13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

The Activator Mechanism of Piperazine in Aqueous Methyldiethanolamine Solutions

Jiru Ying [a]，Stef Raets[b], Dag Eimer[a,b]

[a]Tel-Tek, 3918 Porsgrunn, Norway
[b]University College of Southeast Norway,3901 Porsgrunn, Norway

Abstract

Piperazine (PZ) is added to aqueous methyldiethanolamine (MDEA) solutions to achieve a greater CO_2 absorption in CO_2 capture technology. It is referred to as "activated MDEA solutions" in the industry. However, does PZ really activate rate the CO_2 absorption of MDEA, or do PZ and MDEA just have parallel reactions with CO_2, the mechanism is not clear. In this work, a semi-batch stirred cell with CO_2 continuous operation was used to investigate the "activation" mechanism of PZ in aqueous MDEA solutions. As a comparison, kinetics of CO_2 absorbed in MDEA + MEA solution and PZ aqueous solution respectively were performed at the same conditions as MDEA + PZ solution.

Keywords: Piperazine (PZ); methyldiethanolamine (MDEA); Activator; Mechanism

1. Introduction

One of the important measures to suppress the global warming is the control and cleaning of industrial waste gas in the form of CO_2-emmision control. These waste gases contain a high amount of CO_2 which leads to global warming. A highly effective way to threat waste gas is by using absorption columns using amine solutions. Besides physical absorption, amines also react with the CO_2 and thus remove it effectively from the gas. In order to optimize this absorption process a lot of experimental work has been done on which type or mixture of amine to use.

A well-known method is the process developed by BASF using so called activated MDEA solutions. These mixtures of methyldiethanolamine (MDEA) and an activator (Piperazine, PZ) are very popular due to the fast kinetics at low activator concentrations, the low energy costs and the noncorrosive properties towards carbon steel. However, there is not much data or investigation published on whether PZ is actually an activator in this MDEA + PZ system and how this activation would work.

Figure 1. Molecular structure of PZ (left) and MDEA (right)

To clarify the results and conclusions drawn in this work, it is important to first define the word 'activator'. An activator is considered to be a reactive molecule that reacts with another molecule to form a chemical that has improved properties compared to the two separate reagents. Industry often uses mixed amine solutions in their columns where both of the amines react in parallel to each other. For the authors this is not considered to be an activation mechanism. Two approaches could be employed to investigate the mechanism behind the fast reaction specifically in the mixed MDEA + PZ solutions by stirred cell technology:

- In the first approach, batch experiments are performed in a stirred cell by pressure drop technology [1], and the pseudo 1st order reaction constant k_{ps} and 2nd order reaction constant k_2 can be calculated for aqueous MDEA solutions and aqueous PZ solutions. The theory behind this approach is to first identify the individual kinetics of both the amines, then a mixed solution will be loaded with CO_2 through several batch experiments. If PZ is not an activator but reacts in parallel with MDEA, a decrease in reaction rate should be seen when all the PZ has reacted with CO_2. However, we found the reaction kinetics of PZ with CO_2 cannot be measured by the technique, because the Hatta numbers and enhancement factors do not agree with the pseudo 1st order criterion but describe a fast second order reaction regime as reported by Levenspiel [2]. On the other hand, it was demonstrated that it is difficult to investigate the reaction mechanism by measuring the reaction constant of mixed PZ + MDEA solutions at different CO_2 loadings. Because too little CO_2 was used in the kinetics reaction measurement by this batch method, and the mechanism investigation requires depletion of all PZ, which needs enough CO_2 to react with PZ.
- In the second approach, the stirred cell is modified to a semi-batch running stirred cell, continuous with respect to the gas phase (pure CO_2), and CO_2 absorption rates are measured for aqueous MDEA solutions, aqueous PZ solutions and mixed solutions at room pressure. We expected that the CO_2 absorption rate would be drop very fast and down to MDEA reaction level after PZ is depleted if PZ does not act as activator but reacts in parallel to the MDEA.

In this work, the experiments were done by using the second approach on MDEA solutions, mixed MDEA + PZ solutions, aqueous PZ solutions and mixed MDEA + MEA solutions, and the results between MDEA, MDEA + PZ and MDEA + MEA solutions will be compared to find whether PZ acts as activator.

