

# Measurement of Carbon dioxide (CO<sub>2</sub>) Absorptive Capacity in a Secondary Amine based Aqueous Mixture: Experimental and Modelling Study

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Over the past 30 years, the increasing global temperature due to industrial emissions of greenhouse gases is considered as an immense threat to our environment which needs to be addressed. However, the number of industries has been increasing significantly over the past few decades, leading to the ever increasing emissions and worsening the air pollution situation. Carbon dioxide (CO<sub>2</sub>) is one of the major greenhouse gas contributing to the rapid climate changes and therefore, collective efforts are required to control its emissions. In this study, 20 experiments were conducted to study the solubility of CO<sub>2</sub> in the mixture of two solvents diethanolamine and dimethylformamide (DEA and DMF). Design expert (DOE) software was used to design the solubility experiments in order to optimize the number of experiments and to develop a correlation between various variables such as temperature, pressure and solution concentration. The objective of this work was to measure the CO<sub>2</sub> loading capacity in aqueous solutions of DEA and DMF at various operating conditions of temperature, pressure and solution concentrations. It was observed that by increasing the weight percent of DEA in the aqueous solution, solubility tends to increase. The maximum value of 0.7454 mol/mol of CO<sub>2</sub> solubility was achieved at pressure of 8 bar and at temperature of 313.15 K which is found to be higher than the monoethanolamine (MEA). In addition to that important design property such as density was also measured at the wide range of temperature and concentrations. The new solubility and density data can be a useful contribution to design a better process to mitigate CO<sub>2</sub> from various industrial streams.

## 1. Introduction

The world is facing ever increasing threat from the environmental changes occurring around us and this is consequently linked to the global warming (Shirleen et al 2020). This is due to the rapid increase of greenhouse gases which is eventually caused by the huge industrialization and urbanization. Immense efforts are required to lay down the policies to control this rapid increase. One of the important factor is the rise in CO<sub>2</sub> concentration in the environment and therefore decarbonisation is quite essential to neutralize the ever increasing environmental challenges (Hosein et al 2017). Therefore, the process to capture CO<sub>2</sub> from various gaseous streams become very important and this is considered to be one of the effective approach to minimize the greenhouse gases (Vida and Patricia 2019). The objective of CO<sub>2</sub> capture from industrial streams is to capture it and then convert it to some useful products which can be economical beneficial as well. Additionally, this is the only possible way to use the fossil fuels for a longer period of time along with renewable energy to meet Global energy requirements without compromising over environment (Renjie and Aage 2009).

There are several technologies available to capture CO<sub>2</sub> from various gaseous streams especially from power generation plants run by fossil fuel. However, chemical absorption using aqueous solutions is among the mature technologies to capture CO<sub>2</sub> without effecting the plants footprints (Joao et al. 2015). The most fundamental amine based aqueous solutions which are being employed includes Monoethanolamin (MEA), di-ethanolamine (DEA), Monodiethanolamine (MDEA) and their mixtures (Muhammad et al 2009). The selection of the appropriate solvent is quite critical process due to some drawbacks such as thermal degradation, corrosion and large amount of energy requirements for regeneration of the CO<sub>2</sub> rich amine solvent (Murshid et al. 2018). It is

