CHAPTER 2

LITERATURE REVIEW

This Chapter deals with the history of the alkanolamine technology used in gas treating processes, the background theory of chemical equilibria in solutions and density correlations. A description of reaction mechanisms of CO$_2$ with water, CO$_2$ with aqueous primary and secondary amines, CO$_2$ with amine aqueous piperazine and several models used to represent the solubility data in CO$_2$-alkanolamine-water systems are presented. Several methods to determine the solubility of CO$_2$ in aqueous alkanolamines that have been used by previous investigators were also reviewed. Finally, this chapter presents a critical review of previous works carried out on density measurement and CO$_2$ solubility in aqueous alkanolamine solutions.

2.1 Historical background on amine gas treating process

Historically, alkanolamine technology is one of the oldest and dominant methods employed in removing acidic gases in the industries. R.R. Bottoms was granted a patent in this technology in 1930. Triethanolamine (TEA) was the first to become commercially available alkanolamine in the early gas treating plants. However, it has been replaced largely because of its low absorption capacity, slow reaction rate and relatively poor stability (Kohl and Riesenfeld, 1985). The term gas sweetening process refers to removal of acid gas from process gas stream. In amine technology, the process of separating the acid gas from its many sources involves the absorption
of acid gas into the aqueous amine solution at low temperature followed by stripping the acid gas from the amine solution at a higher temperature. In the absorption process, chemical reaction and physical absorption occur. To enhance the absorption performance, with regards to the type of solvent used, the absorption capacity of the solvent or loading and rate of absorption should be very high. Figure 2.1 illustrates the basic major equipment in an amine gas treating plant.

![Diagram of alkanolamine acid-gas removal process]

**Figure 2.1:** Basic flow diagram of alkanolamine acid-gas removal process.

The acidic gas is being fed at the bottom of the absorber and in contact with the descending amine solution counter currently. The purified gas flows from the top of the absorber. The acidic gas is absorbed by the amine solution and discharged from
the absorber to the regeneration zone. The rich amine solution is heated by hot regenerated lean amine in the heat exchanger where some CO₂ is being liberated. The amine solution is further heated in a regeneration still column where more CO₂ will be liberated and discharged from the system. Steam and acid gases separated from rich amine are condensed and cooled respectively in the reflux condenser. The hot lean amine is being cooled before circulating back to the absorber for a complete cycle.

2.1.1 Structures and properties of alkanolamines

An alkanolamine molecule contains at least one hydroxyl group and one amino group. The hydroxyl group is claimed to be responsible to reduce the vapor pressure and increase the solubility of the amine in water, while the amino group is very important providing the necessary alkalinity in the aqueous solution for the absorption process. Generally, alkanolamines can be divided into three categories namely, primary, secondary and tertiary depending on the number of alkyl groups attached to the nitrogen atom in the molecular structure (Figure 2.2). For example, DEA, which has two alkyl groups attached to the secondary central nitrogen is classified as a secondary amine.

The most commonly alkanolamines used in the gas processing industries are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). MEA is a primary amine, which has been used extensively in gas treatment process due to its high reactivity, thermal stability, low cost and ease of
Figure 2.2: Molecular structures for different types of alkanolamine
reclamion. However, it has high reaction heat with CO₂ that leads to high energy consumption and high vapor pressure that cause more vaporization loss.

Furthermore, it is appreciably more corrosive compared to other amines, which make it less competitive in the market (Liu, et al., 1999b). Generally MEA is used as 10 to 20 % weight in aqueous solution. The acid gas loading is usually limited to 0.3 to 0.35 mol of acid gas to mol of MEA due to the corrosion problem for carbon steel equipment. However, for stainless steel equipment the loading capacity can be as high as 0.9 mol of acid gas/ mol of MEA without any corrosion problem (Polasek and Bullin, 2001). The reaction of MEA with oxidizing agents such as carbonyl sulphide (COS), sulphur disulphide (CS₂), sulphur dioxide (SO₂) and oxygen can form soluble products, which are very corrosive. These products must be removed to avoid serious corrosion problems.

For DEA, it is commonly used in the 25 to 35 % weight aqueous solution. The acid gas loading is also limited to 0.3 to 0.35 mol of acid gas/mol of DEA when employing carbon steel equipment but can be increased to 1 mol of acid gas/mol of DEA when using stainless steel equipment or using corrosion inhibitor (Kohl and Riesenfeld, 1985). Compared to MEA, the degradation products of DEA are much less corrosive. Compared to MEA or DEA, MDEA is commonly used in a higher range of concentration that is between 20 to 50 % weight. Due to the less corrosion problem, in practical the acid gas loading that can be achieved is as high as 0.7 to 0.8 mol of acid gas to mol of MDEA (Polasek and Bullin, 2001). The most distinct advantage of MDEA over other conventional amines is that it is readily selective
towards H$_2$S in the presence of CO$_2$. Other advantages include low vapor pressure, low heat of reaction, less corrosive and high resistance to degradation.

Another interesting alkanolamine solvent is a sterically hindered amine which structurally is a primary amine with the primary amino group attached to a tertiary carbon atom or a secondary amino group is attached to a secondary or tertiary carbon atom. For instance, AMP is a sterically hindered amine which is in the form of hindered MEA. Such amine forms unstable carbamates when reacted with CO$_2$ (Sartori and Savage, 1983, Xu, et al., 1996). The unstable carbamates readily undergo hydrolysis forming bicarbonate and releasing free amine that again reacts with CO$_2$ resulting in higher stoichiometric CO$_2$ loading capacity approaching 1 mol of CO$_2$/mol of amine with appreciable rate of absorption (Sartori and Savage, 1983, Alper, 1990). There is no carbamate ion in the final reaction of CO$_2$ with AMP which was confirmed by the work of Chakraborty et al. (1986) where carbamate ion peak does not exist in their $^{13}$C-NMR spectra analysis. Moreover, hindered amine also has a good selectivity towards H$_2$S in the presence CO$_2$ in the sour gas stream (Saha et al., 1993). Therefore, the use of hindered amine in gas treating plants leads to reduction in amine circulation rate and steam requirement for regeneration process as well as higher mass transfer coefficients. Furthermore, lower equipment cost for new units will provide additional credit (Saw et al., 1984).

In the past twenty years, blended amines have steadily gain popularity in the alkanolamine technology. Numerous investigations (Chakravat, 1985, Li and Shen, 1992, Li and Chang, 1994, Saha et al., 1995, Jane and Li, 1997, Xiao et al., 2000,
Mandal et al., 2003) on blended amines have been done in order to optimize the absorption system to capture CO₂. The basic concept of using the blended amine is to utilize and combine the advantages of the individual amines in the mixture or customizing the amine solution to a particular need. Generally mixtures of MDEA and MEA or DEA are used to improve the CO₂ absorption process. For example, in a mixture of MDEA and MEA, the MDEA helps to increase the absorption capacity while the MEA is responsible to achieve the desired reaction rate. The application of MDEA blended amines are more useful in the area of low pressure condition because the MDEA is less capable of picking up sufficient CO₂ to meet the pipeline specifications, thus the MEA or DEA will carry out the task to achieve the desired CO₂ pick up. At high pressure the blended amine have little or no advantages over the MDEA (Polasek et al, 2001). The problems with the blended amines are to determine and maintain the amine mixture in the operation process of the gas treatment (Polasek and Bullin, 2001).

Recent development in alkanolamine technology is the use of activated amine where the conventional amine is being doped with an activator such as piperazine, which has been the focus of many investigators. Piperazine is a cyclic secondary diamine (Figure 2.4). A pure piperazine is in the form of clear crystal at ambient temperature. It absorbs water and CO₂ when exposed to the air and turn to yellowish color. It is also used as corrosion inhibitor, insecticide, accelerator for curing polychloroprene and enthelmintic (Lewis, 1993). When added to convectional amines, piperazine accelerates the CO₂ absorption reaction due to the formation of dicarbamate (Xu, et al., 1992, 1995, Kaganoï, 1997, Bishnoi and Rochelle, 2000, Seo and Hong, 2000).
Compared with DEA, piperazine has greater effect on enhancing the absorption rate of CO₂ in MDEA solution (Kaganoi, 1997). In the study of kinetics of CO₂ absorption in activated MDEA solution using a disk column, Xu and co-workers (1992, 1995) reported that the process was a rapid pseudo-first order reversible reaction between CO₂ and piperazine, in parallel with reaction between CO₂ and MDEA.

The use of hybrid process is another new potential technology in gas treating processes. The hybrid process technology combines membrane and amine absorbent to remove the acidic gases from process gas stream. The advantages of this technology, it can achieve large ratio of membrane area to module volume, high operating flexibility for handling feed streams of varying compositions or flow rate and easy to scale up (Kim and Yang, 2000, Bhide et al., 1998).

There are several types of membrane used by investigators for separations of CO₂ gas such as polymeric membrane, palladium membrane and zeolite-type membrane. The performances of the membranes are usually based on the selectivity, permeability and durability. Micro porous membrane absorbers made from polytetrafluoroethylene with AMP as the absorbent has shown a promising absorption capacity to separate CO₂ from CO₂-nitrogen mixtures (Kim and Yang, 2000), while a polypropylene hollow fiber membrane contactor with aqueous MEA solution as the absorbent exhibits the highest efficiency in removing CO₂ from CO₂-nitrogen mixtures compared with NaOH and DEA (Xu et al., 2001). The hybrid of polypropylene membrane-DEA absorbent have low efficiency in CO₂ absorption
because there is a reaction of DEA with the membrane in which the membrane suffered changes in terms of pore structure and surface roughness after being exposed to the DEA solution (Wang et al., 2004). The alteration of the surface tension of the membrane reduces the hydrophobic characteristic of the membrane. However, dissolved CO₂ can retard the surface roughening and cause less deformation to the membrane micro-pores. This may be due to the formation of carbamate ions from the reaction of CO₂ with DEA solution (Wang et al., 2004).

More research and development studies are required to improve the effectiveness of hybrid membrane-amine system in CO₂ absorption especially in the field of chemical compatibility of membrane with alkanolamine and the resistance of membrane to high temperature.

2.2 Theoretical background

2.2.1 Development on density correlation.

In this study a Redlich-Kister equation (Prausnitz et al., 1999) of the excess molar volume was applied to correlate the density of amine mixtures.

