CO_2 Solubility In Aqueous Solution Of

2-Amino-2ethyl-1,3-propanediol (AEPD) and

Piperazine (Pz)

By

Muhammad Safwan bin Atan

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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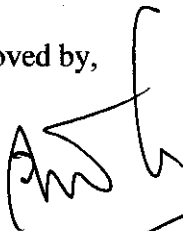
CERTIFICATION OF APPROVAL

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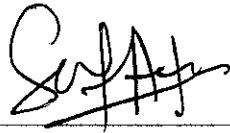(CHEMICAL ENGINEERING)

Approved by,

_____

(Assoc. Prof. Dr Azmi Bustam)

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TRONOH, PERAK

SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MUHAMMAD SAFWAN BIN ATAN)

ABSTRACT

Most of the power plants are using conventional alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA) and N-Methyldiethanolamine (MDEA) to adsorb CO_2 for CCS.[2-6] However, these conventional alkanolamine had some disadvantages and not efficient.[9] With the emerging research of sterically hindered amines (SHA)[7] such as -amino-2ethyl-1,3-propanediol (AEPD) and the usage of activator such as Piperazine (Pz)[8] being introduced to the industry, the alkanolamine used for CCS can be change and the process can be more efficient. Main objective of this project is to measure the CO_2 solubility in aqueous solution of AEPD and Pz Solution. The effects of initial pressure and concentration of aqueous solution of AEPD and Pz towards CO_2 solubility are also studied. The solubility experiment is conducted using High Pressure Gas Solubility Cell. For this experiment, concentration of AEPD used are 1.0 mol, 2.0 mol and 3.0 mol. Each of the different concentration of AEPD will be mixed with Pz with concentration of 0.1 mol, 0.2 mol and 0.3 mol. the mixture of the AEPD and Pz will be in volume ratio of 3:1. All of the experiments are conducted in constant temperature which is 30°C. Different initial pressure of 5 bar2, 10 bars, and 15 bars are also used for each sample. The solubility of CO_2 is determined in terms of CO_2 loading per mole of amine used. Three of the highest CO_2 solubility achieved is 2.4714, 2.3989 and 2.1560 at amine mixture concentration of 1.1 mole, 1.2 mole and 1.3 mole respectively at initial pressure of 15 bars. Meanwhile, three of the lowest CO_2 solubility achieved is 0.3964, 0.4280 and 0.4421 at amine mixture concentration of 3.1 mole, 2.1 mole and 3.3 mole at initial pressure of 5 bars. In addition, as the initial pressure for adsorption process is increased, the rate of CO_2 adsorption will increase and the time taken for the adsorption process to reach equilibrium will be faster. As the concentration of AEPD increases, the CO_2 loading will decrease. However, the trend of CO_2 loading for different concentration of Pz could not be determine as there is no significant changes and trend when the Pz concentration is varied.

ACKNOWLEDGEMENT

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ABBREVIATION

Green House Gas	GHG
Carbon Dioxide	CO_2
Intergovernmental Panel Climate Change	IPPC
Carbon Capture and Storage	CCS
Monoethanolamine	MEA
Diethanolamine	DEA
N-Methyldiethanolamine	MDEA
Sterically Hindered Amines	SHA
Piperazine	Pz
2-amino-2-methyl-1-propanol	AMP
2-amino-2-ethyl-1,3-propanediol	AEPD
2-amino-2-hydroxymethyl-1,3-propanediol	AHPD
Hydroxyl	OH

CHAPTER 1: INTRODUCTION

1.1   BACKGROUND OF STUDY

Nowadays, greenhouse gas (GHG) emissions have become one of the most important environmental issues around the world. Among these GHG, carbon dioxide (CO_2) is the largest contributor of the GHG because of its large amount that present in the atmosphere. The anthropogenic CO_2 from open burning and also industrial work such as coal fired power plant is known to be part of the cause towards large amount of CO_2 emissions. According to Intergovernmental Panel on Climate Change (IPCC) prediction, the worldwide energy demands will increase by 50% thus the energy related CO_2 emissions will rise by 52% in 2030.[1] Recently, carbon capture and sequestration (CCS) has been identified as a potential method of controlling greenhouse gas emission. Most of the current technology of CCS is using chemical adsorbent such as amine to adsorb CO_2 and prevent it from being released towards the atmosphere. Most of the power plants are using conventional alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA) and N-Methyldiethanolamine (MDEA) to adsorb CO_2 for CCS.[2-6] However, these conventional alkanolamine had some disadvantages and not efficient.[9] With the emerging research of sterically hindered amines (SHA)[7] and the usage of activator such as Piperazine (Pz)[8] being introduced to the industry, the alkanolamine used for CCS can be change and the process can be more efficient.

In order to improve the efficiency of the CCS system, various researches had been done to study and investigate the best alkanolamine to be used for the process.[10-17] Researcher had put a lot of effort in order to investigate the effectiveness of using SHA which was first introduced by Guldo and David.[7] Ever since, researchers had discover the importance of SHA and starts to develop more experimental data on SHA.

1.2 PROBLEM STATEMENT

Current data for SHA are very limited and need to be develops in order to optimize the process. The data that are usually collected for CCS system purpose are solid solubility, oxidation, thermal degradation, and corrosion and CO_2 solubility. The present work focus on the solubility data of the alkanolamine. As example, data for 2-amino-2-methyl-1-propanol (AMP), a simple hindrance form MEA; is widely available.[10-12] However, data for 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2ethyl-1,3-propanediol (AEPD), and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD); 3 SHA which are derived from AMP; is very limited and not established yet.[9] There are only data for kinetics of adsorption of CO_2 and CO_2 solubility into AEPD. There is also no data available for CO_2 solubility in AEPD and Pz solution.

1.3 OBJECTIVE

1. To measure the CO_2 Solubility in aqueous solution of AEPD and Pz Solution

2. To investigate the effects of initial pressure and concentration of aqueous solution of AEPD and Pz towards CO2 Solubility

1.4 FEASIBILITY OF THE PROJECT

The time period for the project is 2 semesters, which is approximately 9 month to complete the project. There are also budget given to the student to purchase chemicals and each student is given RM 500 each. The apparatus for the experiment are also available in block 3, UTP. Overall, based on the time period, budget and experimental apparatus, it is feasible to do the project.

CHAPTER 2: LITERATURE REVIEW

2.1   CARBON CAPTURE AND SEQUESTRATION (CCS)

According to the Intergovernmental Panel on Climate Change (IPCC), to avoid dramatic consequences of global warming, global greenhouse gas (GHG) emissions must be reduced by 50 to 80 percent by 2050.[1] According to Bellona (multi-disciplinary international environmental NGO), the strategy for reducing global CO2-emission must be a combination of (1) increased energy efficiency, (2) more renewable energy production, and (3) a wide implementation of CCS. CCS is a vital part of the solution to addressing global climate change. It is the process of dramatically reducing CO2 emissions from power generation and returning it underground. Today, most of the world's economy runs on fossil fuel energy. When carbon-based fossil fuels like coal, oil and natural gas are used to fuel conventional electricity generating plants, CO_2 will be produced and emitted into the atmosphere. Huge amount of CO_2 being release to the atmosphere when the power plant generate energy. In order to capture the CO_2 from being release to the atmosphere, most of the power plants install adsorption and stripping system in their process. Current technology used amines as the adsorbent to adsorb CO_2 and prevent CO_2 emission to the environment.

