent equilibrium constant for amine protonation which incorporates the activity coefficient of the relevant species involved in the reaction. The form of this correlation is based on that proposed by Hu & Chakma (1995) with the addition of the square of the amine concentration for better fitting of the experimental data.

Hosseini (2009) applied a simplified technique to calculate the CO₂ loading in AMP and in mixtures of AMP and ionic liquids. By assuming ideal conditions and neglecting the carbamate formation reaction, she derived a relationship between the overall equilibrium constant K_{OV} and CO₂ loading as follows;

$$P_{CO_2} = \frac{H_{CO_2}[AMP]_t}{K_{OV}} \cdot \frac{\alpha^2}{(1-\alpha^2)} \quad (3.25)$$

According to equation (3.25) the CO₂ partial pressure was plotted against $\frac{\alpha^2}{(1-\alpha^2)}$ using experimental CO₂ loading and the points were fitted to a straight line with slope equals to $\frac{H_{CO_2}[AMP]_t}{K_{OV}}$. This approach was previously suggested by Danckwerts & Sharma (1966) and later referred to and revised by other researchers, Cents *et al.* (2005), Cents *et al.* (2005a) and Rahimpour & Kashkooli (2004), to be used for the design of absorption and stripping columns.

3.5 PROPOSED MATHEMATICAL MODEL

In this work, it is assumed that the activity and fugacity coefficients to be unity (ideal solutions). It is also assumed that K_1 representing dissociation of protonated MAE is a function of temperature only, therefore the data of Table 3.2 are fitted to the form of equation (3.21) which yields the following correlation for MAE;

$$\ln K_1 = 43400.95 - 1.812 \times 10^{-6}/T + 7561.416 \cdot \ln T + 12.1425 \cdot T \quad (3.26)$$

K_2 , representing hydrolysis of carbamate ion to bicarbonate, is then determined by fitting the experimental carbamate ions concentrations, by non-linear regression, to the form of equation (3.24) which includes not only temperature, but also CO₂ partial pressure and amine concentration, as proposed by Haji-Sulaiman *et al.* (1996). This correlation, together with equations (3.12)-(3.20), are then solved simultaneously to find theoretical (or predicted) values for the loading α in (mole CO₂/mole MAE), as well as the concentrations of eight species (i.e. $[R\dot{R}NH]_e$, $[R\dot{R}NH_2^+]_e$, $[R\dot{R}NCOO^-]_e$, $[HCO_3^-]_e$, $[CO_3^{2-}]_e$, $[CO_2]_e$, $[H^+]_e$, $[OH^-]_e$), for known values of $[R\dot{R}NH]_t$, P_{CO_2} , H_{CO_2} , K_1 , K_3 , K_4 and K_5 .

The theoretical (or predicted) results of α using this approach are compared with the experimental data using the coefficient of determination, R^2 and the sum of absolute mean percentage errors (MPE) as measures for assessment of accuracy.

3.6 SUMMARY

This chapter presents a review of most published literature on modeling VLE data for CO₂ absorption in alkanolamine solutions at different conditions.

In view of lack of published literature on VLE data for MAE, this work proposes a simple technique for the determination of CO₂ loading by using non-linear regression to fit experimental data of carbamate ion concentration to a correlation which relates the equilibrium constant, K_2 , of the carbamate hydrolysis with temperature, CO₂ partial pressure and amine concentration as proposed by Haji-Sulaiman *et al.* (1996). The results of this technique are compared with experimental solubility data for assessment of accuracy. Results, comparison and discussion are illustrated in Chapter 6 of this thesis.