

## Kinetics Study of CO<sub>2</sub> Absorption into Blended Reactive and Non-Reactive Solvents System

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### Abstract

Increased levels of greenhouse gases (GHG) like CO<sub>2</sub>, H<sub>2</sub>S and other sulphuric components are usually present in industrials and producer gases and may lead to global warming and climate change. They may have to be removed from the gas stream (sweetening process) for environmental, operational, economical reasons. Many studies on the kinetics of the reaction of CO<sub>2</sub> in aqueous reactive and non-reactive solvents have been reported. But there are still some discrepancies to the values of the reaction rate constants and the influence of absorption conditions (temperature, CO<sub>2</sub> partial pressure, amines concentrations and using single or mixtures of physical and chemicals solvents) on these values. Due to the increasing importance of blended-solvent systems in acid-gas treating process it is necessary to have an understanding of the kinetics phenomena in mixed system. The objective of this work is to quantify the effectiveness of physical solvent as a rate promoter in aqueous PZ –Amine mixture. To study the reaction kinetics and to optimize the absorption process parameters using design of experiment software (DOE). A correct interpretation of the kinetics requires the knowledge of physical solubility and diffusivity of CO<sub>2</sub> in aqueous solvents solutions. The main deliverable of this project is introducing a novel CO<sub>2</sub> absorption solvent together with developing kinetic model to simulate the CO<sub>2</sub> absorption at different process variables.

**KEY WORDS:** Acid gases, kinetic model, Physical solvent-PZ –Amine-H<sub>2</sub>O mixture, CO<sub>2</sub> solubility and diffusivity.

### 1. INTRODUCTION

THE aqueous alkanolamines solution and physical solvents are frequently used for removal of acidic gases such as carbon dioxide and hydrogen sulfide from gas streams in natural or synthesis gas and gaseous effluents released from refineries. Utilizing the

advantages of each physical solvent [dimethyl Ether of Polyethylene Glycol (DEPG), Propylene Carbonate (PC), N-Methyl-2-Pyrrolidone (NMP)] and chemical solvent [ mono-ethanolamine (MEA), di-ethanolamine (DEA), diglycolamine (DGA), di-isopropanolamine (DIPA), , N-methyldiethanolamine

(MDEA), and methyl Piperazine] can add great impact to the solvent absorption capabilities.

Absorption with physical solvents presents the advantage of low energy requirements in the regeneration step. Furthermore they are often preferred for treating gas streams at high pressure with high concentrations of the acid gases (CO<sub>2</sub> and H<sub>2</sub>S), Murrieta *et al.*, (1988).

Some physical solvents such as sulfolane, n-methyl-2-pyrrolidone (NMP) and propylene carbonate (PC) used in the processing of gases which has a strong affinity for acid gases (CO<sub>2</sub> and H<sub>2</sub>S) present in many natural and refinery gas streams. In general, the economics of CO<sub>2</sub> recovery is strongly influenced by the partial pressure of CO<sub>2</sub> in the feed gas. At low partial pressures, physical solvents are uneconomical because the compression of the gas for physical absorption is expensive. However, if the gas is available at high pressure, physical solvents might be a better choice than chemical solvents, Jou *et al.*, (1990).

Kassim *et al.*, (1988) measured the solubility of CO<sub>2</sub> in the extraction solvents 1-methyl-2-pyrrolidone, 4-formylmorpholine,  $\gamma$ -butyrolactone, sulfolane and 1,4-dioxane over the temperature range of 303 to 333K at a partial pressure of 1 atm using falling-film flow technique. For all systems, the solubility was found to be decreased with increasing temperature. The solubility study by Kassim *et al.*, (1988) was compared to that of solubility prediction by Redlich-Kwong equation of state (RK-EOS) for binary system and was found to be within  $\pm 3\%$  accuracy.

The solubility for CO<sub>2</sub> increased with molecular weight of the solvent i.e. from diethylene glycol dimethyl ether (DEGDME) to tetraethylene glycol dimethyl ether (TEGDME). Exception being Ethylene glycol dimethyl ether (EGDME) that had a better capacity for CO<sub>2</sub> than DEGDME at all temperatures, but its vapor pressure was noticeably higher and therefore was not included in the list of the best solvents as reported by

Amr *et al.*, (2005). The solubility increased from EGDME to TEGMME, from DEGME to DEGDEE, and from EGMBE to TEGMBE.

Xia Gui *et al.*, (2010) used constant-volume method to determine the solubility of CO<sub>2</sub> in dimethyl carbonate (DMC) under the pressure of 6 MPa and the temperature variations from 281 to 328 K. The reliability of the experimental apparatus was verified by the measurements of CO<sub>2</sub> solubility in water. It was found by that DMC has greater ability to dissolve CO<sub>2</sub> than propylene carbonate and methanol at the same temperature. Furthermore, the solubility of CO<sub>2</sub> in DMC at room temperature, 298K, is close to that of methanol at 263K. Therefore, DMC can be considered as an effective and low-cost absorbent for pre-combustion CO<sub>2</sub> capture process.