desirable to apply the most reactive amine such as primary amine (MEA) for effective CO<sub>2</sub> capture. However, it would not be desirable when it comes to the regeneration of the CO<sub>2</sub> rich primary amine due to the formation of stable carbamates and consequently increasing the high heat of regeneration (Joao et al. 2015). To overcome the earlier mentioned shortcomings of amines, immense work has been reported on the solubility of CO<sub>2</sub> in the blended mixture of amines (Li and Rochelle 2013). The addition of activators such as piperazine (PZ) to overcome low CO<sub>2</sub> loadings of conventional amines is also reported in literature (Shota et al 2013). Joao (2015) reported the solubility of various amines and concluded that DEA perform better in terms of CO<sub>2</sub> loading (0.4902 mol/mol) compared to the MEA (0.409 mol/mol) which is a bench mark solvent used globally. Among the secondary amines, DEA showed good affection for CO<sub>2</sub> and its widely used to capture CO<sub>2</sub>. Therefore in this work a novel mixture of DEA (secondary amine) with dimethylformamide (DMF) is used to analyse their CO<sub>2</sub> loading capacity. DMF is an organic compound with lower viscosity than water with good affection for CO<sub>2</sub>. Duran et al. 2001 and Michael et al. 2012 reported the solubility of CO<sub>2</sub> in DMF which showed promising results. Despite of being good potential solvent, not much literature has been found on the solubility of CO<sub>2</sub> in the aqueous blend of DEA and DMF. Therefore, the objective of this work to combine both DEA and DMF to prepare different blended solution to measure their physical properties such as density and their CO<sub>2</sub> loading capacity at various temperature and pressure conditions. The properties were measured and correlated using suitable correlations. These properties and solubility data is important in designing and modelling the CO<sub>2</sub> absorption system.

## 2. Methodology

### 2.1 Chemical and solution preparations

All the chemicals and gases including DEA, DMF, CO<sub>2</sub> and N<sub>2</sub> were purchased from sigma Aldrich and Oman gas supplies, Oman respectively. The chemicals were used without any further purification. The total solvent concentration of 30 wt % was used and the amount of DEA was varied from 5 to 25 wt% as shown in Table 2. The physical properties such as density was measured over the range of temperature from 298.15 K to 333.15 K. The solubility of the CO<sub>2</sub> in the blended aqueous solutions of DEA and DMF was measured from the pressure of 4 bar to 8 bar and at three industrially important temperatures 303.15, 313.15 and 333.15 K. All the solubility experiments were designed using the design of experiment (DOE) software and the correlation was developed to understand the relationship of various variables on the CO<sub>2</sub> loading in the aqueous solutions.

### 2.2 Density Measurement

The density of the aqueous solutions of DEA and DMF was measured using Anton Paar DMA4500 digital density meter which can measure density up to 3 g·cm<sup>-3</sup> and temperature of 373.15 K with measuring accuracy of 5 x 10<sup>-5</sup> g·cm<sup>-3</sup>. The measuring tube was cleaned with distilled water and acetone before injecting 1 ml solution. Once the desired temperature was achieved, the density meter was activated to measure the density.

### 2.3 Solubility Measurements

Gas Solubility cell was used to measure the CO<sub>2</sub> solubility for the selected solvents in this work is shown in Figure. 1. The apparatus consists mainly of a CO<sub>2</sub> cell and an equilibrium cell (EC) of volume 156 mL and 70 mL, respectively. The temperature of the cells was regulated by water bath supplied with two heaters (HAAKE D1, A512. Germany).

