CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The capture and sequestration of carbon dioxide has significant global importance due to its escalating damaging effects on the environment and ecosystem. With the recent mandates for CO_2 emissions, new ways to remove and process CO_2 from their product streams must be investigated. The process of separating acid gases from source gases is commonly referred to as *Gas treating*, *Acid Gas Removal*, or *Gas Sweetening*.

 H_2S and CO_2 concentrations in gas streams vary from several parts per million to 50% by volume. Clean-up specifications also vary widely depending on the process and on the nature of impurity. Much of the CO_2 emission reduction effort focuses on large point sources, with fossil fuel fired power plants being a prime target. Green *et al.* (2005) indicated that the CO_2 content of power plant flue gas varies from 4% to 9% by volume, depending on the type of fossil fuel used and on the operating conditions. Although new power generation technologies may result in CO_2 control with minimal economic penalty, these concepts are not generally adopted on most of the existing power plants.

This chapter reviews and summarizes the previous studies related to CO_2 capture by alkanolamines in general with emphasis on 2-methylaminoethanol (MAE) as a good candidate for this purpose. These studies cover reaction mechanism, kinetics and equilibrium solubility at various operating conditions.

2.2 ACID GAS ABSORPTION PROCESSES

Absorption of acid gases with aqueous alkanolamine solvents is characterized as mass transfer enhanced by chemical reaction; following absorption into the aqueous solution, the acid gases react either directly or through an acid-base buffer mechanism with the alkanolamines to form non-volatile ionic species. Si Ali (2007) explained that mass transfer of acidic gases from the bulk gaseous phase to the bulk liquid phase in which chemical reaction occurs, such as an aqueous alkanolamine solution, can be described as follows;

- Diffusion of one or more acidic gas components from the bulk gas phase to the gasliquid interface followed by absorption (dissolution) into the liquid.
- Diffusion of the reactants from the gas liquid interface to the bulk liquid phase.
- Reaction between the dissolved gas and the liquid reactant in the liquid phase occurs simultaneously with mass transfer.
- Diffusion of the reaction products into the bulk liquid phase due to concentration gradients created by the chemical reactions.

Figure 2.1 illustrates the process of mass transfer with chemical reaction that can occur during the absorption of acid gas by aqueous alkanolamine solution.



Figure 2.1: Schematic diagram of the equilibrium process of CO₂ gas absorption into aqueous amine solution (Source: Si Ali, 2007)

A number of processes have been developed for the capture of CO_2 and other acid gases from gas streams. Chemical and physical absorption can be used for the separation of CO_2 from process gas streams or flue gas. The choice of process depends on the composition of the gas stream, the CO_2 partial pressure in addition to other factors.

Figure 2.2 shows some of the most widely used technologies for CO_2 capture with the applicability of each process for different situations, (Shaw & Hughes, 2001).



Figure 2.2: Process selection chart for the CO₂ removal processes (Source: Shaw & Hughes, 2001)

While different processes and technologies are being developed for CO_2 capture, to date, absorption by aqueous alkanolamine solution remains the most widely used technology for this purpose.

Different amine solvents have different reaction rates with different types of acid gases. Also, different amines have different equilibrium solubilities in the various acid gases and have different stability and corrosion profiles. In absorption/stripping of acid gases with aqueous alkanolamine solvents, two types of equilibrium are considered; chemical equilibrium and phase equilibrium. Therefore, it is necessary to determine the concentrations of the various dissolved molecular and ionic species which are in equilibrium with each other.

2.3 ALKANOLAMINE SOLVENTS FOR CARBON DIOXIDE CAPTURE

The structural formulae of the most commonly used alkanolamines are shown in Figure 2.3. Each alkanolamine has at least one hydroxyl group and one amino group. The hydroxyl group reduces the vapour pressure and increases the water solubility, while the amino group increases the pH of the solution which causes reaction with acidic gases such as CO_2 and H_2S (Kohl & Nielsen, 1997).

Alkanolamines are ammonia derivatives, and can be classified as primary, secondary, or tertiary depending on the number of non-hydrogen substituent groups bonded to the nitrogen atom of the amino group.

