

## Solubility of CO<sub>2</sub> in Piperazine (PZ) Activated Aqueous N-Methyldiethanolamine (MDEA) Solvent under High Pressure

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### ABSTRACT

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In this research work, piperazine (PZ) was used to activate the performance of aqueous N-methyldiethanolamine (MDEA) solvent for the capturing of CO<sub>2</sub>. The solubility experiments were conducted at a temperature and pressure ranges of 303.15 to 333.15 K, and 2 to 50 bar, respectively. The solubility of CO<sub>2</sub> was investigated in terms of CO<sub>2</sub> loading capacity as the ratio between the quantities of moles of CO<sub>2</sub> absorbed to the total amount of moles of solvent used. It was observed that CO<sub>2</sub> loading has increased with increasing the partial pressure of CO<sub>2</sub> while increasing the temperature has a negative effect as the loading capacity has decreased with increase in system's temperature. The CO<sub>2</sub> loading capacity of the solvent investigated in this research work has demonstrated better performance as compared to conventionally used alkanolamines solvents.

#### Keywords:

Absorption, carbon dioxide solubility,  
N-methyldiethanolamine, piperazine

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## 1. Introduction

In the recent development of the industrial world, the use of the different kind of fuels resources are explored on large scale to meet the energy requirements. Those fuels sources get much importance in their utilization on industrial scale which are less pollutant to the environment. Among all utilized energy resources, fossil fuel based power plants are the largest stationary source for energy production. About 88 % of the world energy consumption is based on fossil fuels such as coal, natural gas, and oil. Fossil fuels on their burning liberate the oxides of nitrogen, sulfur, and carbon (NO<sub>2</sub>, SO<sub>2</sub>, CO, CO<sub>2</sub>). These gases are collectively termed as the sour gases, which further contribute in the formation of greenhouse gases (GHGs). Among all the sour gases, CO<sub>2</sub> contribute the major part in the greenhouse gases (GHGs). The CO<sub>2</sub> almost comprises 78.6 % of all the sour gases present in the greenhouse gas, which is termed as a major greenhouse gas [1]. The worldwide emissions of CO<sub>2</sub> from fossil fuels is estimated to rise up to 40.2 GT by the year 2030 [2]. With the increasing demand of energy from fossil fuels, environment, and its ecosystems are getting polluted by the emission of greenhouse gases mainly due to CO<sub>2</sub> [3]. The emission of CO<sub>2</sub> related to use of

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energy was estimated to increase from 30.2 billion metric tons to 43.2 billion metric tons in 2035 [2]. Associated with the continuous emission of CO<sub>2</sub>, the life on the earth is effecting irrecoverably by means of global warming, melting of the polar ice cap, glaciers, rising sea level and devastating weather patterns. In order to minimize the effects of CO<sub>2</sub> on the open atmosphere as a sour gas, there is need to capture CO<sub>2</sub> from the flue gases liberated from the industrial processes. Different kind of CO<sub>2</sub> capturing techniques has been reported in the literature such as adsorption [4], cryogenics separation [5], membrane separation [6] and chemical absorption [7].

