Study on CO$_2$ Solubility in Ionic Liquids (DCIL)

by

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Dissertation submitted in partial fulfillment of
the requirements for
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CERTIFICATION OF APPROVAL

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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.

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RABIATUL ADAWIYAH MOHAMAD

ABSTRACT

The objective of this project is to study the solubility of CO_2 in the ionic liquids which acts as a solvent in this experiment. For this purpose, the ionic liquid which is 1,10-Bis (trioctylphosphonium) decane dioctylsulfosuccinate has to be synthesized first in order to conduct the experiment.

Even though many researchers have conducted the same experiments of CO_2 solubility in ionic liquids, many focused on the imidazolium-based ionic liquids compared to phosphonium-based ionic liquids. Therefore, the purpose of this work is to study the solubility of CO_2 in the phosphonium based ionic liquids. Due to its high thermally stable characteristic, phosphonium-based ionic liquids is choose to be the solvent of this study compared to imidazolium-based ionic liquids. Other than that, the price which is less expensive and the availability of the phosphonium based ionic liquids are the traits that attract the researchers to conduct this new study.

This project covers the study of ionic liquids and its unique characteristics that contribute to the gas separation in the academic research and also industries, CO_2 solubility determination by calculating the Henry's law constant from the data and the comparison between the phosphonium-based ionic liquids and imidazolium-based ionic liquids.

This report also consists of background of project, objectives, scopes of study, literature review, methodology, result and discussion and conclusion of the finding.

ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Recently, the growing interest in the application of ionic liquids (ILs) as gas-separation media stems from their exceptional properties, such as negligible vapor pressure, high thermal stability, and tunability of various other properties with the structural changes of the ionic liquids. Besides that, the other unique characteristics of ionic liquids are they are in liquid phase at ambient temperature, excellent solvent power or catalyst for some organic reactions and non-flammable and non-corrosive. Moreover, due to its negligible vapor pressure, ionic liquids are considered as green and environmentally friendly solvent. This is because ionic liquids do not emit any volatile organic compounds (VOCs), thereby reducing the negative impact on the environment, working exposure hazards and contamination of the reaction products can be prevented.

Gas solubility is an important design parameter in equilibrium stage and rate-based separations. Gas solubility was usually measured as a function of temperature and at pressures close to atmosphere, using an isochoric saturation method. Also, from a practical point of view, gas solubility can be helpful in the calculation of (vapor + liquid) equilibria and thus pertinent to the development of new reaction and separation processes. Ionic liquids show, in general, has very high solubility in water and carbon dioxide and a low solubility of hydrogen compared to conventional organic solvents. Thus, ionic liquids have potential for the separation of gases such as carbon dioxide and hydrogen. The very low vapor pressures of ionic liquids make them even more attractive for gas separations since they show almost no solubility in gaseous phase. The researchers have used the different types of ionic liquids such as to study the gas solubility in them which are phosphonium-based ionic liquids, ammonium-based ionic liquids, imidazolium-based ionic liquids and propylcholium-based ionic liquids.

As for the study of the solubility of CO_2 in ionic liquids, phosphonium-based ionic liquids have received less attention compared to imidazolium-based ionic liquids. This is because phosphonium-based ionic liquids have not been produced in large scale. However, they have recently become available in large quantities and generally cost much less than imidazolium-based ionic liquids.

1.2 PROBLEM STATEMENT

Many researches have been conducted to study the solubility of CO_2 using ionic liquids. However, many researchers are focus on the imidazolium-based ILs compared to phosphonium-based ILs due to more documented academic papers. A study has been conducted on the phase behavior of the binary system and the ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([emim][Tf$_2$N]) (Schilderman A. M, 2007). Meanwhile, another study has been conducted a study on the influence of changing the cation of 1-ethyl-3-methylimidazolium ($[C_1C_2Im]^+$) on the gas solubility (Hong *et al.*, 2007).

Based on my research, there are very few journals discussing about the solubility of CO_2 in the phosphonium-based ILs. Kamps *et al.* (2003) have measured for temperatures ranging from (293 to 393) K and for pressures up to about 9.7 MPa to find the solubility of CO_2 in [bmim][PF$_6$] with very limited experimental information found in the literature (Kamps *et al.*, 2003).

Meanwhile, there are no reported work has been conducted on the solubility for the ionic liquid used which is 1, 10-bis(trioctylphosphonium) decane dioctylsulfosuccinate in this study. Thus, the new solubility data for this newly synthesis phosphonium-based ionic liquids is very important since the solubility is the fundamental to most areas of chemistry.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this study are:

1) To synthesis 1, 10-bis (trioctylphosphonium) decane dioctylsulfosuccinate, [$P_{888}C_{10}P_{888}$] docusate for the experiment (Ziyada *et al.*, 2011)

2) To measure CO2 solubility in [$P_{888}C_{10}P_{888}$] docusate at different pressure (10-30 bar).
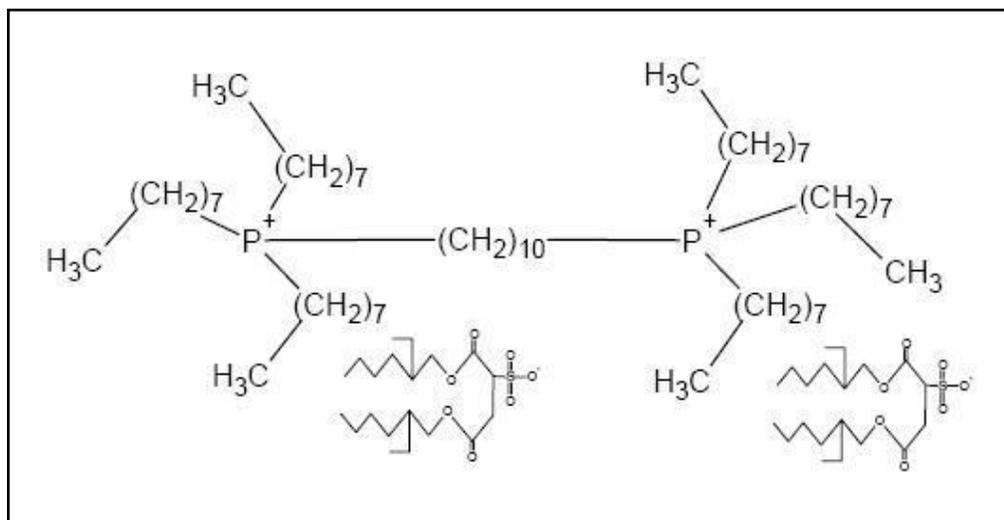
Figure 1: Structure of 1,10-bis (trioctylphosphonium) decane dioctylsulfosuccinate

Meanwhile the scopes of study of this project are:

1) Study on ionic liquids and its unique characteristics that contribute to gas separation which in this case is CO_2.

2) Solubility measurement of CO_2 at different pressure (10-30 bar) at room temperature (298.15 K).

3) Calculation of mole fraction of CO_2 absorbed in [$P_{888}C_{10}P_{888}$] docusate, molality and Henry's law constant.

CHAPTER 2
LITERATURE REVIEW

2.1 WHAT IS IONIC LIQUIDS (ILs) AND DICATIONIC IONIC LIQUIDS (DCILs)?

Ionic liquids are a new generation of solvents for catalysis and synthesis that have been demonstrated as potential successful replacements for conventional ionic liquids. Ionic liquids are a common name given to the organic salts where the molecules composed of ions and having melting points below 100°C and negligible vapor pressure. In general, ionic liquid consists of a salt where one or both ions are large, the cation has a low degree of symmetry. These are the factors that reduce the lattice energy of crystalline form of the salt thus reduce the melting point of the ionic liquids (Earle *et al.*, 2000). In addition, ionic liquids also in liquid phase at room temperature and are often called "room-temperature ionic liquids (RTILs)."

The other synonyms that have been used for ionic liquids in the industries are:

- ambient-temperature ionic liquid
- non-aqueous ionic liquid
- molten organic salt
- fused organic salt
- low melting salt
- neoteric solvent
- designer solvent

Ionic liquids have attracted the attention of chemists around the world for various reasons. Ionic liquids are generally non-flammable and thermally stable at temperatures higher than conventional organic molecular solvents. Ionic liquids also have a wider liquid ranges compared to molecular solvents. Ionic liquids have a wide range of solubilities and miscibilities, and can be used as reaction media and/or catalyst for chemical reactions. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts

are miscible with water at 25°C where alkyl chain length is less than 6, but at or above 6 carbon atoms, they form a separate phase when mixed with water (Earle *et al*, 2000). Moreover, the physical, chemical and biological properties of ionic liquids can be designed by switching anions or cations, by designing specific functionalities into cations and/or cations and lastly, by mixing two or more simple ionic liquids together (Freemantle M., 2010). Properties such as melting points, viscosity, density and hydrophobicity can be varied by simple changes to the structure of the ions (Earle *et al.*, 2000). The properties of "ideal" ionic liquids were thought to include low cost, water stability (as well as stability to the solvent, product, etc.), low toxicity, low environmental impact, noncorrosive and recyclable. Industry representatives suggested a viscosity of less than 100 cP and thermal stability to 973 K (Domanska U., 2005).

Meanwhile, dicationic ionic liquids are new class of molecules containing two head groups linked by a rigid or flexible space (Ding *et al.*, 2007). Dicationic ionic liquids, contains of one dication and two monocationic ionic liquids is lacking relative to monocationic ionic liquids because of much fewer reports on dicationic ionic liquids compared to monocationic ionic liquids. Ionic liquids that are stable at much higher temperatures are the dicationic ionic liquids. They exhibit a much higher thermal stability, with onset temperatures ranging from 330 to over 400°C .