To predict the excess volume of a binary system, the following relation was employed:

\[ V_{12}^E / cm^{-3} \cdot mol^{-1} = x_1 x_2 \sum_{i=0}^{n} A_i (x_1 - x_2)^i \]  \hspace{1cm} (2.2.1)

where,

- \( A_i \) = pair parameter
- \( x_i \) = mole fraction of pure component
The pair parameter \((A_i)\) are assumed to be a function of temperature and expressed as
\[
A_i = a + b(T/K) + c(T/K)^2
\]  
(2.2.2)

The excess volume of a liquid mixture for ternary system can be calculated by the following expression.
\[
V^E = V^E_{12} + V^E_{13} + V^E_{23}
\]  
(2.2.3)

Using the measured density value of the fluid, the excess molar volume \(V^E\) can be calculated as:
\[
V^E = V_m - \sum x_i V^o_i
\]  
(2.2.4)

where

\(V_m\) = molar volume of liquid mixture

\(V^o_i\) = molar volume of pure fluid at the temperature of the system.

The molar volumes of the liquid mixtures are calculated as
\[
V_m = \frac{\sum x_i M_i}{\rho_m}
\]  
(2.2.5)

where

\(M_i\) = molar mass of pure component \(i\)

\(\rho_m\) = measured liquid density

In order to calculate the excess volume, the densities of pure fluids are required. The expression below was used to correlate the density of the pure fluid.
\[
\rho / g \cdot cm^{-3} = a_1 + a_2(T/K) + a_3(T/K)^2
\]  
(2.2.6)

The parameters \((a_i)\) can be determined from experimental data. In this work the parameters of the density equation for pure fluid were quoted directly from the available reference except for the value for pure piperazine which is not available in
the literature. In the case of pure piperazine, a few data points were collected from the literature and fitted into equation (2.2.6) to determine the parameter.

2.2.2 Chemical Equilibrium

"Chemical equilibrium is a condition in which a chemical reaction is occurring at equal rates in its forward and reverse directions, so that the concentrations of the reacting substances do not change with time" (Parker, 1993). In the thermodynamic point of view, it is a condition where there is no change of composition in the system with imposing some form of work upon it. The statistics mechanisms define the equilibrium state as a condition of the maximum freedom (or minimum restraint) which is compatible with composition, volume and energy of the system. By far, the thermodynamic approach is the most powerful and useful tool in treating the quantitative relationships between the position of the equilibrium and the factors which govern it.

Chemical potential $\mu$ is a thermodynamic property which plays important role in the description of both phase and chemical equilibrium. It can be described as the tendency of the substance to undergo chemical or physical change. It is used to relate the driving force of the chemical reaction. For phase equilibrium to exist, the chemical potential of each species in the system must be the same in all phases. This can be expressed by

$$\mu_i = \mu_i'$$  \hspace{1cm} (2.2.7)

where $\mu_i = \text{chemical potential of species } i$
$l, v = \text{liquid and vapor phase respectively}$

Consider a general chemical reaction as below

$$v_A A + v_B B \Leftrightarrow v_C C + v_D D$$

(2.2.8)

where $A, B, C, D$ are the chemical species and $v_i$ are the stoichiometric coefficients.

The stoichiometric coefficient is positive for the product and negative for the reactant. At equilibrium condition, the chemical reaction can be expressed as

$$\sum_{i=1}^{N} v_i y = 0 \quad (y = A, B, \ldots, N)$$

(2.2.9)

For multiple reaction the equation (2.2.8) can be generalized as

$$\sum_{i=1}^{N} v_{ij} B_i = 0 \quad (j = a, b, \ldots, M)$$

(2.2.10)

where $v_{ij}$ = stoichiometric coefficient of species $i$ in the reaction $j$

$M = \text{total reactions}$

$N = \text{total species}$

A general criterion for a closed system to be in thermodynamic equilibrium at constant temperature and pressure is its Gibbs energy is at minimum value and the chemical potential of each species must be equal in every phase.

2.2.3 Equilibrium Constant

Referring to general chemical reaction as shown in equation (2.2.8), at the equilibrium condition the total chemical potential of the product and the reactants are equal, thus the equation represents the equilibrium condition is

$$v_A \mu_A + v_B \mu_B = v_C \mu_C + v_D \mu_D$$

(2.2.11)
At constant T and P, the difference in chemical potential is equal to the change in Gibbs free energy $\Delta G$ (equation (2.2.9)).

$$\Delta G = [v_c \mu_i^c + v_D \mu_D] - [v_A \mu_A + v_B \mu_B] = 0 \quad (2.2.12)$$

The chemical potential $\mu$ can be represented by the equation below

$$\mu_i(T) = \mu_i^o + RT \ln(\gamma_i m_i) \quad (2.2.13)$$

where the subscript $i$ indicates the species, $\mu_i^o$ is the chemical potential of the species in standard state, $R$ is the ideal gas constant, $T$ is absolute temperature, $\gamma_i$ is the activity coefficient and $m$ is the molality of the species $i$.

Substitute equation (2.2.13) into (2.2.12) gives

$$v_A (\mu_A^o(T) + RT \ln(\gamma_A m_A)) + v_B (\mu_B^o(T) + RT \ln(\gamma_B m_B))$$

$$= v_c (\mu_c^o(T) + RT \ln(\gamma_c m_c)) + v_D (\mu_D^o(T) + RT \ln(\gamma_D m_D))$$

This equation is equivalent to

$$\ln \frac{(\gamma_c m_c)^c (\gamma_D m_D)^d}{(\gamma_A m_A)^A (\gamma_B m_B)^B} = \frac{v_A \mu_A^o + v_B \mu_B^o - [v_c \mu_c^o + v_D \mu_D^o]}{RT} \quad (2.2.15)$$

Analogous to equation (2.2.12), the standard Gibbs energy can be defined as,

$$\Delta G_i^o = [v_c \mu_i^o + v_D \mu_D^o] - [v_A \mu_A^o + v_B \mu_B^o] \quad (2.2.16)$$

and the equilibrium constant $K$ is defined as

$$K = \frac{(\gamma_c m_c)^c (\gamma_D m_D)^d}{(\gamma_A m_A)^A (\gamma_B m_B)^B} \quad (2.2.17)$$

Combination of equation (2.2.15) and (2.2.17) gives,

$$\ln K = -\frac{\Delta G_i^o}{RT} \quad \text{or} \quad K = \exp \left( -\frac{\Delta G_i^o}{RT} \right) \quad (2.2.18)$$
2.2.4 The relationship of temperature with equilibrium constant.

The qualitative effect of changing the temperature upon the equilibrium position can be related by the Le Chatelier’s Principle, where changing the conditions of the equilibrium system at equilibrium with respect to reversible process will produce a reaction in the system to offset the change (Brey, 1979). For instance, if one pair of opposing reactions consists of one endothermic reaction and another exothermic, increasing the temperature will tend to increase the amount of material corresponding to the product of endothermic reaction and decreases the product of exothermic one.

The quantitative effect on equilibrium can be related thermodynamically between the equilibrium constant, temperature and heat of reaction as below.

\[ H_i^o = -RT \frac{d}{dT} \left( \frac{G_i^o}{RT} \right) \]  \hspace{1cm} (2.2.19)

where \( H_i^o \) = standard enthalpy of species \( i \)

When equilibrium is achieved after a period of time, equation (2.2.19) becomes

\[ \sum_{i=1}^{N} H_i^o = -\sum_{i=1}^{N} RT^2 \frac{d}{dT} \left( \frac{G_i^o}{RT} \right) = -RT \frac{d}{dT} \sum_{i=1}^{N} \frac{G_i^o}{RT} \]  \hspace{1cm} (2.2.20)

or

\[ \Delta H_i^o = -RT^2 \frac{d}{dT} \left( \frac{G_i^o}{RT} \right) \]  \hspace{1cm} (2.2.21)

Rearranging equation (2.2.21), becomes

\[ \frac{d}{dT} \left( \frac{G_i^o}{RT} \right) = \frac{\Delta H_i^o}{RT^2} \]  \hspace{1cm} (2.2.22)
Combining equation (2.2.18) and (2.2.22)

\[
\frac{d(-\ln K)}{dT} = -\frac{\Delta H_i^o}{RT^2}
\]  

(2.2.23)

Equivalent to

\[
\frac{d(\ln K)}{dT} = \frac{\Delta H_i^o}{RT^2}
\]  

(2.2.24)

From equation (2.2.23), it can be seen that in exothermic reactions, the enthalpy change of reaction is negative, so the equilibrium constant will decrease with an increase in temperature which shift the equilibrium position toward the reactants. On the other hand, for endothermic reactions, the equilibrium position will be shifted toward the product with increasing in temperature.

The enthalpy and entropy changes as function of temperature using integral of heat capacity are expressed as

\[
H_i^o(T) = H_i^o(T_o) + \int_{T_o}^{T} CpdT
\]  

(2.2.25)

\[
S_i^o(T) = S_i^o(T_o) + \int_{T_o}^{T} \frac{CpdT}{T}
\]  

(2.2.26)

where \(T_o\) = reference temperature

\(S\) = entropy

\(Cp\) = heat capacity.