2. Theory Background

By the second approach, the equation defining the gas flux in terms of the overall gas mass transfer coefficient and CO_2 partial pressure driving force:

$$N_{CO_2} = \frac{K_G a}{RT}\left(P_{CO_2} - P_{CO_2}^*\right)$$
(1)

where N_{CO2} stands for the flux of CO_2, K_G is the overall mass transfer coefficient on the gas side, a is the interfacial area and P_{CO2} and P^*_{CO2} are the partial pressures of CO_2 in the gas phase and the liquid bulk respectively. This equation can be written as function of various factors such as concentrations, mole ratios or mole fractions. However for the experiments in this work the equation above is the most suitable and is applied in order to calculate the mass transfer coefficient K_G.

2.1. Reactions and models in aqueous MDEA solutions

The main reaction occurring in an aqueous MDEA solution is the base catalysed CO_2 hydration reaction where

MDEA functions as the base catalyst [3-5]:

$$CO_2 + MDEA + H_2O \rightleftarrows MDEAH^+ + HCO_3^- \tag{2}$$

where the concentration of water is set to unity.
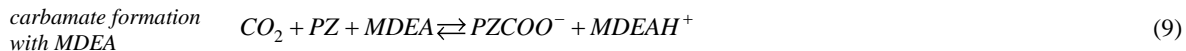
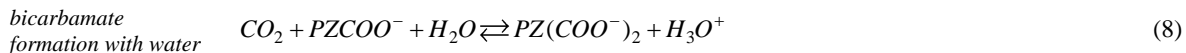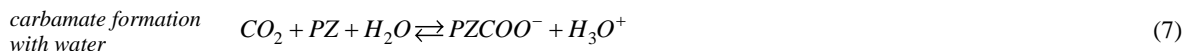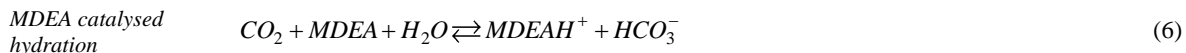*2.2. Reactions in aqueous PZ solutions*

Various reactions occurring during CO_2 absorption in aqueous PZ solutions are described in literature [6-8].The main reactions occurring in an aqueous PZ solution are the carbamate and bicarbamate formations [7]:

$$CO_2 + PZ + B \rightleftarrows PZCOO^- + BH^+ \tag{3}$$

$$CO_2 + PZH^+ + B \rightleftarrows H^+PZCOO^- + BH^+ \tag{4}$$

$$CO_2 + PZCOO^- + B \rightleftarrows PZ(COO^-)_2 + BH^+ \tag{5}$$

Here B could be any base that is available in the solution such as PZ, $PZCOO^-$ (carbamate), PZH^+ (protonated PZ), H_2O and OH^-.

*2.3. Reactions in mixed PZ and MDEA solutions*

Basically the reactions occurring in a mixed amine system of MDEA + PZ are a summary of the previous two paragraphs about reactions. However there are some main reactions going on: the carbamate formation, bicarbamate formation and the MDEA catalysed hydration. All of them are given below:

MDEA catalysed hydration	$CO_2 + MDEA + H_2O \rightleftarrows MDEAH^+ + HCO_3^-$	(6)

carbamate formation with water	$CO_2 + PZ + H_2O \rightleftarrows PZCOO^- + H_3O^+$	(7)

bicarbamate formation with water	$CO_2 + PZCOO^- + H_2O \rightleftarrows PZ(COO^-)_2 + H_3O^+$	(8)

carbamate formation with MDEA	$CO_2 + PZ + MDEA \rightleftarrows PZCOO^- + MDEAH^+$	(9)

bicarbamate formation with MDEA	$CO_2 + PZCOO^- + MDEA \rightleftarrows PZ(COO^-)_2 + MDEAH^+$	(10)

However, not all these reactions are significant related to mass transfer. The difference lies in both the reaction rate and basicity of the molecules. First of all as will be explained later in this work, the reaction rate of the PZ reactions is much higher than the MDEA catalysed hydration reaction. Therefore the main reactions occurring in a mixed MDEA + PZ solution are the carbamate and bicarbamate formations. Similar to aqueous PZ solutions, the carbamate formation reaction will mainly occur first while afterwards the bicarbamate formation will occur. Both of these

