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จากก๊าซเผาไหม้จากโรงไฟฟ้าเพื่อลดภาวะโลกร้อน

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### บทคัดย่อ

ในปัจจุบัน การเปลี่ยนแปลงสภาพภูมิอากาศ และภาวะโลกร้อน เป็นประเด็นที่สำคัญในเรื่องของสิ่งแวดล้อม เนื่องจากปริมาณก๊าซคาร์บอนไดออกไซด์ที่เพิ่มสูงขึ้นมากในบรรยากาศ แหล่งของคาร์บอนไดออกไซด์ที่สำคัญ คือ กิจกรรมที่เกี่ยวข้องกับพลังงาน เช่น การผลิตไฟฟ้า ณ ขณะนี้เทคโนโลยีที่มีประสิทธิภาพในการกำจัดคาร์บอนไดออกไซด์จากแหล่งเหล่านี้ คือ การดูดซึมโดยเฉพาะอย่างยิ่งด้วยสารละลายเอมีน สารละลายเอมีนที่ใช้ในเชิงพาณิชย์คือ โมโนเอทานอลามีน (เอ็มอีเอ) และ เมทิลไดเอทานอลามีน (เอ็มดีอีเอ) อย่างไรก็ตามสารเหล่านี้ยังมีข้อด้อย เช่น ความจุต่ำ การกัดกร่อน และความต้องการในการใช้พลังงานสูง ดังนั้น สารละลายชนิดใหม่ๆ ได้ถูกพัฒนาขึ้นมาเพื่อที่จะปรับปรุงประสิทธิภาพในการจับคาร์บอนไดออกไซด์ ดังนั้นจุดประสงค์ของงานนี้ คือ การวัดค่าการละลายของคาร์บอนไดออกไซด์ในสารละลายน้ำของ ไดเอทิลอะมิโนเอทานอล (ดีอีเออี) ในฐานะที่เป็นสารตัวใหม่ โดยทำการวัดที่อุณหภูมิจาก 30 องศาเซลเซียส ถึง 80 องศาเซลเซียส ความดันย่อยของคาร์บอนไดออกไซด์ อยู่ในช่วง 5 ถึง 100 กิโลปาสกาล และความเข้มข้นของสารละลายจาก 3 ถึง 5 โมลาร์ ผลของการละลายของคาร์บอนไดออกไซด์ในสารละลายดีอีเออี จะถูกเปรียบเทียบกับผลที่ได้จากสารละลายของเอ็มอีเอ และ เอ็มดีอีเอ สำหรับความจุวัฏภาค ผลที่ได้แสดงให้เห็นว่า ดีอีเออีจะมีศักยภาพสูงถึง 861 เปอร์เซ็นต์ และ 151 เปอร์เซ็นต์ เมื่อเทียบกับ เอ็มอีเอ และ เอ็มดีอีเอ ตามลำดับ นั้นหมายความว่าดีอีเออีจะช่วยประหยัดพลังงานได้มากขึ้นและสามารถลดค่าใช้จ่ายในการฟื้นฟูสภาพสารละลาย และทำให้เทคโนโลยีในการจับคาร์บอนสามารถเป็นไปได้

**Research Topic:** Solubility Study of Carbon Dioxide in Aqueous Amine Solution of Diethyl Monoethanolamine  
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**Period of research:** December 2014

### **Abstract**

Currently, climate change and global warming are the main issues on environmental concern due to the higher amount of carbon dioxide in the atmosphere. The main sources of carbon dioxide are energy-related activities such as power generation. Now, the effective technology to remove CO<sub>2</sub> from these sources is absorption especially with amine solution. The commercially used amine solutions are monoethanolamine (MEA) and methyldiethanolamine (MDEA). Nevertheless, they also have disadvantages such as low capacity, corrosion and high energy requirement. Therefore, many new solvents have been developed to improve efficiency for CO<sub>2</sub> capture. Consequently, the objective of this work is to measure the solubility of CO<sub>2</sub> in an aqueous solution of 2-(Diethylamino)ethanol (DEAE) as a novel solution at the temperature from 30 °C to 80 °C, CO<sub>2</sub> partial pressures ranging from 5 to 100 kPa and solution concentration from 3 to 5 molar. The solubility results of CO<sub>2</sub> in DEAE solution are compared with those of aqueous solution of MEA and MDEA. For cyclic capacity, the results present that DEAE provides higher performance which is up to 856% and 151% higher than that of MEA and MDEA, respectively. This means that DEAE can save more energy and cost for solution regeneration and makes carbon capture technology viable.