Analogous to equation (2.2.25) and (2.2.26), the corresponding property changes can be written as;
\[ \Delta H^\circ(T) = \Delta H^\circ(T_o) + \int_{T_o}^{T} \Delta C_p^{\circ} dT \]  
\[ \Delta S^\circ(T) = \Delta S^\circ(T_o) + \int_{T_o}^{T} \frac{\Delta C_p^{\circ} dT}{T} \]  
(2.2.27)
(2.2.28)

The basic relationship to the change in properties as function of temperature are given as

\[ \Delta G^\circ(T) = \Delta H^\circ(T) + T\Delta S^\circ(T) \]  
(2.2.29)

Combining equation (2.2.27), (2.2.28) and (2.2.29), gives

\[ \Delta G^\circ(T) = \Delta H^\circ(T_o) + \int\Delta C_p^{\circ} dT - T\Delta S^\circ(T) - T\int_{T_o}^{T} \frac{\Delta C_p^{\circ}}{T} dT \]  
(2.2.30)

Analogous to equation (2.2.29)

\[ \Delta S^\circ(T_o) = \frac{\Delta H^\circ(T_o) - \Delta G^\circ(T_o)}{T_o} \]  
(2.2.31)

Substitute equation (2.2.31) into (2.2.30), yields

\[ \Delta G^\circ(T) = \Delta H^\circ(T_o) + \int\Delta C_p^{\circ} dT - T\left(\frac{\Delta H^\circ(T_o) - \Delta G^\circ(T_o)}{T_o}\right) - T\int_{T_o}^{T} \frac{\Delta C_p^{\circ}}{T} dT \]  
(2.2.32)

Rearranging equation (2.2.33), gives

\[ \Delta G^\circ(T) = \Delta G^\circ(T_o) \left(\frac{T}{T_o}\right) + \Delta H^\circ(T_o) \left(1 - \frac{T}{T_o}\right) + \int_{T_o}^{T} \Delta C_p^{\circ} dT - T\int_{T_o}^{T} \frac{\Delta C_p^{\circ}}{T} dT \]  
(2.2.33)

To relate equation (2.2.33) with equilibrium constant, it is divided by \(RT\), which gives,

\[ \frac{\Delta G^\circ(T)}{RT} = \frac{\Delta G^\circ(T_o)}{RT_o} + \frac{\Delta H^\circ(T_o)}{RT} \left(1 - \frac{T}{T_o}\right) + \frac{1}{RT} \int_{T_o}^{T} \Delta C_p^{\circ} dT - \int_{T_o}^{T} \frac{\Delta C_p^{\circ}}{RT} dT \]  
(2.2.34)
Multiply negative sign and exponential to both sides of equation (2.2.34), gives

$$\exp\left(-\frac{\Delta G^o(T)}{RT}\right) = \exp\left[\frac{\Delta G^o(T_o)}{RT_o}\right] \left(1 - \frac{T}{T_o}\right) - \frac{1}{RT} \int_{T_o}^{T} \Delta C_p^o \, dT + \int_{T_o}^{T} \frac{\Delta C_p^o}{RT} \, dT$$

(2.2.35)

Since $K = \exp\left(-\frac{\Delta G^o}{RT}\right)$, equation 2.2.35 become

$$K = K_o \exp\left[\frac{\Delta H^o(T)}{RT} \left(1 - \frac{T}{T_o}\right)\right]$$

$$\exp\left[\frac{\Delta C_p^o}{RT} \int_{T_o}^{T} \Delta C_p^o \, dT + \int_{T_o}^{T} \frac{\Delta C_p^o}{RT} \, dT\right]$$

(2.2.36)

Equation (2.2.36) can be written in a simplified form as

$$K = K_o K_a K_b$$

where $K_o = \exp\left(-\frac{\Delta G^o(T)}{RT_o}\right)$ which is the value of equilibrium constant at the reference temperature.

$$K_a = \exp\left[\frac{\Delta H^o(T)}{RT} \left(1 - \frac{T}{T_o}\right)\right]$$ which is the most temperature dependent part.

$$K_b = \exp\left[\frac{1}{RT} \int_{T_o}^{T} \Delta C_p^o \, dT + \int_{T_o}^{T} \frac{\Delta C_p^o}{RT} \, dT\right]$$

In general the heat capacities of reactants and products are different, therefore the enthalpy of reaction changes with temperature, as a result $K_b$ has less dependence on temperature.
The partial derivative of Gibbs energy is zero with respect to reaction coordinate at
equilibrium condition with constant temperature and pressure. This equilibrium
condition can be described by the following equation.

\[
\frac{\partial G}{\partial \xi} \bigg|_{T,P} = \sum_{i=1}^{\bar{N}} V_i \mu_i = 0
\] (2.2.37)

The chemical potential of a chemical can be written in terms of fugacity as below.

\[
\mu_i = \Gamma_i(T) + RT \ln f_i
\] (2.2.38)

Analogous to equation (2.2.38) the Gibbs energy of species \(i\) in its standard state can
be written as

\[
G_i^\circ = \Gamma_i(T) + RT \ln f_i^\circ
\] (2.2.39)

Subtracting equation (2.2.39) from (2.2.38)

\[
\mu_i = G_i^\circ + RT \ln \left( \frac{f_i}{f_i^\circ} \right)
\] (2.2.40)

Substitute equation (2.2.40) into (2.2.37)

\[
\sum_{i=1}^{\bar{N}} V_i \left( G_i^\circ + RT \ln \left( \frac{f_i}{f_i^\circ} \right) \right) = 0
\] (2.2.41)

Rearranging the equation (2.2.41)

\[
- \frac{\sum_{i=1}^{\bar{N}} V_i G_i^\circ}{RT} = \sum_{i=1}^{\bar{N}} V_i \ln \left( \frac{f_i}{f_i^\circ} \right) = \ln \left( \prod_{i=1}^{\bar{N}} \left( \frac{f_i}{f_i^\circ} \right) \right)
\] (2.2.42)

The standard Gibbs energy change of reaction is define as

\[
\Delta G_i^\circ = \sum_{i=1}^{\bar{N}} V_i G_i^\circ
\] (2.2.43)
Substitute equation (2.2.43) into (2.2.42), gives

\[ -\sum_{i=1}^{N} \frac{\Delta G^o_i}{RT} = \ln \left( \prod_{i=1}^{N} \left( \frac{f_i}{f_i^o} \right)^{x_i} \right) \]  \hspace{1cm} (2.2.44)

Taking exponential for both side of the equation (2.2.44), gives

\[ K = \exp \left( \frac{\Delta G^o}{RT} \right) = \prod_{i=1}^{N} \left( \frac{f_i}{f_i^o} \right)^{x_i} \]  \hspace{1cm} (2.2.45)

The activity coefficient of species \( i \) in the solution is given by a symbol \( \gamma_i \). By definition,

\[ \gamma_i = \frac{f_i}{x_i f_i^o} \text{ where } f_i = \text{liquid phase fugacity component } i \]

\[ f_i^o = \text{standard state fugacity for pure component } i \]

Therefore, \[ \frac{f_i}{f_i^o} = \gamma_i x_i \]

From equation (2.2.45), the value of \( K \) can be written as

\[ K = \prod_{i=1}^{N} (\gamma_i x_i) \]  \hspace{1cm} (2.2.46)

If the liquid is an ideal solution, the activity coefficient will be equal to 1, thus equation (2.2.46) will be simplified to be:

\[ K = \prod_{i=1}^{N} (x_i) \]  \hspace{1cm} (2.2.47)

This relationship is called 'law of mass action'.
2.2.5 Characteristics of electrolyte solutions

The absorption of CO₂ in aqueous alkanolamine solutions involves an electrolyte system. The liquid solutions containing ionic species in which charged particles interact with coulombic forces at small separations (distance between the ions). The formation of ion clouds around each ion, will damp the coulombic forces at larger separation distances. These forces are larger in magnitude compared to those involved in the interaction of neutral molecules. For electrolyte solutions the electrolyte activity coefficient is not unity even at a very low concentration. The activity coefficient varies with the total ionic population of the solution. The total ionic population of the solution is measured in a quantity called ionic strength, \( \mu \). The ionic strength of a solution containing ion \( i \) with charge of \( Z_i \) is defined by the following equation.

\[
\mu = \frac{1}{2} \sum_i [i] Z_i^2
\]  

(2.2.48)

where \([i] = \text{ion concentration}\)

\( Z_i = \text{charge of ion } i \)

The activity coefficient of a single ion cannot be measured since the concentration of single ion cannot be varied without varying the concentration of opposite charged thus the mean activity coefficient of a substance, \( \gamma_s \), is used to related the individual ionic activity coefficient of substance \( M_mN_n \) as follows

\[
\gamma_{M_mN_n} = \gamma_M^m \gamma_N^n = \gamma_s^{m+n}
\]

(2.2.49)
For infinite dilution solutions, the ions in the solution are too far apart to exert any significant influence on each other; therefore the mean ionic activity coefficient of the electrolyte can be considered as unity. However, in dilute solution (not infinitely dilute), the coulombic forces are important because the electrostatic and repulsive forces between the ions are significant even at large distances of separation (Prausnitz et al, 1999). Actually, there are a number of factors that may affect the activity coefficient such as formation of complex ion, changes in the dielectric constant of the solvent but the most major cause of deviation of the activity coefficient from actual concentration in dilute solution is the electrical effect (Bard, 1966). The electrostatic forces produce an extra free energy in addition to the free energy of the reaction in the absence of electrostatic effect and this addition energy is related to activity coefficient. The Debye-Hückel theory succeeded in developing quantitatively treatment for the electrostatic interactions. Using a statistical mechanical model to obtain the average ion distribution around ions in the solution Debye and Hückel derived the following expression.

\[
\ln \gamma_i = -\alpha \left| Z_i Z_j \right| \sqrt{\mu}
\]  

(2.2.50)

where \( \alpha \) is the parameter that depends on solvent and temperature and the bracket term is the absolute value of the product of ion valences. The important features of this equation are that all the ions in the solution influence the ionic strength factor. However, equation (2.4.46) is only accurate at low ionic strength and is usually known as the Debye-Hückel Limiting Law. Significant error can be observed at ionic strength as low as 0.01 molal (Sandler, 1989). This is due to the existing of repulsive forces between the finite sizes of the ion and interaction forces other than the electrostatic forces such as dispersion forces. Nevertheless, the assumption of the
solvent is a dielectric continuum (characterized by its dielectric constant) is invalid because there are no explicit terms for solvent-solvent and ion-solvent interactions taken into account. It is only assumed that these interactions are lumped into the dielectric constant which is only satisfactory for infinite dilute solution but a large divergence are observed for concentrated ionic solutions. However, for higher electrolyte concentrations, some modification has been applied to equation (2.2.50), as shown below.

\[
\ln \gamma_1 = -\frac{\alpha|Z_1 Z_2|^{1/2}}{1 + \beta \alpha \sqrt{\mu}}
\]  

(2.2.51)

where \(\beta\) = interaction parameter for the aqueous solutions

\[\alpha = \text{constant related to average hydrated radius ions}\]

In practice, the product of \(\beta \alpha\) is sometimes set equal to unity or treated as an adjustable parameter.