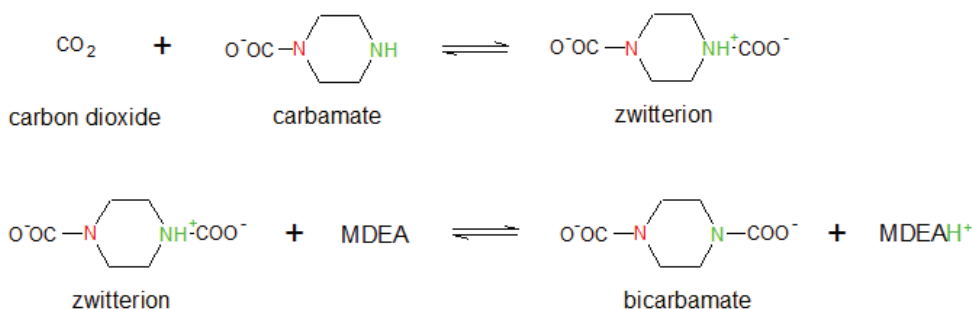reactions are shown in Figure 2.
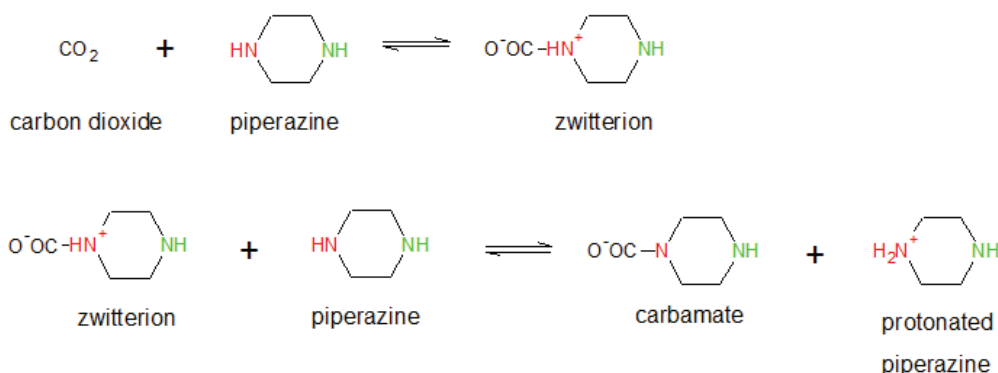
Figure 2. Reaction scheme applying the zwitterion mechanism and showing the main reactions occurring in mixed MDEA + PZ solutions.

Compared to aqueous PZ Solution, the difference with aqueous PZ solutions lies in the presence of MDEA. With a pK_a value of 8.52 for MDEA and 5.33 for the carbamate (PubChem, 2015), the first proton acceptor in the carbamate formation reaction is still PZ. But for the bicarbamate formation the base will be MDEA instead of carbamate because of the higher pK_a value for MDEA. Unlike for aqueous PZ solutions it is harder here to say how many moles of PZ react with one mole of CO_2. Worth mentioning is that whether MDEA or carbamate is the proton acceptor also depends on the concentration that they are present at.

Furthermore the potential activator mechanism or regeneration reaction which is probably present in the mixed amine solution is given by:

$$PZCOO^- + H_2O + MDEA \rightleftharpoons PZ + HCO_3^- + MDEAH^+ \tag{11}$$
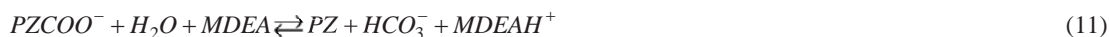
PZ will transfer the CO_2 onto a water molecule while MDEA will function again as a proton acceptor. This mechanism lets the PZ to regenerate itself. Using the fast reaction kinetics of PZ in a low concentration and the proton acceptor abilities of MDEA present in a high concentration makes this mixture a very effective CO_2 removal solution.

3. Experimental section

3.1. Experimental set-up and procedure

The experimental setup used for measuring the absorption data is based on our previous work [1]. The experimental setup has been modified by adding a gas bag supply system and a flow meter between this bag and the stirred cell reactor. The schematic diagram of the reworked stirred cell is shown in Figure 3. Furthermore some equipment dimensions and data are given in Table 1:

Table 1. Dimension of the stirred cell reactor

Parameters	Symbol	Value	Unit
Volume of reactor	V	1.986×10^{-6}	m³
Volume liquid phase	V_L	$\pm 0.6 \times 10^{-6}$	m³
Interfacial area	A	1.227×10^{-2}	m²
Stirrer revolutions per minute(rpm)	ω	120	min^{-1}
Diameter of liquid stirrer	d	8.85×10^{-2}	m