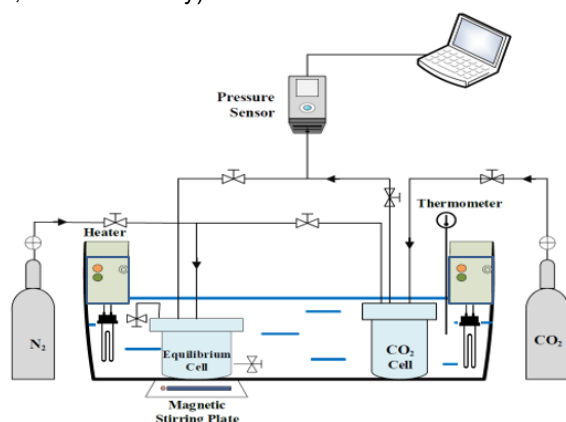


Figure 1: Schematic Diagram of the Gas Solubility Cell

Before each experiment, both cells were washed with distilled water and acetone and then purged with pure Nitrogen gas to remove any unwanted remaining gases or chemical traces. After the desired temperature was reached, 6 mL of the solvent was injected into EC followed by the injection of the CO<sub>2</sub> from CO<sub>2</sub> cell at the desired pressure. The pressure of the system was measured using digital pressure sensor (nVision Reference Recorder) with a precision of 0.025%. Magnetic stirring plate (Stuart scientific) located under the EC was used to increase the rate of mass transfer between the gas and liquid phases, and to decrease the time of reaching equilibrium. The pressure of the cell was observed to decrease with time, and it gets stabilized in about 4 to 6 hours. After the equilibrium was achieved, the solubility of CO<sub>2</sub> ( $\alpha$ ) in the solvent was calculated in terms of moles of CO<sub>2</sub> absorbed per moles of solvent using the following Eq(1). The further details of the solubility measurement procedure can be found in our previously published work (Pishro et al. 2021).

$$\alpha = \frac{n_{CO_2}^l}{n_{solvent}} \quad (1)$$

## 2.4 Calibration of the Equipment

All the equipment used in this work were calibrated in order to validate the experimental work. The density meter and the solubility cell both were calibrated using distilled water and aqueous solution (30 %) MEA respectively. The measured values of this work for both density and CO<sub>2</sub> solubility were compared with literature as shown in the Table 1. The smaller values of average absolute deviation (%AAD) shows a good agreement between measured and literature values. The AAD was calculated using the following Eq(2).

$$\%AAD = \frac{100}{n} * \sum_{i=1}^{i=n} \left| \frac{x_{exp} - x_{Lit}}{x_{exp}} \right| \quad (2)$$

The density of the aqueous solutions was measured over the wide range of temperature ranging from 298.15 to 333.15 K. All the density measurements were made at atmospheric pressure due to the incompressible nature of the liquid solutions. The density data is useful in mass transfer and gas solubility calculations which is consequently essential to design the gas liquid absorber.

Table 1: Calibration of Density and Solubility Cell Equipment

T/K	Density ( $\rho$ ) g·cm <sup>-3</sup>			Solubility ( $\alpha$ mol/mol) 30 wt% MEA solution			
	This Work	Literature*	% AAD	P/kPa	This Work	Literature**	% AAD
303.15	0.9957	0.9956		5.115	0.652	0.675	
308.15	0.9942	0.9940		8.838	0.718	0.728	
313.15	0.9925	0.9922	0.018	12.712	0.739	0.763	1.82
323.15	0.9882	0.9880		15.945	0.759	0.772	
333.15	0.9833	0.9832		19.876	0.785	0.806	

\*Al-Ghawas et al. 1989

\*\*Shen et al. 1992

## 3. Results and discussion

The measured density data of aqueous solution (DEA+DMF) is presented in the Table 3 as a function of temperature and DEA concentration. Results show that density values increase with increase in concentration of DEA in the aqueous solution at any fixed temperature. The density values decreased as the temperature was increased from 298.15 K to 333.15 K for all studied concentration of the aqueous solution. The maximum range of the density data measured were in between 1.0185– 1.0304 g·cm<sup>-3</sup> at 298.15 K while the lowest density was recorded at 333.15 K for 5 wt% DEA. In addition to that, the density tend to decrease by increasing temperature which could be due to the volume expansion of the aqueous solution at higher temperatures (Garg et al 2017). The solubility of CO<sub>2</sub> was measured in five different solutions (DEA + DMF) where the concentration of the solution was kept 30 wt% which is the standard concentration of amine solution used in industry. The solubility experiments were designed using design of experiment (DOE) software as shown in Table 2 along with the measured CO<sub>2</sub> solubility data. The solubility of CO<sub>2</sub> is presented in Table 2 as a function of pressure, temperature and solvent concentration. It can be observed from that the highest CO<sub>2</sub> solubility was recorded for runs which have low temperature, high concentration of DEA, and high pressure. The highest solubility of 0.7454 mol/mol of CO<sub>2</sub> was recorded at DEA concentration of 25 wt%, at a pressure of 8 bar and at a middle range temperature 313.15 K as shown in Figure 3. The lowest value of solubility of 0.1809 mol/mol was recorded at