- 1. Primary alkanolamines; where one hydrogen atom of the ammonia molecule is replaced by an ethanol group. The best known example of primary alkanolamine is monoethanolamine, MEA (HOCH₂CH₂NH₃)
- 2. Secondary alkanolamines; where two hydrogen atoms of the ammonia molecule are replaced by ethanol groups, such as diethanolamine, DEA, ((HOCH₂CH₂)₂NH) or MAE, (HOCH₂CH₂NH)
- 3. Tertiary alkanolamines; where all hydrogen atoms are replaced by either alkyl or alkanol groups. The most popular amines in this category are triethanolamine, TEA, (HOCH₂CH₂)₃N and methyldiethanolamine, MDEA (HOCH₂CH₂)₂NCH₃.



Monoethanolamine (MEA)



Triethanolamine (TEA)

 H_2N OH

2-amino,2-methylpropanol (AMP)



2-(2-aminoethylaminoethanol) (AEEA)



Triisopropylamine (TIPA)



Diethanolamine (DEA)



Methyldiethanolamine (MDEA)



2-amino,2-methylpropan 1,3 diol (AMPD)

HO

2-methylaminoethanol (MAE) or (MMEA)

HN NH

Piperazine (PZ)

Figure 2.3: Structures of some commercially famous amines (Source: www.chemicalbook.com)

In aqueous solutions, primary, secondary and tertiary alkanolamines show different behavior towards CO_2 due to their molecular structure. Primary and secondary alkanolamines react with CO_2 forming a carbamate species according to the following overall equation, Derks (2006);

$$2RR \square NH + CO_2 \rightleftharpoons RR \square NH_2^+ + RR \square NCOO^-$$

where $R\square$ is H in the case of primary amine or another alkyl group in the case of secondary amine. This reaction is reversible, allowing the CO₂ gas to be liberated by heating in a separate stripping column and therefore the amine is not consumed and may be continuously recycled through the process, Strazisar *et al.* (2001)

The reaction of tertiary amines with CO_2 is considered to be a hydrolysis catalyzed reaction as they cannot form a carbamate;

$$RR \square K + CO_2 + H_2O \rightleftharpoons RR \square RNH^+ + HCO_3^-$$

The characteristics of the reaction of the three classes of alkanolamines with CO_2 including kinetics and heat of solution are studied by many scientists. Research showed that primary amines have the highest rate of reaction compared to the other two classes, whereas tertiary amines have the highest capacity (CO_2 loading) and the lowest heat of solution (lowest heat required for regeneration). These different absorption characteristics are some of the reasons that aqueous MEA is a popular solvent in flue gas treatment, where the CO_2 content is below 15%, while aqueous MDEA is usually used in CO_2 bulk removal processes as it requires less energy for regeneration.

According to Veawab *et al.* (2001) the key factors in the assessment of amine solvents are absorption and regeneration characteristics, acid gas loading, corrosion profile and solvent stability. Solvents that require less regeneration energy usually require large contacting surface areas. Also, solvents that have higher loading capacity are most probably more difficult to regenerate.

Some other developments in the use of amine solutions for the absorption of CO_2 gas involve the use of amine blends (tertiary with primary or secondary) or adding activated amine using an accelerator (activator) such as piperazine (PZ). Many research studies also focus on sterically hindered amines which showed enhanced acid gas absorption.

2.3.1 Monoethanolamine and Methyldiethanolamine

Aqueous monoethanolamine (MEA) solutions are the most commonly used alkanolamine absorbents due to their low cost, low molecular weight, high absorbing capacity and good thermal stability, (Tourneux, 2007). MEA is a relatively strong base with a fast reaction rate removing more than 96% of CO_2 from natural gas and combustion gas streams. A number of investigators have studied the solubility and kinetics of CO_2 in aqueous MEA, (Jou et al, 1995, Lee et al. 1976, Li & Shen, 1992, Dankwerts & Sharma, 1966, Versteeg & Swaaij, 1988, Laddha & Danckwerts, 1981, Dang & Rochelle, 2001). However, aqueous MEA solutions are characterized by high regeneration energy and high corrosivity, Veawab *et al.* (2001). In addition, because of the formation of a stable carbamate, the stoichiometry of the reaction limits the amount of CO_2 that can be absorbed to a maximum of 0.5 mole CO_2 per mole of amine. Another problem with MEA absorption is the degradation of the amine over time. The byproducts of MEA degradation are known to decrease the efficiency of CO_2 capture and have also implicated in the corrosion on machinery, Dupart *et al.* 1993.