2.2 PROPERTIES OF IONIC LIQUIDS

2.2.1 LIQUID RANGE AND THERMAL STABILITY

Ionic liquids have higher ranges than molecular solvents. Liquid range is the temperature range between melting point or glass transition temperature and boiling point or thermal decomposition temperature. Many ionic liquids slowly form glasses at low temperatures. Because they have negligible vapor pressure they generally do not evaporate or boil at high temperatures. The upper limit of their liquidus range is determined by the thermal decomposition temperature.

For example, 1-alkyl-3-methylimidazolium salts have glass transition temperatures in the range -70 to -90°C and thermal decomposition temperature ranging from 250 to over 450°C. They have liquid ranges of over 300°C. Meanwhile, water is in liquid from 0 to 100oC at atmospheric pressure, therefore has liquid ranges of 100°C.

The higher the thermal stability temperatures of ionic liquids means that the study can be carried out in these solvents without any solvent degradation (Freemantle M., 2010).

2.2.2 MELTING POINTS

The melting points of room-temperature ionic liquids tend to decrease as the size of the anion or cation increases. For example, the melting point of [C$_2$mim]Cl is 87°C meanwhile [C$_2$mim][AlCl$_4$] which has larger anion, is 7°C. Therefore, small variations in the alkyl chain in a cation can also lead to huge differences in the melting points.

The symmetry of the cation also significantly influences melting point. As symmetry increases, the ions pack more efficiently and the melting point of the ionic liquid increases. For example, tetraalkylammonium bromide [N $_{5\ 5\ 5\ 5}$]Br has four straight-chain pentyl groups, has a melting point of 101.3^{o}C. In contrast, [N $_{1\ 5\ 6\ 8}$]Br, which has four different alkyl groups is liquid at room temperature.

It has been known that melting point depression of some organic solids can be induced by compressed gasses. For example, lipids and polymers are known to melt at temperatures 10-25°C lower than their normal melting point, when they are exposed to

high pressure gases (Manic *et al.*, 2010). Kazarian et al. observed liquid-crystal transition for an imidazolium salt, [C$_{16}$mim][PF$_6$] with carbon dioxide. Scurto et al. reported that high pressure carbon dioxide can induce surprisingly high melting point depression up to 120°C (Scurto *et al.*, 2003).

2.2.3   **VAPOR PRESSURE**

The major reason for the interest in ionic liquids is their negligible vapor pressure, which decreases the risk of technological exposure and the loss of solvent to the atmosphere. The lack of measurable vapor pressure at temperatures up to their thermal decomposition temperatures arises from the strong coulombic interactions between ions in the liquids.

However, it is possible to distil certain ionic liquids at high temperature and low pressure. Using experimental surface tension and density data, Rebelo *et al.* predicted that it should be possible to distil ionic liquids with [NTf$_2$]$^-$ anion and imidazolium cations containing long alkyl chain lengths at temperatures between their estimated boiling and decomposition temperatures. They subsequently carried out distillations of [C$_{10}$mim][NTf$_2$] at reduced pressure and 70°C (Freemantle M., 2010).

In general, the vapor pressures of ionic liquids, notably the widely-used imidazolium ionic liquids with short cationic alkyl chains, are negligible at ambient temperatures and pressures.

2.2.4   **VISCOSITY**

Viscosity is a measure of a liquid's resistance to flow. Liquids with lower viscosity flow more readily. Generally, ionic liquids are more viscous than molecular solvents. The viscosities of ionic liquids at room temperature (20-25°C) typically lie in the range of 10 to over 500 cP. For example, the viscosities of [C$_2$mim][BF$_4$] and [C$_4$mim][PF$_6$] at 25°C are 34 and 270 cP, respectively.

The viscosities of ionic liquids increase with increasing size of the cation and particularly with increasing alkyl chain lengths. For example, the viscosities of [N $_{6\,2\,2}$ $_2$][NTf$_2$] and [N $_{8\,2\,2\,2}$][NTf$_2$] at 25°C are 167 and 202 cP, respectively.

Meanwhile, the ionic liquids with weakly coordinating anions, such as $[BF_4]^-$, $[PF_6]^-$ and $[NTf_2]^-$ have lower viscosities than those with strongly coordinating anions. For example, the room temperature viscosities of $[C_6mim][PF_6]$ and $[C_6mim][NO_3]$ are 314 and 804 cP, respectively (Freemantle M., 2010)

2.2.5   DENSITY

Ionic liquids are denser than water. If an ionic liquid does not mix with water, it forms the lower phase when the two liquids are mixed. Ionic liquids with shorter alkyl chains or less buly cations have higher densities compared to ionic liquids with longer alkyl chains or more bulky cations. The changes of temperature have small impact to the density of an ionic liquid.

2.2.6   SOLUBILITY AND MISCIBILITY

Ionic liquids can be selected or designed to dissolve a wide range of organic and inorganic gases, liquids and solids. The ability of an ionic liquid to dissolve a substance depends on several factors, most notably its polarity and the coordination ability of its ions. The coordination ability of ionic liquid anions, for example, influences the solubility of metal salts in ionic liquids.

The miscibility of ionic liquids with water is one of the particular interests. The coordination ability of the ions in an ionic liquid will determine an ionic liquid's miscibility with water. Ionic liquids with basic anions such as Cl^- and $[NO_3]^-$ are strongly coordinating, whereas those with acidic anions such as $[Al_2Cl_7]^-$ are non-coordinating. As the coordinating ability of the anion decreases, the hydrophobicity of the ionic liquids increases (Freemantle M., 2010)

2.2.7   CONDUCTIVITY

The two properties of ionic liquids which are ionic conductivity and electrochemical stability combined with other properties, such as tune-ability of the ions, low volatility and high thermal stability make ionic liquids attractive as potential electrolytes for batteries, solar cells, fuel cells and other electrochemical devices and also as potential solvents for electrochemical redox reactions.

2.2.8   REFRACTIVE INDICES

The refractive index of a substance is a measure of its ability to refract light when it travels from the substance into another medium. Substances with refractive index more than 1.6 are considered having high refractive index.

The refractive index of ionic liquids are depends on the nature of both cation and anion. For example, as the refractive index increase, branching and length of alkyl length in the cation increases.

2.2.9   IMPACT OF IMPURITIES

Impurities such as traces of water, acids, halide ions, residual solvents and unreacted volatile organic compounds arising from the preparation of the liquids. For example, the viscosities if $[C_2mim][BF_4]$ and other 1-methylimidazolium salts have increase dramatically when small amounts of chloride impurities are present. Halide impurities deactivate transition metal-based catalysts immobilized in ionic liquids.

2.3 CO_2 SOLUBILITIES IN IONIC LIQUIDS

Carbon dioxide, CO_2, is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm. Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous world-wide consumption of such fossil fuels, the amount of CO_2 in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in CO_2 concentration.

Carbon dioxide was chosen as the gases in this study because they have higher solubilities in ionic liquids than those of simple gases such as oxygen, nitrogen and helium.

From the study conducted by Muldoon *et al.*, there are number of factors that controlled the CO_2 solubility in the ionic liquids, both cation and anion related. In the previous study, anion played the biggest role in CO_2 solubility. Anions that contain fluoroalkyl groups have the highest CO_2 solubility. Also, as the quantity of fluoroalkyl groups increased, CO_2 solubility also increased. For the cations, there were two factors that influenced the CO_2 solubility. As the alkyl chain length on the cation increases, the CO_2 solubility also increased. This may be due to entropic reasons whereas the density of ionic liquids decreases with increasing alkyl chain length. Thus, there is more free volume within the longer chain ionic liquids (Muldoon *et al.*, 2007).

Next, one of the factors that controlled CO_2 solubility is the enthalpy and entropy of dissolution of CO_2. The partial molar enthalpy and entropy of CO_2 dissolution in the ionic liquids can be estimated from the temperature dependence of the Henry's law constants. A larger negative value for the enthalpy indices stronger IL/CO_2 interactions. For example, the partial molar enthalpies of dissolution of CO_2 in [hmim][Tf_2N] and [hmpy][Tf_2N] are -12.2 and -11.4 kJ/mol, respectively. Therefore, [hmim][Tf_2N] has higher IL/CO_2 interaction, leading to higher solubilities.

The solubility of CO_2 can also be determined by fluorination of the anion. The positive effect of fluorination of the anion can be seen by comparing the solubility of CO_2 in [hmim][PH_6], [p_5-mim][bFAP] and [hmim][eFAP]. The FAP-type anion is analogous to the [PH_6] anion where replacement of three fluorine atoms with fluoroethyl groups increases the CO_2 solubility considerably. The solubility in CO_2, [p_5-mim][bFAP] is the highest been observed compared to [hmim][PH_6] and [hmim][eFAP] when the dissolution is by the physical absorption.

The CO_2 solubility can be calculated by using Henry's law constant. The lower the value of the Henry's law constant, the higher the solubility in the ionic liquids. For example, Kamps *et al.* using different range of temperature (293-393 K) to measure the CO_2 solubility in the [bmim][PF_6] where Henry's law constant at 293 K and 393 K is 1.20 MPa and 5.49 MPa, respectively. The results showed that the CO_2 solubility at 293 K is higher compared to 393 K. Also, the results showed that as the temperature increased, the solubility of CO_2 in ionic liquids decreased (Kamps *et al*., 2003).

In addition, CO_2 could increase the solubility of gases which normally not very soluble on their own in ionic liquids. It is found that the solubility of CH_4 and O_2 increased in ionic liquids even at low partial pressures of CO_2. High pressure NMR showed that the addition of CO_2 increased the amount of H_2 dissolved in the ionic liquids. Others studying the enantioselective hydrogenation of imines using a cationic iridium catalyst in an IL/CO_2 biphasic system found that the catalyst performance was increased dramatically in the ionic liquids when CO_2 pressure was added (Muldoon *et al.*, 2007).