Numerous models have been developed to correlate the activity coefficient in aqueous electrolyte solutions. Additional terms that account for the ion-ion interactions and ion pairing (incomplete dissociation) to that of Debye-Hückel model was used to describe the electrolyte solutions at high concentrations. The contribution of long range forces between ions and short range forces between all species involved in the electrolyte solution are very important parameter to determine the accuracy of the model to the experimental values.
In mixed electrolyte solutions, the ion-interaction model of Pitzer has been widely used for the system of interest in many chemical industries. In fact, with the availability of a substantial model-parameter database and powerful computer software, this model is more versatile to be used to describe the thermodynamic properties of electrolyte solutions. The Pitzer model (1975) represents the excess Gibbs energy as the following equation (2.2.52).

\[
\frac{G^e}{n_w} = f(\mu) + \sum_{i,j} \lambda_{ij}(\mu) M_i M_j + \sum_{i,j,k} \delta_{ijk} M_i M_j M_k + \ldots \quad (2.2.52)
\]

where

\[
\frac{G^e}{n_w} \quad \text{excess Gibbs free energy per kg of solvent}
\]

\[M_i\] = molality of each ion or neutral solute

\[f(\mu)\] = Debye-Hückel coefficient

\[\lambda_{ij}\] = second virial coefficient

\[\delta_{ijk}\] = third virial coefficient

The function of \(f(\mu)\) depends on temperature, solvent properties and ionic strength which represent the long range electrostatic forces. It is in the form of modified Debye-Hückel term.

\[
f(\mu) = -A_d \frac{4\mu}{b} \ln\left(1 + b\sqrt{\mu}\right) \quad (2.2.53)
\]

where \(b\) is the empirical universal constant which is equal to \(\sqrt{\frac{1.2\text{kg}}{mol}}\) used to all electrolytes, while \(A_d\) is the Debye-Hückel parameter for the osmotic coefficient.
\[ A_{\phi} = \frac{1}{3} \left( \frac{1}{2\pi N_A ds} \right)^2 \left( \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r kT} \right)^2 \]  \hspace{1cm} (2.2.54)

where,

- \( N_A \) = Avogadro’s constant.
- \( ds \) = solvent density (g/cm\(^3\)).
- \( e \) = electronic charge = 1.60218 \times 10^{-19} \text{ C}.
- \( \varepsilon_0 \) = permittivity of free space = 8.85419 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}.
- \( \varepsilon_r \) = dielectric constant of solvent.
- \( k \) = Boltzmann constant.
- \( T \) = absolute temperature.

The \( \lambda_{ij} \) represents the short range interaction between the two solute molecules in the solution, where it facilitates rapid convergence in this viral expansion and finally, the \( \delta_{ijk} \) represent the three-body ion interactions which are only important at high concentrations (usually > 2 mol kg\(^{-1}\)). Higher order of interaction may be required in this equation for more highly concentrated solutions (Prausnitz et al, 1999). The \( \lambda_{ij} \) and \( \delta_{ijk} \) matrices are assumed to be symmetric where \( \lambda_{ij} = \lambda_{ji} \) and \( \delta_{ijk} = \delta_{ikj} = \delta_{jki} \). The interaction parameter of \( \lambda_{ij}(\mu) \) and \( \delta_{ijk} \) are analogous to second and third viral coefficients because they represent the effect of short range forces between the two and three ions respectively.

Another popular model that have been frequently used to describe the activity coefficient in aqueous alkanolamine solutions is the Non-random two-liquid (NRTL) equation. This model is based on local composition concept. The effect of Van der
Waals interaction forces between the ions is not expressed as a function of the bulk composition but as a function of the local composition. The NRTL model is used to represent the short range forces in the activity coefficient and written as follows for a solution of \( m \) components:

\[
\frac{G_j^E}{RT} = \frac{\sum_{i=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{i=1}^{m} G_{ji} x_j} \tag{2.2.55}
\]

with \( \tau_{ji} = \frac{b_{ji}}{RT} \) and \( G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \)

The \( \alpha, b_{ji} \) parameters are specific to a particular pair of species which are independent of composition and temperature.

The activity coefficient of the component \( i \) is given as:

\[
\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{j=1}^{m} G_{ji} x_j} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{j=1}^{m} G_{ji} x_j} \left[ \tau_{ij} \frac{\sum_{j=1}^{m} x_j \tau_{ij} G_{ij}}{\sum_{j=1}^{m} G_{ij} x_j} \right] \tag{2.2.56}
\]

This equation contains three parameters, \( \tau_{ij}, \tau_{ji} \) and \( \alpha_{ij} \) for each pair of components in the solution. The interesting features about this model is that all the parameters can be determined from the activity coefficient data of a binary mixture. For example, by correlating activity coefficient for species 1-species 2 mixture the 1-2 parameters can be determined. Similarly, from data for species 2-species 3 and species 1-species 3 binary mixtures, the 2-3 and 1-3 parameters can be found. Based on these coefficients, it can be used to estimate the activity coefficients for the ternary mixture of 1,2-3 without any experimental data for the three component system. However, for high accuracy prediction of multicomponent behavior in ternary mixtures, binary
data and some ternary data would be required to determine the activity coefficient model parameters (Sandler, 1989).

The activity coefficient based on Universal quasichemical (UNIQUAC) model of Abrams and Prausnitz (1975), also used the local composition concept to account for the non randomness of the molecules. The recent application of this model have been employed by Kaewsichan et al., (2001) in representing the solubility of CO₂ and H₂S in monoethanolamine and methyldiethanolamine solutions. The model consists of two parts, a combinatorial term \( g^c \), accounting for molecular size and shape differences and a residual term \( g^R \) describing the intermolecular interaction forces. The UNIQUAC equation for multicomponent is written as:

\[
g = g^c + g^R \tag{2.2.57}
\]

where \( g = \frac{G^E}{RT} \)

The \( g^c \) term requires pure species parameters only because this part is determined by the composition and by the shape and sizes of the molecules. The \( g^R \) term incorporates two adjustable binary parameters for each pair of molecules. For multicomponent system,

\[
g^c = \sum_{i=1}^{m} x_i ln \left( \frac{\Phi_i}{x_i} \right) + \frac{1}{2} \sum_{i=1}^{m} q_i ln \left( \frac{\theta_i}{\Phi_i} \right) \tag{2.2.58}
\]

\[
g^R = -\sum_{i=1}^{m} x_i ln(\sum_{j=i}^{m} \theta_j \tau_{ij}) \tag{2.2.59}
\]

where,
\[ \Phi_i = \frac{x_i r_i}{\sum_{j=1}^{m} x_j r_j} = \text{segment or volume fraction of species } i. \]

\[ \theta_j = \frac{x_j q_j}{\sum_{j=1}^{m} x_j q_j} = \text{area fraction of species } i. \]

\[ \ln \tau_{ij} = -\left( \frac{U_j - U_{ij}}{RT} \right) \]

\( r_i \) = volume parameter for species \( i \)

\( q_i \) = surface area parameter for species \( i \)

\( U_j \) = average interaction energy for species \( i \)-species \( j \) interaction

\( z \) = average coordinate number, usually equal to 10

Combining equations (2.2.57), (2.2.58) and (2.2.59) gives

\[ \ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \]  \hspace{2cm} (2.2.60)

\[ \ln \gamma_i^c = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_j}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{m} x_j l_j \]  \hspace{2cm} (2.2.61)

\[ \ln \gamma_i^R = q_i \left[ 1 - \ln \sum_{j=1}^{m} \frac{\theta_j \tau_{ij}}{\sum_{j=1}^{m} \theta_j \tau_{ij}} - \sum_{k=1}^{m} \frac{\theta_k T_{kj}}{\sum_{k=1}^{m} \theta_k T_{kj}} \right] \]  \hspace{2cm} (2.2.62)

where,

\[ l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \]

This equation contain only two adjustable parameters, \( \tau_{ij} \) and \( \tau_{ij} \) for each binary pair.

The size and surface area parameter \( r_i \) and \( q_i \) can be evaluated from molecular structure information which may be extracted from available literature. The UNIQUAC model cannot always represent data with high accuracy. However, it
provides satisfactory description for many typical mixtures encountered in chemical practices (Gmehling et al., 1977, Prausnitz et al., 1980). This model is relatively simple since it only uses two adjustable parameters and it has a wide range of applicability in the industry.

### 2.2.5 Phase Equilibrium

The fugacity of species \( i \) in the liquid phase is given by

\[
f_i^L = \gamma_i x_i f_i^L
\]  

(2.2.63)

where \( f_i \) = liquid phase fugacity

while in the vapor phase is given by

\[
f_i^V = \phi_i y_i p_i
\]  

(2.2.64)

where \( f_i \) = vapor phase fugacity

\[ \phi_i = \text{vapor fugacity coefficient} \]

The criterion for phase equilibrium at constant \( T \) and \( P \) in the vapor-liquid of alkanolamine system can be expressed as

\[
f_i^V = f_i^L
\]  

(2.2.65)

Substitute equation (2.2.63) and (2.2.64) into (2.2.65), gives

\[
\gamma_i x_i f_i^L = \phi_i y_i p_i \quad (i = 1,2,\ldots,N)
\]  

(2.2.66)

The application of equation (2.2.66) is known as gamma/phi approach to VLE calculation which is usually used at low to moderate pressures.
For pure component liquid, the fugacity $f_i^L$ can be expressed as

$$f_i^L = f_i^{sat} \exp \left[ \frac{v_i^L (P - P_i^{sat})}{RT} \right] = \phi_i^{sat} P_i^{sat} \exp \left[ \frac{v_i^L (P - P_i^{sat})}{RT} \right]$$

(2.2.67)

where, $v_i^L$ = liquid phase molar volume

$P_i^{sat}$ = saturated vapor pressure

$\phi_i^{sat}$ = saturated vapor fugacity coefficient

Substituting equation (2.2.67) into (2.2.66), we obtain,

$$\phi_i y_i P = \gamma_i x_i \phi_i^{sat} P_i^{sat} \exp \left[ \frac{v_i^L (P - P_i^{sat})}{RT} \right]$$

(2.2.68)

The exponential term is known as Poynting factor. For low to moderate temperatures, the Poynting factor is very close to unity and it can be neglected. Therefore, the phase equilibrium equation becomes

$$\phi_i y_i P = \gamma_i x_i \phi_i^{sat} P_i^{sat}$$

(2.2.69)

For a dilute system the fugacity of the species is experimentally found to be linearly proportional to its mole fraction, that is

$$f_i^L = x_i H_i$$

(2.2.70) as $x_i \to 0$

$H_i$ is known as Henry’s Law Constant which is the function of solute-solvent pair, temperature and pressure. At higher concentrations a new activity coefficient $\gamma_i^*$ is introduced into equation (2.2.70)

$$f_i^L = \gamma_i^* x_i H_i$$

(2.2.71)

where the activity coefficient $\gamma_i^*$ is equal to the ratio of activity coefficient $\gamma_i$ to its value at infinite dilution.
2.2.6 Equilibrium associated with CO₂ – activated alkanolamine – water systems.