2.2   AVAILABLE CO₂ ADSORBENT

Various alkanolamines are used to adsorb CO_2 from the process such as monoethanolamine (MEA), diethanolamine (DEA) and N-Methyldiethanolamine (MDEA). Conventional alkanolamine used for CCS had its disadvantages; whether it is a primary amine (MEA), secondary amine (DEA) or tertiary amine (MDEA). In order to choose the best amine for the process, several factors can be considered which are the adsorption capacity, reaction kinetics, and regeneration potential.[2] Thus, it is important to search for an alkanolamine that suit all the criteria so that the CO_2 adsorption process will be optimized. Amine is actually an organic compounds and functional groups that contain a basic nitrogen atom with a lone pair.[18] Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group.[18] MEA is a

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primary alkanolamine, DEA is a secondary alkanolamine, while MDEA is a tertiary alkanolamine. These three alkanolamine are widely used in the industry for CO_2 adsorption purpose. However, due to some disadvantage when using these amine, there are needs to find another alternative to improve the efficiency of the process.[2]

(a)   (b)   (c)
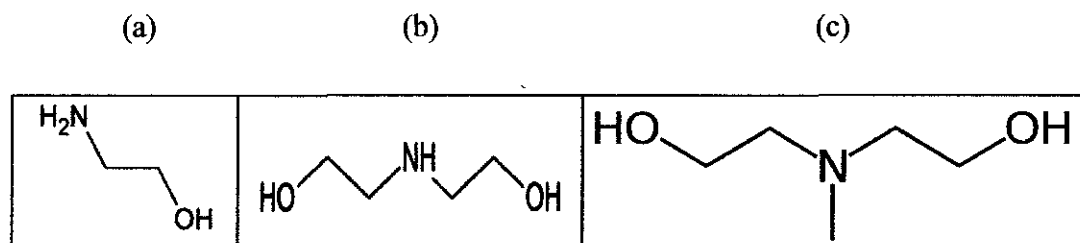
Figure 2.1 Molecular structure of (a)MEA, (b)DEA, and (c)MDEA

Primary and secondary amines have almost the same properties, which both having fast reactivity due to the formation of carbamates.[9] However, the solvent generation cost is very high and both of the alkanolamines have relatively low CO_2 loading compared to the other alkanolamines.[9] Meanwhile, tertiary amine have a low reactivity with CO_2 due to formation of bicarbonates by CO_2 hydrolysis. On the bright sight, tertiary have low solvent regeneration cost and high CO_2 loading capacity.[9]

Mixed amines are also used as the adsorbent for CO_2 adsorption. Mixtures of amines are generally mixtures of MDEA and DEA or MEA and are used to enhance CO2 removal by MDEA.[21] Such mixtures are referred to as MDEA-based amines with DEA or MEA as the secondary amine. The secondary amine generally comprises less than 20% of the total amine on a molar basis. At lower concentrations of MEA and DEA, the overall amine concentration can be as high as 55 wt % without the implementation of exotic metal equipment system. Amine mixtures are particularly useful for lower pressure applications since the MDEA becomes less capable of picking up sufficient CO2 to meet pipeline specifications at lower pressures. At higher pressures, amine mixtures appear to have little or no advantage over MDEA.[21]

Researchers had tried to improve the alkanolamine so that the system can be optimized. The discovery of sterically hindered alkanolamines (SHA) gives more choices for the solvent in the system.[7]

2.3   STERICALLY HINDERED AMINE (SHA)

SHA refers to a new type of amine which is derived from the conventional amine by addition of other functional group such as methyl and hydroxyl. The addition of these functional groups will create a steric effect which can improve the adsorption capability of the amine. Steric effect refers to the fact that each atom within a molecule occupies a certain amount of spaces.[19] Steric hindrance refers to a situation where the size of a group within the molecule are preventing the chemical reaction that are suppose to happen in related smaller molecule.

It is a very useful tool and as the reactivity pattern can be exploited and unwanted side reaction can be avoided. SHA have high carbon adsorption capacity, adsorption rates, selectivity and also degradation resistance. SHA will form unstable carbamates due to the hindrance of the bulky group adjacent to the amino group. [2,9] SHA is actually combining both the quality of each amine advantage which is fast reactivity from primary or secondary amine and also high adsorption capacity and low solvent generation cost from tertiary amine.

Structure		Description
H_2N, CH_2—C—CH_3, HO, CH_3	AMP	2-amino-2-methyl-1-propanol Simple hindrance form of MEA Addition of hydroxyl group
H_2N, CH_2—C—CH_2—OH, HO, CH_3	AMPD	2-amino-2-methyl-1,3-propanediol Derive from AMP Addition of hydroxyl group
H_2N, CH_2—C—CH_2—OH, HO, H_2C—OH	AHPD	2-amino-2-hydroxymethyl-1,3-propanediol Derive from AMPD Addition of hydroxyl group
H_2N, CH_2—C—CH_2—OH, HO, H_2C—CH_3	AEPD	2-amino-2ethyl-1,3-propanediol Derive from AMPD Addition of methyl group

Figure 2.2 Sterical Hindrance Amine derivations

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Figure 2.2 shows the example of SHA which are 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2ethyl-1,3-propanediol (AEPD), and 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD). AMP is a simple hindrance from MEA, which one Hydrogen H in the MEA structure is substituted with Hydroxyl (OH). Then, the AMP can be exploited to produce another three alkanolamines which are AMPD, AEPD, and AHPD.[2,9] One H is substituted with OH in AMP to produce AMPD. Next, another H from AMPD is substituted with OH to produce AHPD. Another H from AMPD is substituted with CH3 to produce the last alkanolamine which is AEPD.

2.4   2-AMINO-2ETHYL-1,3-PROPANEDIOL (AEPD)
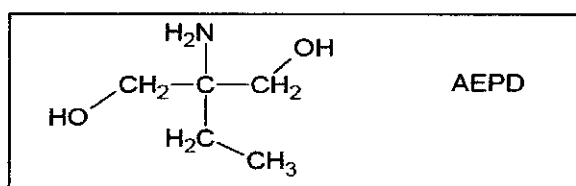
Figure 2.3 Molecular structure of AEPD

As mentioned in the problem statement, the chosen SHA for this project will be AEPD. AEPD is the derivation of AMPD, which is addition of one methyl group into the AMPD structure. The formula for AEPD is $C_5H_{13}NO_2$ and figure 2.3 shows its molecular structure. The density of AEPD is 1.099 and the molecular weight is 119.16. AEPD is soluble in water and it can cause irritation if get in contact with skin or eye. In order to adsorb CO_2, AEPD will react with CO_2 to adsorb the CO_2 from its initial gas stream. The reaction between aqueous AEPD and CO_2 can represented as follows:

$$CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^- [2.1]$$
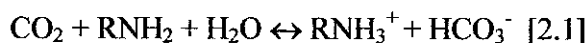
In addition, the reaction of CO_2 with primary and secondary alkanolamine can be described by zwitterions equation. Zwitterion refers to is a neutral molecule with a positive and a negative electrical charge at different locations within that molecule. Zwitterions are sometimes also called inner salts.[22]

$$CO_2 + RNH_2 \leftrightarrow RNH_2^+COO^- [2.2]$$

$$RNH_2^+COO^- + B \rightarrow RNHCOO^- + BH^+ [2.3]$$

Based on reaction [3], B can be the amine, water or the hydroxyl ion. These three substances can contribute to deprotonation of the zwitterions in the aqueous solution:

$$RNH_2^+COO^- + RNH_2 \rightarrow RNHCOO^- + RNH_3^+ \quad [2.4]$$

$$RNH_2^+COO^- + H_2O \rightarrow RNHCOO^- + H_3O^- \quad [2.5]$$

$$RNH_2^+COO^- + OH^- \rightarrow RNHCOO^- + H_2O \quad [2.6]$$

Table 2.1 Solubility data for aqueous AEPD

Type of amine	Concentration	Pressure	Temperature	Solubility α= Mole CO_2/mole Amine
Aqueous AEPD [3]	10 mass% AEPD	1-3000 kPa	313.151	Highest : 1.289 Lowest : 0.632
			323.15	Highest : 1.189 Lowest : 0.664 Highest : 1.108 Lowest : 0.179
	30 mass% AEPD	1-3000 kPa	333.15	Highest : 1.026 Lowest : 0.202

2.5   PIPERAZINE (PZ)

Several studies had been done in order to improve the quality of the CO_2 adsorbent. The addition of a primary or secondary (alkanol) amine to an aqueous MDEA solution has found widespread application in the removal and absorption of carbon dioxide. The principle of such an aqueous blend of a so-called 'activator' with a tertiary amine is based on the relatively high rate of reaction of CO2 with the primary or secondary alkanolamine combined with the low heat of reaction of CO2 with the tertiary alkanolamine, which leads to higher rates of absorption in the absorber column and lower heats of regeneration in the stripper section. In this project, piperazine will be used as the activator in the AEPD solution.
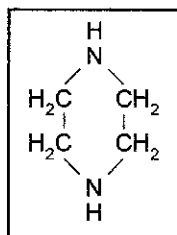
Figure 2.4 Molecular structure of Piperazine

Based on the research done by Sanjay Bishnoi and Gary T. Rochelle, aqueous piperazine has two reaction zones. At low solution loading, the dominant reaction products are piperazine carbamate and protonated piperazine. At high loading, the dominant reaction product is protonated piperazine carbamate. Although piperazine dicarbamate is present, it is never the dominant reaction product. Pz is an effective promoter for CO_2 removal from gas stream mainly because the rate constant is an order of magnitude higher than primary amines such as MEA and other primary amine while the first carbamate stability constant is comparable. Figure 2.5 shows the molecular structures of piperazine species.