2.4 COMPARISON OF IMIDAZOLIUM-BASED IONIC LIQUIDS AND PHOSPHONIUM-BASED IONIC LIQUIDS

The ionic liquid that is used for this study is 1,10-bis (trioctylphoshonium) decane dioctylsulfosuccinate, $[P_{888}C_{10}P_{888}]$ docusate, which is a phosphonium-based ionic liquid.

From the previous report about the CO_2 solubility, an imidazolium-based ionic liquid has widely used to investigate the solubility of carbon dioxide compared to phosphonium-based ionic liquids. For example, Kamps *et al.* conducted CO_2 solubility in the [bmim][PF_6] and Kilaru *et al.* conducted CO_2 solubility at low pressure in [emim][Tf_2N], [emim][TfO], [bmim][PF_6], [bmim][Tf_2N], [bmim][BETl], [desmim][TfO] and [C_6mim][Tf_2N].

From study conducted by Ferguson *et al.*, phosphonium-based ionic liquids could become another alternative to imidazolium-based ionic liquids. Phosphonium-based ionic liquids generally differ from imidazolium-based ionic liquids in three categories; first, ring-cations (imidazolium) vs alkyl-cations; second, phosphonium ionic liquids as a group has viscosities larger than imidazolium ionic liquids, and finally, the phosphonium molar volumes are larger (Ferguson *et al.*, 2007).

Also, the gas permeabilities of the phosphonium-based ionic liquids are similar to imidazolium-based ionic liquids, except that the phosphonium CO_2 permeabilities are

significantly lower than the imidazolium CO_2 permeabilities. The gas solubilities and diffusivities of the phosphonium-based ionic liquids are of the same order of magnitude as the gas solubilities and diffusivities for imidazolium-based ionic liquids. However, the Henry's law constants for the phosphonium-based ionic liquids are, generally, less than their respective values for imidazolium-based ionic liquids. The phosphonium-based liquid diffusivities also have a similar gas molar volume correlation power as the imidazolium-based ionic liquids. However, the phosphonium-based liquid diffusivities do not have the same viscosity correlation power as the imidazolium-based ionic liquids (Ferguson *et al.*, 2007)

Lastly, phosphonium based ionic liquids have the following advantages. First of all they are thermally more stable than ammonium or imidazolium salts that may be important for processes performed above 100 °C. And secondly, they have no acidic protons and are stable under basic conditions. Moreover, their density is lower than that of water that may be beneficial for work-up procedures.

CHAPTER 3
METHODOLOGY

3.1 CO_2 SOLUBILITY MEASUREMENT

The objectives of this methodology are to calculate the CO_2 solubility in term of mole fraction of CO_2 absorbed, molality and Henry's law constants.

Below is the process flow diagram for the proposed methodology:

Run FTIR analysis before and after DEA/ionic liquid is tested with CO_2

Applied vacuum to whole system and run leakage system

Preparing the binary system ionic liquid/CO_2:
1,10-bis(trioctylphosphonium) decane dioctylsulfosuccinate

Setting values of temperature (in ^{o}C) and pressure (in bar).
Run the solubility measurement using DEA and ionic liquid

Record the pressure reading (for 10 bar, 20 bar and 30 bar) for 24 hours.

Figure 2: Process flow diagram for methodology

3.2 SOLUBILITY MEASUREMENT EXPERIMENTAL SETUP

Below are the list of the apparatus that is used for the CO_2 solubility measurement experiment:

1. Stainless steel pressure cell
2. CO_2 gas storage tank
3. Magnetic stirrer– to stirs the mixture
4. Pressure gauge/transducer (range: 0-25 bar) – to measure the bubble point pressure
5. Vacuum pump
6. Bomb

3.3 EXPERIMENTAL SETUP
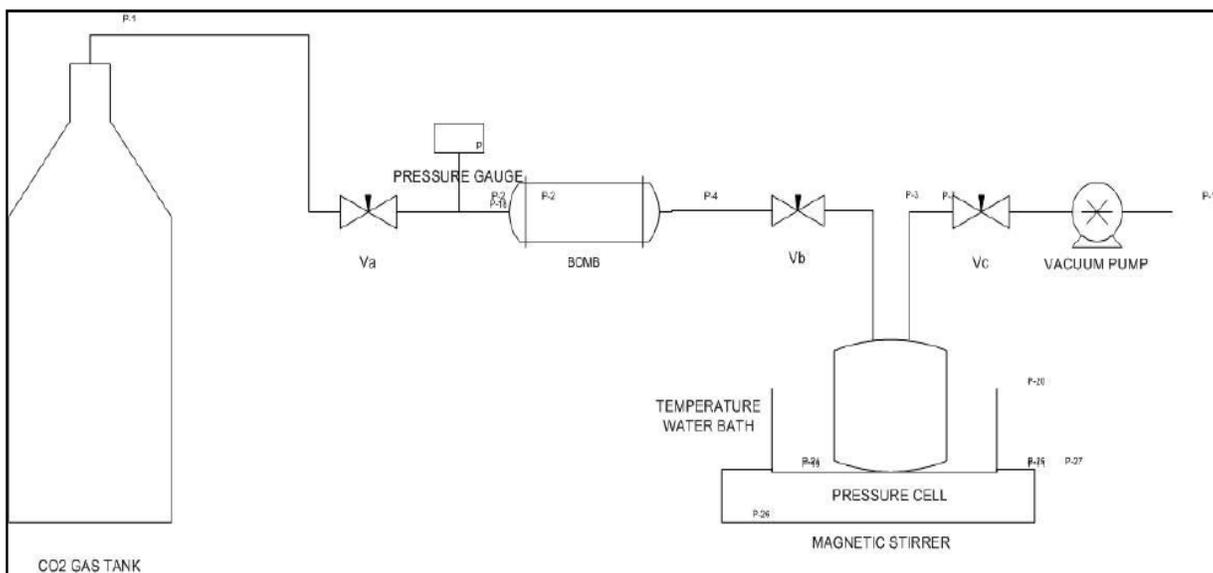
Figure 3: Schematic diagram of the overall experimental setup

3.3.1 **PRESSURE CELL**

Pressure cell is designed as the container for $[P_{888}C_{10}P_{888}]$ docusate. The pressure cell will attaches to:

- Valve b, V_b
- Release Valve, V_c

The o-ring will be used between the cover and the pressure cell itself in order to prevent any leakage occurs.

3.3.2 **OVERALL EXPERIMENTAL SETUP**

The pressure cell that has been designed is attached to the frame work. Vacuum pump and CO_2 tank also are connected to the setup. Below is the overall experimental setup for CO_2 solubility measurement.
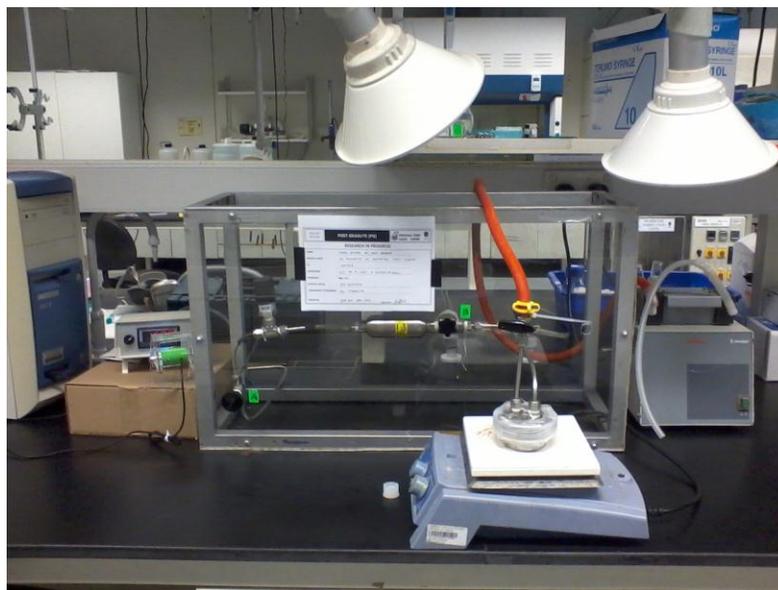
Figure 4: Overall experimental setup

3.4 RESEARCH METHODOLOGY

3.4.1   SPECTROSCOPY TEST

1. FTIR spectrum is taken before and after the CO_2 is introduced to the ionic liquid.
2. For the ionic liquid without CO_2, the sample is dried in vacuum oven and directly put into the Shimadzu model IR Spectrometer.
3. For the ionic liquid contacted with CO_2, it is collected after the solubility measurement is finished.
4. The broadband trend of the ionic liquid with and without CO_2 contact is evaluated.

3.4.2   PROCEDURE OF EXPERIMENTAL SETUP LEAKAGE TEST

1. Vacuum is applied to the whole system to ensure no other gases in the system.
2. 10 bar CO_2 gas is introduced to the first line of the system by opening valve a, V_a while valve b, V_b and valve c, V_c is closed.
3. The pressure reading showed by pressure gauge is monitored for 5-8 hours.
4. V_b is opened to let the CO_2 exposed to the whole system. V_c is maintain closed all the time.
5. The pressure reading showed by pressure gauge is monitored for 24 hours.