The absorption process of CO₂ into aqueous activated amine involves two stages. Firstly, the CO₂ molecules in the vapor phase are being absorbed physically into the aqueous activated amine solution. Secondly, the CO₂ molecules that have been absorbed react with the activated amine forming non volatile ionic species as shown in figure 2.3. As a result many chemical species in this system participate in the chemical reaction. When this system reaches equilibrium condition, it experiences the phase and chemical equilibrium states.
Figure 2.3: Absorption conditions of CO₂ in the vapor and liquid phase of activated DEA system.

2.3 Reaction Mechanism

2.3.1 Reaction of CO₂ with water.

When CO₂ gas dissolves in water, the concentration of CO₂ in the solution can be determined by its partial pressure and the interaction of dissolved CO₂ with other solutes in water (Butler, 1982). The concentration of CO₂ physically absorbed in solution can be calculated using Henry’s Law:
\[ [CO_2] = H_{CO2}P_{CO2} \]  \hspace{1cm} (2.3.1)

where,

\[ [CO_2] = \text{concentration of CO}_2 \text{ (mol/liter)} \]
\[ H_{CO2} = \text{Henry's law constant (mol/liter.atm)} \]
\[ P_{CO2} = \text{CO}_2 \text{ partial pressure (atm)} \]

At 25 °C the \( H_{CO2} \) value is about \( 10^{-1.5} \) and it decreases to \( 10^{-1.7} \) at 50 °C when the
\[ [CO_2] \] is in mol per liter and the \( P_{CO2} \) is in atmosphere. It varies slightly with ions
composition in the solution as the value for fresh water and sea water is \( 10^{-1.47} \) and
\( 10^{-1.54} \) respectively.

At pH less then 8 the main mechanism is a direct hydration of dissolved CO\(_2\) (Astarita et al., 1981)
\[ CO_2 + H_2 \Leftrightarrow H_2CO_3 \quad \text{(slow reaction)} \]  \hspace{1cm} (2.3.2)
\[ HCO_3^- + OH^- \Leftrightarrow HCO_3^- \quad \text{(instantaneous)} \]  \hspace{1cm} (2.3.3)

Reaction (2.3.2) is very slow where the k (rate constant) value is 0.026 s\(^{-1}\) at 25 °C
(Pinsent et al., 1956) and is usually neglected (Blauwhoff et al., 1984).

The most predominant reaction is the formation of bicarbonate.
\[ CO_2 + OH^- \Leftrightarrow HCO_3^- \]  \hspace{1cm} (2.3.4)

This reaction is fast and can increase the mass transfer rate.
2.3.2 Reaction of CO₂ with aqueous primary and secondary alkanolamine.

The reaction mechanism which describes the reaction between CO₂ with the primary and secondary amines is originally proposed by Caplow (1968) and reintroduced by Dankwerts (1979). This reaction mechanism has been used in many research works of CO₂ reaction with aqueous alkanolamine solutions (Blauwhoff et al., 1984, Saha et al., 1995, Xu et al., 1996, Riker et al., 1996).

The main reaction is the formation of carbamate,

\[ CO₂ + 2R₁R₂NH ⇌ R₁R₂NCOO⁻ + R₁R₂NH₂⁺ \] (2.3.5)

This reaction takes place in two steps. The first step is the formation of a zwitterion,

\[ CO₂ + R₁R₂NH ⇌ R₁R₂NH⁺COO⁻ \] (2.3.6)

followed by deprotonated by a base B to produce carbamate.

\[ R₁R₂NH⁺COO⁻ + B ⇌ R₁R₂NCOO⁻ + BH⁺ \] (2.3.7)

where R₁ is an alkyl group and R₂ is hydrogen for primary amines and alky group for secondary amine. Theoretically, any base that is present can deprotonate the zwitterion. Hence, the bases in the aqueous solution of the alkanolamine could be the hydroxide, amine or water (Blauwhoff et al., 1983) as shown in the following equations.

Deprotonation reactions.

\[ R₁R₂NH⁺COO⁻ + OH⁻ ⇌ R₁R₂NCOO⁻ + H₂O \] (2.3.8)

\[ R₁R₂NH⁺COO⁻ + R₁R₂NH ⇌ R₁R₂NCOO⁻ + R₁R₂NH₂⁺ \] (2.3.9)

\[ R₁R₂NH⁺COO⁻ + H₂O ⇌ R₁R₂NCOO⁻ + H₃O⁺ \] (2.3.10)

However, Versteeg and Van Swaaij (1988) claimed that the contribution of hydroxyl ion in the aqueous amine solution can be neglected, in view of the fact that it is
present at low concentration in the solution. Laddha and Danckwerts (1981) account only the amine as base in aqueous alkanolamine solution. Therefore, the equilibrium loading capacity of CO₂ in the primary and secondary amine solutions are limited to 0.5 mole of CO₂/mol of amine. This is due to formation of stable carbamate. In the case of tertiary amine, they lack the extra hydrogen, thus they do not form stable carbamate as in reaction 2.3.5.

The OH functional group in the alkanolamine is likely to react with CO₂, according to the following equations,

\[ R_1 - OH + OH^- \rightarrow R_1 - O^- + H_2O \]  \hspace{1cm} (2.3.11)

\[ R_1 - O^- + CO_2 \rightarrow R_1 - O - COO^- \]  \hspace{1cm} (2.3.12)

These reactions are generally neglected because the amount of product formed is very small (Jensen et al., 1954). According to Astarita (1967), these reactions can only take place in basic solution where the pH is 11 or greater, where as, in a slightly carbonated solution the pH is less than 10. Therefore, these reactions are not going to be considered in the reaction of CO₂ into the aqueous alkanolamine in this work.

The main reactions of the primary or secondary amine with CO₂ is governed by the following sets of equations.

Dissociation of the protonated amine

\[ R_1R_2NH \leftrightarrow R_1R_2NH + H^+ \]  \hspace{1cm} (2.3.14)
Formation of carbamate

\[ R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NCOO^- + H^+ \]  \hspace{1cm} (2.3.15)

Dissociation of carbon dioxide

\[ H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \]  \hspace{1cm} (2.3.16)

Ionization of water

\[ H_2O \rightleftharpoons H^+ + OH^- \]  \hspace{1cm} (2.3.17)

2.3.3 Reaction of CO₂ with aqueous piperazine

The reaction mechanism that occurs in the CO₂-H₂O-PZ system is very much similar to the reaction of CO₂ with aqueous primary or secondary amines, where it experiences amine protonation, carbamate formation, dissociation of carbon dioxide, dissociation of bicarbonate ion and ionization of water. The chemical reaction for protonation of piperazine and formation of carbamates (Bishnoi and Rochelle, 2000) are shown in equation 2.3.18 – 2.2.21, where else other related chemical reaction can be found in section 2.3.2.

Protonation of piperazine

\[ PZ + H_3O^+ \rightleftharpoons PZH^+ + H_2O \]  \hspace{1cm} (2.3.18)

Formation of carbamates

\[ PZ + CO_2 + H_2O \rightleftharpoons PZCOO^- + H_3O^+ \]  \hspace{1cm} (2.3.19)

\[ H_2O + H^+ PZCOO^- \rightleftharpoons H_3O^+ + PZCOO^- \]  \hspace{1cm} (2.2.20)

\[ PZCOO^- + CO_2 + H_2O \rightleftharpoons OOCPZCOO^- + H_3O^+ \]  \hspace{1cm} (2.2.21)
The pH of carbonated alkanolamine solution in the commercial application is usually in the range of 8 – 10, therefore the formation of diprotonated piperazine from protonated piperazine can be neglected since the pKa value is 5.56 at 23 °C. The detail chemical reaction equilibria used in this work is described in section 5.2. The molecular structure of piperazine and its carbamates are shown in figure 2.4.

![Molecular structures of piperazine species.](image)

**Figure 2.4** Molecular structures of piperazine species.

### 2.3.4 Modeling of VLE data in H$_2$O-CO$_2$-alkanolamine system.

There are several models reported in the literature used to predict the solubility data in CO$_2$-alkanolamine-water system. The first approach to correlate the solubility data for aqueous alkanolamine/CO$_2$ system was done by Mason and Dodge (1936) using curve fitting method but the reactions between the alkanolamine and CO$_2$ had not been studied. Danckwerts and McNeil (1967) used pseudoequilibrium constants which relate to the ionic strength of the solution but did not contain the activity
coefficient. In this model the ionic strength alone is not sufficient to determine the concentration dependence of pseudo equilibrium constant. Kent and Eisenberg (1979) modified this method. They correlate the solubility data without any dependence on ionic strength but the amine equilibrium constants were found by fitting the experimental data. Today, there are various models that have been developed to represent the VLE (vapor-liquid-equilibrium) data for the CO2-alkanolamine-water system. Generally, it can be divided into three types of approaches (Chunxi and Furst, 2000).

The first approach corresponds to empirical expression such as the Kent and Eisenberg model (1979). Apparent equilibrium constants were used to relate the components concentration in the equilibrium governing the chemical equilibria. The carbamates and protonated amine constants are fitted on the experimental data to represent the effect of ionic strength. Owing to its simplicity, which is based on Henry’s Law and several equilibrium constants, until today, this model have been widely used sometimes with some modifications by many investigators (Li et al., 1994, Haji Sulaiman et al., 1998, Liu et al., 1999b, Seo and Hong, 2000, Park et al., 2003) to represent their solubility data of acid gases in aqueous alkanolamine systems where the non-idealities that are present in the system are lumped together into the K values. Hu and Chakma (1990) modified the Kent and Eisenberg model and proposed the expression for the equilibrium constants governing the main amine reaction as a function of temperature, amine concentration and acid gas partial pressure. They used this model to analyze solubility data of CO2 and H2S in the sterically hindered amine AMP solutions. Similarly, Kritpiphath and
Tontiwachwuthikul (1996) also fitted their experimental data on the equilibrium of CO$_2$ in AMP using this model. In the recent published literature, Park et al. (2002) had applied this model to correlate the solubility data of CO$_2$ in aqueous mixtures of AMP with MEA or DEA. Bishnoi and Rochelle (2000) also used this model to represent the solubility of CO$_2$ in aqueous piperazine solutions.