## TABLE OF CONTENTS

<b>Acknowledgement</b>	i
<b>Abstract (THAI)</b>	ii
<b>Abstract (ENGLISH)</b>	iii
<b>Table of Contents</b>	iv
<b>List of Tables</b>	vi
<b>List of Figures</b>	vii
<b>CHAPTER ONE: INTRODUCTION</b>	<b>1</b>
1.1 Effects and Uses of CO <sub>2</sub>	1
1.2 Sources of Flue Gas	2
1.3 Flue Gas from Coal-Fired Power Plants	2
1.4 Flue Gas Control Technologies	4
1.4.1 Absorption process	6
1.4.2 Adsorption	6
1.4.3 Cryogenics	7
1.4.4 Membrane	7
1.5 Objectives of This Research	9
<b>CHAPTER TWO: THEORIES AND LITERATURE REVIEWS</b>	<b>11</b>
2.1 Absorption Process	11
2.1.1 Basic concept of absorption	11
2.1.2 Types of absorption	12
2.1.3 Cyclic Capacity	13
2.1.4 Process description	15
2.2 Solvents for Acid Gas Absorption	15
2.2.1 Chemical solvents	19
2.2.2 Physical solvents	23
2.2.3 Mixed physical-chemical solvents	24
2.3 Literature Review of Solubility of CO <sub>2</sub> in MEA	26
2.4 Literature Review of New Solvents	27
2.4.1 New solvents for acid gas removal	28

<b>CHAPTER THREE: EXPERIMENT</b>	32
3.1 Chemicals and equipment	32
3.2 Experimental procedure	34
<b>CHAPTER FOUR: RESULTS AND DISCUSSION</b>	36
4.1 Verification of solubility study	36
4.2 Solubility results	36
4.2.1 Effect of types of solvents	43
4.2.2 Effect of CO <sub>2</sub> partial pressure	46
4.2.3 Effect of temperature	46
4.2.4 Effect of solvent concentration	47
<b>CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS</b>	49
5.1 Conclusions	49
5.2 Recommendations for Future Work	49
<b>REFERENCES</b>	51

## List of Tables

Table 1.1 Composition of flue gas evolved in burning bituminous coal	4
Table 2.1 Commercial CO <sub>2</sub> scrubbing solvents used in the industry	17
Table 2.2 Conventional alkanolamines	20
Table 3.1 Experimental operating conditions for solubility studies	35
Table 4.1 Solubility results of CO <sub>2</sub> in MEA, MDEA and DEAE at 3M concentration and 30-80°C	38
Table 4.2 Absorption capacity difference of DEAE compared with MEA and MDEA at 3M concentration and 30-80°C	39
Table 4.3 Solubility results of CO <sub>2</sub> in MEA, MDEA and DEAE at 4M concentration and 30-80°C	40
Table 4.4 Absorption capacity difference of DEAE compared with MEA and MDEA at 4M concentration and 30-80°C	41
Table 4.5 Solubility results of CO <sub>2</sub> in MEA, MDEA and DEAE at 5M concentration and 30-80°C	42
Table 4.6 Absorption capacity difference of DEAE compared with MEA and MDEA at 5M concentration and 30-80°C	43

## List of Figures

Figure 1.1 GHGs emission by sectors	3
Figure 1.2 CO <sub>2</sub> emissions from power plants in Thailand comparison with power generation	3
Figure 1.3 CO <sub>2</sub> capture technologies	5
Figure 1.4 Principles of gas separation and gas absorption membranes	8
Figure 2.1 Film theory of mass transfer across the interface	12
Figure 2.2 Schematic flow diagram of the absorption process	16
Figure 3.1 Schematic diagram of solubility apparatus	33
Figure 3.2 CO <sub>2</sub> loading measurement equipment	35
Figure 4.1 Comparison of solubility of CO <sub>2</sub> in 5.0M MEA solution at 40°C	37
Figure 4.2 Comparison of solubility of CO <sub>2</sub> in 5.0M MEA solution at 80°C	37
Figure 4.3 Solubility of CO <sub>2</sub> in 5.0M MEA, MDEA and DEAE at 40°C	44
Figure 4.4 Solubility of CO <sub>2</sub> in 5.0M MEA, MDEA and DEAE at 80°C	44
Figure 4.5 Cyclic capacities of CO <sub>2</sub> in 5.0M MEA, MDEA and DEAE at 15 and 100 kPa	45
Figure 4.6 Solubility of CO <sub>2</sub> in 5.0M DMAE from 30 to 80°C and CO <sub>2</sub> partial pressure from 5-100 kPa	47
Figure 4.7 Effects of solution concentration on solubility of CO <sub>2</sub> in DEAE from 30 to 80°C	48