3.4.3   **PROCEDURE OF VOLUME, V_1 DETERMINATION**

Figure 6 and 7 show initial and Volume 1, V_1.
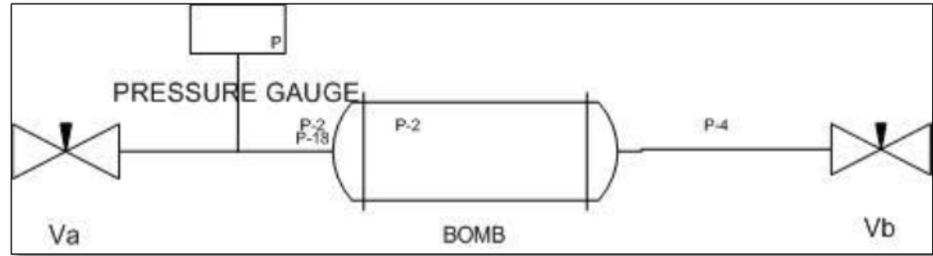
Figure 5: Initial Volume, V_i (V_a to V_b)
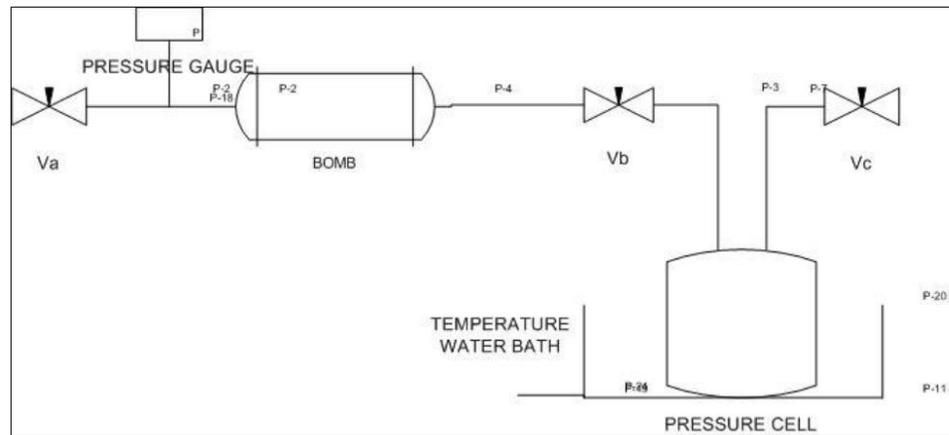
Figure 6: Volume 1, V_1 (V_a to V_c)

1. Vacuum is applied to the whole system to ensure no other gases in the system.
2. 10 bar CO_2 is introduced to the system as P_1.
3. V_a and V_b is closed.
4. V_c is opened to release the left CO_2.
5. The pressure reading is observed till it stable.
6. V_b is opened.
7. The pressure reading is taken as P_2.
8. V_1 is determined by using formula $\mathbf{P_iV_i = P_1V_1}$

3.4.4 PROCEDURE OF SOLUBILITY MEASUREMENT

1. Ionic liquid is dried for 24 hours at 80^oC in the vacuum oven.

2. 1 ml of the ionic liquid was put in the pressure cell directly from the oven, and immediately the pressure cell is closed and attached to the unit.

3. Valve a, V_a is closed while valve b, V_b and valve c, V_c are opened.

4. The unit was connected to a vacuum pump and the system is evacuated for 10 minutes.

5. The vacuum pump is switch off.

6. V_c and V_b are closed.

7. CO_2 is introduced to the system by opening V_a. (The equilibrium condition was judged when the pressure was unchanged).

8. V_b is opened so that ionic liquid sample could be in contact with CO_2.

9. After equilibrium as indicated by negligible pressure change, the pressure is measured again to determine the amount of CO_2 gas left in vapor phase. The different in the amount of CO_2 is taken as the amount of CO_2 dissolves.

10. Valve V_c is kept closed throughout series of run.

11. Pressures are measured before opening valve V_b and after equilibration with valve V_b is opened.

12. The procedure is repeated for measurement at different pressures.

13. The mol of ionic liquid, n_i is calculated based of pure ionic liquid used in this solubility measurement.

3.5 **DATA INTERPRETATIONS**

The solubility of CO_2 in diethanolamine (DEA) and $[P_{888}C_{10}P_{888}]$ docusate is calculated by using the Ideal Gas Law. Ideal Gas Law is used to determine the amount of mole of CO_2 absorbed in DEA/$[P_{888}C_{10}P_{888}]$ docusate, which in this experiment, at constant temperature (assume to be at room temperature $= 25^{o}C = 298.15$ K). For non-ideal gas, compressibility factor is used to calculate the the real P-V. Compressibility factor, Z is a function of the reduced temperature and reduced pressure of the gas (or gas mixture) at high pressure (for more than 5 bar) and temperature. Thus, the equation used is as below:

$$PV = ZnRT \qquad (1)$$

Where;

P = Pressure of CO_2 in bar

V = Volume of solvent in cm^3

n = Number of moles of CO_2

R = Constant for all gases = 8.314 J/K.mol

T = Absolute temperature in K = 298.15 K

Z = Compressibility factor

Thus, to calculate the number of moles of CO_2 in DEA/$[P_{888}C_{10}P_{888}]$ docusate:

The volume of CO_2 introduced to the system, V_1 is:

$$P_iV_i = P_1V_1 \qquad (2)$$

The number of moles of CO_2 introduced to the system, n_1 is:

$$n_1 = P_1V_1/ZRT \qquad (3)$$

The number of moles of CO_2 absorbed into DEA/[$P_{888}C_{10}P_{888}$] docusate, n_{absorb} is:

$$\mathbf{P_1V_1/n_1 = P_2V_2/n_2} \tag{4}$$

$$\mathbf{n_{absorb} = n_2 - n_1} \tag{5}$$

The number of moles of DEA/[$P_{888}C_{10}P_{888}$] docusate is calculated as below:

$$\mathbf{n_i = m_i / M_i} \tag{6}$$

As for the mole fraction of moles of CO_2 absorbed, $\mathbf{X_{CO2}}$:

$$\mathbf{X_{CO2(absorb)} = n_{absorb} / (n_{absorb} + n_i)} \tag{7}$$

Finally, CO_2 gas molality, m_{CO2} which is the number of moles of CO_2 absorbed per kilogram of DEA/[$P_{888}C_{10}P_{888}$] docusate:

$$\mathbf{m_{CO2} = n_{absorb} / kg\ of\ solvent} \tag{8}$$

Next, to calculate the Henry's law constant, $\mathbf{K_H}$ is as below:

$$\mathbf{K_H = p / x_{CO2(absorb)}} \tag{9}$$

$$\mathbf{p = X_i P_T} \tag{10}$$

Where;

K_H = Henry's Law Constant

P = partial pressure

X_{CO2} = mole fraction of CO_2 absorbed in DEA/[$P_{888}C_{10}P_{888}$] docusate

X_i = mole fraction of CO_2 in the gas mixture

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 DETERMINATION OF INITIAL VOLUME, $V_{initial}$

Leakage Test:

Date	P_{CO_2} Introduced(bar)	P_{CO_2} Equilibrium(bar)	Date
15/4/2011	20	16.1	18/4/2011
18/4/2011	10	7.8	20/4/2011

Table 1: Leakage test result

The results show that there is no leakage in the system. Thus, to determine the initial volume of solubility cell without ionic liquid:

$$(P_{initial}) (V_{initial}) = (P_{1 \text{ without IL}}) (V_{1 \text{ without IL}})$$

$$V_{initial} = V_{\text{tube from valve A to valve B}} + V_{bomb}$$

$$= \pi (0.414cm/2)^2 (25.7cm) + 75 \text{ cm}^3$$

$$= 78.46 \text{ cm}^3$$

At 10 bar;

$$V_{1 \text{ without IL}} = (10 \text{ bar})(78.46 \text{ cm}^3) / 7.8 \text{ bar}$$

$$= 100.56 \text{ cm}^3$$

$$V_{DEA \text{ used}} = 1 \text{ ml} = 1 \text{ cm}^3$$

Therefore,

$$V_{1 \text{ with DEA}} = 100.56 - 1$$

$$= 99.56 \text{ cm}^3$$

Back calculation to determine $P_{1 \text{ with DEA}}$:

$$(P_{\text{initial}}) \, (V_{\text{initial}}) = (P_{1 \text{ with DEA}}) \, (V_{1 \text{ with DEA}})$$

$$P_{1 \text{ with DEA}} = (10 \text{ bar}) \, (78.46 \text{ cm}^3) \, / \, 99.56 \text{ cm}^3$$

$$= \textbf{7.88 bar}$$

Therefore, 7.88 bar will be used as the first pressure at time = 0 h. Meanwhile, 15.76 bar will be used for first pressure at 20 bar, time = 0 h and 23.63 bar will be used for the first pressure at 30 bar, time = 0 h.