Tertiary amines like methyldiethanolamine (MDEA) solutions have higher loading capacity of up to 1.0 mole of CO_2 /mole of amine and less regeneration energy, and higher resistance to thermal and chemical degradation. However, they are also known to have low reaction rate with CO_2 , (Bishnoi & Rochelle, 2000).

2.3.2 Activated Amines with Piperazine

The addition of an activator such as piperazine (PZ) to an aqueous alkanolamine has found a wide spread application in the removal of carbon dioxide. Derks *et al.* (2010) indicated that the blend of PZ is based on the combined effect of the relatively high rate of reaction of CO_2 with PZ with the low heat of reaction of CO_2 with the tertiary alkanolamine. This results in higher rate of absorption in the absorber column and lower heat of regeneration in the stripper column.

Bishnoi & Rochelle, (2000) reported experimental carbon dioxide solubilities in 4 M MDEA activated with 6 M PZ at temperatures of 313 and 343 K and partial pressures up to around 7.5 kPa. The paper included kinetics study of the amine blend and reported rate constants.

Bishnoi *et al.* (2000) studied the absorption of CO_2 into aqueous solutions of piperazine (PZ) in a wetted wall contactor. Absorption was studied at temperatures from 298 to 333 K in solutions of 0.6 and 0.2 M aqueous PZ. The rate order, constants, activation energy and solubility were determined. The equilibrium data were then modeled and compared with those of MEA, DEA and diglycolamine (DGA). The study showed evidence that the reactivity of PZ is due to its combined effect of the cyclic and diamine structure.

Dugas *et al.* (2007) studied the effect of blending MEA with PZ at 40 $^{\circ}$ C and at pressures ranging from 0.1 to 100 kPa. The study showed that 7 M MEA/2 M PZ has 45% greater CO₂ capacity than 7 M MEA. Also the 7 M MEA/2 M PZ showed faster rate and higher stability compared to 7 M MEA.

Si Ali (2007) investigated the solubility of CO_2 in activated amine solutions using PZ. He varied the PZ concentration from 0.01 M to 0.1 M to activate DEA and MDEA keeping the amine total concentration at 2.0 M and ranging the temperature from 40 to

80 °C and CO₂ partial pressure from 0.05 to 95.7 kPa. He found that the solubilities of CO₂ in activated PZ/MDEA blends and in activated PZ/DEA blends are greater than in DEA/MDEA blends. However, the solubility of CO₂ in MDEA/PZ is lower than in MEA/MDEA blends.

Besides the literature mentioned above, several other studies are reported on the solubility of CO_2 in aqueous PZ solutions, (Aroua & Salleh, 2004), and blends of aqueous PZ-MDEA solutions, (Si Ali & Aroua, 2004). These studies proved the ability of PZ to enhance the solubility of CO_2 in aqueous alkanolamines.

2.3.3 Sterically Hindered Amines

A sterically hindered amine is defined as a primary amine in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to a secondary or tertiary carbon atom.

The use of sterically hindered amines was first proposed by Sartori & Savage (1983), who investigated 2-amino,2-methyl, 1-propanol (AMP) as a possible candidate for CO_2 capture.

Wong & Bioletti, (2002) illustrated that hindered amine concept is based on the reaction rates of the acid gases with different amine molecules. They explained that in the case of CO_2 removal, the loading capacity of the solvent can be improved significantly if the carbamate formation reaction can be slowed down by providing stearic hindrance to the reacting CO_2 . This hindrance can be achieved by attaching a bulky substitute to the nitrogen atom of the amine molecule. As a result, the overall reaction will be slowed down and the carbamates produced will be less stable. Therefore, by making the amine carbamate unstable, the loading capacity of the amine solvent can be theoretically doubled.

The main concept of CO_2 absorption by sterically hindered amines is that, by control of the molecular structure, amines can be synthesized to form a stable carbamate ion, an unstable carbamate ion or no carbamate ion. Therefore, by an appropriate molecular configuration an unstable carbamate ion would be formed with CO_2 which can be readily hydrolyzed, producing bicarbonate. This would result in a theoretical loading ratio of one mole of CO_2 per mole of amine. It is claimed that better selectivity can be obtained with sterically hindered amines than with commonly used tertiary or secondary alkanolamines, (Kohl & Nielsen, 1997). Some of these amines were found to have advantages over MDEA with regard to selectivity, acid gas loading, kinetics and product gas purity.