## CHAPTER ONE

### INTRODUCTION

The production and use of fossil fuels contributes to an increase in emissions of greenhouse gases (GHGs), especially carbon dioxide (CO<sub>2</sub>) and other pollutants such as oxides of sulfur (SO<sub>x</sub>) and oxides of nitrogen (NO<sub>x</sub>). CO<sub>2</sub> constitutes the largest fraction of greenhouse gas emissions, accounting for 77.2% of the total greenhouse gases emitted in Canada (Environment Canada, 2006).

#### 1.1 Effects and Uses of CO<sub>2</sub>

As a chemical, CO<sub>2</sub> is used in various ways. It has great potential as a chemical feedstock for a variety of commodity chemicals. Moreover, CO<sub>2</sub> is used in the food industry in carbonated beverages and brewing. Its industrial uses include feedstock for chemical manufacture, inert gas, and firefighting. It is an essential ingredient in medical oxygen, where, in low concentrations, it acts as a breathing stimulant, and in the growth of plants or algae. Currently, there are also extensive uses of CO<sub>2</sub> in enhanced oil recovery processes (EOR) to recover more oil from petroleum reservoirs (Gupta et al., 2003).

In contrast, CO<sub>2</sub> has adverse effects as well. CO<sub>2</sub> is a significant factor in climate change and global warming. The increased concentrations of greenhouse gases in the atmosphere are enhancing global warming. The direct result of climate change is likely to be a global warming. Climate scientists around the world agree that average global temperatures could rise by 1.4 to 5.8 degrees Celsius by the end of this century (Williams, 2002). However, climate change is more than a warming trend. Increasing temperatures will lead to changes in many aspects of weather, such as wind patterns, the amount and type of precipitation, and the types and frequency of severe weather events that may be expected to occur in many areas.

In addition, the impact of climate change on agricultural regions will vary: some regions will benefit from longer growing seasons and more rain, but poorer soil conditions and reduced water resources will make it more difficult to feed growing populations in poorer areas.

In addition, warmer temperatures could increase the range of some parasites and diseases, bringing new infectious diseases to communities. For example, the extremely rapid and unexpected spread of West Nile virus across the US and Canada can in part be attributed to a warmer climate in which disease-carrying mosquitoes are able to thrive (Williams, 2002).

These ultimate effects of increased CO<sub>2</sub> in the atmosphere underscore the need for technologies to significantly reduce these emissions. One such technology is post-combustion CO<sub>2</sub> capture, which involves separating CO<sub>2</sub> from various sources such as flue gas from power plants, refineries, cement manufacture, etc. in order to prevent the CO<sub>2</sub> from being emitted to the atmosphere.

## 1.2 Sources of CO<sub>2</sub>

Flue gas and CO<sub>2</sub> from natural gas processing contribute significantly to the total CO<sub>2</sub> emitted by anthropogenic sources. As shown in Figure 1.1, energy-related activities are by far the largest sources of CO<sub>2</sub> emissions. These industries consist of fossil fuel production and electricity and heat production. Furthermore, recently, the use of coal as a huge source of energy has become more important for power generation because of its greater availability and lower cost compared to oil and gas. However, the amount of CO<sub>2</sub> from oil and gas production in Thailand has less than that from power plants and is more difficult to capture. Therefore, carbon capture technology development, including this work focuses mainly on CO<sub>2</sub> capture from fossil-fired power plant flue gas. In Thailand, CO<sub>2</sub> emission from power plants is presented in Figure 1.2 which shows the amount of CO<sub>2</sub> emitted to the atmosphere compared to the power generated each year.

## 1.3 Flue Gas from Fossil-Fired Power Plants

The combustion process of coal or natural gas in fossil-fired power plants leads inevitably to the production of CO<sub>2</sub> and other pollutants. The composition of flue gas given in Table 1.1 is typical of flue gas generated from burning western Kentucky coal (Slack, 1975), which is mainly bituminous. From the table, the concentration of CO<sub>2</sub> from coal-fired power plants is around 12%, which is similar to typical flue gas that normally has 10-18% for coal and 5-12% for natural gas (Gupta et al., 2003).