Aqueous solutions of alkanolamines are the most widely used chemical absorbents for the removal of acidic gases from natural, refinery, and synthesis gas streams. The processes utilizing

aqueous alkanolamines as an absorption agent have become well established in this area.

The kinetics of the reaction of carbon dioxide with 2-amino-2-methyl- 1-propanol solutions was investigated by Shuo *et al.*, (1996). The authors determined the reaction rate constants from measurements of the rate of absorption of CO<sub>2</sub> into both aqueous and non-aqueous (1-propanol) AMP solutions. The zwitterion mechanism was found to be suitable for modeling the absorption of CO<sub>2</sub> into the aqueous AMP solutions and into the 1-propanol-AMP solvent. The partial order in amine is greater than one for both cases. The kinetic parameters for aqueous AMP solutions were obtained for temperatures ranging from 288 to 318K and over a concentration range of 0.25-3.5 kmol m<sup>-3</sup> of AMP with stirring speed in the range of 70-85 rpm.

Sanjay *et al.*, (2000), studied the absorption of carbon dioxide into aqueous solutions of Piperazine (PZ) in a wetted wall contactor at temperature range between 298 to 333 K in solutions of 0.6 and 0.2M

aqueous Piperazine. The apparent reaction rate is first order in both carbon dioxide and Piperazine with a value of  $53,700 \text{ m}^3/\text{kmol s}$  at  $526\text{K}$  ( $253^\circ\text{C}$ ). The apparent second-order rate constant follows Arrhenius temperature dependence over the range studied with an activation energy of  $3.36 \times 10^4 \text{ kJ/kmol}$ .

Aqueous monoethanolamine (MEA) solutions are the most frequently used chemical absorbents because of high reactivity to acid gases like carbon dioxide. However, it is known that these solutions can also react with materials in reactor vessels, tubing lines, and several process compartments. For this reason, highly concentrated aqueous MEA solutions should be avoided if possible. MEA is a relative strong base with a fast reaction rate, yielding a low  $\text{CO}_2$  concentration. A number of investigators have studied on the solubility and reaction kinetics of  $\text{CO}_2$  in aqueous MEA. Even though MEA reacts relatively fast with  $\text{CO}_2$ , the rate of absorption is still controlled by reaction kinetics

as described by Hongyi *et al.*, (2001).

The selective absorption of  $\text{H}_2\text{S}$  from  $\text{N}_2$  streams containing  $\text{H}_2\text{S}$  and  $\text{CO}_2$  into aqueous solutions of 2-amino-2-methyl-1-propanol (AMP) as well as *N*-methyldiethanolamine (MDEA) was investigated by Mandal *et al.*, (2004). Their results showed that, the rates of absorption of  $\text{H}_2\text{S}$  and the selectivity factor decreased with the contact time for both alkanolamine solutions. With increasing amine concentration in the range  $2.0\text{--}3.0 \text{ kmol/m}^3$ , the rates of absorption of both  $\text{CO}_2$  and  $\text{H}_2\text{S}$  increased. In the temperature range between  $293\text{--}313 \text{ K}$ , the rates of  $\text{CO}_2$  absorption increased marginally with the increase in temperature while the rates of  $\text{H}_2\text{S}$  absorption and selectivity factor decreased. The maximum selectivity observed in their work was 17.57 and 23.02 for AMP and MDEA, respectively for  $\text{H}_2\text{S}$ .

Compared to the most common alkanolamines, tertiary MDEA (methyldiethanolamine) amine is known for its lower regeneration cost, its thermal and chemical degradation

resistance, and lower corrosion rate. In addition, it has capability for selective H<sub>2</sub>S removal in the presence of CO<sub>2</sub> and the removal of both H<sub>2</sub>S and CO<sub>2</sub> as indicated by Hassan *et al.*, (2009).

Since the mid-nineteen eighties, in order to further improve absorption performance of MDEA solvent, blended alkanolamines solvents have been developed by adding another alkanolamines into MDEA. These blended solvents include MDEA–MEA, MDEA–DEA, MDEA–DIPA, MDEA–DGA, and MDEA–AMP, etc. (Pacheco *et al.*, 2000; Mandal *et al.*, 2001; Xia *et al.*, 2003; Rinker, 1997). The blended solvents have the compatibility advantages of each single solvent in blended mixture (Aroonwilas and Veawab, 2004). For example, a blended solvent, consisting of a mixture of primary or secondary amine with MDEA, combines the advantage of higher CO<sub>2</sub> reaction rates of the primary or secondary amine with the higher CO<sub>2</sub> loading capacity of the MDEA.

The experimental and theoretical investigation of the

absorption of carbon dioxide into aqueous blends of monoethanolamine and N-methyldiethanolamine has been conducted by Daniel *et al.*, (1995). The mathematical model was used to estimate the rate coefficient of the reaction between CO<sub>2</sub> and monoethanolamine at 313K from experimentally measured absorption rates.