Another popular modeling approach is the method of Deshmukh and Mather (1981). This model is based on the extended Debye-Hückel theory of electrolyte solutions. The activity coefficient is calculated using the Guggenheim equation where it represent the long range ion-ion interactions and a short range Van der Waals forces between the solute species in the liquid phase. The adjusted binary interaction parameters of the model are fitted to the experimental data of the system. Haji Sulaiman and Aroua (1996) used this model to correlate their solubility data for CO$_2$ in aqueous DEA and AMP system. Jane and Li (1997) employed this model to represent the solubility of mixtures of CO$_2$ and H$_2$S in the H$_2$O + DEA + AMP solution which produced reasonably good results. Similarly, Carroll and Mather (1996) utilized this model in acid gases equilibrium between an aqueous alkanolamine solution and LPG where they used a modified Henry’s Law approach. The fugacity coefficients of the compounds in the hydrocarbon-rich liquid were calculated using the Peng-Robinson equation of state. For the aqueous phase, for molecular species other than amine and water, the fugacity is estimated by using simple Henry’s law equation. Liu et al. (1999b) employed this model for their CO$_2$ solubility study in MDEA + PZ + H$_2$O solution. The average deviation between the
model and the experimental data is about 9.8% in which the effect of the salts on Henry's constant is taken into consideration.

The second type of approach in modeling the acid gases with aqueous alkanolamine system is based on excess Gibbs free energy model. This approach may use the NRTL (Non Random Two Liquid) model or UNIQUAC or simplified Clegg-Pitzer equation (Clegg and Pitzer, 1992) and three-suffix Margules equation, to treat the short range binary interactions. Austgen et al. (1989) applied the NRTL model to represent the H₂S and CO₂ equilibrium partial pressures reported in the literature for aqueous solutions of MEA and DEA over the temperature range 25 - 120 °C and amine concentration between 0.5 to 5 kmol m⁻³. The model rigorously account for the chemistry to increase the accuracy of predicting all the liquid phase species, ionic and molecular concentration. Liu et al. (1999a) adopted a similar electrolyte NRTL model used by Austgen et al. (1989) to represent the vapor-liquid equilibrium of CO₂ + MEA + H₂O system with vigorous chemical equilibria considerations. They discussed in detail the influence of chemical equilibrium constants, Henry's Constant, experimental data and data regression in representing the VLE of the system. The equilibrium constants of the carbamate reversion reaction and interaction parameters of the electrolyte-NRTL model were fitted to experimental data using two-stage procedure proposed by Weiland et al. (1993). They claimed that their model has been successfully applied to simulate three industrial cases for CO₂ removal. In 1991, Austgen and Rochelle, utilized the electrolyte-NRTL equation to estimate the activity coefficients for the solubility of CO₂ in aqueous mixture of MDEA with MEA or DEA. The same approach had been
adopted by Posey and Rochelle (1997) but they added other thermodynamic properties such as pH, conductivity, freezing point and heat of mixing to improve the degree of accuracy of the regression work. Kaewsichan et al. (2001) used a modified UNIQUAC model to predict the solubility of acid gases in MEA, MDEA and their mixtures. They adopted the Debye-Hückel equation to represent the long-range ion-ion interactions contribution and the UNIQUAC model to represent the short range ion-ion interactions. To avoid excessive numbers of ion pair interaction parameters, they assumed that the short range interaction occurs between ion pairs with surface area fraction randomly distributed to those of the individual ions, resulting in forming ion-ion specific interaction parameter which simplified the activity coefficient expression.

Li and Mather (1994) applied the Clegg-Pitzer equation to represent the CO$_2$ + MDEA + MEA + H$_2$O system. Their model consists of an extended Debye- Hückel term which is a function of composition and three suffix level Margules expansion with some simplifications. They also applied this model to several aqueous amine system (Li and Mather, 1995, 1996, 1997) in which they neglected the ionic species such as H$^+$, OH$^-$, CO$_3^{2-}$, S$^2$ and unreacted molecular species, H$_2$S and CO$_2$ in the aqueous phase. The gas phase was treated as an ideal condition. This model predict reasonably well; however, its application is limited to acid gas mole loadings less than one.

In the recent published work, Aroua et al. (2002) utilized the NRTL model for the CO$_2$ with aqueous solution of AMP and MDEA and their mixtures using the Aspen
plus software. They used the model parameters generated from a single amine experimental data to predict the binary AMP-MDEA mixtures without further regression. The model gives a good CO$_2$ solubility prediction especially for the mixture ratio of 1:1 (AMP : MDEA).

The third approach is using the equation of state (EOS). Huang et al. developed the equation of state for CO$_2$ that yields high accuracy in PVT calculation. It was reported to be accurate around the critical region due to the ‘nonanalytical’ term to model the critical isotherm which is suitable to be applying in the supercritical states. Furst and Renon (1993) developed a new equation of state for electrolyte solution based on an expression of Helmholtz free energy which contain of a non-electrolyte part and a part relative to ions. The EOS approach is claiming to be attractive because it is well adapted to the calculating of VLE involving supercritical compounds and no Henry’s constant is needed (Chunxi and Furst, 2000). Among the recent published work that presented their solubility data using EOS are Kuranov et al. (1997) for CO$_2$ $+$ MDEA $+$ H$_2$O and H$_2$S $+$ MDEA $+$ H$_2$O. Similarly, Valee et al. (1999) used this model for CO$_2$ $+$ DEA $+$ H$_2$O and H$_2$S $+$ DEA $+$ H$_2$O systems. They extended the classical Redlich-Kwong-Soave equation of state associated with Wong-Sandler mixing rule for the ionic interaction.
2.4 Method used to determine the solubility of CO\(_2\) in aqueous alkanolamines.

There are several methods used to determine the concentration of CO\(_2\) in aqueous alkanolamine solutions. The most common method that is being employed is the wet chemistry titration. In this method, the carbonated amine sample is precipitated by adding appropriate metal salt such as BaCl\(_2\) and mixed with an excess of standard base to convert the free CO\(_2\) gas into non volatile ionic species. The mixture is heated to ensure complete reaction. An aliquot of the filtrate is titrated with standard acid solution to determine the concentration of uncarbonated amine in the sample. An indicator such as Bromocresol green and phenolphthalein are commonly used to indicate the end point (Jensen et al., 1954, Hikita et al., 1977, Chan and Danckwerts, 1981, Austgen and Rochelle, 1991, Shen and Li, 1992, Jane and Li, 1997). The total amine concentration of the solution is determined by titrating the liquid sample with standard acid solution such as HCl with the presence of indicator such as methyl orange (Hikita et al., 1977, Camacho et al., 1997, Mandal et al., 2001). The CO\(_2\) that is being absorbed in the solution is calculated as the difference of total amine and the uncarbonated amine. A similar method was also employed in this work; however, the solubility of CO\(_2\) in the solutions was calculated directly from the titration of the carbonated amine precipitate with standard HCl solutions. An autotitrator which utilized the Dynamic Equivalence Point Titration technique was used to determine the end point of the titration process for achieving higher accuracy results.

Haji Sulaiman et al. (1996), developed a technique based on titration using NaOH to determine the solubility of CO\(_2\) in aqueous solutions of alkanolamine. The amount of
NaOH required to neutralize the sample was related to the bicarbonate, protonated amine ions and free CO$_2$. The total amine concentration and the equilibrium pH can be determined from the experiment. By solving relevant sets of equations simultaneously, the concentration of different species and CO$_2$ loading in the solution can be calculated. However, this method is more reliable for measuring the solubility of CO$_2$ in the tertiary amine solutions.

Haimour and Sandall (1984), measured the solubility of CO$_2$ in aqueous MDEA based on volumetric method in an equilibrium cell. This technique have been used by several investigators (Al Ghawas et al., 1989, Li and Lee, 1996, Hageswiesche et al., 1995, Li and Lai, 1995, Ko and Li, 2000, Xiao et al., 2002, Mandal et al., 2003) in their work measuring the CO$_2$ solubility in aqueous alkanolamine. The principle of this method is based on the measurement of volume change of the gas where a known volume of liquid sample is bring in contact it in a close system at constant temperature and pressure. The liquid sample is continuously agitated until there is no change in the volume, indicating that the equilibrium stage is attained. The amount of absorbed gas is measured volumetrically by calculating the different between the initial and final reading of the gas volume which is indicated by the level of mercury meniscus in the set of burette. Figure 2.7 show the solubility apparatus used by Al Ghawas et al., (1989), which is a modified version of the apparatus used by Haimour and Sandall, (1984).
Several investigators (Kagano, 1997, Bishnoi and Rochelle, 2000, 2002a, 2002b, Pacheno at al., 2000) have used the carbon analyzer to determine the CO$_2$ solubility in aqueous alkanolamine solutions. This is done by injecting small amount of the liquid sample into a solution of phosphoric acid which frees all the carbon dioxide in the solution as a gas. This gas was swept by a carrier gas (nitrogen) to an IR analyzer where the total carbon dioxide was determined. Bishnoi and Rochelle, (2000, 2002a, 2002b), used this method in series of their study on CO$_2$ absorption in aqueous alkanolamine. They plotted a graph of CO$_2$ flux as a function of CO$_2$ interfacial
partial pressure at constant loading. Then, the equilibrium solubility of CO₂ is determined by interpolation of the equilibrium partial pressure correspond to a value of the flux equal to zero.