For the physical description of the stirred cell, reference is made to the description in earlier work [1]. Description of the modified parts follows here. The CO_2 flow rate is measured by a N_2 mass flow meter (Sierra Top-Trak 820, 0-5 Lpm) and coupled to the data acquisition system. To introduce the CO_2 into the reactor a metal pipe system was installed starting from the flow meter, through a copper pipe in the water bath, and around the metal flange. The temperature for the gas to be introduced is thus controlled by the water bath. The metal flange is heated by an independent controller (electric heater). This whole part and the gas introduction pipe around the flange are isolated with thermal isolation material to ensure a decent temperature stability and control. For each experiment the CO_2 flow rate, the gas-, liquid- and metal temperature and the pressure inside the cell were recorded. This was done by the data acquisition system (data logger, Agilent BenchLink, 34972A) which records this data every second.
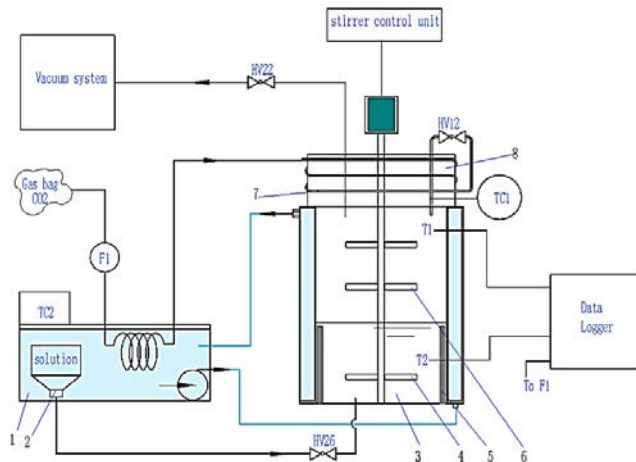

Figure 3. Schematic diagram of the stirred cell reactor with semi-batch operation. (1)water bath, (2)solution tank, (3)stirred cell chamber, (4)stirrer for the liquid, (5)baffles, (6)stirrer for the gas, (7)preheat pipe for the gas, (8)metal flange, (F1) gas flow meter

3.2. Experimental procedure

The stirred cell reactor described above is operated batch wise for the liquid phase and semi-continuous for the gas phase. Approximately 600 mL of a freshly prepared solution is fed into the reactor and vacuumed at 400 mbar for

around 15 minutes. The solution is vacuumed to remove most the gases present. The solution is kept under vacuum for 45 minutes while ensuring that the gas and liquid phase reach the desired temperature. Meanwhile the gas bag was filled with CO_2 and the metal section above the stirred cell that contains the gas introduction pipe was heated and kept on the required temperature. This is to make sure that there is no heat/temperature loss of the gas during transportation from the water bath to the stirred cell.

The valve HV12 between the gas bag and the stirred cell reactor is opened and the pressure in the cell will be close to room pressure throughout the experiment. Because the CO_2 will be absorbed into the solution, the pressure in the cell will be lower than room pressure, and change as the room pressure fluctuates (not significant) during the measurement. Meanwhile the flow rate of CO_2 is measured by a flowmeter continuously. After the pressure in the cell is close to the room pressure, the gas and liquid stirrer are turned on to provide a sufficient renewal of the gas surface to make the availability of free amine possible. The stirrer speed is set at approximately 120 rpm. This causes a strong mixing of the liquid without formation of any turbulence.

Because the solution was vacuumed at 400 mbar before introducing CO_2 into the cell, the CO_2 partial pressure will be around 600 mbar after the introduction of CO_2. The big double gas stirrers at 120 rpm were expected to reduce the gas phase resistance [9].

3.3. Reagent and solution preparation

MDEA, MEA and PZ were obtained from Sigma Aldrich with a purity of respectively ≥ 99 %, ≥99 % and 90 %. All were used without any further treatment. The carbon dioxide gas was purchased from AGA Gas GmbH and has a purity of ≥ 99,995 mol%. Solutions were made using deionised water and an analytical balance (Mettler Toledo XS403S, accuracy ± 1 mg) in a flask. Products were weighed and the solutions were mixed with a magnetic stirrer on a stirring plate in the vacuum hood. Stirring was maintained until a clear solution was obtained.