The kinetics of the absorption of CO<sub>2</sub> into a blend of 2-amino-2-methyl-1-propanol (AMP), mono-ethanolamine (MEA) and water were investigated by Jimmy *et al.*, (2000) at 303, 308 and 313K, using a laboratory wetted wall column. Ten systems consisting of 1.7 and 1.5 kmol m<sup>-3</sup> AMP was mixed with various MEA concentrations (0.1, 0.2, 0.3, and 0.4 kmol m<sup>-3</sup>) were studied. The N<sub>2</sub>O analogy was applied to estimate the solubilities and diffusivities of CO<sub>2</sub> in amine systems. Assuming pseudo-first-order for the CO<sub>2</sub> absorption, the overall reaction rate constants (pseudo-first-order) were determined from kinetic measurements. The addition of small amounts of MEA to AMP results in a

significant enhancement of CO<sub>2</sub> absorption rates. A hybrid reaction rate model assuming first-order reaction for MEA and a zwitterion mechanism for AMP was used to model the kinetic data. The model produced a satisfactory representation of CO<sub>2</sub> absorption rates in AMP + MEA aqueous systems.

The kinetics of the CO<sub>2</sub> absorption into monoethanolamine (MEA) and N-methyl-diethanolamine (MDEA) together with water were investigated by, Chen and Meng (2002), at 303, 308 and 313K using a laboratory wetted wall column. A similar approach to that of Jimmy *et al.*, (2000) was performed. The hybrid reaction rate model using a zwitterion mechanism for MEA and a pseudo first-order reaction model for MDEA was used to model the kinetic data. Based on the pseudo first order for the CO<sub>2</sub> absorption, the overall pseudo first-order reaction rate constants were determined. Ten systems with various MEA concentrations (0.1, 0.2, 0.3, 0.4, and 0.5 kmol m<sup>-3</sup>) mixed with aqueous MDEA (1.0 and

1:5 kmol m<sup>-3</sup>) solutions were studied. The addition of small amounts of MEA to aqueous MDEA results in a significant enhancement of CO<sub>2</sub> absorption rates. The N<sub>2</sub>O analogy was again applied to estimate the solubilities and diffusivities of CO<sub>2</sub> in amine systems.

Mandal *et al.*, (2005) investigated the simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S into aqueous blends of 2-amino-2-methyl-1-propanol (AMP) and diethanolamine (DEA). From their results, it can be concluded that the blended amine solvent (AMP+DEA+H<sub>2</sub>O) has been found to display an efficient mixed solvent for simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S, and it was suggested that, for simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S, it will be desirable to use AMP alone or AMP with small concentration of DEA.

Mohamed *et al.*, (2007), studied the absorption of carbon dioxide in CO<sub>2</sub> loaded mixed solutions of mixed MDEA and MEA (with MEA/MDEA weight ratio of 27/03 to 23/07, over a

concentration range for MDEA of 2.316-1.996 kmol m<sup>-3</sup> and for MEA of 0.490-1.147 kmol m<sup>-3</sup>, they were found that, the reaction rate constant ( $k_{\text{MEA}}$ ) obtained for MEA blended into MDEA at 298–333 K was  $k_{\text{MEA}} = 5.127 \times 10^8 \exp(-3373.8/T)$ .

Their results showed that, an addition of small amounts of MEA to MDEA results in significant enhancement in the rates of CO<sub>2</sub> absorption for this mixed solvent. It also showed that, the smaller the concentration of MDEA, (i.e. the higher the MEA/MDEA ratio), the higher the enhancement factor observed for CO<sub>2</sub> absorption into the aqueous blend of MEA and MDEA blend.

The kinetics of CO<sub>2</sub> absorption was investigated by Ardi *et al.*, (2009) in an unloaded aqueous solution using diethylenetriamine (DETA) concentrations ranging between 1.0 and 2.9 kmol m<sup>-3</sup> and at temperature range between 298.1 and 332.3 K. It was found that the reaction rates strongly increased by increasing the concentrations and temperatures. Both the

termolecular and the zwitterion models were applied to interpret the experimental data. Both models gave identical results for all practical approach. It was found that fitting of experimental data to the termolecular mechanism gave statistically more robust results than fitting to the zwitterion mechanism.

Arunkumar *et al.*, (2011) study was on the absorption of CO<sub>2</sub> into Piperazine (PZ) activated aqueous N-methyldiethanolamine (MDEA) solvent. The absorption experiments are performed over the MDEA concentration range of 1.89–2.41 kmol m<sup>-3</sup> along with PZ concentrations of 0.24, 0.60 and 0.95 kmol m<sup>-3</sup>. The rates of absorption of CO<sub>2</sub> into this solvent have been measured over the CO<sub>2</sub> partial pressure range of 2–14 kPa and temperature range of 298–313K under atmospheric pressure. They concluded that, the addition of small amounts of PZ to an aqueous solution of MDEA results in significant increase in the rate of absorption and enhancement factor.

Since equilibrium data are indispensable for design of gas absorption units, many researchers have reported the solubility of acid gases in various types of solvents (physical and chemical). Furthermore most of the solvents have low absorption rate and absorbents capacity, low reactivity with poor thermal stability and suffers from degradation and amine salts formation.