A potential method to analyze CO₂ solubility in aqueous amine solutions is using Gas Chromatography (GC). Robbin and Bullin, (1984), claimed that the advantages of using this method is that, it can produce results in a shorter time, can be employed in on-line sampling and less interference in the analysis process. In their work on “Analysis of amine solution by gas chromatography”, they reported that two columns in series were required to get a good separation between the amine and light components. The first column contained Tenax-GC, which is an organic polymer bead used to separate the amine and the light components. The second column contained Poropak Q which is made up from a cross-linked between an ethylvinylbenzene and divinylbenzene copolymer. It can withstand high temperature, up to 250 °C before polymer degradation occurs and is used to separate all the light components. Helium was used as the carrier gas. The optimum operating condition that have been described by Robbins and Bullin, (1984) are as follows:

- Injector/detector temperature = 270 °C
- Initial column temperature = 120 °C
- Final column temperature = 240 °C
- Rate of temperature program = 20°C/min
- Detector current = 60 mA
- Carrier gas flow rate = 40 ml/min
- GC attenuation = 1
- Integrator attenuation = 4
- Oven temperature at actuated switching valve = 180 °C

The results of the analysis can be detected in 8 minutes with reproducibility of each analysis about 2% using a Shimadzu GC-8A chromatograph with a Shimadzu model C-RIB integrator.

Even though the GC method has been claimed to have many advantages over the titration or volumetric method, it is still not a popular method used by investigators to measured CO₂ solubility in aqueous alkanolamine. This can be confirmed, where the availability of published literature using this method is very scarce until today. This may be due to several problems which arise due to the sensitivity of amine solution to thermal degradation because GC columns operate at high temperature and using the right column is very important in order to achieve sharp distinct peaks with good separation. In fact another important feature that needs serious attention is in the configuration of the column to accommodate the elution of each component existing in the sample. Finally, the operating conditions are another factor that can affect the results of the analysis using the GC technique. However, it is not impossible this method can be the most frontier method used in future if all the above problems can be resolved since it does not only analyze the CO₂ content in the sample but also other components that exist in the solution in a shorter time frame.
2.5 A literature review of previous work.

2.5.1 Density

The physical properties information such as density, viscosity, heat capacities and surface tension are useful data in rational designing of acid gas treatment unit. In process design, accurate thermo physical properties data are necessary to produce high efficiency plant which will reduce the cost of production. Due to the significant contribution of the alkanolamine to the industries, many physical data properties of these compounds have been reported in the literature for the past few decades. Until today, these efforts are still being continued.

Al Ghawas et al. (1989) measured the densities of pure MDEA and aqueous MDEA solutions over the temperature range of 15 to 60 °C using a Gay-Lussac pycnometer. A series of ethanolamine densities and viscosities measurements at temperature range from 25 °C to 198 °C have been reported by DiGuilio et al. (1992). They used a high pressure pycnometer to measure the density and used simple expressions to correlate the data. A modified rough hard sphere model was used to represent the viscosity of the ethanolamines. Maham et al. (1994, 1995) have studied the volumetric properties of binary mixtures of water with monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA), ethyldiethanolamine (EDEA), dimethylethanolamine (DMEA) and diethylethanolamine (DEEA). Teng et al. (1994) also measured the viscosities of aqueous DEA and MDEA solutions at five temperatures in the range of 25 to 80 °C and correlated their data as a function of composition to be used in industrial calculations. Rinker et al. (1994) also studied the viscosity, density and surface
tension of aqueous MDEA, DEA and their mixtures over a temperature range of 20 to 100 °C. The density and viscosity of binary mixtures of MDEA with triethylene glycol monomethyl ether and MDEA with ethanol have been reported by Henni et al. (2000), while Li and Lie (1994) measured the densities and viscosities of ternary amine mixtures, MEA + MDEA + H₂O and MEA + AMP + H₂O at temperatures ranging from 30 to 80 °C. They employed the Redlich-Kister equation of excess volume to correlate their density data and used the equation of Grunberg and Nissan to represent the viscosity of the liquid mixtures.

The densities of the ternary system of DEA + MDEA + H₂O, DEA + AMP + H₂O and MEA + 2-piperidinemethanol (2PE) + H₂O have been investigated by Hsu and Li (1997) at a temperature range of 30 to 80 °C. They also used the Redlich-Kister equation of the excess volume to represent their density data where their overall absolute deviation is 0.04 % for a total of 686 data points used. Recently an extension data on densities and volumetric properties of aqueous binary mixtures of MEA, monomethylethanolamine (MMEA), dimethylethanolamine (DMEA) (Maham et al. 2002), AMP, n-butyldiethanolamine (n-BDEA) n-propyethanolamine (n-PEA) (Chan et al., 2002), monoethyethanolamine (MEEA) and diethylethanolamine (DEEA) (Lebrette et al, 2002) over the full range of compositions have been published. A modified Redlich-Kister equation was used to describe the excess function. They found that the density behavior of the liquid mixtures could be classified into two distinct zones that are composition dependent. For example, in MEA + H₂O and DMEA + H₂O mixtures the separation line occurs at x = 0.2 and x = 0.12 respectively (Maham et al., 2002). At lower concentration the
density increases until it passes through a maximum value where it decreases smoothly to the density of the pure alkanolamine. The excess molar volumes and excess molar enthalpies of the mixtures are claimed to be dependent on the size of the alkyl group present in the liquid mixtures (Lebrette et al., 2002). Zhang et al. (2002) investigated extensively on the thermodynamic properties of aqueous solution of MDEA and AMP which include excess molar heat capacities, volume and the expansibilities of the binary system. They used heat flux differential scanning calorimeter to measure the heat capacities and vibrating tube densimeter to determine the densities of the aqueous amine solutions over the whole fraction range. They found that the mole fraction dependence of the reduced excess heat is most pronounced at temperature greater than 298.15 K and the behavior of excess molar heat capacity for the two binary amine mixture is different but the excess molar volume is similar.

The physical properties of primary interest in this work focus on volumetric properties of the amine system. At present there is no data available in the open literature on density of aqueous piperazine and activated DEA. The information related to density correlation is elaborated in section (2.2.1).

2.5.2 Solubility of CO₂ in alkanolamine

The solubility data of CO₂ in alkanolamine is very important for the design and optimization of the CO₂ absorption process. For the past few decades, numerous investigations on the solubility of CO₂ in aqueous alkanolamine solutions have been published. This include the conventional amine such as MEA, DEA and MDEA, the
common sterically hindered amine, AMP and blended amines as MEA + DEA, DEA + MDEA and MEA + MDEA. An overview of some experimental solubility of CO\textsubscript{2} in aqueous DEA, MDEA (Sidi-Boumedine et al., 2004) and blended amine (Teng, T.T., 1998) are presented in Table 2.1, 2.2 and 2.3 respectively.

**Table 2.1:** Experimental work on solubility of CO\textsubscript{2} in aqueous DEA solutions.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>DEA concentration (wt %)</th>
<th>Temperature (K)</th>
<th>CO\textsubscript{2} Partial Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottoms (1931)</td>
<td>50</td>
<td>298, 303, 318, 328</td>
<td>0 – 101.3</td>
</tr>
<tr>
<td>Dawodu and Meisen (1994)</td>
<td>42.1</td>
<td>373</td>
<td>93 - 3742</td>
</tr>
<tr>
<td>Kennard and Meisen (1984)</td>
<td>10, 20, 30</td>
<td>373, 383, 393, 403, 413, 423</td>
<td>70 - 4000</td>
</tr>
<tr>
<td>Lal et al., (1985)</td>
<td>20.6</td>
<td>313, 373</td>
<td>0.003 – 3.3</td>
</tr>
<tr>
<td>Lee et al., (1973)</td>
<td>5.2, 20.6, 35.4, 49.7, 63.7, 77.6</td>
<td>373, 298, 323, 348, 373, 393, 413</td>
<td>0.7 - 5702</td>
</tr>
<tr>
<td>Lee et al. (1973)</td>
<td>5.2, 20.6, 35.4, 49.7</td>
<td>298, 323, 348, 373, 393</td>
<td>0.7 - 5702</td>
</tr>
<tr>
<td>Maddox et al. (1987)</td>
<td>5.2, 20.6</td>
<td>298</td>
<td>6.9 - 2013</td>
</tr>
<tr>
<td>Maddox and Elizondo (1989)</td>
<td>20, 35, 50</td>
<td>300, 339, 389</td>
<td>0.0221 – 64.9</td>
</tr>
<tr>
<td>Investigator</td>
<td>MDEA concentration (wt %)</td>
<td>Temperature (K)</td>
<td>CO₂ Partial Pressure (kPa)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------------------</td>
<td>-----------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Mason and Dodge (1936)</td>
<td>5.2, 20.6, 49.7, 77.6</td>
<td>273, 298, 323, 348</td>
<td>1.3 – 101.3</td>
</tr>
<tr>
<td>Oyevaar et al. (1989)</td>
<td>10.3 – 25.2</td>
<td>298</td>
<td>1.9 – 14.8</td>
</tr>
<tr>
<td>Reed and Wood (1941)</td>
<td>26</td>
<td>373, 413</td>
<td>137.9 – 2068.4</td>
</tr>
<tr>
<td>Rogers et al. (1997)</td>
<td>20.2</td>
<td>323</td>
<td>0.0003 – 0.6</td>
</tr>
<tr>
<td>Seo and Hong (1996)</td>
<td>30</td>
<td>313, 333, 353</td>
<td>4.8 – 357.3</td>
</tr>
</tbody>
</table>