Chemical absorption technique using aqueous solution of alkanolamines is one of the mostly utilized, well established and economical approach towards separation of CO<sub>2</sub> from flue gases [8, 9]. In USA about 95 % separation process are based on the amine scrubbing process in which the aqueous alkanolamines solvents are utilized as chemical solvent [10]. The commercially utilized alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), diglycolamine (DGA), diisopropanolamine (DIPA), 2-amino-2-methyl-1-propanol (AMP) [11]. Despite the fact that the alkanolamines are widely utilized solvents in the absorption technique to capture CO<sub>2</sub> gas possesses some drawbacks such as limited loading capacity, high vapor loss, corrosive nature of the amines and high thermal and oxidative degradation limits their applications on the industrial scale for CO<sub>2</sub> capture [12]. Primary (MEA) and secondary amines (DEA) are mostly utilized solvents on the industrial scale but their stoichiometric study proposed their limited loading capacity up to 0.5 mole of CO<sub>2</sub> per mole of amine [10]. In the recent times, tertiary amine (MDEA) has become much important amine due to its some favorable characteristics of high CO<sub>2</sub> equilibrium loading capacity (up to 1.0 mole of CO<sub>2</sub> per mol of amine), high thermal stability, low vapor losses and low enthalpy of reaction with CO<sub>2</sub>, which is much important property in regeneration process [13]. Besides these several advantages over other amines, the absorption rate of CO<sub>2</sub> in aqueous MDEA is quite slow, it does not react directly with CO<sub>2</sub>, since it just promotes CO<sub>2</sub> hydrolysis to form carbonate [14]. In order to enhance the absorption rate of tertiary amine (MDEA), different type of activators such as piperazine (PZ), monoethanolamine (MEA) and diethanolamine (DEA) are used [14]. Recently, PZ was used with MDEA as an activator in the activated MDEA process of BASF to absorb CO<sub>2</sub> more efficiently [15]. This favorable application of MDEA+PZ system might be due to the higher reaction rate of PZ and lower heat of reaction of MDEA with CO<sub>2</sub>, resulting in overall higher absorption rate and lower energy requirements for regeneration process throughout CO<sub>2</sub> capture process. Therefore, aqueous solution of MDEA+PZ system could be utilized as an alternative solvent in CO<sub>2</sub> removal systems of chemical absorption.

In this research study the solubility of CO<sub>2</sub> in the aqueous solution of piperazine activated MDEA was investigated at three different temperatures (303.15, 313.15, and 333.15) K and pressure ranges of 2 to 50 bar. The experimental results were compared with the literature data for the suitability of the utilized solvents.

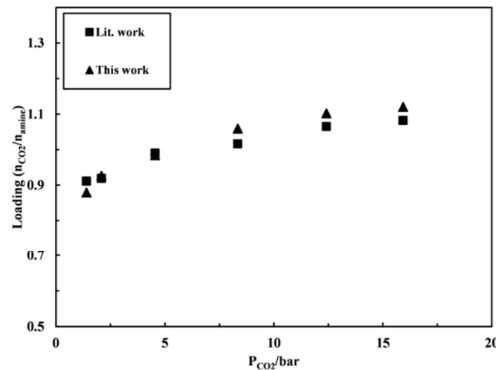
## 2. Materials

The chemicals used in this research work were N- methyldiethanolamine (MDEA) with a purity of 98% mol %, piperazine (PZ) 99%, were purchased from Merck Sdn. Bhd. All the chemicals were reagent grade and used as received without any further purification. The carbon dioxide gas (CO<sub>2</sub>) purity (≥99.99%) and nitrogen (N<sub>2</sub>) with purity (≥99.99 %) were purchased from Gas walkers (Malaysia). The Millipore quality of water was used for sample preparation. The details description of the purchased chemical and gases is tabulated in Table 1. The concentration of MDEA and PZ were kept constant at 30 wt. % and 3 wt. % respectively. All the samples were freshly prepared and retained for 24 h to ensure complete miscibility.

**Table 1**

Description of chemicals and gases used in this work

Chemical Name	Purity (%)	Molar Mass (g)	Source
MDEA	98%	119.163	Merck
PZ	99%	86.136	Merck
Millipore water	≥ 99%	18.01	-
Carbon dioxide	≥99.99%	44.01	Gas walkers
Nitrogen	≥99.99%	28.01	Gas walkers



**Fig. 1.** CO<sub>2</sub> loading of 30 wt% aqueous MDEA at 313.15 K

### 3. Math Ands

A SOLTEQ BP-22 high pressure solubility cell was used to measure the solubility of CO<sub>2</sub> in piperazine (PZ) activated aqueous N-methyldiethanolamine (MDEA). The high pressure solubility cells comprise of two equilibrium cells (EC) and one mixing vessel (MV). Before starting the experiments, the equilibrium cells were cleaned with the acetone and water to remove the residue left in the cells. After cleaning N<sub>2</sub> gas was purged into both the equilibrium cells so as to avoid any contamination and then the CO<sub>2</sub> was pressurized into mixing vessel. In order to measure the pressure inside the vessels, a digital pressure indicator (Druck DPI 150) was utilized with an accuracy of ± 1.0 kPa for a pressure range of 0 to 10,000 kPa. Thermostatic water baths were utilized to maintain the temperature of pressure vessels within ± 0.1°C accuracy range, while the internal temperature of pressure vessels was recorded using digital thermometer (YOKOGAWA 7653) with ± 0.01°C precision. Vacuum is created inside equilibrium cells to remove any vapors or gases left inside the cells. A sample of 5 mL volume of aqueous solution of piperazine activated MDEA was fed using metering pump in equilibrium cell (EC1) and 7 ml aqueous solution in equilibrium cell (EC2). The temperature of the cell is then adjusted to the required value and pressure is recorded. At this point, solvent exists under its own vapor pressure P<sub>v</sub>. The CO<sub>2</sub> gas is then transferred from mixing vessel to equilibrium cells with the stirrer on.