In this work, the new novel solvent -CO<sub>2</sub>- H<sub>2</sub>O systems at various process variable will be introduced. The process variables will be optimized using design of experiment software (DOE). A workable reaction kinetics model will be developed to simulate CO<sub>2</sub> absorption into novel solvent.

## **2. MATERIALS AND EXPERIMENTAL METHODS**

### **2.1 MATERIALS.**

Physical solvents include: - Dimethyl Ether of Polyethylene Glycol (DEPG), Propylene Carbonate (PC), N-Methyl-2-

Pyrrolidone (NMP), and Methanol (MeOH).

Chemical solvents are, (MDEA), DEA, MEA, (DIPA), (DGA) &MPZ The blends of these solvents will be use for the absorption of acid gases namely CO<sub>2</sub>.

### **2.2 EXPERIMENTAL SET-UP AND PROCEDURE**

The SOLTEQ High Pressure Gas Solubility Cell (Model: BP 22) consists of a gas mixing vessel and an equilibrium cell, each immersed in a heating jacket. Other supporting components include the magnetic stirrer, circulation pumps, vacuum pump, thermostat heating bath, liquid feed pump, liquid degassing unit and instrumentations such as mass flow controllers, pressure and temperature indicators. A gas chromatograph is provided for online gas composition analysis while a liquid titrator with autosampler is available for offline liquid composition analysis. The process flow diagram of cell is provided below.

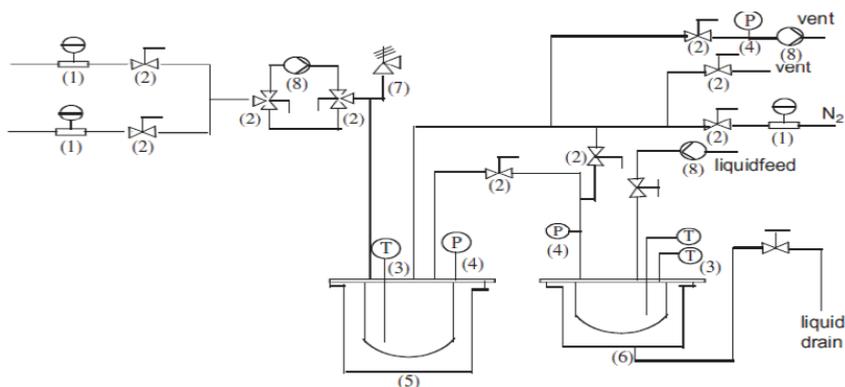


Figure1. Schematic of the high pressure solubility cell unit: 1—mass flow controller; 2—non-return valve; 3—thermocouple; 4—pressure transducer; 5—mixing vessel; 6—equilibrium cell; 7—pressure relief valve; 8—pump.

Pressurized gas mixture in mixing vessel will be charged into the equilibrium cell up to the desired pressure. The liquid is then introduced into cell using a liquid feed pump. The equilibrium cell contains a magnetic stirring bar seated on top of a magnetic stirrer will be used to agitate the liquid to contact with the gas mixture. Furthermore, a circulation pump attached to the equilibrium cell will circulate gases from the top of the cell into the liquid at the bottom to increase contact between the two phases. Both mixing vessels and equilibrium cell are immersed in a

circulating bath inside individual heating jackets, which are connected to a thermostat heating bath to maintain constant temperature throughout the unit.

Saturation of the gas and liquid components in the equilibrium cell is measured by a constant pressure drop. Once the minimum pressure is constant (assuming that a steady state (saturation) between the gas and liquid has occurred), the experiment is stopped. The samples can then be carried out to determine the solubility of gas in the liquid.