**Table 2.2**: Experimental work on solubility of CO₂ in aqueous MDEA solutions.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature (°C)</th>
<th>Concentration (ppm)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meisen (1994)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jou et al. (1982)</td>
<td>11.8, 23.4, 48.9</td>
<td>298, 313, 343, 373, 120</td>
<td>0.001 - 6570</td>
</tr>
<tr>
<td>Jou et al. (1993)</td>
<td>35, 50</td>
<td>313, 373</td>
<td>0.004 - 236</td>
</tr>
<tr>
<td>Kuranov et al. (1996)</td>
<td>19.2, 32.1</td>
<td>313, 333, 373, 393, 413</td>
<td>70 - 5000</td>
</tr>
<tr>
<td>Lemoine et al. (2000)</td>
<td>11.8, 23.6</td>
<td>298, 313</td>
<td>0.02 - 1.64</td>
</tr>
<tr>
<td>Liu et al. (1999a)</td>
<td>40</td>
<td>303, 323, 343, 363</td>
<td>18.3 - 353.1</td>
</tr>
<tr>
<td>MacGregor and Mather (1991)</td>
<td>23.4</td>
<td>313</td>
<td>0.5 - 3770</td>
</tr>
<tr>
<td>Maddox et al. (1987)</td>
<td>11.8, 20, 23.4</td>
<td>298, 311, 313, 339, 389</td>
<td>11.1 - 6164.2</td>
</tr>
<tr>
<td>Mathonat et al. (1997)</td>
<td>30</td>
<td>313, 353, 393</td>
<td>2000 - 10000</td>
</tr>
<tr>
<td>Park et al. (2001)</td>
<td>50</td>
<td>298, 323, 348, 373</td>
<td>0.8 - 140</td>
</tr>
<tr>
<td>Perez-Salado Kamps et al. (2001)</td>
<td>32, 48.8</td>
<td>313, 353, 393</td>
<td>228 - 7565</td>
</tr>
<tr>
<td>Rho et al. (1997)</td>
<td>5, 20, 50, 75</td>
<td>323, 348, 373</td>
<td>0.8 - 268.3</td>
</tr>
<tr>
<td>Rogers et al. (1998)</td>
<td>23</td>
<td>323</td>
<td>0.0004 -1</td>
</tr>
<tr>
<td>Shen and Li (1992)</td>
<td>30</td>
<td>313, 333, 353, 373</td>
<td>1 - 2000</td>
</tr>
<tr>
<td>Silkenbäeumer et al. (1998)</td>
<td>23.9</td>
<td>313</td>
<td>12 - 4080</td>
</tr>
<tr>
<td>Xu et al. (1993)</td>
<td>23.4, 39.8, 48.9</td>
<td>313, 328, 343, 353, 373</td>
<td>0.876 - 1041</td>
</tr>
</tbody>
</table>
Table 2.3: Experimental work on solubility of CO₂ into blended amines solutions.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>System</th>
<th>Temperature (°C)</th>
<th>CO₂ Partial Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shen &amp; Li (1992)</td>
<td>MDEA – MEA</td>
<td>40 - 100</td>
<td>0.9 – 2016</td>
</tr>
<tr>
<td>Li &amp; Shen (1992)</td>
<td>MDEA – MEA</td>
<td>40 100</td>
<td>1.1 – 2080</td>
</tr>
<tr>
<td>Jou et al. (1994)</td>
<td>MDEA – MEA</td>
<td>25 – 120</td>
<td>0.001 – 19930</td>
</tr>
<tr>
<td>Dawodu &amp; Meisen (1994)</td>
<td>MDEA – MEA</td>
<td>70 - 180</td>
<td>65 – 3876</td>
</tr>
<tr>
<td>Li &amp; Chang (1994)</td>
<td>MEA – AMP</td>
<td>40 – 100</td>
<td>1 – 200</td>
</tr>
<tr>
<td>Li &amp; Chang (1995)</td>
<td>MEA – AMP</td>
<td>40, 80</td>
<td>0.9 – 149</td>
</tr>
<tr>
<td>Seo &amp; Hong (1996)</td>
<td>DEA – AMP</td>
<td>40 – 80</td>
<td>1.6 – 281</td>
</tr>
<tr>
<td>Jane &amp; Li (1997)</td>
<td>DEA – AMP</td>
<td>40, 80</td>
<td>0.1 – 101</td>
</tr>
<tr>
<td>Song et al (1997)</td>
<td>MEA – EG*</td>
<td>60</td>
<td>2 - 2300</td>
</tr>
<tr>
<td>Song et al (1997)</td>
<td>MEA – PEG*</td>
<td>60</td>
<td>2 - 2300</td>
</tr>
<tr>
<td>Park et al. (2002)</td>
<td>MEA + AMP</td>
<td>40, 60, 80</td>
<td>0.69 – 344.64</td>
</tr>
<tr>
<td>Park et al. (2002)</td>
<td>DEA + AMP</td>
<td>40, 60, 80</td>
<td>0.69 – 344.64</td>
</tr>
</tbody>
</table>

EG* = Ethylene glycol
PEG* = Polyethylene glycol.

Recently, the considerable interest in development of CO₂ absorption using amine technology has identified activated amine as a potential absorbent where piperazine was used as the activator (Kagano, 1997; Liu et al., 1999b; Xu et al. 1998; Bishnoi and Rochelle, 2002a). However, the information on this technology is still scarce.

Among the research works that have been done related to the activated amine is the work of Liu et al. (1999b) and Xu et al. (1998) on solubility of CO₂ in activated MDEA. They claimed that piperazine has a significant effect on CO₂ loading. However, they have not considered the formation of piperazine carbamate as one of their reaction product in their model. This will affect the species profiles since the fitted parameters do not correspond to the chemistry of the system (Weiland, 2000). Besides, Bishnoi and Rochelle (2000) and Dang and Rochelle (2003) have clearly shown the formation of piperazine carbamates in their speciation studies on solubility of CO₂ in aqueous piperazine and mixtures of piperazine with MEA respectively. Bishnoi and Rochelle (2002a) also reported that piperazine carbamate is the major product at low loading (< 0.1), while protonated carbamate is the major product at high loading in their solubility model for PZ + MDEA + H₂O + CO₂ system. They used the electrolyte NRTL model to represent the solubility data and verified the high loading data by NMR. The formation of various piperazine carbamates have also been studied by Ermatchkov et al. (2003). They used ¹H-NMR spectroscopy to quantify the species that exist in the aqueous solution of piperazine with CO₂. These experimental results were used to determine the chemical equilibrium constant for the formation of respective piperazine carbamate. Table 2.2 shows some related work.
on absorption of CO₂ into activated amine that has been published in the open literature.

Table 2.4: Experimental works on CO₂ absorption in aqueous activated amine solutions.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>System</th>
<th>Temperature (°C)</th>
<th>Study</th>
<th>CO₂ Partial Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu et al., (1999b)</td>
<td>MDEA + PZ + H₂O</td>
<td>30 - 90</td>
<td>Solubility</td>
<td>13.6 - 935.3</td>
</tr>
<tr>
<td>Xu et al., (1992)</td>
<td>MDEA + PZ + H₂O</td>
<td>30 - 70</td>
<td>Kinetic</td>
<td>33070 - 694300</td>
</tr>
<tr>
<td>Xu et al., (1995)</td>
<td>MDEA + H₂O, MDEA + PZ + H₂O</td>
<td>30 - 70</td>
<td>Kinetic</td>
<td>ΔP* = 1.94 - 56.54</td>
</tr>
<tr>
<td>Xu et al., (1998)</td>
<td>MDEA + H₂O, MDEA + PZ + H₂O</td>
<td>40 - 100</td>
<td>Solubility</td>
<td>0.876 - 1013</td>
</tr>
<tr>
<td>Bishnoi and Rochelle, (2000)</td>
<td>PZ + H₂O</td>
<td>25 - 50</td>
<td>Kinetic, Solubility, mass transfer</td>
<td>0.032 - 40</td>
</tr>
<tr>
<td>Seo and Hong, (2000)</td>
<td>AMP + PZ + H₂O</td>
<td>30 - 40</td>
<td>Kinetic</td>
<td>-</td>
</tr>
<tr>
<td>Bishnoi and Rochelle, (2002a)</td>
<td>MDEA + PZ + H₂O</td>
<td>40 - 70</td>
<td>Solubility</td>
<td>0.033 - 7.48</td>
</tr>
<tr>
<td>Bishnoi and Rochelle, (2002b)</td>
<td>MDEA + PZ + H₂O</td>
<td>22 - 70</td>
<td>Kinetic</td>
<td>0.01 - 61.10</td>
</tr>
<tr>
<td>Dang and Rochelle, (2003)</td>
<td>MEA + PZ + H₂O</td>
<td>40 - 60</td>
<td>Kinetic, Solubility</td>
<td>0.0002 - 7.73</td>
</tr>
<tr>
<td>Ermatchkov et al., (2003)</td>
<td>PZ + H$_2$O</td>
<td>10 – 60</td>
<td>Speciation</td>
<td>100</td>
</tr>
<tr>
<td>--------------------------</td>
<td>--------------</td>
<td>---------</td>
<td>------------</td>
<td>-----</td>
</tr>
<tr>
<td>Zhang et al., (2003)</td>
<td>MDEA + PZ + H$_2$O</td>
<td>60</td>
<td>Kinetic</td>
<td>200 - 625</td>
</tr>
</tbody>
</table>

$\Delta P^*$ = difference between input and output CO$_2$ partial pressure.

In the study of CO$_2$ solubility and absorption rate in aqueous piperazine system, it has been noted that the piperazine carbamate stability constant is comparable to that of other secondary amines such as DEA (Bishnoi and Rochelle, 2000). Dang and Rochelle (2003) reported that at 24% mole of piperazine content in the total amine, the CO$_2$ equilibrium pressure decreased by 50% and the reaction rate enhanced from 50% to 100%. In fact, the absorption rate of CO$_2$ into blended PZ + MDEA is faster compared to blended MEA + MDEA or DEA + MDEA with similar concentration (Bishnoi and Rochelle, 2002b).

A thermodynamic model based on a modified Pitzer's equation describing the phase equilibrium in absorption of hydrogen sulphide in aqueous piperazine and activated MDEA was reported by Xia et al. (2003). This model was also extended for presenting the solubility of carbon dioxide in aqueous piperazine and activated MDEA system by Kamps et al., (2003) at temperature ranging from 313 K to 393 K and pressure up to about 9.6 MPa with piperazine concentration up to 4 mol per Kg of water. The prediction model dictates that the solubility of CO$_2$ is much higher in aqueous solutions of piperazine than in aqueous MDEA, especially in the low to moderate region of amine loading. The higher basic character of aqueous piperazine
solutions and the formation of carbamate species was claimed to be responsible for increasing capability of dissolving the sour gas chemically.

2.6 Conclusion

A comprehensive literature review revealed that there are relatively few investigations on solubility of CO₂ in aqueous activated amine solutions and there are no data available on density measurement of activated amine solutions. At present, the solubility of CO₂ in aqueous activated DEA solutions has not been reported in any open literature. Pertinent to the limited information on density measurements of activated amine solutions and solubility data on absorption of CO₂ in aqueous activated amine, it is the interest of this work to focus on the density measurement of aqueous piperazine, PZ + DEA, PZ + DEA + H₂O system and the solubility of CO₂ into aqueous piperazine and activated amine solutions.