low concentration of DEA (5 wt %), low pressure (4 bar) and high temperature (333.15 K). These findings show that high temperatures do not favor the gas solubility. This could be due to the increase in kinetic energy of the gas molecules at higher temperatures causing the weakening of intermolecular bond and helping gas molecules to escape from the solution (Yan et al 2022). The higher temperatures are usually used in gas strippers to release CO<sub>2</sub> from the CO<sub>2</sub> rich amine solution. These findings are also depicted in the Figure 3 where the effect of various variables such as pressure and temperature on CO<sub>2</sub> loading is presented.

Table 2: Solubility of CO<sub>2</sub> in aqueous solutions of DEA and DMF; DOE designed experiments

DEA wt%	DMF wt%	T(K)	Desired pressure (bar)	Recorded P <sub>1</sub> (bar)	α (mol of CO <sub>2</sub> /mole of solvent)
5	25	333.15	4	4.047	0.1809
5	25	303.15	4	4.065	0.2172
5	25	313.15	6	6.278	0.2732
5	25	313.15	6	6.384	0.2747
5	25	333.15	8	8.013	0.4299
10	20	303.15	8	8.141	0.5139
10	20	303.15	8	8.230	0.4519
15	15	333.15	4	4.123	0.2721
15	15	313.15	4	4.029	0.3405
15	15	333.15	6	6.064	0.3896
15	15	313.15	6	6.371	0.4602
15	15	313.15	6	6.195	0.4935
15	15	313.15	6	6.186	0.4469
15	15	333.15	8	8.142	0.4994
25	5	333.15	4	4.022	0.3699
25	5	313.15	4	4.223	0.4411
25	5	303.15	6	6.104	0.6277
25	5	303.15	6	6.117	0.663
25	5	333.15	8	8.085	0.6663
25	5	313.15	8	8.079	0.7454

In addition, the effect of each parameter (T, P, C) on the CO<sub>2</sub> loading was examined by Analysis of Variance (ANOVA), which was obtained from DoE. This technique is useful in determining the significance of each parameter on the CO<sub>2</sub> loading and it gives a better explanation of the experimental results statistically. The following correlation was obtained resulted from ANOVA analysis;

$$\alpha = 0.436995 + -0.035788 * A + 0.120157 * B + 0.142349 * C + 0.00967738 * AB + -0.0340105 * AC + 0.0215035 * BC \quad (3)$$

Where A, B and C are temperature, pressure, and mass concentration, respectively. The plot in Figure 4 shows the comparison of the experimental and the correlated data of CO<sub>2</sub> loading. There is a good agreement between measured CO<sub>2</sub> loading values and predicted from the correlation. The reported coefficient of determination (R<sup>2</sup>) was 0.989 which indicates the adequacy of the regression model on representing the experimental data.

Table 3: Density of aqueous solutions of DEA and DMF

T/K	DEA 5 wt%	DEA 10 wt%	DEA 15 wt%	DEA 25 wt%
298.15	1.0185	1.0238	1.0275	1.0304
303.15	1.0173	1.0227	1.0262	1.0295
308.15	1.0165	1.0215	1.0251	1.0283
313.15	1.0157	1.0204	1.0239	1.0274
323.15	1.0148	1.0193	1.0227	1.0264
333.15	1.0139	1.0181	1.0218	1.0258

The solubility of CO<sub>2</sub> in the aqueous solution (DEA + DMF) was compared with literature. The highest solubility of 0.7454 mol/mol of CO<sub>2</sub> was measured for 30 wt% aqueous solution (DEA + DMF) at 8 bar pressure and temperature of 313.15 K which is 3.5 % higher than the solubility of CO<sub>2</sub> in MEA (0.72 mol/mol) at the same pressure, temperature and solution concentration (Shen et al 1992). These results shows that the addition of DMF into DEA aqueous solution has improved the solubility of CO<sub>2</sub> which can be useful to overcome the drawbacks associated with the application of primary amines such as high regeneration energy consumption.