## 2.3 RESEARCH METHODOLOGY

A schematic of the methodology is given in Figure 2 below

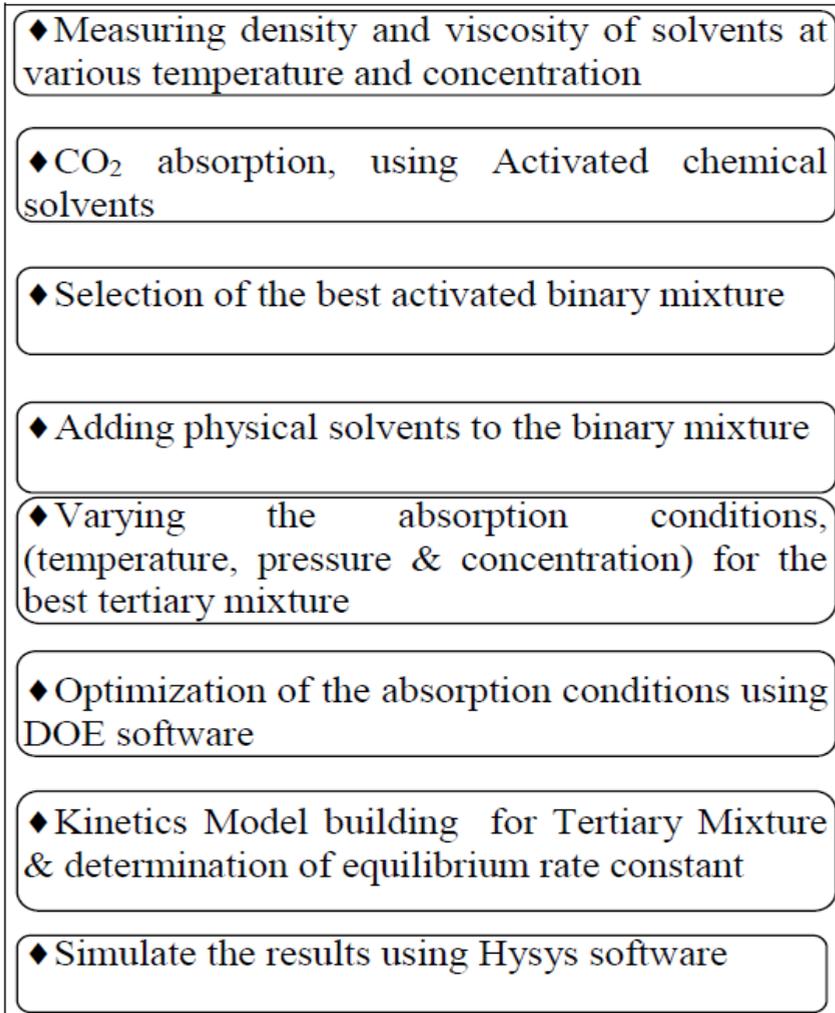


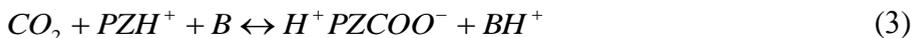
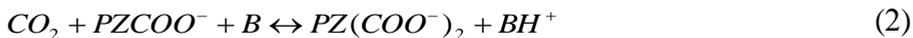
Figure 2 Schematic of methodology of this research.

The selection of the best binary mixture and optimum conditions (concentrations, pressure and temperature) with regards to its enhancement effect on CO<sub>2</sub> absorption rate can be summarized as follows:

(1) All experiments will be carried out at 25-45 °C and 7000 – 10000 KPa.

(2) The change in gas pressure will be recorded versus time and the profile of CO<sub>2</sub> loading in the solution will be obtained as a function of time.

(3) The activator percentage with the fastest increase in CO<sub>2</sub>



Where *B* is the base (PZ, PZCOO<sup>-</sup>, PZH<sup>+</sup>, H<sub>2</sub>O and OH<sup>-</sup>) present in solution

### 3.1 REACTION RATE DEPENDENCE ON PZ

The kinetics of primary and secondary alkanolamines with CO<sub>2</sub> can be described using the zwitterion mechanism, as originally proposed by Caplow (1968) and later reintroduced by Danckwerts (1979). It is

loading will be identified as the best binary mixture.

### 3. REACTION CHEMISTRY AND KINETICS STUDY

In aqueous environment, Piperazine can react with CO<sub>2</sub> to form many different reaction products, as shown by Bishnoi and Rochelle (2000) and Ermatchkov et al. (2002). In aqueous Piperazine solutions, carbon dioxide can react according to reactions below:

assumed that this mechanism is also applicable to PZ although it is not an alkanolamines: Piperazine will react with CO<sub>2</sub>, under a first order rate both in CO<sub>2</sub> and PZ, respectively. This results in the formation of a zwitterion, which is consequently deprotonated by any base *B* present in the liquid. The overall reaction rate is

second-order (first with respect to  $PZH^+COO^-$  and  $B$ ).



$$r_{CO_2} = \frac{k_2[CO_2][PZ]}{1 + \frac{k_{-1}}{\sum k_B B}} = \frac{[PZ][CO_2]}{\frac{1}{k_2} + \left(\frac{k_{-1}}{k_2}\right)\left(\frac{1}{\sum k_B B}\right)} \quad (6)$$

Where,  $k_B B$  is the contribution of all the bases present in the solution ( $PZ$ ,  $PZCOO^-$ ,  $PZH^+$ ,  $H_2O$  and  $OH^-$ ) for the removal of the protons. Kumar et al. (2003) pointed out, there are two asymptotic situations for amines in aqueous solution:

(I) In case the deprotonation of the zwitterion is very fast, or  $\frac{k_{-1}}{\sum k_B B} \ll 1$ , the kinetic equation reduces to simple second-order kinetics, as found for primary alkanolamines.

$$r_{CO_2} = k_2[CO_2][PZ] \quad (7)$$

(II) The reversed situation of case I occur when  $\frac{k_{-1}}{\sum k_B B} \gg 1$ , now the kinetic rate expression reduces to:

$$r_{CO_2} = k_2[CO_2][PZ] \left( \frac{\sum k_B B}{k_{-1}} \right) \quad (8)$$

### 3.2 REACTIONS OF CO<sub>2</sub> IN AQUEOUS SOLUTIONS

Two reactions occur for  $CO_2$  in aqueous solutions. The first reaction is the hydration of  $CO_2$ :



The second reaction is the bicarbonate formation:



This reaction is fast and can enhance mass transfer even when the concentration of hydroxyl ion is low. The forward reaction can be described as (Pinsent et al., 1956):

$$r_{CO_2-OH^-} = k^*_{OH^-} [CO_2][OH^-] \quad (11)$$

$$\log_{10} k^*_{OH^-} \left( \frac{m^3}{(kmol.s)} \right) = 13.635 - \frac{2895}{T(K)} \quad (12)$$

### 3.3 REACTION RATE DEPENDENCE ON DEA

The zwitterion mechanism originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979), is generally accepted as the reaction mechanism for the carbamate formation between CO<sub>2</sub> with primary and secondary alkanolamines. The

zwitterion mechanism has been used successfully in aqueous alkanolamine solutions by Blauwhoff et al. (1984) and Barth et al. (1984) as well as in some organic and viscous solutions by Alvarez-Fuster et al. (1980,b), and Versteeg and van Swaaij (1988a).

The reaction steps successively involve the formation of a “zwitterion”,



and the subsequent removal of the proton by a base B (base catalysis):



Where, B is a base that could be an amine, OH<sup>-</sup>, or H<sub>2</sub>O (Blauwhoff et al., 1984).

For this mechanism, Danckwerts (1979) derived the forward reaction rate equation at quasi-steady state as:

$$r_{CO_2-Amin e} = \frac{k_{2,R_1R_2NH} [CO_2][R_1R_2NH]}{1 + \frac{k_{-1}}{\left( k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{R_1R_2NH}[R_1R_2NH] \right)}} \quad (15)$$

In the present work, the zwitterion mechanism will be applied to the reaction of CO<sub>2</sub> into PZ + DEA + H<sub>2</sub>O, the base could be DEA, PZ, OH<sup>-</sup>, or H<sub>2</sub>O.

### 3.4 OVERALL REACTION RATE

$$r_{ov} = r_{CO_2-PZ} + r_{CO_2-DEA} + r_{CO_2-OH^-} \quad (16)$$

$$r_{ov} = k_{ov}[CO_2] \quad (17)$$

$$r_{CO_2} = k_{2,PZ}[CO_2][PZ] + k_{OH^-}[CO_2][OH^-] + \quad (18)$$

$$\frac{k_{2,DEA}[CO_2][DEA]}{1 + \frac{k_{-1}}{\left( k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k_{PZ}[PZ] + k_{DEA}[DEA] \right)}}$$

From the above equation and the overall reaction rate constant  $k_{ov}$ , can be determined and the apparent reaction rate constant,  $k_{app}$ , is defined as follows:

$$k_{app} = k_{ov} - k_{OH^-}[OH^-] \quad (19)$$

### 3.5 RATE OF THE PHYSICAL ABSORPTION

The partial pressure CO<sub>2</sub> in the gas at the surface of the liquid is such that the solubility of CO<sub>2</sub> is C\*. It is assumed that the gas and liquid are in equilibrium at the surface, so the concentration of CO<sub>2</sub> at the surface will be C\*. The

concentration in the bulk of the layer is C<sub>o</sub>. It is in a common ground between the film and the surface renewal models. Therefore the concentration falls from C\* to C<sub>o</sub> in a region close to the surface. The resulting concentration gradient controls the rate of absorption. The film model predicts that the rate of absorption, R<sub>o</sub> per unit area of the surface will be:

$$R_o = \frac{D}{\delta}(C^* - C_o) \quad (20)$$

The surface renewal models lead to expressions of the form:

$$R_o = K \sqrt{\frac{D}{\tau}} (C^* - C_o) \quad (21)$$

Both models thus predict that the rate of absorption is proportional to the driving force

$$R_o = K_L (C^* - C_o) \quad (22)$$

$K_L$ : liquid film coefficient (depend of D, flow rate, and size of packing).

### 3.6 DETERMINATION OF THE ABSORBED CO<sub>2</sub> CONCENTRATION IN THE MIXED SOLVENT

The synthetic method proposed by Habchi Tounsi *et al* (2002), for the determination of CO<sub>2</sub> concentration absorbed in the liquid phase utilizes the knowledge of introduced or initial concentration of CO<sub>2</sub> and the concentration of CO<sub>2</sub> in the vapour phase. The acid gas mole number introduced in the equilibrium cell can be calculated by using a specific equation of state, the

knowledge of the reserves volume, the pressure and the temperature of the system before and after the acid gas introduction in the equilibrium cell. In order to determine the absorbed concentration of acid gas in the solvent, we write the mass conservation equation (for the present demonstration the acid gas used is CO<sub>2</sub>). The quantity of carbon dioxide introduced in the cell is divided into two parts: a concentration of CO<sub>2</sub> in the vapour phase and the concentration of carbon dioxide absorbed by the solvent.