3.4. Analysis clarification

As mentioned in the system description the temperature of the gas, liquid and metal are measured as well as the pressure inside the reactor and the gas flow. Temperatures are mainly measured to make sure the system remained stable during the experiment. It is important to mention is that the moment the system reached room pressure, that moment is considered to be the start of the gas flow measurements and therefore the time starts counting from that moment. The assumption has been made that during the prior time there is no CO_2 absorbed into the liquid. Thus all the CO_2 flow measured is considered to be contributing to the increase of the pressure till room pressure and that only. The goal is to calculate the overall mass transfer coefficient K_G in *m/s* from formula (1) as function of both the time and the loading on PZ. Therefore it's necessary to calculate the molar flux and the amount of moles CO_2 absorbed at any moment in the corresponding units.

The final step in the calculation is to determine the overall mass transfer coefficient in unit (*m/s*). The backpressure of CO_2 in the solution is assumed to be negligible. This means that $P_{CO2}{}^{*}$ in equation (1) is assumed to be zero. This assumption was made based on the loading values. It was measured in this work that the CO_2 loading was 0.06 mol CO_2 /mol amine for 4M MDEA + 0.05 M PZ solution after 50 min CO_2 absorption process in the stirred cell at 30 °C, and this loading is the maximum among the all measurements. The small loading for the long time (50 min) was mainly caused by the small gas-liquid contact area in the cell. Therefore the backpressure can be neglected for K_G calculation by equation (1).

4. Results and discussion

4.1. Influence of PZ concentration on CO_2 absorption of PZ in MDEA solutions

In order to see the influence of the concentration of PZ on the mixed amine solutions, measurements were done at 30°C at various concentrations of PZ and only PZ aq. solution. The corresponding progress of the K_G as function of the time, is presented in Figure 4. It can be seen from Figure 4 (a) that all K_G are non-linear decreasing curves as function of time. Considering that the total CO_2 loading in the solution is assumed negligible, the decrease could mean a saturation of PZ. With respect to the MDEA solution (black curve), there is slight decrease in K_G between

the beginning and at 50 min, the decrease in K_G was caused by the increase of CO_2 loading and consumption of MDEA, the slight decrease implies that the assumption of $P^*_{CO2}=0$ is acceptable. Known from kinetic measurements and literature [3, 6, 8], PZ reacts CO_2 much faster than MDEA, and thus the general increase of K_G seen between the different curves as function of the concentration confirms this.
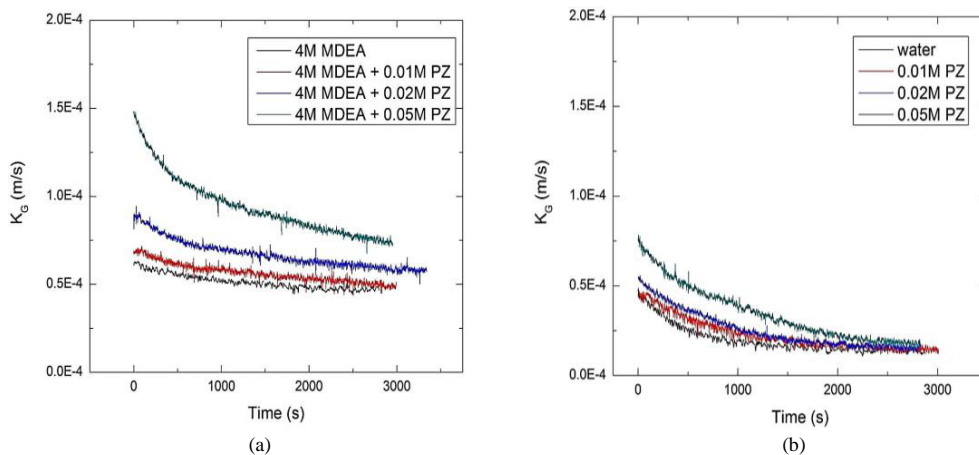

Figure 4. K_G is as function of the time at 30°C. (a) 4M MDEA with PZ at different concentrations; (b) Aqueous PZ solutions at different concentrations.