The moles of CO<sub>2</sub> transferred were calculated using pressure drop, volume of mixing vessel and temperature by the using equation (1).

$$n_{CO_2} = \frac{V_T}{RT} \left( \frac{P_1}{z_1} - \frac{P_2}{z_2} \right) \quad (1)$$

where  $VT$  (ml) represents the volume of the mixing vessel,  $z_1$  and  $z_2$  are the compressibility factors for pressure's  $P_1$  and  $P_2$ ,  $R$  is the real gas constant and  $T_a$  is the ambient temperature. The compressibility factors can be calculated using Peng Robinson equation of state (EOS). After almost 3-4 hrs, when there is no change in pressure drop in the equilibrium cell, then it was assumed that the thermodynamic equilibrium has been achieved. Pressure value recorded at this time is termed as equilibrium pressure ( $PCO_2$ ). And the equilibrium pressure was calculated by the following equation (2).

$$P_{CO_2} = P_T - P_v \quad (2)$$

where  $PT$  (MPa) and  $PV$  (MPa) represents the total pressure and vapor pressure of solutions respectively. The remaining moles of  $CO_2$  in the gas phase  $n_g$  were calculated by equilibrium pressure ( $PCO_2$ ), temperature and overhead gas volume by using equation (3).

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{z_{CO_2} RT} \quad (3)$$

So, the effective number of moles of  $CO_2$  absorbed into the solvent can be calculated using the following equation (4)

$$n_{CO_2}^l = n_{CO_2} - n_{CO_2}^g \quad (4)$$

The solubility was then calculated as mol of  $CO_2$  per mol of amine by using the following equation (5).

$$\alpha = \frac{n_{CO_2}^l}{n_{MDEA+PZ}} \quad (5)$$

where  $n_{MDEA+PZ}$  represents the moles of MDEA+PZ solvent in the liquid and calculated by the following equation (6)

$$n_{MDEA+PZ} = \frac{\rho V_l m}{M} \quad (6)$$

where  $\rho$  ( $g/cm^3$ ) is the density of the aqueous solution of MDEA, PZ solution,  $V_l$  (ml) is the liquid volume in the cell,  $m$  is the mass fraction and  $M$  is the molecular weight of the corresponding solvent

#### 4. Results and Discussion

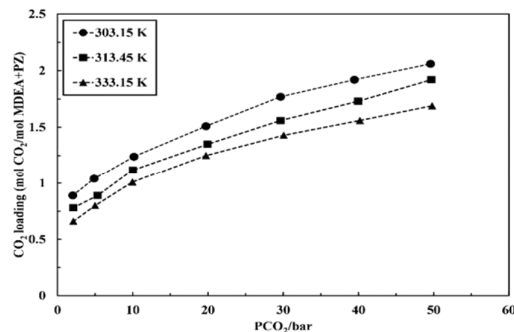
Before investigating the solubility of  $CO_2$  in piperazine activated aqueous MDEA solution. The solubility of  $CO_2$  in 30 wt% aqueous MDEA solution was investigated for the calibration of the high pressure solubility cell. The temperature was selected as 313.15 K and the results were compared with the literature data in the graphical form. The compared results showed in Figure 1 confirmed the validity of the equipment and reproducibility of the work. It was shown a good agreement between the experimental and literature data.