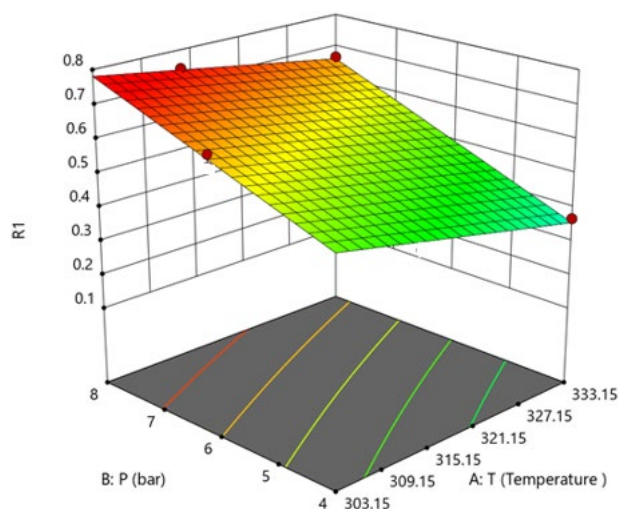


Figure 3: Effect of temperature, pressure and concentration of CO<sub>2</sub> solubility in aqueous solution (DEA + DMF)

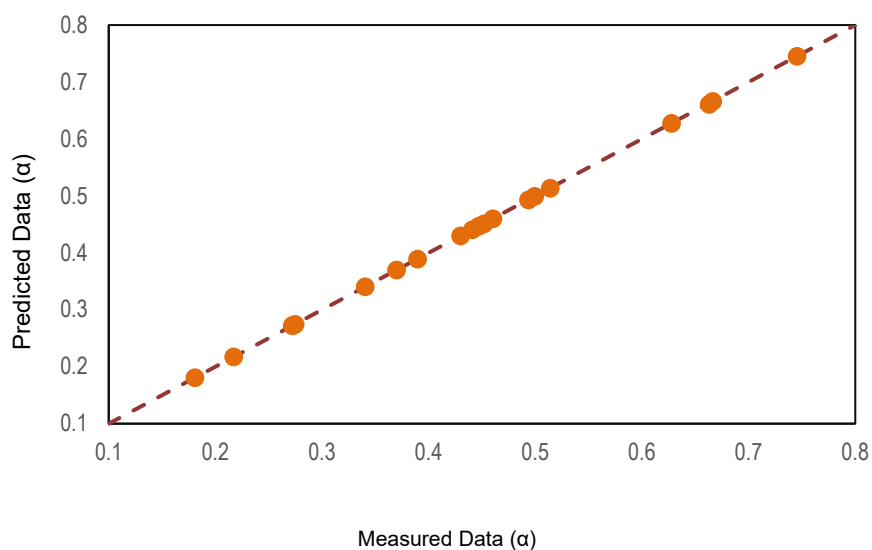


Figure 4: Comparison between measured and predicted CO<sub>2</sub> solubility in aqueous solution (DEA + DMF)

#### 4. Conclusion

The new aqueous solutions of DEA and DMF were prepared and their density and CO<sub>2</sub> solubility was measured at a wide range of temperature and pressure. The density of the aqueous solution decreases linearly at all studied concentrations which is align with the data reported in literature. This density data can be useful in mass transfer and modelling of gas absorber system. In addition to that, the addition DMF in to DEA aqueous solution has shown great prospects as the solubility increased by 3.5 % compared to the conventional primary amine (MEA) under the same operating conditions of temperature, pressure and concentration. This new findings can open new doors to apply alternate solvents to capture CO<sub>2</sub> from various gaseous streams with improved and better properties compared to conventional amines.

## Acknowledgments

The authors would like to thank Sultan Qaboos University for providing the financial and technical assistance to accomplish this work.

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