4.2 RESULT FOR Diethanolamine (DEA)

4.2.1 Initial pressure, $P_1 = 10$ bar
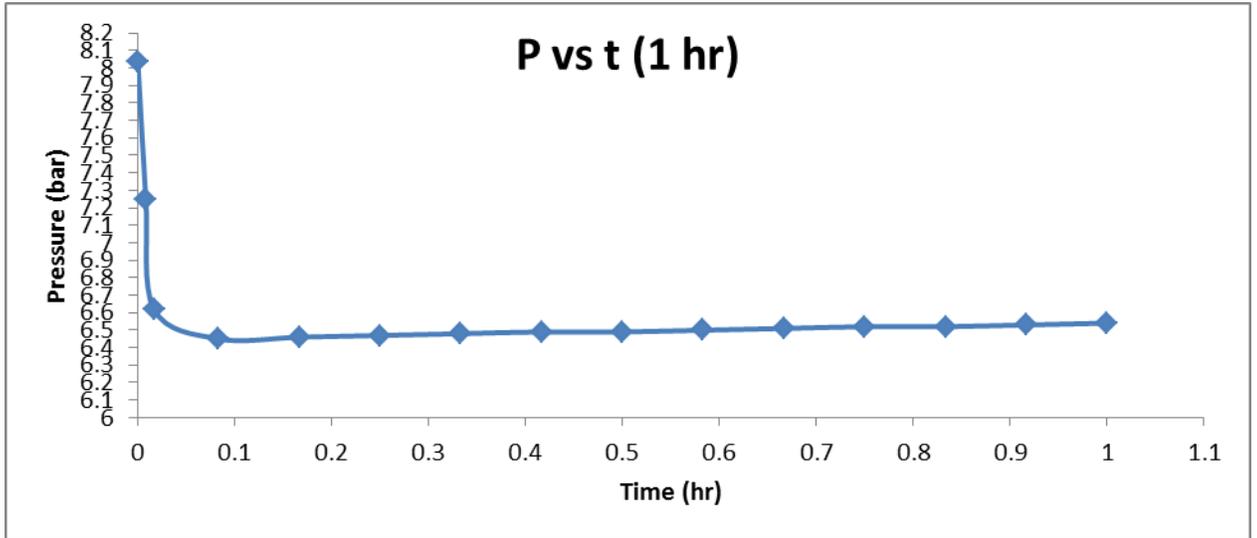
Figure 7: Pressure vs time for DEA at 10 bar (1 hour)
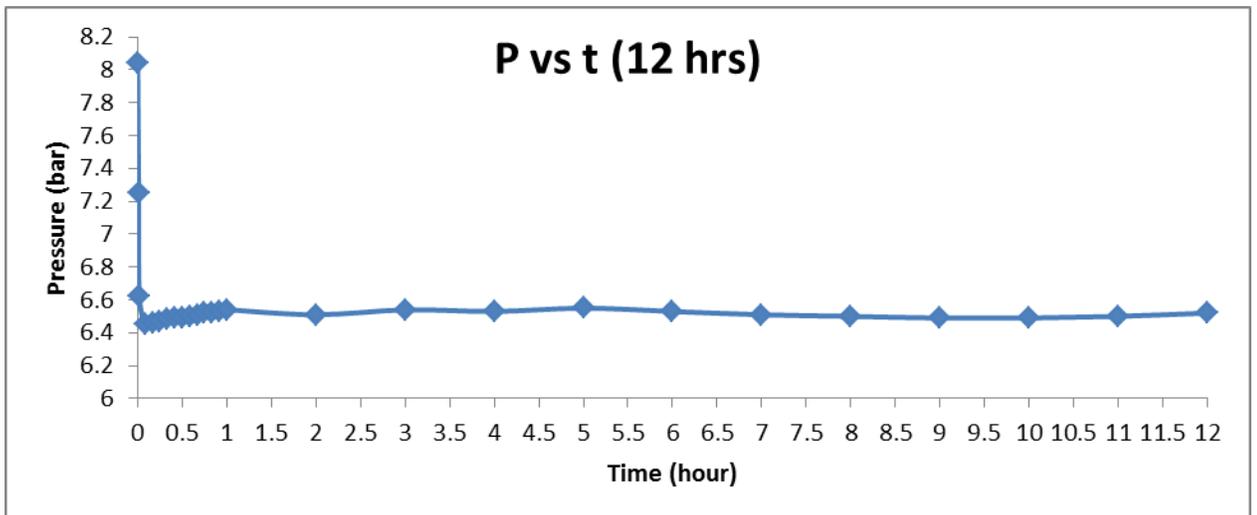
Figure 8: Pressure vs time for DEA at 10 bar (12 hour)

4.2.2   **Initial pressure, P_1 = 20 bar**
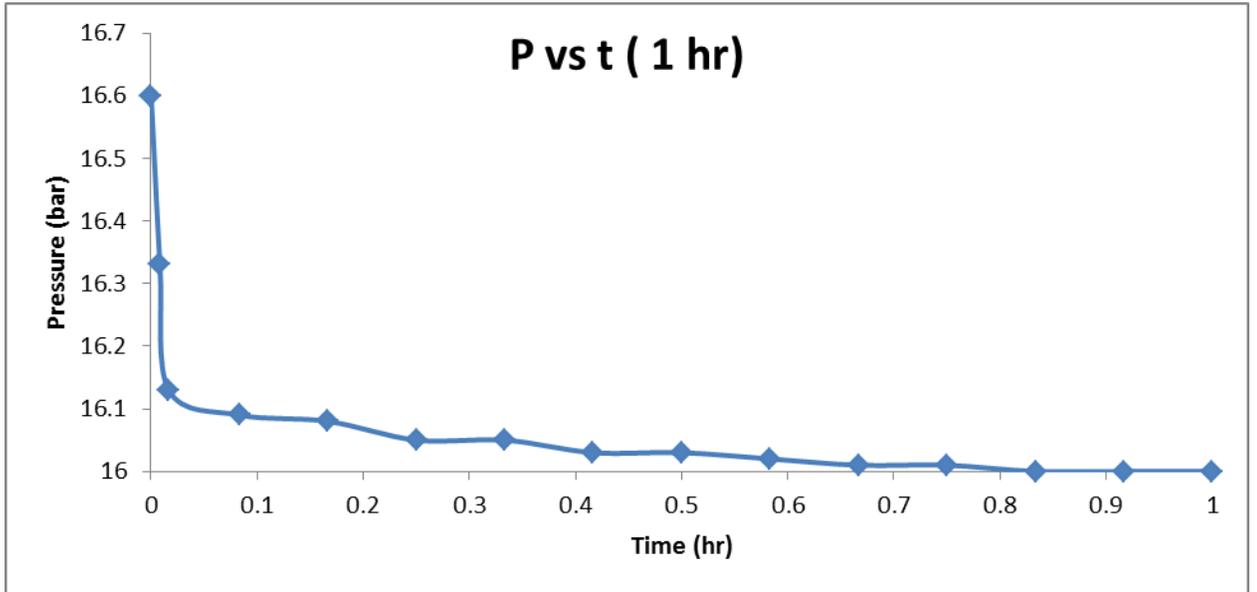
Figure 9: Pressure vs time for DEA at 20 bar (1 hour)
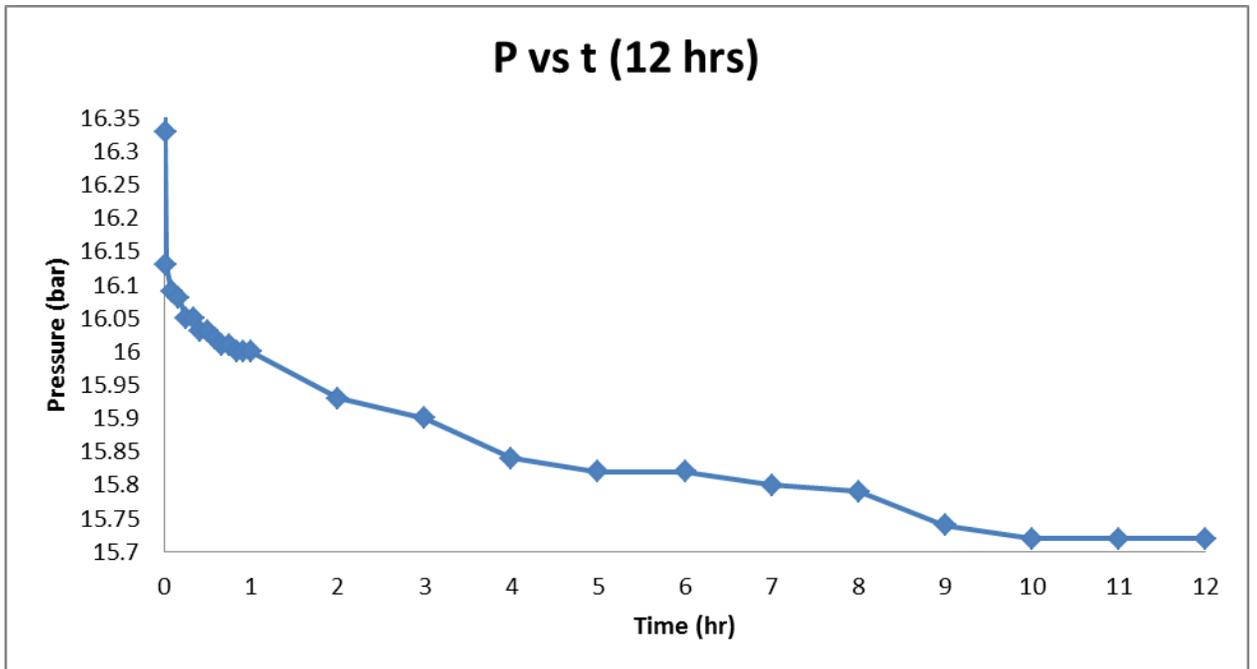
Figure 10: Pressure vs time for DEA at 20 bar (12 hour)