Table 2.2 Rate Constant comparison between amine

Amine	Rate Constant at 25°C	Source
Piperazine	53,700	Bishnoi and Rochelle (2000)
Ethylenediamine	15,000	Sharma (1965)
Monoethanolamine	7,000	Hikita et al. (1979)
Morpholine	20,000	Sharma (1965)
Diethanolamine	1,200	Sada et al. (1976)
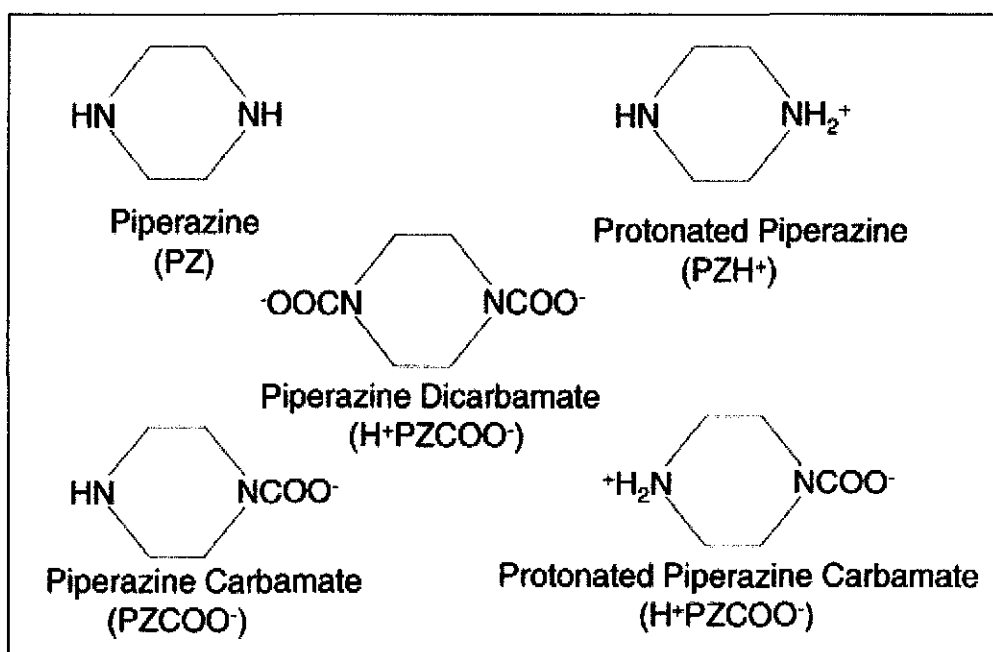
Figure 2.5 Molecular structure of piperazine species

CHAPTER 3: METHODOLOGY

3.1 RESEARCH METHODOLOGY
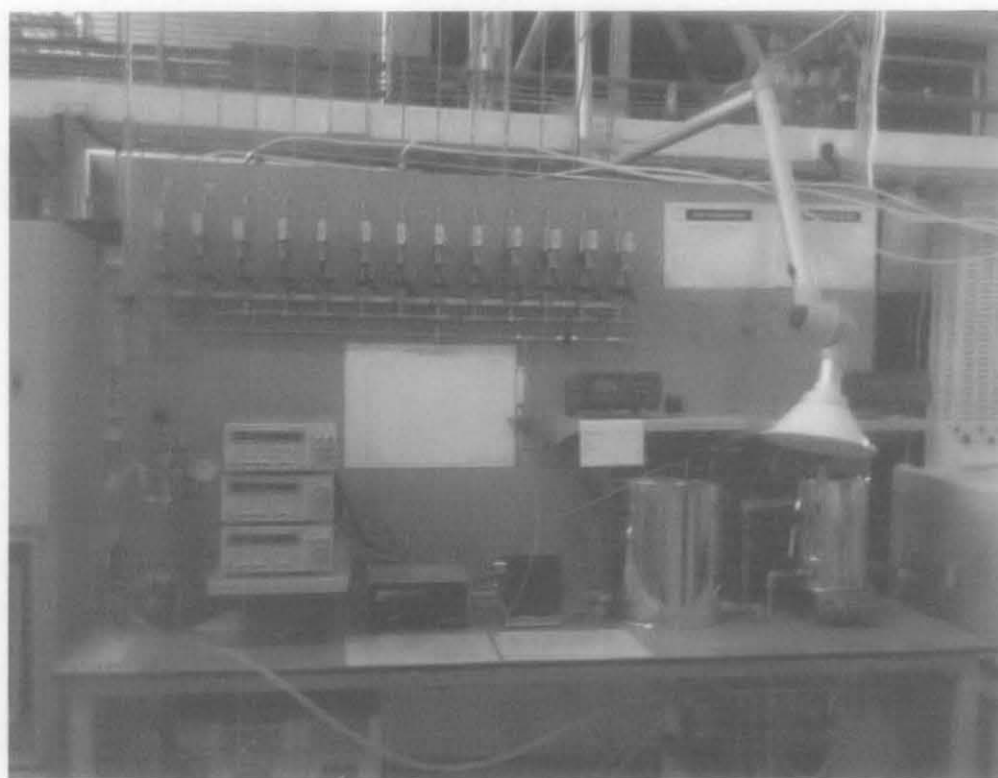
Figure 3.1 High Pressure Gas Solubility Cell

Figure 3.1 shows the equipment used to determine the solubility of CO_2 in AEPD and Pz mixture. There are 2 phases in conducting this experiment which are preparation of the amine to be used, and solubility determination.

3.1.1 Preparation of the amine

For this experiment, concentration of AEPD used are 1.0 mol, 2.0 mol and 3.0 mol. Each of the different concentration of AEPD will be mixed with Pz with concentration of 0.1 mol, 0.2 mol and 0.3 mol. the mixture of the AEPD and Pz will be in volume ratio of 3:1. In order to prepare the solution, the AEPD and Pz will be diluted to achieve the desired concentration. The calculations are as follows:

$$Molarity = \frac{Number\ of\ Moles\ x\ 1000}{Volume(ml)}$$

$$Number\ of\ moles = \frac{Mass}{Molecular\ Weight}$$

Table 3.1 Mass of AEPD and Pz to be diluted

Type of Amine	Concentration	Volumetric Flask Used	Mass to be diluted
AEPD	1.0	500 ml	59.6 g
Mw : 119.2	2.0	500 ml	119.6 g
	3.0	500 ml	179.25 g
Pz	0.1	100 ml	0.8614 g
Mw : 86.14	0.2	100 ml	2.5842 g
	0.3	100 ml	4.307 g

Next, the amines are mixed together with volume ratio of 3:1 and the density of the mixtures is calculated. Volume for each mixture is 80 ml, thus, 60 ml of AEPD and 20 ml of Pz will be mixed. The Refractive index for each mixture is also determined.

Table 3.2 Density of AEPD and Pz mixture

Mixture (mol)		Weight (g)				Density (g/ml)
AEPD	**Pz**	**1**	**2**	**3**	**Average**	
1.0	0.1	22.1	22.15	22.1	22.11	2.7645
1.0	0.2	22.24	22.17	21.97	22.12	2.7658
1.0	0.3	22.14	21.94	22.30	22.12	2.7658
2.0	0.1	22.07	22.19	22.33	22.19	2.7745
2.0	0.2	22.30	22.23	22.12	22.21	2.7770
2.0	0.3	22.11	22.20	22.40	22.23	2.7795
3.0	0.1	22.25	22.04	22.35	22.21	2.7766
3.0	0.2	22.37	22.28	22.04	22.23	2.7787
3.0	0.3	22.30	22.23	22.30	22.27	2.7838

Table 3.3 Density of AEPD and Pz mixture

Mixture (mol)		Refractive Index			
AEPD	**Pz**	**1**	**2**	**3**	**Average**
1.0	0.1	1.34476	1.34476	1.34476	1.34476
1.0	0.2	1.34474	1.34475	1.34476	1.34475
1.0	0.3	1.34477	1.34473	1.34476	1.34475
2.0	0.1	1.35747	1.35759	1.35726	1.35744
2.0	0.2	1.35731	1.35735	1.35652	1.35706
2.0	0.3	1.35624	1.35790	1.35755	1.35723
3.0	0.1	1.36104	1.36899	1.36665	1.36556
3.0	0.2	1.36104	1.36871	1.37000	1.36658
3.0	0.3	1.36304	1.36765	1.36871	1.36647

3.1.2 Solubility Determination

The solubility of CO_2 is determined according to several conditions which are temperature at $30°C$, and pressure at 5 bars, 10 bars and 15 bars. Equipment used for determination of CO_2 solubility is high pressure gas solubility cell. This equipment consist of a gas mixing vessel and a equilibrium cell, each emerged in a heating jacket. Other supporting component of this equipment include the magnetic stirrer, circulation pumps, vacuum pump, thermostat heating bath, liquid degassing unit, mass flow controllers, pressure indicator and temperature indicator. High accuracy pressure sensors and platinum RTD sensors are used for high accuracy pressure and temperature measurements.