$$n_{CO_2 \text{ Introduced}} = \frac{P_1 CO_2 \text{ reserve } V_{\text{Circuit } CO_2}}{Z_{CO_2} R T_1 \text{ reserve}} - \frac{P_2 CO_2 \text{ reserve } V_{\text{Circuit } CO_2}}{Z_{CO_2} R T_2 \text{ reserve}} \quad (23)$$

$$= n_{CO_2 \text{ Cell}} = n_{CO_2 \text{ Liquid}} + n_{CO_2 \text{ Vapour}}$$

#### 4. CONCLUSION

The investigation into acid gases solubility in liquid solvents is fundamentally important for the design of gas absorption processes to purify industrial and natural gases which frequently contain large quantities of carbon dioxide (CO<sub>2</sub>). In this work the reaction kinetics and the optimization of the absorption process, using tertiary mixture of reactive (chemical) and non-reactive (physical) solvents will be investigated. Introduction of a novel solvent for syngas and natural gases purification treatment and optimization of acid gases absorption conditions, are very critical issues in this work. Due to the increasing importance of blended-solvent systems in acid-gas treating process it is

necessary to have an understanding of the kinetics phenomena in mixed system. The potential contributions of this novel solvent are:

I Allow decreasing equilibrium pressure of acid gases in relation to their pressure over pure physical solvent.

II Allows the achievement of better technical and economical performance compared with the technology which uses pure solvent.

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## Notation

$k_{ov}$	Overall reaction rate constant
$k_{app}$	Apparent reaction rate constant
$K_L$	liquid film coefficient
$D$	Diffusivity of $CO_2$ in solution
$K$	Numerical constant of order unity
$\delta$	Thickness of the stagnant film
$n_{CO_2 Vapour}$	$CO_2$ mole number in the vapor phase
$n_{CO_2 Liquid}$	$CO_2$ mole number absorbed by the solvent.
$P_{1CO_2 reserve}$	$CO_2$ pressure in the reservoir before introduction,
$P_{2CO_2 reserve}$ ,	$CO_2$ pressure in the reservoir after introduction

## REFERENCES

- [1] Alvarez-Fuster, C, N, Midoux, A, Laurent, and J.C Charpentier, "Chemical Kinetics of the Reaction of Carbon Dioxide with Amines in Pseudo m-nth Order Conditions in Polar and Viscous Organic Solutions," *Chem. Eng. Sco.*, 36, 1513 (1980).
- [2] Amr Henni1, Paitoon Tontiwachwuthikul1 and Amit Chakma" Solubilities of Carbon Dioxide in Polyethylene Glycol Ethers" *The Canadian journal of chemical engineering* Vol 83. (2005).
- [3] Ardi Hartonoa, EirikF.daSilvab, HallvardF.Svendsen "Kinetics of carbon dioxide absorption in aqueous solution of diethylenetriamine (DETA)" *Chemical Engineering Science* 64, 3205 – 3213, (2009).
- [4] Arunkumar Samanta, S.S. Bandyopadhyay "Absorption of carbon dioxide into piperazine activated aqueous N-methyl diethanolamine" *Chemical Engineering Journal* 171, 734– 741, (2011).
- [5] Barth, D., C. Tondre, and . J. Delpuech "kinetics and Mechanisms of the reactions of carbon dioxide with alkanolamines: A discussion concerning the cases of MDEA and DEA," *Chem, Eng. Sci.*, 39, 1753 (1984).
- [6] Bishnoi, S., Rochelle, G., "Absorption Of Carbon Dioxide Into Aqueous Piperazine: Reaction Kinetics, Mass Transfer and Solubility". *Chemical Engineering Science* 55, 5531–5543, (2000).
-

- [7] Blauwhoff, P.M.M., C.F. Versteeg, and W.P.M. Van Swaaij, "A study on the reaction between CO<sub>2</sub> and alkanolamines in Aqueous solution," *Chem. Eng. Sci.*, 39, 207 (1984).
- [8] B.P. Mandal, S.S. Bandyopadhyay, "Simultaneous absorption of carbon dioxide and hydrogen sulfide into aqueous blends of 2-amino-2-methyl-1-propanol and diethanolamine" *Chemical Engineering Science* 60, 6438 – 6451, (2005).
- [9] B.P. Mandal a, A.K. Biswas b, S.S. Bandyopadhyay "Selective absorption of H<sub>2</sub>S from gas streams containing H<sub>2</sub>S and CO<sub>2</sub> into aqueous solutions of N-methyldiethanolamine and 2-amino-2-methyl-1-propanol" *Separation and Purification Technology* 35,191–202, (2004).
- [10] Caplow, M., "Kinetics of Carbamate Formation and Breakdown," *J. Am. Chem. Soc.*, 90, 6795 (1968).
- [11] Chen-Hung Liao, Meng-Hui Li" Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + N-methyldiethanolamine" *Chemical Engineering Science* 57, 4569 – 4582, (2002).
- [12] Dackwerts, P.V., "The reaction of CO<sub>2</sub> with Ethanolamines" *Chemi. Eng. Sci.*, 34, 443, (1979).
- [13] Daniel P. Hagewiesche, sami S. Ashour, hani A. Al-ghawas and orville C. Sandall "Absorption of Carbon Dioxide Into Aqueous Blends of Mono ethanolamine and n-Methyldiethanolamine", *Chemical Engineering Science*, Vol. 50, No. 7, pp. 1071-1079, (1995).
- [14] Ermatchkov, V., Perez-Salado Kamps, A., Maurer, G., "Chemical Equilibrium Constants for the Formation of Carbamates in (Carbon Dioxide + Piperazine + Water) from H-NMR-Spectroscopy," *Journal of Chemical Thermodynamic* 35, 1277-1289, (2002).
- [15] Habchi Tounsi, K.N., Barreau, A., Lecorre, E., Mougin, P., Neau, E. "Thermodynamic modelling of the Absorption of acid gas in a mixed solvent By electrolyte NRTL equation: new Equipment and measuring" *Fluid phase equilibria*, (2002).
- [16] Hassan E. Alfadala, and Essa Al-Musleh "Simulation of an Acid Gas Removal Process Using Methyldiethanolamine; an Equilibrium Approach" *Proceedings of the 1st Annual Gas Processing Symposium* H. Alfadala, G.V. Rex Reklaitis and M.M. El-Halwagi (Editors), (2009).
- [17] Hongyi Dang, and Gary T. Rochelle "CO<sub>2</sub> Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water" May 14-17, *First National Conference on Carbon Sequestration*, Washington, (2001).
- [18] Jimmy Xiao, Chih-Wei Li, Meng-Hui Li "Kinetics of absorption of carbon dioxide into aqueous solutions of 2-amino -2-methyl-1-propanol + monoethanolamine" *Chemical Engineering Science* 55, 161-175,(2000).
-