4.2.3   Initial pressure, P_1 = 30 bar
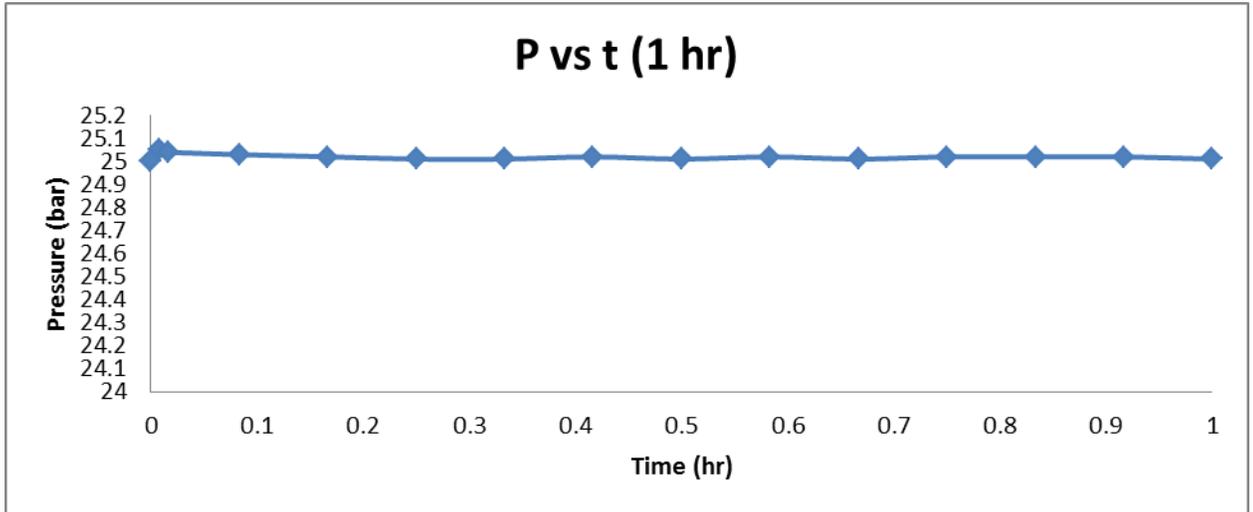
Figure 11: Pressure vs time for DEA at 30 bar (1 hour)
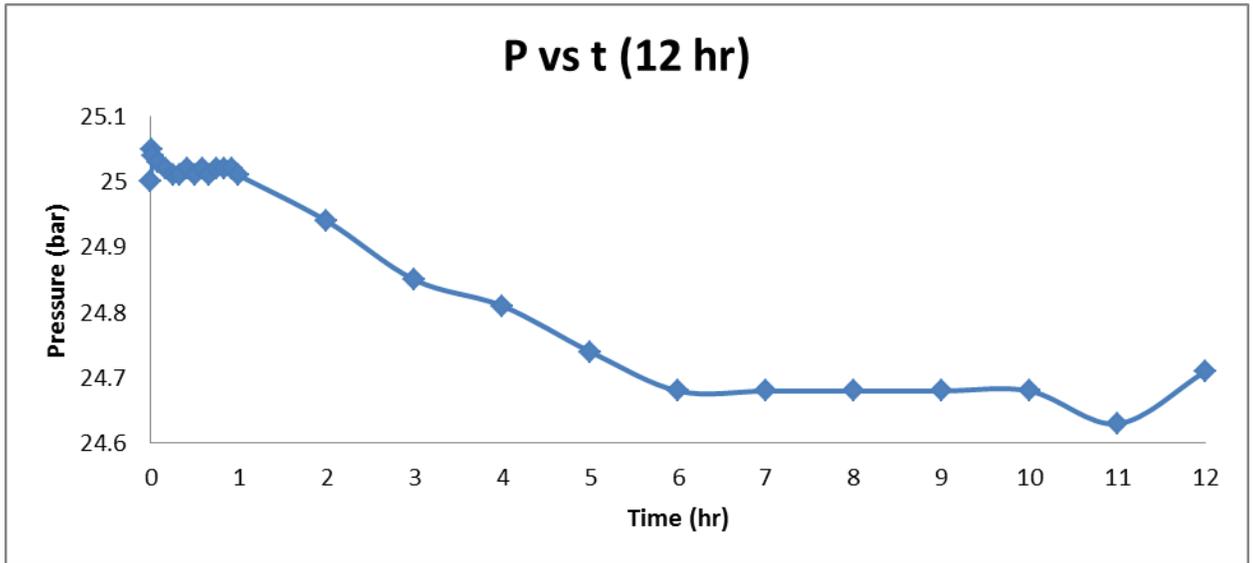
Figure 12: Pressure vs time for DEA at 30 bar (12 hour)

4.3 RESULT FOR [P$_{888}$C$_{10}$P$_{888}$] docusate

4.3.1   Initial pressure, Pi = 10 bar
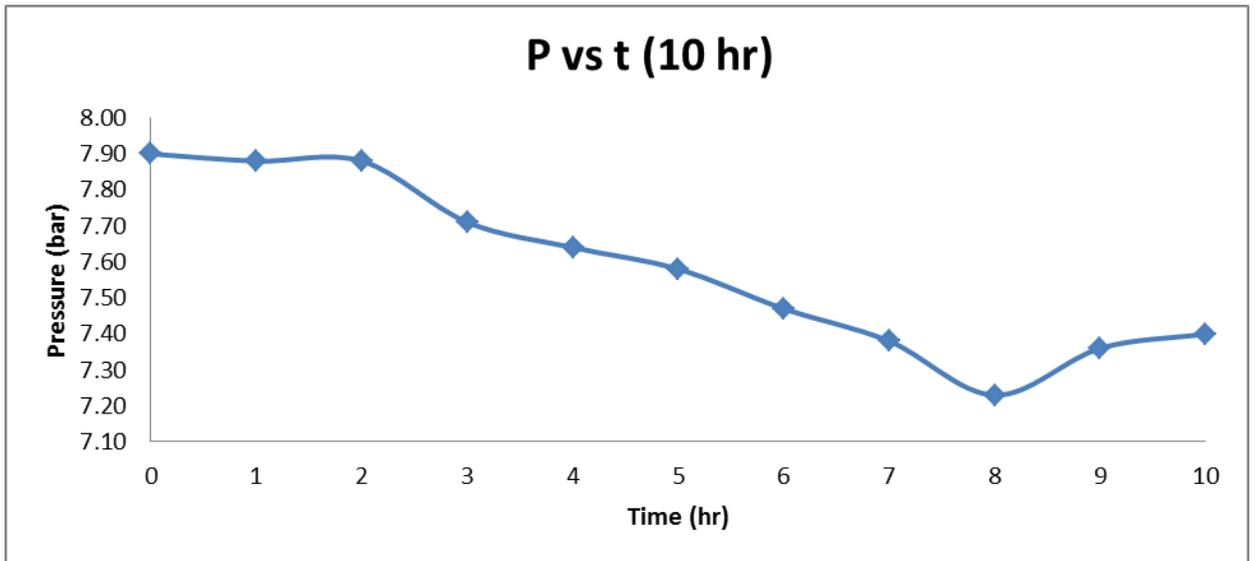
Figure 13: Pressure vs time for [P$_{888}$C$_{10}$P$_{888}$] docusate at 10 bar (10 hour)

4.3.2   Initial pressure, Pi = 20 bar
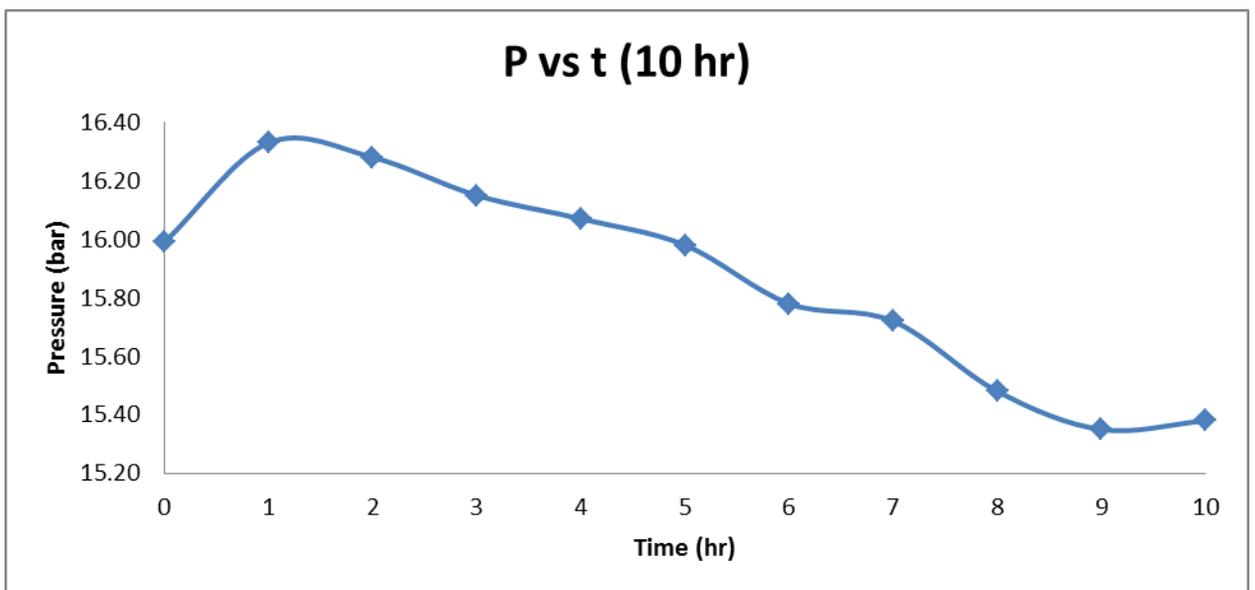
Figure 14: Pressure vs time for [P$_{888}$C$_{10}$P$_{888}$] docusate at 20 bar (10 hour)