It is noted that at the end of the experiment, after 50 min, there is still a difference between the K_G for the mixed amine solutions and the aqueous MDEA. This implies that there could be a sort of regeneration reaction occurring that generates free PZ, the so called "activator mechanism" as described in section 2.3, that keeps the K_G higher than a solution without PZ. If there was only parallel reaction with CO_2 of PZ and MDEA, the K_G of the solution (PZ+MDEA) should as same as that of MDEA solution because of the depletion of PZ after 50 min reaction. The difference at the end with the MDEA curve increases with higher PZ concentrations. This is can be explained by the fact that a higher concentration of PZ forms a higher concentration of carbamate and thus the equilibrium of the carbamate reversion reaction will lean more to the right. Overall there is still a big decrease in K_G throughout the experiment indicating that this regeneration i.e. carbamate reversion is rather slow compared to carbamate formation.

A way to get a better insight in the behaviour of PZ is to measure its behaviour individually. Therefore the K_G of aqueous PZ solutions were measured at the same temperature (30°C) as the mixed amine solutions and using the same PZ concentrations in order to get a better comparison, as shown in Figure 4 (b). On first glance the trends of the different curves are in line with mixed amine solutions at 30°C. There is strong decrease in K_G at the beginning and in general a difference between the PZ curves and the water curve. However an important difference between the mixed amine solutions and the aqueous PZ solutions is at the end of the experiment. Here all the solutions end up at a K_G value which is nearly the same as the one for water. This indicates that at the end of the experiment the PZ is saturated with CO_2. The lack of offset at the end also indicates that there is no regeneration or carbamate reversion occurring. Having no real proton acceptor available in the solution makes PZ act as any other amine in CO_2 absorption.

4.2. Comparison of the K_G of PZ and MEA in mixed amine solutions with MDEA during CO_2 absorption

To check if PZ is a parallel reacting amine, a known parallel reacting amine, MEA [10], was used in mixed amine solutions for comparison. The progress of K_G is measured for mixed solutions of MDEA and MEA at the same concentrations as used before for MDEA + PZ solutions as shown in Figure 5.

Compared to the absorption trends of MDEA + PZ solutions at 30°C in Figure 4 (a), it is found from Figure 5 that the difference in K_G between the MDEA + MEA curves and the MDEA curve is less and the K_G value is also significantly less than the MDEA + PZ system at the level of a same concentration. MEA is known to be a fast

reacting amine with CO_2, especially compared to MDEA, but is still tenfold slower (comparing reaction rate constants) than PZ. Therefore the overall increase in K_G with higher MEA concentrations is lower than for PZ. The lack of strong drop in K_G of MDEA + PZ system in the beginning might also be explained by this. Another way to show there is a difference between PZ and MEA in mixed amine solutions with MDEA is the difference in K_G at the end of the experiment. Clearly the difference between the MDEA+MEA solutions and the aqueous MDEA solution is rather small. This indicates the fact that there is no reaction present in the MDEA+MEA solutions that sets MEA free to react with CO_2 whereas this probably does occur in the MDEA+PZ solutions.
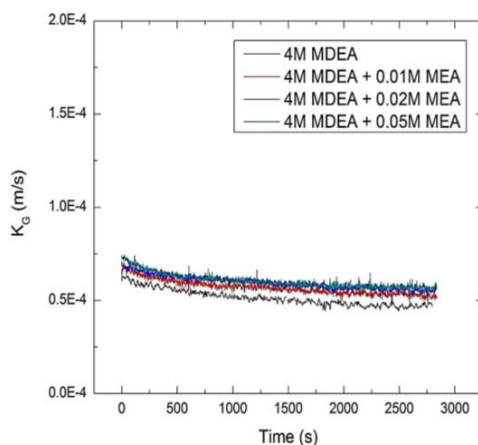

Figure 5. Progress of K_G of several MDEA + MEA solutions at different concentrations as function of the time at 30°C.

4.3. Investigation of the different systems as function of the relative loading of CO_2 on PZ

To find indications of depletion or regeneration of PZ, the same K_G are presented but as function of the relative loading of CO_2 on PZ instead of the time, see Figure 6. It must be kept in mind that the possible activator mechanism is that PZ can react twice with CO_2: first to form carbamate, secondly to form bicarbamate, then transfer CO_2 to MDEA by reaction (11) and assuming all absorbed CO_2 in MDEA should react with PZ first. Therefore, the relative loading is here defined by

$$\text{Relative loading} = \frac{\text{the amount of moles } CO_2 \text{ absorbed in solution}}{\text{moles of amine (e.g. PZ or MEA)}} \qquad (12)$$

This means assuming the carbamate formation occurs the fastest, compared to the hydration reaction with MDEA and the bicarbamate formation. At a relative loading of 0.5 all of the free PZ has reacted to form carbamate. The theoretical loading to know whether all the carbamate has reacted to bicarbamate is much more difficult since MDEA is the base for the bicarbamate formation and the influence of the hydration reaction will become more significant. It is hoped to find indications around a loading of 0.5 in the curves or just in general significant changes that might indicate something. It is important to remember if there is regeneration of PZ, i.e. 'activation' present, these indications might be different or shift to other regions in the curves.