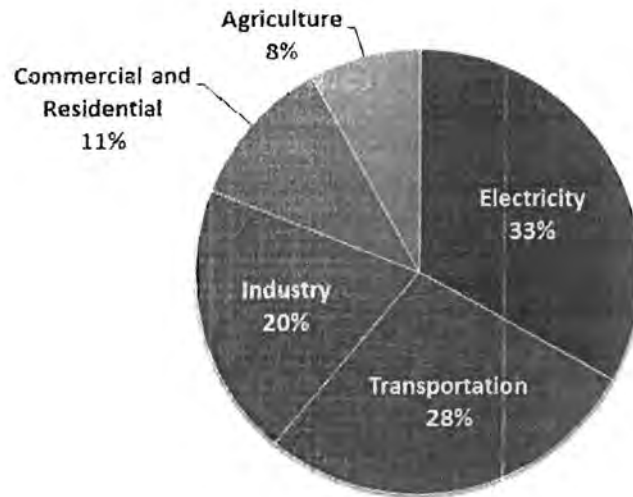


Figure 1.1 GHGs emission by sectors (www.epa.gov, 2011)

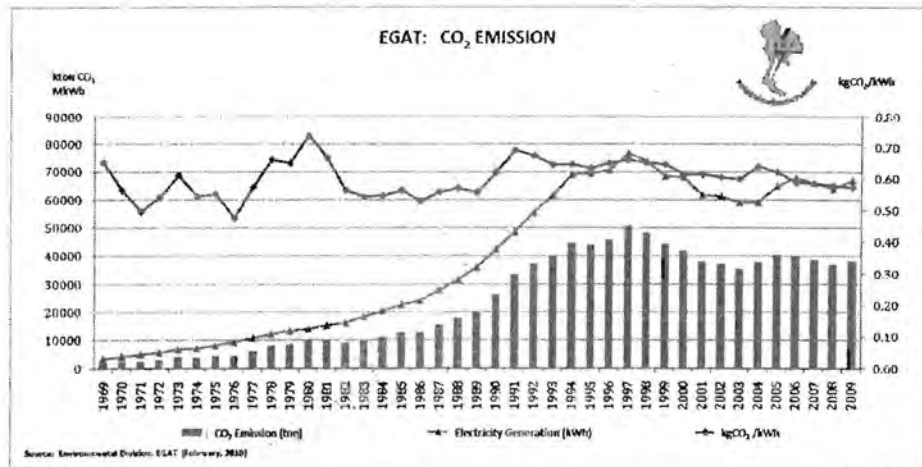


Figure 1.2 CO<sub>2</sub> emissions from power plants in Thailand comparison with power generation (www.egat.co.th)

Table 1.1 Composition of flue gas evolved in burning bituminous coal (Slack, 1975)

Constituent	Typical flue gas from western Kentucky coal * (% vol)
Nitrogen (N <sub>2</sub> )	74.56
Carbon dioxide (CO <sub>2</sub> )	12.55
Oxygen (O <sub>2</sub> )	4.87
Water vapor (H <sub>2</sub> O)	7.76
Sulfur oxides (SO <sub>x</sub> )	
-Sulfur dioxide (SO <sub>2</sub> )	0.22
-Sulfur trioxide (SO <sub>3</sub> )	0.001
Nitrogen oxide (NO <sub>x</sub> )	0.04
Particulate matter	
-Percent by weight	0.66
-Grains per standard cu.ft.(scf)	3.59

\* Composition (%wt): 66.0% C; 3.3% S; 12.0% ash; 1.3% N.

Fisher et al. (2002), report the distribution of CO<sub>2</sub> concentration emitted from industrial sources that 75% of CO<sub>2</sub> emissions have a concentration of 10-20%. More specifically, flue gas streams containing less than 20% CO<sub>2</sub> concentrations make up about 90% of the emission sources. As CO<sub>2</sub> capture is being designed for application at various concentrations, there is tremendous potential for CO<sub>2</sub> capture from fossil-fire power plant flue gas.

Several mature technologies are available for effectively capturing CO<sub>2</sub>, including absorption, adsorption, cryogenics, and membrane technologies.

#### 1.4 Flue Gas Control Technologies

Any of several proven technologies could be used to remove CO<sub>2</sub> from gas streams. Depending on the nature of the problems and economic considerations, the selection of a technology for a given capture application depends on many factors: pressure of the gas stream, partial pressure of CO<sub>2</sub> in the gas stream, extent of CO<sub>2</sub> recovery required, purity of desired CO<sub>2</sub> product, capital and operating costs of the

process, and the cost of additives necessary to overcome fouling and corrosion. Based on the method of CO<sub>2</sub> removal, capture technologies can be broadly classified into a number of categories as shown in Figure 1.3.