Hook (1997) introduced a number of sterically hindered amines as potential CO_2 scrubbing compounds and compared their performance with MEA. He verified that methyl groups substituted adjacent to the amine increase solution absorption capacities but with overall reduction in absorption rate.

Hindered amines can be classified as either moderately hindered or severely hindered amines. The moderately hindered amines are used for bulk non-selective removal of H_2S and CO_2 while the severely hindered amines are employed in the selective removal of H_2S . These amines have a high thermodynamic capacity that approaches 1.0 mole of CO_2 per mole of amine (Bishnoi & Rochelle, 2000).

Aroua *et al.* (2002) compared between the loadings of AMP which is a primary sterically hindered amine and MDEA and introduced the use of aqueous solutions of a mixture of two amines in varying compositions. They found that CO_2 loading in AMP can reach 1 mole/mole AMP, especially at low absorption temperature. They also showed that adding AMP to MDEA at the same total concentration shows an improvement in CO_2 loading over the entire range of CO_2 partial pressures.

Park *et al.* (2003) investigated aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), a sterically hindered amine, as a potential CO₂ absorbent and compared it with monoethanolamine (MEA) solution. The solubilities of CO₂ in aqueous 10 mass % AHPD solutions were higher than those in aqueous 10 mass % MEA solutions above 4 kPa at 298.15 K, but below 4 kPa, the solubility behavior appeared to be the opposite. AHPD contains more hydroxyl groups than non-hindered MEA, and hence, the chemical shifts in its C-13 NMR spectra were strongly influenced by the solution pH values. In contrast, MEA appeared to be insensitive to pH.

Mamun (2005) investigated new absorbents for CO_2 capture at 40 °C. He found that an aqueous 30% mass 2-(2-aminoethyl-amino)ethanol, (AEEA) solution could be a potentially good absorbent for capturing CO_2 from atmospheric flue gases as it offers high absorption rate combined with high absorption capacity.

Mitsubishi Heavy Industries, Ltd. and Kansai Power Co. have developed a proprietary blend of hindered amines that was used for acid gas removal from flue gas streams. The proposed hindered amine blend is said to have 67% higher CO_2 absorption capacity and 20% lower heat of regeneration than that of MEA. The solvent was also claimed to be less corrosive and more resistant to degradation by oxidation, such that make-up requirements are one-fifth of those of MEA (Iijima, et al., 2004).

2.3.4 Methylaminoethanol

Methylaminoethanol (MAE) is a secondary alkanolamine that is widely used in pharmaceuticals and industries. Recent studies mentioned this amine as being a potential absorber of acid gases from various gas streams. However, detailed VLE and kinetics data on this amine are still scarce. Bavbec & Alper (1999) studied the mechanism and kinetics of the reaction of CO_2 with MAE and other amines. The fractional reaction order found in this study proved that carbamate formation takes place according to a zwitterions mechanism rather than a one-step reaction.

Ohno *et al.* (1999) studied the reaction mechanism of MAE with CO₂ using vibrational spectroscopy and ab initio theories. The study showed that, in the CO₂-MAE-H₂O system, MAE reacts with CO₂ to form MAECO₂⁻ and MAEH⁺. The former subsequently reacts with H₂O and CO₂ to form MAEH⁺ and HCO₃⁻.

Mamun (2005) focused on selecting new absorbents for CO_2 capture. MAE and other alkanolamine solvents were investigated and their performance was compared with that of MEA. The study showed that MAE could have a good potential when used in contactors where the two phases are separated. His study also indicated that MAE showed foaming tendencies that could make it difficult to use in ordinary towers.

2.4 SOLUBILITY OF CARBON DIOXIDE IN ETHANOLAMINES

The absorption of CO_2 in aqueous solutions of alkanolamines involves both physical absorption and chemical reaction where the gas loading can be determined from reaction kinetics and thermodynamic equilibrium.