Procedure:

1. Both gas mixing vessel and equilibrium cell are immersed in circulating water bath inside individual heating jacket which are connected to a thermostat heating bath. The temperature is set to $30°C$ and maintain throughout the experiment.

2. Both gas mixing vessel and equilibrium cell are evacuated using turbo molecular vacuum pump.

3. CO_2 is charged into the gas mixing vessel until the pressure reach slightly above 5 bars. A gas booster is used to pressurize the gas into the gas mixing vessel.

4. The pressure in the gas mixing vessel is recorded.

5. The valve connecting the gas mixing vessel and equilibrium cell are opened until the pressure of both cells is the same and stable. The valve is then closed and the pressure in the gas mixing cell is recorded.

6. Liquid is the introduced to the equilibrium cell using a liquid feed pump.

7. Magnetic stirrer is turned on. This will agitate the liquid to contact with the gas mixture.

8. The gas component will dissolve in liquid and the pressure will start to drop. Once the pressure is stable the pressure is recorded as the solubility process has reached steady state.

3.2 PROJECT TIMELINE

Final Year Project 1

No	Detail Work	1	2	3	4	5	6	7	Mid-semester break	8	9	10	11	12	13	14
1	Selection of Project Topic	■	■													
2	Preliminary Research Work		■	■	■											
3	Submission of Extended Proposal Defence						●									
4	Proposal Defence									■						
5	Project work continues											■	■			
6	Submission of Interim Draft Report														●	
10	Submission of Interim Report															●

Table 3.4 FYP 1 Project Timeline

The important key milestones of this semester project are submission of Submission of extended proposal defence, proposal defence and Interim Report.

Final Year Project 2

No	Detail Work	1	2	3	4	5	6	7	Mid-Semester Break	8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■									
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■				
4	Pre-EDX											●					
5	Submission of Draft Report												●				
6	Submission of Dissertation (soft bound)													●			
7	Submission of Technical Paper													●			
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

Table 3.5 FYP 2 Project Timeline

The Key milestone for FYP 2 will be performing the experimental work and achieve the solubility data for CO_2 in AEPD and Pz solution and to submit the project dissertation at the end of week 15.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 RESULTS

The results were obtained from CO_2 solubility experiment using the equipment as discussed earlier. From the equipment, the pressure drop during each experiment can be determined and the CO_2 solubility can be calculated based on the pressure drop.

4.1.1 Pressure drop for each sample

Table 4.1 Results from Solubility Experiment

Pressure	Mixture (mol)		P_{1A} (bar)	P_{2A} (bar)	P_{2B} (bar)
	AEPD	Pz			
5 bar	1.0	0.1	5.59	5.43	3.69
	1.0	0.2	5.44	5.33	3.65
	1.0	0.3	5.32	5.17	3.75
	2.0	0.1	5.30	5.20	2.83
	2.0	0.2	5.30	5.19	2.38
	2.0	0.3	5.46	5.35	2.53
	3.0	0.1	5.36	5.25	1.96
	3.0	0.2	5.38	5.26	1.63
	3.0	0.3	5.34	5.22	1.57
10 bar	1.0	0.1	10.61	10.38	8.53
	1.0	0.2	10.33	10.09	8.45
	1.0	0.3	10.28	10.04	8.39
	2.0	0.1	10.27	10.02	7.42
	2.0	0.2	10.31	10.07	6.90
	2.0	0.3	10.47	10.23	7.09
	3.0	0.1	10.41	10.16	6.42
	3.0	0.2	10.35	10.11	5.97
	3.0	0.3	10.43	10.18	6.25
15 bar	1.0	0.1	15.45	15.09	12.67
	1.0	0.2	15.44	15.06	13.33
	1.0	0.3	15.42	15.05	12.98
	2.0	0.1	15.41	15.04	12.35
	2.0	0.2	15.38	14.99	12.24
	2.0	0.3	15.45	15.07	12.13
	3.0	0.1	15.40	15.05	12.27
	3.0	0.2	15.31	14.94	11.23
	3.0	0.3	15.35	14.98	10.76

P_{1A} = Initial Pressure in the Gas Mixing Cell

P_{2A} = Final Pressure in the Gas Mixing Cell

P_{2B} = Final Pressure in the Equilibrium Cell

4.1.2   Solubility of CO_2 in AEPD and Pz solution

The solubility of CO_2 in AEPD and Pz solution is calculated in terms of CO_2 loading per mole of amine. The calculations to obtain the CO_2 are as follows.

<u>Amount of CO_2 transferred into the equilibrium cell</u>

$$\text{Pressure Difference in the Gas Mixing Cell} = P_{1A} - P_{2A} = \Delta P$$

$$\Delta P = \frac{nRT}{V}$$

Volume   = 3 L

R   = 0.08314

T   = 303 K

Thus,

$$n = \frac{V\Delta P}{RT}$$

n = number of mole transferred into equilibrium cell

<u>Amount of CO_2 that is left after adsorption</u>

$$\text{Final Pressure in the Equilibrium Cell} = P_2B$$

$$P_{2B} = \frac{nRT}{V}$$

Volume   = 0.042 L

R   = 0.08314

T   = 303 K

Thus,

$$n = \frac{VP_{2B}}{RT}$$

n = number of mole CO_2 left after adsorption

Amount of CO_2 adsorbed during adsorption process

= Number of mole transferred into equilibrium cell - number of mole CO_2 left after adsorption

Table 4.2 CO_2 loading calculated from the pressure drop

Initial Pressure	Mixture (mole)		Pressure (bar)		Mol of CO_2 transferred	Mol of CO_2 left	Mol of amine	CO_2 loading
	AEPD	Pz	ΔP	P_{2B}				
5 bar	1	0.1	0.16	3.69	0.0191	0.0062	0.0088	1.4661
	1	0.2	0.11	3.65	0.0131	0.0061	0.0096	0.7307
	1	0.3	0.15	3.75	0.0179	0.0063	0.0104	1.1165
	2	0.1	0.1	2.83	0.0119	0.0047	0.0168	0.4280
	2	0.2	0.11	2.38	0.0131	0.0040	0.0176	0.5188
	2	0.3	0.11	2.53	0.0131	0.0042	0.0184	0.4827
	3	0.1	0.11	1.96	0.0131	0.0033	0.0248	0.3964
	3	0.2	0.12	1.63	0.0143	0.0027	0.0256	0.4521
	3	0.3	0.12	1.57	0.0143	0.0026	0.0264	0.4422
10 bar	1	0.1	0.23	8.53	0.0274	0.0142	0.0088	1.4965
	1	0.2	0.24	8.45	0.0286	0.0141	0.0096	1.5097
	1	0.3	0.24	8.39	0.0286	0.0140	0.0104	1.4032
	2	0.1	0.25	7.42	0.0298	0.0124	0.0168	1.0358
	2	0.2	0.24	6.9	0.0286	0.0115	0.0176	0.9703
	2	0.3	0.24	7.09	0.0286	0.0118	0.0184	0.9109
	3	0.1	0.25	6.42	0.0298	0.0107	0.0248	0.7689
	3	0.2	0.24	5.97	0.0286	0.0100	0.0256	0.7276
	3	0.3	0.25	6.25	0.0298	0.0104	0.0264	0.7330
15 bar	1	0.1	0.36	12.67	0.0429	0.0211	0.0088	2.4714
	1	0.2	0.38	13.33	0.0453	0.0222	0.0096	2.3989
	1	0.3	0.37	12.98	0.0441	0.0216	0.0104	2.1560
	2	0.1	0.37	12.35	0.0441	0.0206	0.0168	1.3972
	2	0.2	0.39	12.24	0.0464	0.0204	0.0176	1.4794
	2	0.3	0.38	12.13	0.0453	0.0202	0.0184	1.3603
	3	0.1	0.35	12.27	0.0417	0.0205	0.0248	0.8558
	3	0.2	0.37	11.23	0.0441	0.0187	0.0256	0.9898
	3	0.3	0.37	10.76	0.0441	0.0179	0.0264	0.9895