The solubility of the CO<sub>2</sub> in the aqueous solution of piperazine activated solvent were investigated at three different temperatures and various pressures. The high pressure range of 2-50 bar was selected for the solubility of CO<sub>2</sub> in the aqueous solution. It was investigated from the experimental results that the CO<sub>2</sub> in aqueous solution is effected by changing the temperature and pressure conditions. The solubility of CO<sub>2</sub> is determined in terms of loading capacity of the solvent, which is the ratio between the numbers of moles of CO<sub>2</sub> capture in a solvent to the number of moles of utilized solvents. The experimental high pressure solubility data is tabulated in Table 2.

**Table 2**  
 CO<sub>2</sub> solubility of aqueous solution of piperazine activated MDEA

T = 303.15 K		T = 313.15 K		T = 333.15 K	
P (bar)	αCO <sub>2</sub>	P (bar)	αCO <sub>2</sub>	P (bar)	αCO <sub>2</sub>
		30 wt. % MDEA+3 wt. % PZ			
2.0	0.89	2.11	0.78	2.11	0.66
4.87	1.04	5.33	0.89	4.99	0.80
1.016	1.24	10.02	1.12	9.96	1.01
19.73	1.51	19.94	1.35	19.73	1.25
29.64	1.77	29.65	1.56	30.06	1.43
39.45	1.92	39.95	1.73	40.18	1.56
49.57	2.06	49.67	1.92	49.78	1.69

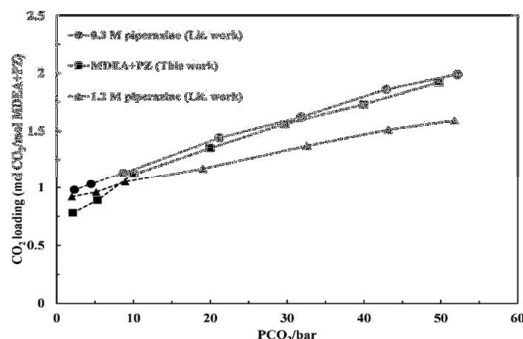
The results showed that the loading capacity of the solvent increased with the increase in the partial pressure of the CO<sub>2</sub> gas, and the loading capacity was tend to decrease with the increase in the temperature of the system. The trend in the loading capacity with the increase in the temperature and the pressure was shown in Figs. 2 and 3.



**Fig. 2.** Effect of temperature on the solubility of CO<sub>2</sub> in aqueous solution of piperazine (PZ) activated MDEA

From figures 2 it was observed that there is marginal decrease in the loading capacity of the solvent with the increase in the temperature of the system from 303.15 to 333.15 K. It was concluded that the increased pressure have a negative effect on the absorption process of capturing gases. At increased pressure the less number of molecules of gases are diffused in a solvent. In a result of the less diffusion of the gas molecules in a chemical solvent the loading capacity of the solvent reduces. From Figure 3, it was observed that, the increased in the partial pressure of the system from 2 bar to 50 bar the loading capacity of the solvents was drastically increased. At increased pressure the higher number of molecules of the CO<sub>2</sub> gas are diffused in the aqueous solution of piperazine activated MDEA solvent. In a result of increased pressure the loading capacity of the aqueous solution increases. It was also concluded that the increased

pressure is in the favor of the absorption process using chemical solvents. The experimental results were compared with the loading capacity of the solvents reported in literature. In Figure 3, the aqueous solution of piperazine activated MDEA solvent showed better solubility in terms of loading capacity.



**Fig. 3.** Comparison of the solubility data of this work with the literature data (Lit. work [16])

## 5. Conclusion

In this study, the solubility of CO<sub>2</sub> in aqueous solution of piperazine activated MDEA solvent was investigated. The solubility experiments were carried out between the temperature and pressure ranges of 303.15-333.15 K and 2-50 bar respectively. The temperature and the pressure condition effect the solubility of the CO<sub>2</sub> in terms of loading capacity. The loading capacity of the solvent increases with increase in the partial pressure of the CO<sub>2</sub> gas. And the loading capacity showed a negative trend with the increase in the temperature of the system. The high pressure solubility results of the aqueous solution of piperazine activated MDEA solvent were compared with the solvents reported in literature. The loading capacity of the aqueous solution of piperazine activated MDEA solvent was higher at same temperature and pressure conditions. The high loading capacity of the investigated solvents makes it as good potential solvent to capture CO<sub>2</sub> in absorption process. Thus it can be utilized as an effective solvent for CO<sub>2</sub> capture at high pressure.

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