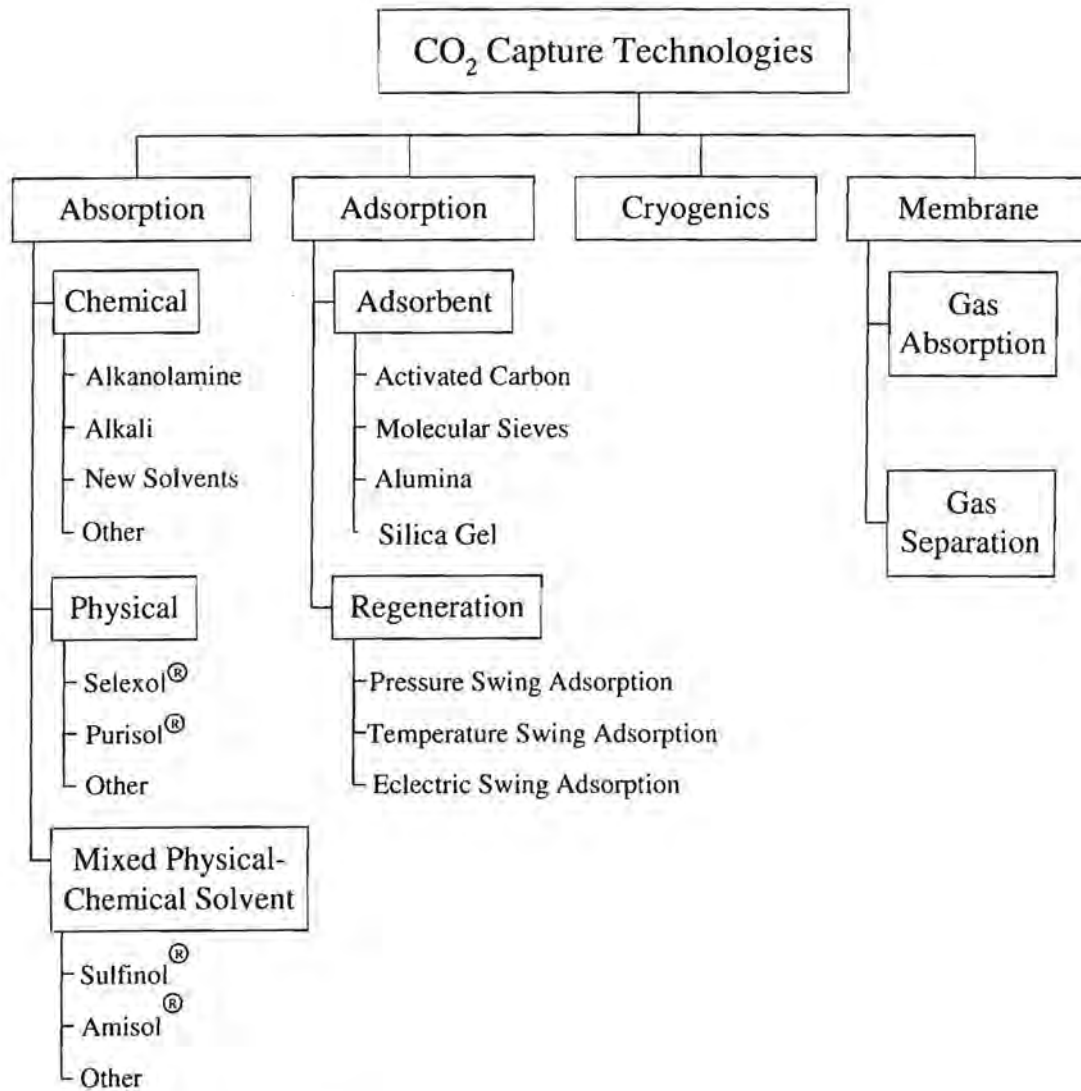


Figure 1.3 CO<sub>2</sub> capture technologies

#### 1.4.1. Absorption process

Absorption systems are the most common CO<sub>2</sub> capture processes currently in use (Gupta et al., 2003). Indeed, chemical absorption at present is the only commercially proven process for CO<sub>2</sub> capture from low CO<sub>2</sub> concentration gas streams. In this approach, absorption occurs when the gas solute transfers from the gas phase into a liquid solvent across a gas-liquid interface. Absorption involves the direct contact of a solvent with the target gas stream in an absorber. In a physical absorption system, the absorption is a function of the solubility of the solute in the solvent; therefore, physical solvents are usually used when the partial pressure of the solute in the feed gas is high (Gupta et al., 2003). Regeneration is accomplished by applying heat, reducing the pressure, or both.