Austgen (1989) explained that, the use of aqueous alkanolamine solutions for gas treating results in two important effects that make these solutions preferable to physical solvents for acid gas absorption; The first effect is that the presence of an alkanolamine drastically affects the solubility of an acid gas in water. That is, at equilibrium, the solubility of an unreacted acid gas in an aqueous solution containing a reaction solvent is governed by the partial pressure of that gas above the liquid. If the gas reacts in the aqueous phase to form non-volatile products, then additional gas can dissolve at a given acid gas partial pressure. As a result, alkanolamines significantly enhance the solubility of acid gases in aqueous solutions. The second is the effect of alkanolamines on the rates of absorption of acid gases into aqueous solution. When an acid gas is absorbed into aqueous solution it is partially consumed by chemical reaction so that its concentration in the bulk liquid remains low. Since the driving force for mass transfer is the difference between the concentration of the gas in the liquid at the gas-liquid interface and the concentration of the unreacted acid gas in the bulk liquid phase, chemical reaction results in a higher driving force for mass transfer compared to no chemical reaction. This further enhances the rate of absorption of the acid gases into the aqueous solution.

2.4.1 Effect of Temperature

The effect of temperature on equilibrium constant can be related to Le Chatelier's Principle, where changing the conditions of a system at equilibrium with respect to a reversible process will produce a reaction in the system to reverse the change. The effect can be related thermodynamically between the equilibrium constant, temperature and heat of reaction. The temperature dependency of equilibrium constants for all the reactions occurring at equilibrium is given by the following equation (Kim *et al.* 2009)

$$lnK = a + b/T + blnT + cT \tag{2.1}$$

where K is the equilibrium constant, T is the temperature in Kelvin and a, b, and c are constants that depend on the type of amine solvent.

In general, gas solubility in liquids usually decreases by increasing the temperature. It is also known that the solubility of CO_2 in alkanolamine solvents decreases when temperature increases (Benamor, 1998). In addition, since the reaction of alkanolamine with CO_2 is exothermic, then increasing the temperature will favor the

backward reaction yielding lower CO_2 loading. Therefore, the variation of CO_2 loading is inversely proportional with temperature and this relationship is verified in the results of this work.

2.4.2 Effect of CO₂ Partial Pressure

The CO₂ partial pressure is considered a significant factor in the choice of the process design parameters of an amine absorber/stripper unit. According to Kohl & Nielsen (1998), physical absorption is generally favored at acid gas partial pressure above 200 psia (1380 kPa), while alkaline solution absorption is favored at lower partial pressures. Therefore, there is a boundary line between physical and chemical solvents at lower partial pressure (60-100 psia) or (414-690 kPa) above which physical solvents are favored. As CO₂ in flue gas streams generally have low partial pressure, absorption with chemical reaction will be considered in this work.

Dependency of CO_2 loading in amine solvents on CO_2 partial pressure was studied and proved by many researchers, (Hook, 1997), (Deshmukh & Mather, 1981), (Park *et al.*, 2003), (Benamor & Aroua, 2005), (Si Ali, 2007) and others.

Increasing the CO₂ partial pressure causes more CO₂ diffusion from the bulk gaseous phase into the bulk liquid phase and hence more CO₂ reacting with the amine which results in higher CO₂ loading. This relationship is more obvious at lower partial pressures (\leq 5 kPa), but the variation becomes less significant at higher partial pressures.

2.4.3 Effect of Amine Concentration

Variation of CO_2 loading with amine concentration was studied extensively, (Si Ali, 2007), (Mamun, 2005), (Benamor, 1998) and others. It was found that increasing

the amine concentration has a small but negative effect on CO_2 loading, however, amine concentration was found to have a considerable effect on the value of the equilibrium constant for the dissociation of the protonated amine and that for the carbamate formation, (Haji-Sulaiman *et al.* 1996). It should be noted, however, that many studies use mass% rather than molar concentration for ease of cost comparison. The amines with lower molar mass like MEA and MAE have higher molar concentration for the same mass% which results in better loading and kinetics performance.

Huang *et al.* (2000) studied the CO_2 absorption capacity of MEA and MAE with and without the addition of sodium chloride (NaCl). Their experimental results showed that an increase in MAE concentration led to a slight decrease in CO_2 absorption capacity in the absence of NaCl. Their results also showed that, with NaCl, the absorption capacity increased with increasing amine concentration.

2.4.4 Carbamate Ion Concentration

Studying carbamate concentration is very important in predicting the reaction mechanism and kinetics. Such data are vital in deciding the type of amine to be chosen for CO_2 absorption processes.