Figure 6 shows K_G is a function of the relative loading at 30°C. The high values of the relative loading are attributed to CO_2 absorption in the solution (MDEA) and lower PZ concentration according to equation (12). It can be seen from Figure 6 (a) that after running the experiments for 50 minutes there is still a difference in K_G at the end of each experiment. This indicates that regeneration of PZ in reaction (11) is probably present in this time frame. Looking at the curve of 4M MDEA + 0.05M PZ there might be something happening around a loading of 0.5 because of a difference in slope after that value. This might mean that carbamate formation does mainly occur first before bicarbamate formation. With respect to the 4M MDEA + 0.02M PZ solution, there is a small change in slope around a loading of 2. This could possibly indicate that there has been a lot of carbamate and bicarbamate formation and

therefore the absorption rate might be afterwards controlled by the hydration reaction. Also the influence of regeneration might be bigger and therefore the difference between carbamate/bicarbamate formation and hydration may not be so clear to observe. However these are all assumptions, as was the goal of this investigation in this work. More clear observations definitely can be done from the aqueous PZ solutions in Figure 6 (b).
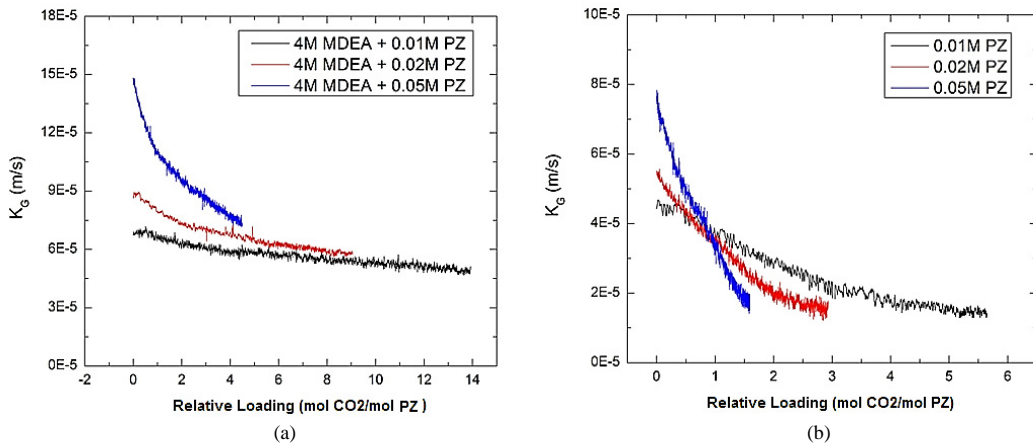

Figure 6. K_G progress as function of the relative loading at 30°C (a) mixtures of MDEA and PZ at different concentrations; (b) aqueous PZ solutions at different concentrations.

Figure 6 (b) shows that K_G is as function of the relative loading at 30°C. The high values of the relative loading in lower PZ concentrations (e.g. 0.01 M PZ) are because of the physically dissolved CO_2 in the solution and lower concentration of PZ. There are two clear observations that can be made from Figure 6 (b). First of all the curves all end up at approximately the same value for K_G at the end of the experiments. This indicates the depletion of PZ in the solutions due to the lack of MDEA and thus the lack of regeneration. The second observation is the course of the 0.02M and 0.05M PZ curves. Both of them drop under the 0.01M curve after the relative loading is around 1. This shows that at a higher concentration of PZ the reaction occurs much faster and reaches the end point faster as well, probably proving that regeneration is not present in only PZ solution, and thus again affirming the idea of PZ being a parallel reacting amine with regeneration when mixed with MDEA.
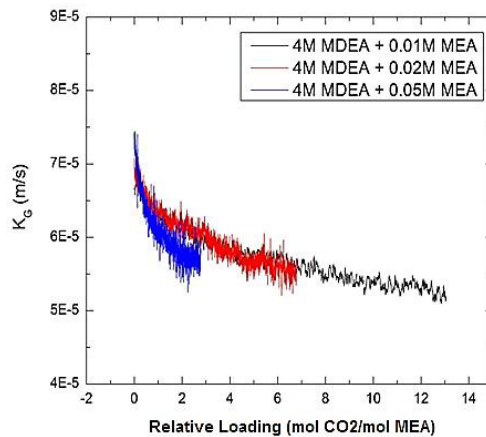

Figure 7. K_G progress of MDEA + MEA solutions at different MEA concentrations as function of the relative loading at 30°C.