4.2 DISCUSSION

Based on the results from the experiment, there are several points that can be discussed to increase the understanding on the experiment result and to meet the objective that had been set.
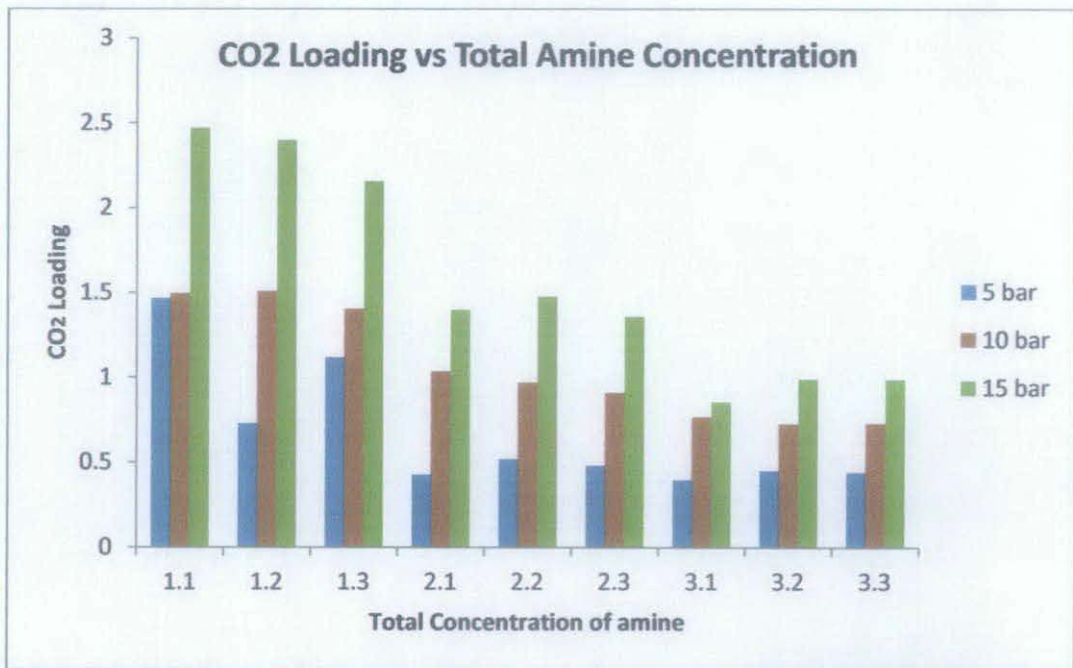
4.2.1 CO$_2$ Loading Trend

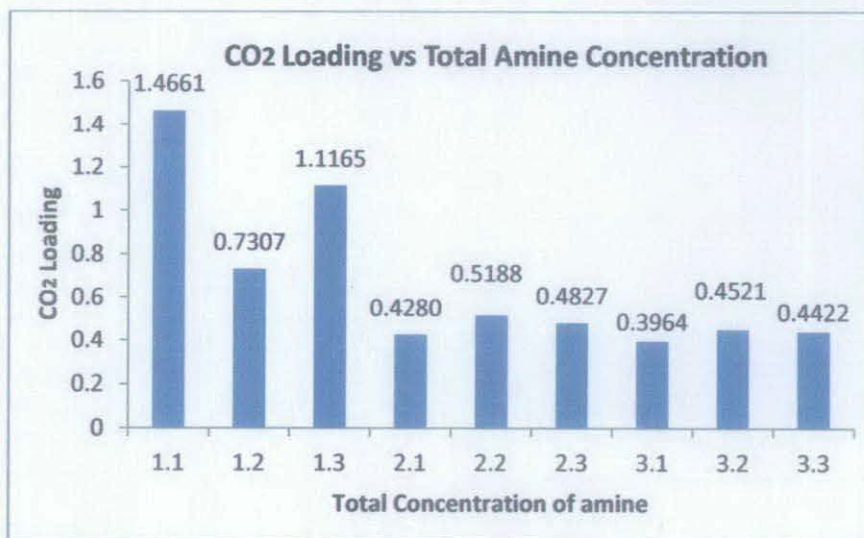*Figure 4.1 CO$_2$ Loading vs Total Amine Concentration at 5, 10 and 15 bar*

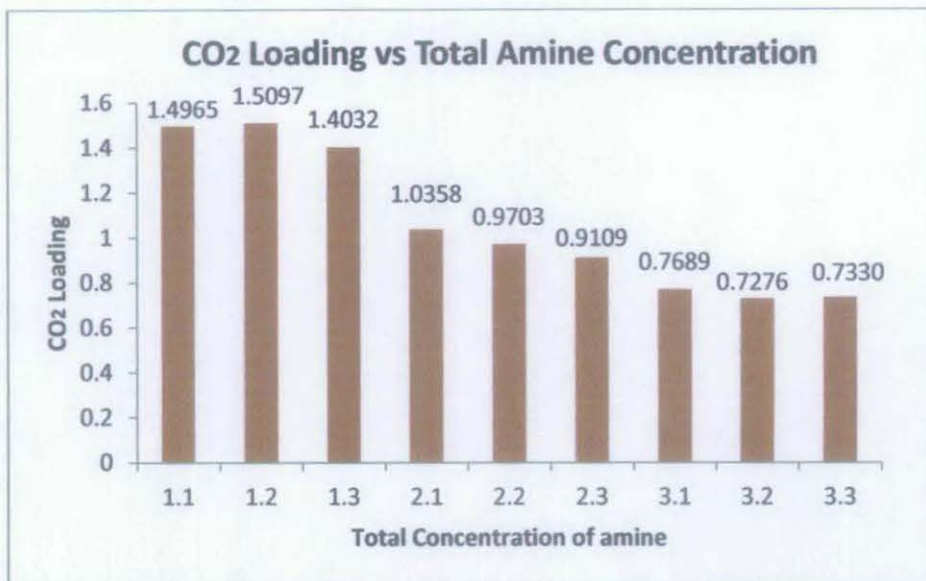*Figure 4.2 CO$_2$ Loading vs Total Amine Concentration at 5 bars*

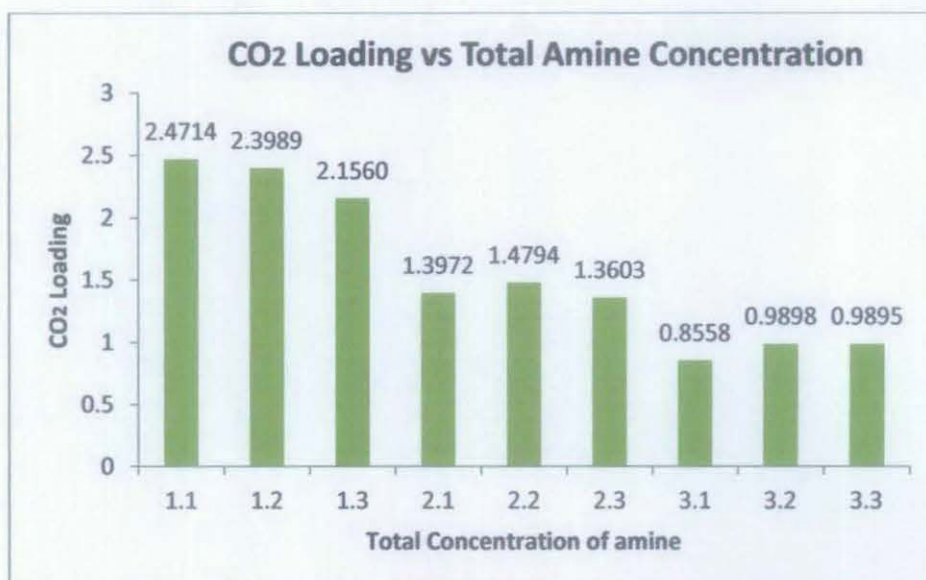*Figure 4.3 CO₂ Loading vs Total Amine Concentration at 10 bars*

Figure 4.4 CO₂ Loading vs Total Amine Concentration at 10 bars

Figure 4.1 shows the CO_2 loading per mol of amine for different amine concentration at different initial pressure. The concentration of amine is the mixture of amine that were prepared earlier, as example, amine concentration of 1.1 indicates that it contain 1.0 mole of AEPD and 0.1 mole of Pz. The concentrations used are 1.0 mole, 2.0 mole, 3.0 mole of AEPD and 0.1 mole, 0.2 mole, 0.3 mole of Pz. The initial pressures used for the experiment are 5 bars, 10 bars and 15 bars. Based on figure 4.1, we can observed that the CO_2 loading with initial pressure 15 bar is the highest at all concentration compared to 10 bars and also 5 bars. This is

followed by initial pressure of 10 bars, and the CO2 loading at 5 bars is the lowest in all concentration. From this observation, we can detect a trend which is the CO_2 loading will increase of the initial pressure of the adsorption process is increased.