4.3.3   **Initial pressure, Pi = 30 bar**
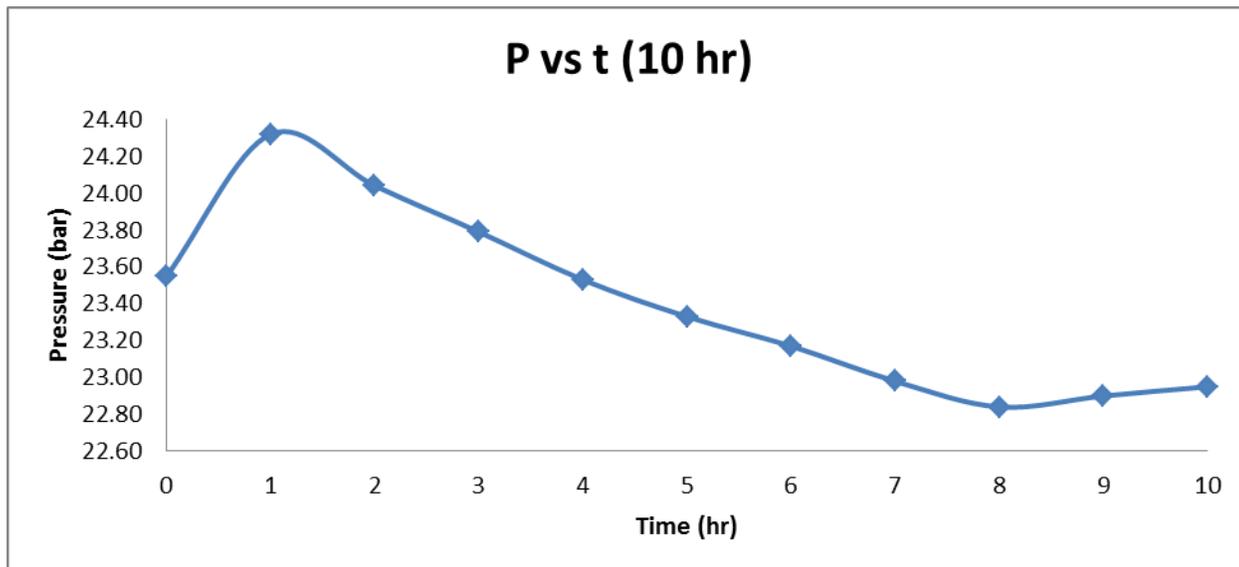
Figure 15: Pressure vs time for [$P_{888}C_{10}P_{888}$] docusate at 30 bar (10 hour)

4.4 NUMBER OF MOLES OF CO_2 ABSORBED, MOLE FRACTION AND MOLALITY

From the data obtained, the solubility of CO_2 in DEA/[$P_{888}C_{10}P_{888}$] docusate is calculated by using the Ideal Gas Law. The solubility of CO_2 is measured at room temperature, assumed to be at 25°C (298.15 K) and at pressure ranging from 10 bar to 30 bar. The solubility of CO_2 at 298.15 K in DEA is tabulated as below:

P (bar)	$n_{absorbed}$	X_{CO2}	m_{CO2} (mol CO_2/kg DEA)	CO_2 loading (mol CO_2/mol DEA)
10	0.0072	0.1891	2.2106	0.2332
20	0.0077	0.1992	2.3575	0.2487
30	0.0082	0.2098	2.5173	0.2655

Table 2: Solubility data for DEA at 298.15 K

Meanwhile, the solubility of CO_2 at 298.15 K in [$P_{888}C_{10}P_{888}$] docusate is tabulated as follows:

P (bar)	$n_{absorbed}$	X_{CO2}	m_{CO2} (mol CO_2/kg IL)	CO_2 loading (mol CO_2/mol IL)
10	0.0027	0.8071	2.3625	4.1844
20	0.0029	0.8191	2.5570	4.5289
30	0.0032	0.8311	2.7799	4.9220

Table 3: Solubility data for [$P_{888}C_{10}P_{888}$] docusate at 298.15 K

As for Henry's law constant, the results calculated are as belows:

Solvent	Henry's law constant (atm)
DEA	117
[$P_{888}C_{10}P_{888}$] docusate	19 ± 10
[P(14)666][Cl]	36 ± 4
[P(14)666][DCA]	29 ± 1
[P(14)666][Tf$_2$N]	37 ± 4
[P(2)444][DEP]	59 ± 6
[P(14)444][DBS]	29 ± 4
[bmim][Pf$_6$]	70.1

Table 4: Comparison of ionic liquids (Kilaru *et al.*, 2008)

Comparison Results between DEA and [$P_{888}C_{10}P_{888}$] docusate
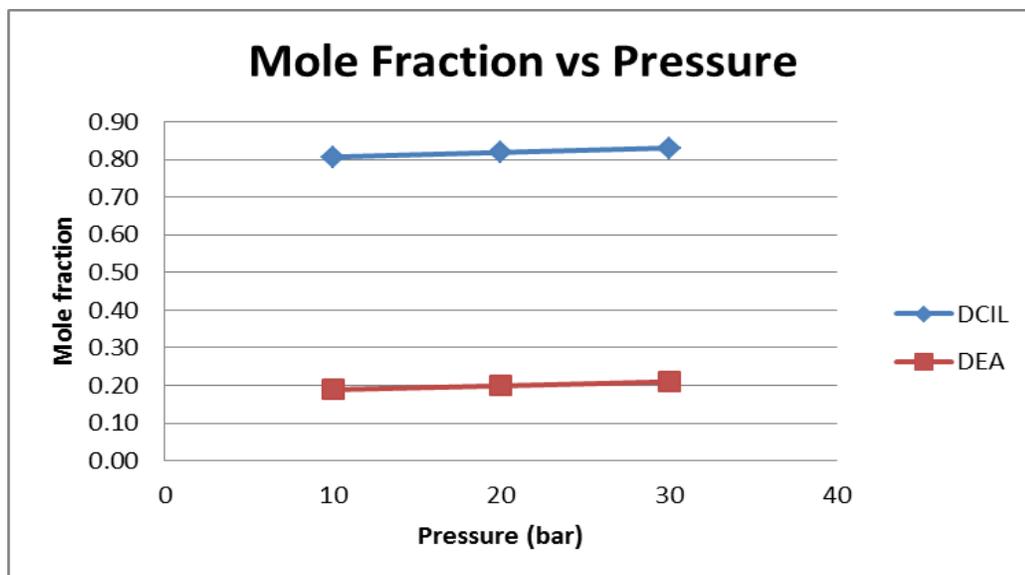
Figure 16: Mole fraction vs pressure for DEA and [$P_{888}C_{10}P_{888}$] docusate
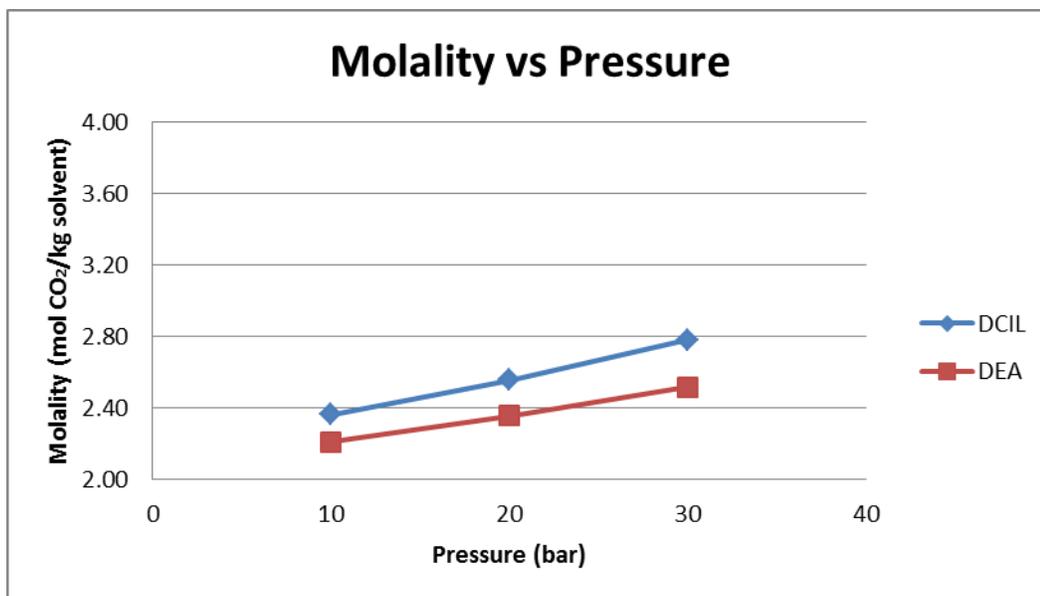
Figure 17: Molality vs pressure for DEA and [$P_{888}C_{10}P_{888}$] docusate
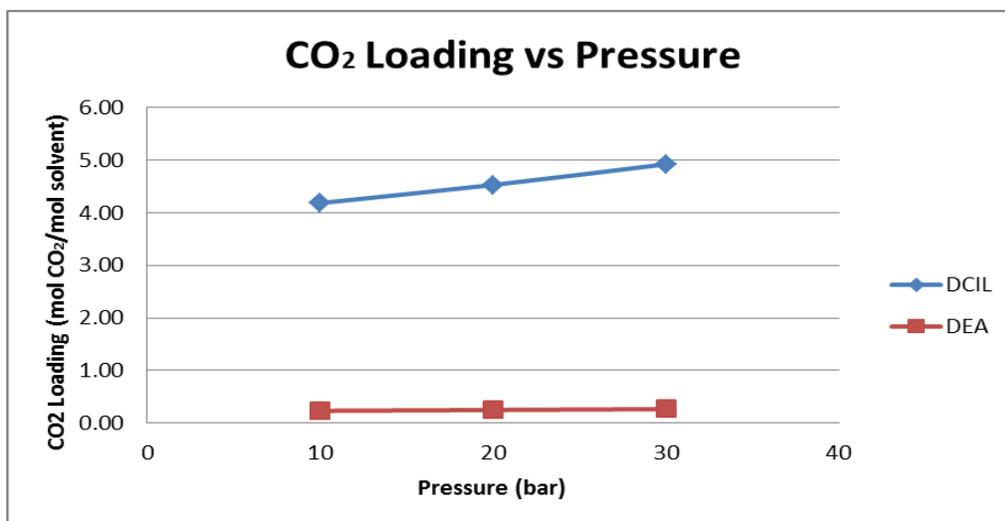
Figure 18: CO_2 loading vs pressure for DEA and [P$_{888}$C$_{10}$P$_{888}$] docusate

In this work, phase behavior of CO_2 in [P$_{888}$C$_{10}$P$_{888}$] docusate were measured in a pressure range from (10 to 30) bar in 10 bar interval at 298 K. The experimental results of CO_2 + DEA and CO_2 + [P$_{888}$C$_{10}$P$_{888}$] docusate system are presented in Table 2 and 3, respectively. Figures 13, 14 and 15 also show their mole fraction, molality and CO_2 loading versus pressure, respectively. Throughout the paper, molality (i.e, number of moles per kilograms of solvent) is used for describing the solute concentration.