- [19] Jou, F. Y.; Deshmukh, R. D.; Otto F.D. and Mather, A. E.; Solubility of hydrogen sulfide, carbon dioxide, methane, and ethane in sulfolane. *Fluid phase Equilibria*, 56, pp:313-324, (1990).
- [20] Kassim, D. M.; Zainel, H. A.; Al-Asaf, S. A. and Talib, E. K.; The temperature dependence of the solubility of carbon dioxide in several extraction solvents. *Fluid phase Equilibria*, 41, pp:287-294, (1988).
- [21] Kumar, P., Hogendoorn, J., Timmer, S., Feron, P., Versteeg, G., "Kinetics of the reaction of CO<sub>2</sub> with aqueous potassium salt of taurine and glycine," *A.I.Ch.E. Journal* 49, 203–213, (2003).
- [22] Maizatul S. Shaharun, Hilmi Mukhtar, Binay K. Dutta "Solubility of carbon monoxide and hydrogen in propylene carbonate and thermomorphic multicomponent hydroformylation solvent" *Chemical Engineering Science* 63. 3024– 3035, (2008).
- [23] Mandal BP, Guha M, Biswas AK, Bandyopadhyay SS. Removal of carbon dioxide by absorption in mixed amines: Modelling of absorption in aqueous MDEA/MEA and AMP/MEA solutions. *Chem. Eng. Sci.*, 56: 6217-24, (2001).
- [24] Mohamed Edali<sup>1</sup>, Ahmed Aboudheir<sup>2</sup>, Raphael Idem<sup>3</sup> "Kinetics of Carbon Dioxide Absorption into Mixed Aqueous Solutions of MDEA and MEA using Laminar Jet Apparatus and Numerically Solved Absorption-Rate/Kinetic Model" Excerpt from the Proceedings of the COMSOL Conference, Bosto, pp 1-7, (2007).
- [25] Murrieta-Guevara F.; Romero-Mrtinez.,A. and Terjo A. ; Solubilities of carbon dioxide and hydrogen sulfide in propylen carbonate, N-methylpyrrolidone, and sulfolane. *Fluid phase Equilibria*, 44, pp:105-115, (1988).
- [26] Pacheco MA, Kaganoi S, Rochelle GT. "CO<sub>2</sub> absorption into aqueous mixtures of diglycolamine and methyldiethanolamine". *Chem Eng. Sci.*, 55, 5125-40, (2000).
- [27] Pinsent, B. R. W., L Pearson, and F. W.J.Roughton, "The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions," *Trans. Faraday Soc.*, 52, 1512 (1956).
- [28] Sanjay Bishnoi, Gary T. Rochelle" Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility" *Chemical Engineering Science* 55 5531-5543, (2000).
- [29] Shuo xu, yi-wei wang, frederick d. Otto and alan e. Mather "kinetics of the reaction of carbon dioxide with 2-amino-2-methyl- 1-propanol solutions" *chemical engineering science*, vol. 51, no. 6, pp. 841-850, (1996).
- [30] Rinker, E.B.,. Acid gas treating with blended alkanolamines. Ph.D. Dissertation. University of California, Santa Barbara, USA, (1997).
- [31] Versteeg, G. F. and W. P. M. Van Awaaij, "On the Kinetics between CO<sub>2</sub> and Alkanolamines Both in Aqueous and non Aqueous Solution-1. Primary and Secondary Amines," *Chem. Eng. Sci.*, 43,573 (1988).
-

[32] Xia Gui, ZhiGang Tang, and Weiyang Fei “CO<sub>2</sub> Capture with Physical Solvent Dimethyl Carbonate at High Pressures” *J. Chem. Eng. Data*, 55, 3736–374, (2010).