Figure 4.2 until 4.4 shows the CO_2 loading per mol of amine for different amine concentration at 5 bars, 10 bars and 15 bars. For initial pressure of 5 bars (figure 4.2), the highest CO_2 loading is **1.4661**, which occurs when 1.1 mole of amine is used. Meanwhile, the lowest CO_2 loading is **0.3964**, which occurs when 3.1 moles of amine is used. For initial pressure of 10 bars (figure 4.3), the highest CO_2 loading is **1.5097**, which occurs when 1.2 mole of amine is used. The lowest CO_2 loading is **0.7276**, which occurs when 3.2 moles of amine is used. Lastly, for initial pressure of 15 bars (figure 4.4), the highest CO_2 loading is **2.4714**, which occurs when 1.1 mole of amine is used. The lowest CO_2 loading is **0.8558**, which occurs when 3.1 moles of amine is used. From this result, we can observe the trend for CO_2 loading with regards to amine concentration. As the concentration of AEPD increases, the CO_2 loading will decrease. There are significant drop of CO_2 loading if the AEPD concentration increases. Meanwhile, the concentration of Pz did not show any trend in CO_2 loading. Figure 4.2 until figure 4.4 shows that there are no significant changes in CO_2 loading when the Pz concentration is increased. Thus, based on this observation, the Pz concentration did not give any significant effect on the CO_2 loading.

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4.2.2   Effect of AEPD concentration on pressure drop during adsorption

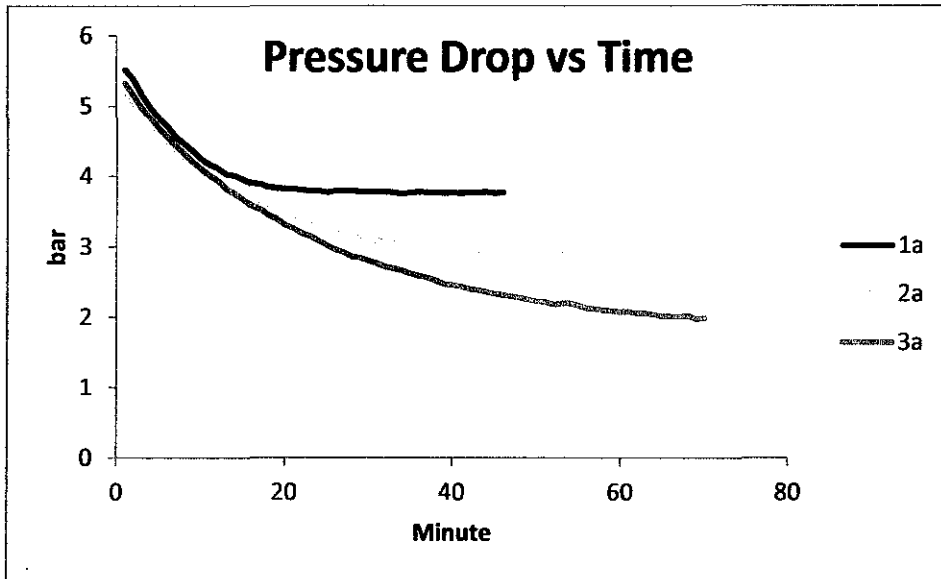At initial pressure of 5 bars, Pz concentration of 0.1 mole

Figure 4.5 Pressure Drop vs Time at 5 bars, Pz concentration of 0.1 mole

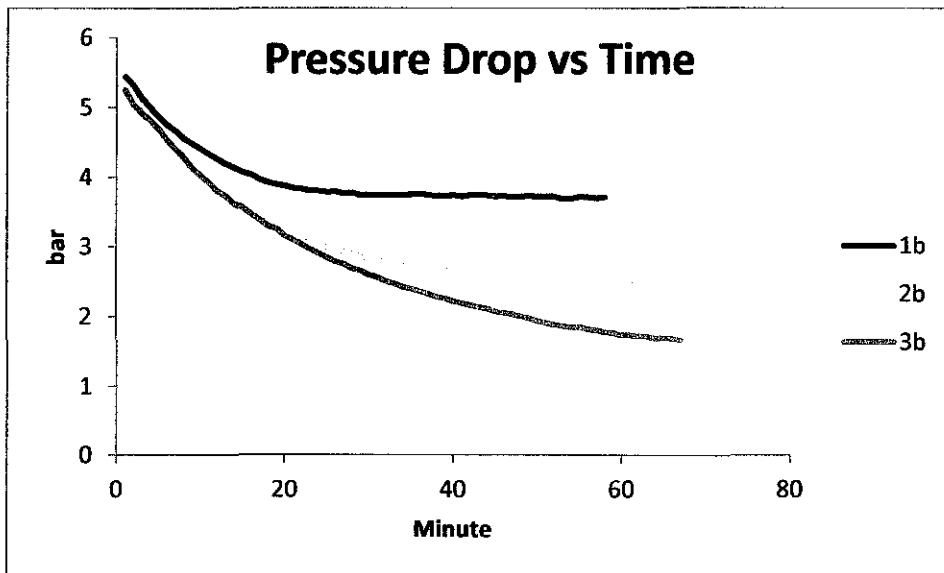At initial pressure of 5 bars, Pz concentration of 0.2 mole

Figure 4.6 Pressure Drop vs Time at 5 bars, Pz concentration of 0.2 mole

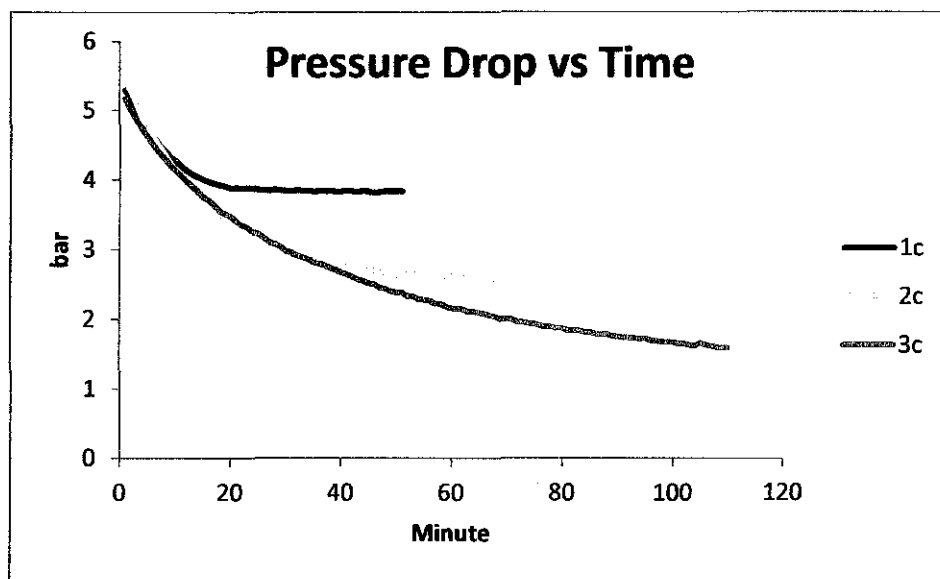At initial pressure of 5 bars, Pz concentration of 0.2 mole

Figure 4.7 Pressure Drop vs Time at 5 bars, Pz concentration of 0.3 mole

Figure 4.5 until 4.7 shows the pressure drop over time for the adsorption process with the concentration of AEPD used vary from 1.0 mole until 3.0 mole at same initial pressure. For figure 4.5, the concentration of AEPD used is 1.1 mole, 2.1 mole, and 3.1 mole, which indicates that the concentration of amine keeps changing from 1.0 mole, to 3.0 mole but the concentration of the Pz remains the same which is 0.1 mole. For figure 4.6 and 4.7, the initial pressure is the same at 5 bars but the Pz concentration is higher which is 0.2 mole and 0.3 mole respectively. From the graph, we can observe that the initial rate of pressure drop for the first 15 minute of the absorption process is almost the same for all concentration of AEPD. However, after 15 minutes, there is significant difference in the rate of adsorption and also the time for the pressure settle. For AEPD concentration of 1.0 mole, the time taken to reach equilibrium is faster than AEPD concentration of 2.0 and 3.0. The rate of pressure drop for AEPD concentration of 1.0 mole is also lower than the rate of pressure drop for AEPD concentration of 2.0 mole and 3.0 mole. This trend can be observed clearly in figure 4.6 and 4.7, which indicates that this trend is valid even though the concentration of Pz is changed.