As can be seen in Figure 13, CO_2 mole fraction increases with increasing pressure at fixed temperature. This means that carbon dioxide solubility increases commensurate to rises in pressure. Figure 13 also showed that CO_2 + [P$_{888}$C$_{10}$P$_{888}$] docusate system has higher solubilities compared to carbon dioxide + DEA system dua to large value of mole fraction of CO_2 absorbed by [P$_{888}$C$_{10}$P$_{888}$] docusate. It also can be concluded that CO_2 solubility in DEA/[P$_{888}$C$_{10}$P$_{888}$] docusate at 30 bar > 20 bar > 10 bar.

Figure 14 shows that as the molality of CO_2 absorbed linearly increases with increasing pressure in the system. This is the typical behavior for a purely physical solubility. Figure 14 also showed that CO_2 + [P$_{888}$C$_{10}$P$_{888}$] docusate system has higher molality thus mean that it has higher solubility than CO_2 + DEA system.

Meanwhile, Figure 15 showed that CO_2 loading of [P$_{888}$C$_{10}$P$_{888}$] docusate also increases with the increasing pressure. However, CO_2 loading for DEA has very small increases

when the pressure is increases. CO_2 loading for $[P_{888}C_{10}P_{888}]$ docusate ranging from 4.18 to 4.92 mole CO_2/mole $[P_{888}C_{10}P_{888}]$ docusate meanwhile CO_2 loading for DEA ranging from 0.23 to 0.27 mole CO_2/mole DEA.

Calculated Henry's law constant in 10 K interval showed in Table 4. Henry's law constant of $[P_{888}C_{10}P_{888}]$ docusate is 19 ± 10 atm which is lower than other Henry's law constant of DEA and other phosphonium-based ionic liquids which are [P(14)666][Cl], [P(14)666][DCA], [P(14)666][Tf$_2$N], [P(2)444][DEP] and [P(14)444][DBS] as stated by Kilaru *et al*. in his report.

This showed that $[P_{888}C_{10}P_{888}]$ docusate has higher solubility compared to DEA and other phosphonium-based ionic liquids. This is because the lower the value of Henry's law constant, the higher the solubility of CO_2.

Moreover, to explain the Henry's law constant, the concentration of dissolved gas depends on the partial pressure of the gas. The partial pressure controls the number of gas molecule collisions with the surface of the solution. If the partial pressure is doubled the number of collisions with the surface will double. The increased number of collisions produces more dissolved gas. The dissolving process for gases is equilibrium. The solubility of a gas depends directly on the gas pressure. The number of molecules leaving the gas phase to enter the solution equals the number of gas molecules leaving the solution. If the temperature stays constant increasing the pressure will increase the amount of dissolved gas.

In addition, from the literature review, the loading for amine should increases from 0 to 0.5 mole CO_2/mole amine (Dang, 2001). However, the highest value of carbon dioxide loading achieved for DEA is 0.2655 mole carbon dioxide per mole DEA in this experiment. It is because this experiment is conducted using pure DEA instead of mixing it with water. This phenomenon could be explained by using Joule-Thomson Effect. Joule-Thompson describes the temperature change of a gas when it is forced through a valve while kept insulated so that no heat is exchanged with the environment. Therefore, to achieve 0.5 mol CO_2/mol DEA of loading, the experiment should be conducted using DEA mixture.

CHAPTER 6
CONCLUSION AND RECOMMENDATION

The solubility of carbon dioxide in ionic liquid [$P_{888}C_{10}P_{888}$] docusate were determined by measuring the pressure drop of the binary mixture (CO_2 + [$P_{888}C_{10}P_{888}$] docusate) at constant temperature, 298.15 K which showing purely physical solubility. The solubility of CO_2 in ionic liquid [$P_{888}C_{10}P_{888}$] docusate was observed from 10 to 30 bar in 10 bar interval. The CO_2 loading for [$P_{888}C_{10}P_{888}$] docusate is 4.50 $\pm$ 0.4 mole CO_2 per mole [$P_{888}C_{10}P_{888}$] docusate with Henry's law constant at 19 $\pm$ 10 atm.

The solubility of carbon dioxide can also be obtained using the different temperature range to measure the effect of temperature at CO_2 solubility. The solid support such as silica gel can also be used to improve the CO_2 solubility.

CHAPTER 7
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CHAPTER 8

APPENDICES

8.1 PRESSURE READING FOR Diethanolamine (DEA)

At 10 bar:

Time, hr	P, bar	Time, hr	P, bar
0	8.04	18	6.4
0.008333	7.25	19	6.34
0.016667	6.62	20	6.3
0.083333	6.45	21	6.27
0.166667	6.46	22	6.27
0.25	6.47	23	6.27
0.333333	6.48	24	6.25
0.416667	6.49	25	6.24
0.5	6.49	26	6.22
0.583333	6.5	27	6.21
0.666667	6.51	28	6.2
0.75	6.52	29	6.19
0.833333	6.52	30	6.19
0.916667	6.53	31	6.16
1	6.54	32	6.14
2	6.51	33	6.14
3	6.54	34	6.15
4	6.53	35	6.15
5	6.55	36	6.16
6	6.53	37	6.16
7	6.51	38	6.16
8	6.5	39	6.16
9	6.49	40	6.13
10	6.49	41	6.12
11	6.5	42	6.03
12	6.52	43	5.99
13	6.52	44	5.95
14	6.52	45	5.92
15	6.51	46	5.9
16	6.5	47	5.88
17	6.49	48	5.86

Table 5: Pressure reading of DEA at 10 bar

At 20 bar:

Time, hr	P, bar	Time, hr	P, bar
0	16.6	18	15.75
0.008333	16.33	19	15.75
0.016667	16.13	20	15.75
0.083333	16.09	21	15.75
0.166667	16.08	22	15.75
0.25	16.05	23	15.75
0.333333	16.05	24	15.74
0.416667	16.03	25	15.74
0.5	16.03	26	15.73
0.583333	16.02	27	15.72
0.666667	16.01	28	15.72
0.75	16.01	29	15.72
0.833333	16	30	15.72
0.916667	16	31	15.72
1	16	32	15.72
2	15.93	33	15.72
3	15.9	34	15.68
4	15.84	35	15.67
5	15.82	36	15.67
6	15.82	37	15.67
7	15.8	38	15.67
8	15.79	39	15.67
9	15.74	40	15.54
10	15.72	41	15.52
11	16	42	15.5
12	16	43	15.5
13	16	44	15.5
14	16	45	15.5
15	15.66	46	15.43
16	15.73	47	15.43
17	15.75	48	15.39

Table 6: Pressure reading of DEA at 20 bar

At 30 bar:

Time, hr	P, bar	Time, hr	P, bar
0	25	18	24.82
0.008333	25.05	19	24.54
0.016667	25.04	20	24.44
0.083333	25.03	21	24.42
0.166667	25.02	22	24.42
0.25	25.01	23	24.42
0.333333	25.01	24	24.42
0.416667	25.02	25	24.42
0.5	25.01	26	24.39
0.583333	25.02	27	24.37
0.666667	25.01	28	24.34
0.75	25.02	29	24.31
0.833333	25.02	30	24.29
0.916667	25.02	31	24.24
1	25.01	32	23.2
2	24.94	33	24.21
3	24.85	34	24.24
4	24.81	35	24.33
5	24.74	36	24.43
6	24.68	37	24.48
7	24.68	38	24.51
8	24.68	39	24.53
9	24.68	40	24.54
10	24.5	41	24.59
11	24.63	42	24.59
12	24.71	43	24.37
13	24.75	44	24.2
14	24.75	45	24.18
15	24.74	46	24.21
16	24.74	47	24.14
17	24.84	48	24.14

Table 7: Pressure reading of DEA at 30 bar

8.2 PRESSURE READING FOR [$P_{888}C_{10}P_{888}$] docusate

At 10 bar:

Time, hr	P, bar
0	7.90
1	7.88
2	7.88
3	7.71
4	7.64
5	7.58
6	7.47
7	7.38
8	7.23
9	7.36
10	7.4
11	7.56
12	7.74
13	7.95
14	7.96
15	7.97
16	7.96
17	7.97
18	7.97
19	7.99
20	7.98
21	7.91
22	7.88
23	7.88
24	7.87

Table 8: Pressure reading of [$P_{888}C_{10}P_{888}$] docusate at 10 bar

At 20 bar:

Time, hr	P, bar
0	15.99
1	16.33
2	16.28
3	16.15
4	16.07
5	15.98
6	15.78
7	15.72
8	15.48
9	15.35
10	15.38
11	15.47
12	15.52
13	15.71
14	15.92
15	16.15
16	16.15
17	16.16
18	16.17
19	16.21
20	16.20
21	16.12
22	16.01
23	15.99
24	16.00

Table 9: Pressure reading of [$P_{888}C_{10}P_{888}$] docusate at 20 bar

At 30 bar:

Time, hr	P, bar
0	23.55
1	24.32
2	24.04
3	23.79
4	23.53
5	23.33
6	23.17
7	22.98
8	22.84
9	22.90
10	22.95
11	23.00
12	23.03
13	23.04
14	23.06
15	23.06
16	23.07
17	23.12
18	23.12
19	23.12
20	23.12
21	23.15
22	23.17
23	23.18
24	23.21
25	23.23

Table 10: Pressure reading of [$P_{888}C_{10}P_{888}$] docusate at 30 bar