Finally the MDEA + MEA solutions, as shown in Figure 7, were also presented as function of the relative loading to

find similarities between PZ and MEA indicating the parallel reagent idea. The behaviour of MEA shows some interesting phenomena. Despite being in the presence of 4M MDEA the graph shows similar trends with the aqueous PZ graph indicating that MDEA and MEA react in parallel in their mixed solution. The solutions with 0.02M and 0.05M MEA react faster (big decrease in the beginning) and the K_G curve drops under the 0.01M curve. This indicates the lack of regeneration and thus the presence of regeneration in the PZ solution system.

5. Conclusions

From the measurements, the CO_2 absorption rate in these mixed MDEA + PZ solutions is strongly influenced by the concentration of PZ. Higher concentrations of PZ in MDEA + PZ solution give a higher K_G value at the beginning of the experiments.

Regarding the behaviour of PZ, it is clear that PZ regeneration is present when mixed with MDEA in the long time scale of the experiments. In the aqueous PZ solutions it was clear that there was no such thing as regenerating PZ. Looking at the influence of adding PZ to MDEA solutions and comparing this with mixed MDEA + MEA solutions, it is noticeable that PZ has a significant effect on the absorption course throughout the experiments. On one side the addition enhances the gas absorption and on the other side it maintains the overall gas absorption rate to a moderate level compared to adding MEA. These indicate that PZ reacts parallel to MDEA, and PZ draws its CO_2 absorption qualities from its fast reaction kinetics and ability to regenerate in the presence of MDEA or any other strong base present in a sufficient concentration.

References

[1]   Ying, J.; Eimer, D. A., Determination and measurements of mass transfer kinetics of CO2 in concentrated aqueous monoethanolamine solutions by a stirred cell. *Industrial & Engineering Chemistry Research* **2013,** *52* (7), 2548-2559.

[2]   Octave, L., Fluid-Fluid Reactions: Kinetics. In *CHEMICAL REACTION ENGINEERING*, 3th ed.; Wiley India Pvt. Limited: 2006; pp 530-534.

[3]   Rinker, E. B.; Sami, S. A.; Sandall, O. C., Kinetics and modelling of carbon dioxide absorption into aqueous solutions of N-methyldiethanolamine. *Chemical Engineering Science* **1995,** *50* (5), 755-768.

[4]   Littel, R. J.; Swaaij, W. P. M. v.; Versteeg, G. F., Kinetics of Carbon Dioxide with tertiary Amines in aqueous solution. *AIChE Journal* **1990,** *36* (11), 1633-1640.

[5]   Versteeg, G. F.; Swaaij, W. P. M. v., On the kinetics between CO2 and alkanolamines both in aqueous and non-aqueous solutions II. Tertiary amines. *Chemical Engineering Science* **1988,** *43* (3), 587-591.

[6]   Bishnoi, S.; Rochelle, G. T., Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chemical Engineering Science* **2000,** *55* (22), 5531-5543.

[7]   Derks, P. W. J.; Kleingeld, T.; van Aken, C.; Hogendoorn, J. A.; Versteeg, G. F., Kinetics of absorption of carbon dioxide in aqueous piperazine solutions. *Chemical Engineering Science* **2006,** *61* (20), 6837-6854.

[8]   Samanta, A.; Bandyopadhyay, S. S., Kinetics and modeling of carbon dioxide absorption into aqueous solutions of piperazine. *Chemical Engineering Science* **2007,** *62* (24), 7312-7319.

[9]   Ying, J.; Eimer, D. A., A study of mass transfer kinetics of carbon dioxide in (monoethanolamine+ water) by stirred cell. *Energy Procedia* **2013,** *37*, 2180-2187.

[10] Versteeg, G.; Kuipers, J.; Van Beckum, F.; Van Swaaij, W., Mass transfer with complex reversible chemical reactions—II. Parallel reversible chemical reactions. *Chemical engineering science* **1990,** *45* (1), 183-197.