4.2.3 Effect of Pz concentration on pressure drop during adsorption

At initial pressure of 5 bars, AEPD concentration of 1.0 mole
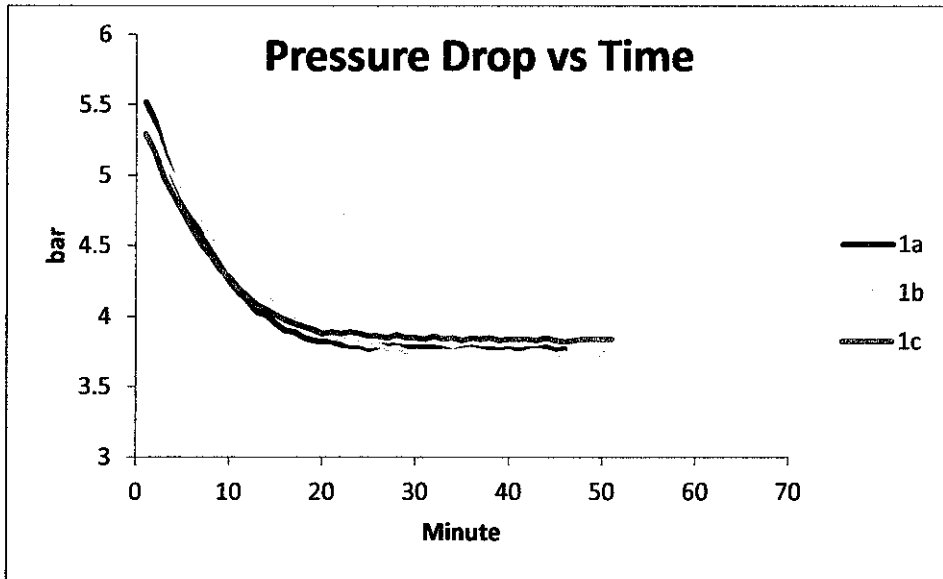

Figure 4.8 Pressure Drop vs Time at 5 bars ,AEPD concentration of 1.0 mole

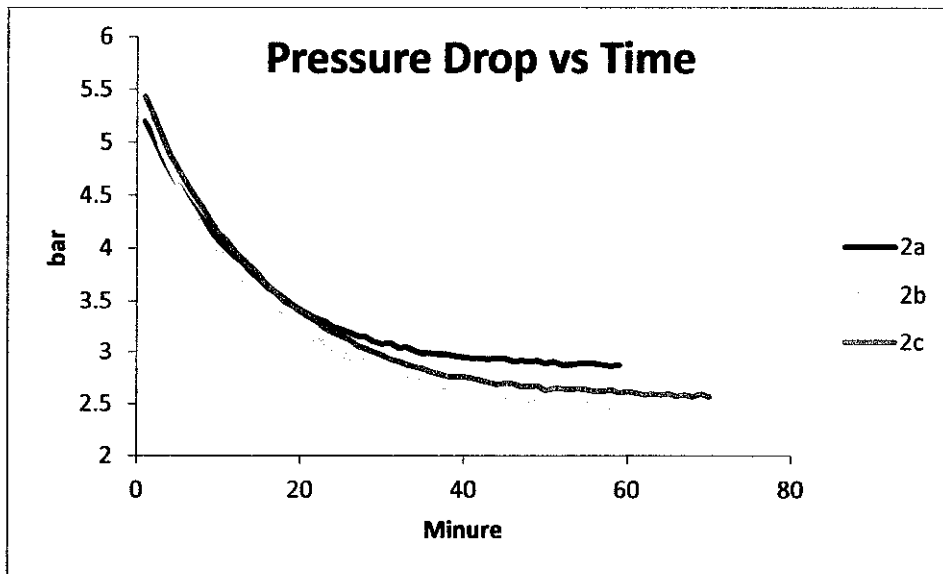At initial pressure of 5 bars, AEPD concentration of 2.0 mole

Figure 4.9 Pressure Drop vs Time at 5 bars , AEPD concentration of 2.0 mole
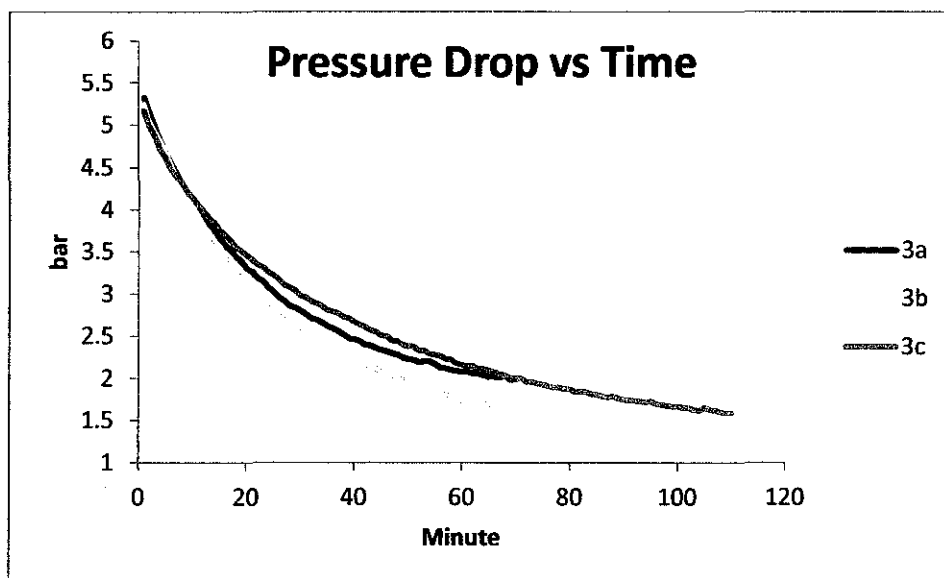
Figure 4.10 Pressure Drop vs Time at 5 bars, AEPD concentration of 3.0 mole

Figure 4.8 until 4.10 shows the pressure drop over time for the adsorption process with the concentration of Pz used vary from 0.1 mole until 0.3 mole at same initial pressure. For figure 4.8, the concentration of amine used is 1.1 mole, 1.2 mole, and 1.3 mole, which indicates that the concentration of Pz keeps changing from 0.1 mole, to 0.3 mole but the concentration of the AEPD remains the same which is 1.0 mole. For figure 4.9 and 4.10, the initial pressure is the same at 5 bars but the AEPD concentration is higher which are 2.0 mole and 3.0 mole respectively. In figure 4.8, the graph shows that the pressure drop during adsorption for all 3 different concentration of Pz is almost the same. There is no significant difference in the rate of pressure drop and also the time taken to reach equilibrium for each of the different concentration. Figure 4.9 and 4.10 also shows the same observation, where all 3 sample for each graph have almost the same curve with only minor difference in the pressure drop rate. Due to this observation, it can be concluded that the addition of Pz in the AEPD solution did not give any significant effect on the pressure drop during the adsorption process and also the CO_2 loading of the amine.