Huang *et al.* (2000) suggested that for primary amines like MEA, the main reaction product is a carbamate according to the following equation;

 $2HOCH_2CH_2NH_2 + CO_2 \Rightarrow HOCH_2CH_2NHCO_2^-H^+ + H_2NCH_2CH_2OH \qquad (2.2)$ Experimental results gave a loading of 0.58 mole CO₂ / mole MEA, which suggests that a small portion of bicarbonate is present as a result of hydrolysis of carbamate ions according to the following equation;

 $HOCH_2CH_2(CH_3)NCOO^- + H_2O \Rightarrow HOCH_2CH_2(CH_3)NH + HCO_3^-$ (2.3) On the other hand, CO_2 absorption capacity of MAE was 0.75 indicating the presence of more bicarbonate and less carbamate in MAE solutions than that in the MEA solutions. Their results showed that the absorption capacity peaked at 0.78 when the feed gas was 230 ml/min at 10% CO_2 . These results can be described by an equilibrium between MAE and carbamate and between carbamate and bicarbonate, according to the following equations;

$2 \text{ HOCH}_2(\text{CH}_3)\text{NH} + \text{CO}_2 \rightleftharpoons \\ \text{HOCH}_2(\text{CH}_3)\text{NCO}_2\text{HHN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ (2.4)

$HOCH_{2}CH_{2}(CH_{3})NCO_{2}HHN(CH_{3})CH_{2}CH_{2}OH + H_{2}O \Leftrightarrow HOCH_{2}CH_{2}(CH_{3})NHH^{+} \square \square HCO_{3}^{-} + HOCH_{2}CH_{2}(CH_{3})NH$ (2.5)

The free MAE leads to an increase in pH, which in turn, causes more CO_2 absorption. Therefore, the higher CO_2 absorption capacity can be attributed to the lower carbamate concentration at equilibrium for both secondary and sterically hindered amines.

Si Ali (2007) illustrated that when reacted with primary amines, CO₂ forms stable carbamates which are responsible for limiting the maximum stochiometric carbon dioxide loading to 0.5 mole CO₂ / mole amine. However, at high CO₂ partial pressure loading higher than 0.5 can be obtained due to the hydrolysis of carbamate ions which generate free amines. On the other hand, tertiary amines do not form carbamates and consequently are characterized by high CO₂ loading capacity approaching 1.0 mole CO₂/mole amine.

2.4.5 Foaming

Kohl & Nielsen (1997) described foaming as the most common problem in amine treating plants. Foaming may result in higher loss of amine and decrease in liquid-gas inter-phase area, which reduces the efficiency of separation. They attribute foaming mainly to impurities in the system which is different in natural gas than in flue gas.

da Silva (2005) explained that foaming is caused by some components acting as surfactants. In an aqueous solution, amines with hydrophobic functionalities can act as surfactants and cause foaming. To reduce foaming characteristics of amine solution, he proposed to keep the ratio of hydrophilic to hydrophobic groups high, meaning high number of hydroxyl groups and low number of carbon-based groups.

Mamun (2005) indicated that although MAE has a higher absorption rate combined with high absorption capacity of CO_2 compared to all other well known amines like MEA, DEA, MDEA, it showed high foaming tendencies. His work also included adding a foam inhibitor which had a negative impact on the mass transfer characteristics, both by reducing the interfacial area and increasing the surface resistance. He concluded that MAE may be a good candidate for CO_2 capture if it is used in contactors where the two phases are separated.

A summary of some of the literature review related to CO₂ absorption by amine solvents, particularly, MEA, DEA, MDEA, AMP, AMPD, PZ and MAE is shown in Table 2.1.