4.2.4 Effect of initial pressure on pressure drop during adsorption
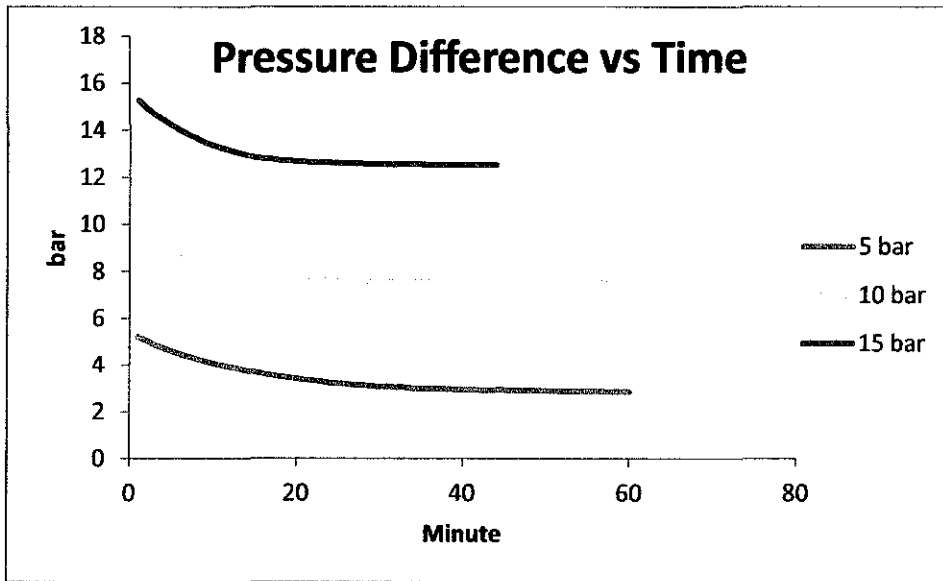
Amine concentration of 2.1 mole

Figure 4.11 Pressure Drop vs Time at amine concentration of 2.1 mole

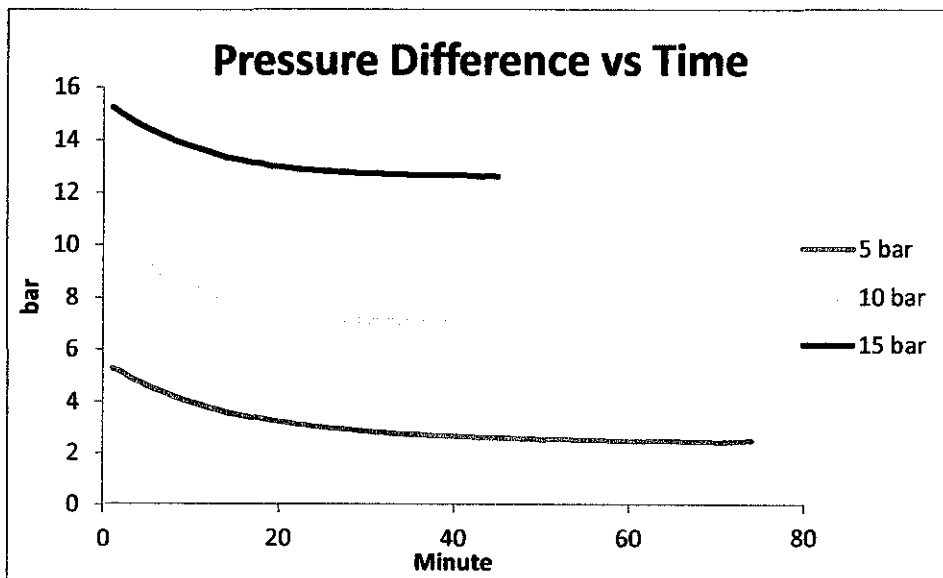Amine concentration of 2.2 mole

Figure 4.12 Pressure Drop vs Time at amine concentration of 2.2 mole
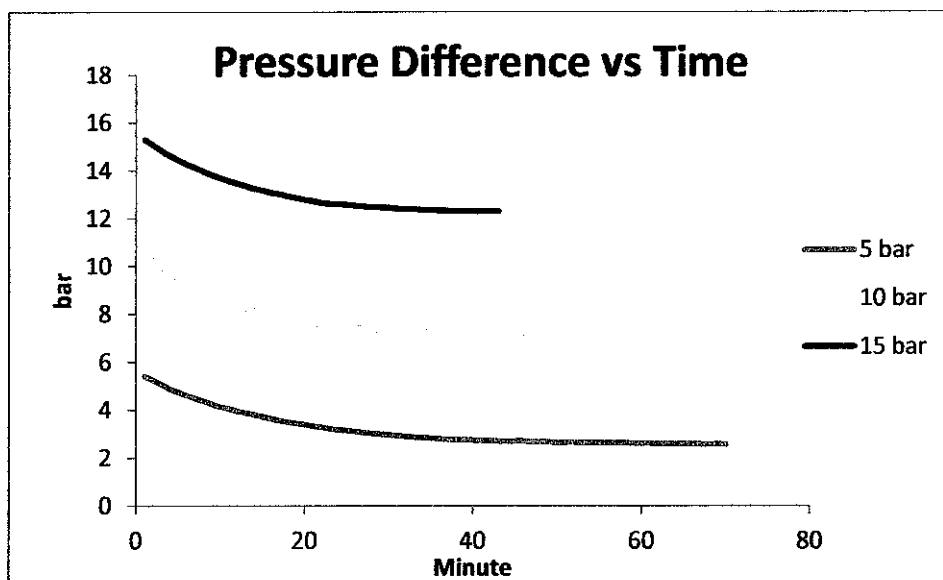
Amine concentration of 2.3 mole

Figure 4.13 Pressure Drop vs Time at amine concentration of 2.3 mole

Figure 4.11 until 4.13 shows the pressure drop over time for the adsorption process with initial pressure used are 5 bars, 10 bars, and 15 bars. The concentration of amine used are2.1 mole, 2.2 mole and 2.3 mole for figure 4.11, 4.12 and 4.13 respectively. From this graph, the relationship between initial pressure and the pressure drop during the adsorption process can de observed. From figure 4.11, it is noticeable that the time taken for the pressure to stable decrease as the initial pressure increases. The same trend can also be observed when using amine concentration of 2.2 mole and 2.3 mole. The rate of pressure drop is also another factor that is affected by the initial pressure change. From figure 4.11, the rate of pressure drop is fast when high initial pressure is used, and the rate of pressure drop is slow when low initial pressure is used. This trend is consistent even when the concentration of amine is change in figure 4.12 and 4.13. Thus, the initial pressure gives direct effect to the rate of pressure drop and the time taken to reach adsorption equilibrium.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Overall, this project is able to achieve the initial objective which is to measure the CO_2 solubility in aqueous solution of AEPD and Pz Solution. The solubility of CO_2 is determined in terms of CO_2 loading per mole of amine used. Based on the experiment result, three of the highest CO_2 solubility achieved is 2.4714, 2.3989 and 2.1560 at amine mixture concentration of 1.1 mole, 1.2 mole and 1.3 mole respectively at initial pressure of 15 bars. Meanwhile, three of the lowest CO_2 solubility achieved is 0.3964, 0.4280 and 0.4421 at amine mixture concentration of 3.1 mole, 2.1 mole and 3.3 mole at initial pressure of 5 bars.

The second objective of the experiment which is to investigate the effects of initial pressure and concentration of aqueous solution of AEPD and Pz towards CO_2 solubility is also completed. Based on the result, as the initial pressure for adsorption process is increased, the rate of CO_2 adsorption will increase and the time taken for the adsorption process to reach equilibrium will be faster. The effect of changing concentration of AEPD and Pz are also determined during the experiment. As the concentration of AEPD increases, the CO_2 loading will become lower. However, the trend of CO_2 loading for different concentration of Pz could not be determine as there is no significant changes and trend when the Pz concentration is varied.

5.2   RECOMMENDATION

There are several recommendations that can be done to achieve better results for this experiment. The recommendations are as follows:

1. Repetition for each sample to produce accurate result

   For the experiment, there is no repetition done for each sample. The CO_2 loading for each sample are calculated by a sole rune of experiment for each sample. By having repetition, more accurate data can be produce.

2. Use higher concentration of Pz

   Higher concentration of Pz might be needed to see the trend if the Pz concentration is change. For this experiment, the Pz concentrations used are 0.1 mole, 0.2 mole and 0.3 mole, which is to close to each other. The recommended concentrations Pz to be used are 0.1 mole, 0.3 mole and 0.5 mole.

3. Study the effect of temperature towards the CO_2 solubility

   Temperature effect is one of the important factors in the CO_2 adsorption. In the current experimental setup, the temperature of the adsorption process is the same for the entire sample. Thus, the recommended temperature changes are $30^{\circ}C$, $50^{\circ}C$ and $70\,^{\circ}C$

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