Reference	Parameters/Method	Findings
Derks <i>et al.</i> (2010)	$T=298, 323, 313K P_{CO2} = 0.68-8.37kPa Conc.= 0.5M MDEA+1.5M PZ 0.5M MDEA+1.5M PZ Method; NMR spectroscopy$	Solubility, pH and conductivity of CO ₂ in MDEA/PZ
Si Ali (2007)	Solubility of CO_2 DEA, MDEA, PZ, DEA/PZ, MDEA/PZ T= 40 - 80 °C P _{CO2} = 0.05-95.7 kPa Method; Stirred Cell Reactor	CO ₂ solubility is greater in PZ activated amines.
Mamun (2005)	T= 32-49 °C Method; String of disc contactor, NMR analysis	AEEA has high absorption rate and capacity, high cyclic capacity and lower regeneration energy MMEA has high absorption and high foaming tendencies
Mamun <i>et al.</i> (2004)	30 mass% MEA and 50 mass% MDEA P= 7 - 192 kPa @ 120 °C P= 66 - 813 kPa at 55,70 and 85 °C	P_{CO2} 7 - 192 kPa at 120 °C Loading 0.16 - 0.42, 50% MDEA, Loading 0.17 - 0.81, 30% MEA Estimated H _{sol} . CO ₂ in MDEA
Mandal <i>et al.</i> (2003)	AMP & DEA blends T=313 K, 100% CO ₂ , Flow; $2x10^{-6}$ m ³ /s Method; Wetted wall steel reactor	kinetic and equilibrium model using Higbies penetration theory
Park et al (2003)	10% AHPD & MEA T=298.15K $P_{CO2} = 0.01 - 3000$ kPa method; C-13 NMR spectroscopy	Solubility Chemical shift influenced by pH
Aroua <i>et al.</i> (2002)	T= 30, 40 and 50 °C $P_{CO2} = 0.1-100$ kPa Total amine conc. = 2.0M	AMP has better loading than MDEA
Baek <i>et al.</i> (2000)	T= 30-60 °C P= 1-100 kPa Conc. = 10 & 30% AMPD	K_1 as function of T, α and M by modified Kent- Eisenberg model

Table 2.1: Selected Literature Review on CO₂ absorption by amine solvents

Kinetics of CO ₂ with PZ	K for 1st order, K for 2nd order,
Conc. = $0.6 \& 0.2M PZ$ T= 298 - 333K P _{CO2} = $0.032-40 kPa$ Method; Wetted wall contact	E_A , Solubility and carbamate stability constant
T=298K 10% CO ₂ Feed gas 230 ml/min, MEA and MAE with and without NaCl	Presence of NaCl increases CO_2 solubility but decreases the rate o CO_2 absorption
Mechanism of CO ₂ -MAE- H ₂ O system Vibrational spectroscopy	Carbamate is formed in the first stage but it dissociates in the subsequent stages to form the protonated amine and bicarbonate
T= 30, 40 and 60 °C, $P_{CO2} = 0.5-3065$ kPa Total amine conc. =10 & 30 mass%	Loading of 30% AMPD at 40 °C is the same as 30% MDEA at 30 °C
Kinetics of CO_2 with MAE, and EAE T= 298 K Method; Stirred tank absorber	Solubility and diffusivity parameter, K_{EAE}
Method; 13C NMR spectroscopy	Methyl groups substituted adjacent to amine increase absorption capacity bu decrease absorption rate.
2M DEA & AMP with NaHCO ₃ at 30 °C	Titration with NaOH to find CO ₂ loading $p\dot{K}_a$ as a function of T, P _{CO2} and M
30 mass% MEA T= 0 – 150 °C P _{CO2} = 0.001 – 20,000 kPa	Correlation using Deshmukh-Mather model
DGA, MMEA, TBAE, AMP, MDEA, DMMEA, DEMEA, DIPMEA T=293, 303, 318 and 333K Method; Potentiometric titration	Values of <i>pKa</i>
	P _{CO2} = 0.032-40 kPa Method; Wetted wall contact T=298K 10% CO ₂ Feed gas 230 ml/min, MEA and MAE with and without NaCl Mechanism of CO ₂ -MAE- H ₂ O system Vibrational spectroscopy T= 30, 40 and 60 °C, P _{CO2} = 0.5-3065 kPa Total amine conc. =10 & 30 mass% Kinetics of CO ₂ with MAE, and EAE T= 298 K Method; Stirred tank absorber Method; 13C NMR spectroscopy 2M DEA & AMP with NaHCO ₃ at 30 °C 30 mass% MEA T= 0 – 150 °C P _{CO2} = 0.001 – 20,000 kPa DGA, MMEA, TBAE, AMP, MDEA, DMMEA, DEMEA, DIPMEA T=293, 303, 318 and 333K Method; Potentiometric

Table 2.1: 0	Continued
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