Unlike physical absorption, in chemical absorption systems, the absorption rate is enhanced by the chemical reaction, making chemical solvents more suitable for processes that have a low solute partial pressure. This is usually the case in coal-fired power plants, where the flue gas is emitted at atmospheric pressure and typically contains 10-15% CO<sub>2</sub>. The solvent is usually an alkanolamine such as Monoethanolamine (MEA) or Diethanolamine (DEA) in an aqueous solution (Kohl and Nielsen, 1997). By applying heat, the amine solution can be regenerated and a purified CO<sub>2</sub> stream is produced. The details of the absorption process, as well as various types of the absorbing agents, will be discussed extensively in the next chapter.

#### 1.4.2. Adsorption

Adsorption relies on an attraction between the CO<sub>2</sub> in a gas stream and the active sites on a solid adsorbent bed. Selective adsorption of gases like CO<sub>2</sub> depends on temperature, partial pressures, surface forces, and adsorption pore size. Solid adsorbents, usually, are made of activated carbon (Quicker et al., 1989; Martin-Martinez et al., 1993; Moreno-Castilla et al., 1997; Zhou and Wang, 2000), molecular sieves (Crosser and Hong, 1980), alumina (Yong et al., 2000), zeolite, and silica gel (Olivier and Jadot, 1997).

The process operates on a repeated cycle with the basic steps being adsorption and regeneration. In the adsorption step, gas is fed to a bed of solids that adsorbs CO<sub>2</sub> and allows the other gases to pass through. When a bed becomes fully loaded with CO<sub>2</sub>, the feed gas is switched to another clean adsorption bed and the fully loaded bed is

regenerated to remove the CO<sub>2</sub>. For regeneration processes, in pressure swing adsorption (PSA), the adsorption is regenerated by reducing pressure, in temperature swing adsorption (TSA), the adsorption is regenerated by raising its temperature, and in electric swing adsorption (ESA), regeneration takes place by passing a low-voltage electric current through the adsorbent (McKee, 2002).

Adsorption may not be attractive for large-scale separation of CO<sub>2</sub> from power plant flue gas because of low capacity and CO<sub>2</sub> selectivity (McKee, 2002). However, it may be successful in combination with another capture technology.

#### 1.4.3. Cryogenics

Cryogenic separation has been widely used commercially for purification of CO<sub>2</sub> from streams that already have high CO<sub>2</sub> concentrations, typically more than 50% (Gupta et al., 2003). It is not normally used for low CO<sub>2</sub> concentration streams such as flue gas from coal/natural gas-fired boilers, as the amount of energy required for refrigeration is uneconomic for the plant.

Cryogenic separation has the advantage that it enables direct production of high-purity liquid CO<sub>2</sub>, which is needed for economic transport, such as transport by ship or pipeline. However, the disadvantages for cryogenic CO<sub>2</sub> capture from low CO<sub>2</sub> concentration streams are significant, since combustion flue gas is delivered at near atmospheric pressure, with several by-products that require removal. A severe energy penalty also comes with lowering the temperature to the range for separation.

The most promising applications for cryogenics are expected to be for separation of CO<sub>2</sub> from high partial pressure gases, such as in pre-combustion capture processes in which the input gas contains a high concentration of CO<sub>2</sub>.

#### 1.4.4. Membrane

A membrane is a barrier film that allows selective and specific permeation under conditions appropriate to its function. With regards to CO<sub>2</sub> capture, two types of membrane systems have been considered:

##### 1. Gas separation membranes

Gas separation membranes rely on differences in physical interactions between gases and a membrane material, causing one component to pass through the membrane faster than another. Various types of gas separation membranes are currently available, including ceramic, polymeric, and a combination of both (McKee, 2002). The separation of the gases relies on diffusivity of the gas molecules in the membrane – the difference in the partial pressure from one side of the membrane to other acts as a driving force for gas separation, as shown in Figure 1.4.

## 2. Gas absorption membrane

Gas absorption membranes are micro-porous solid membranes that are used as contacting devices between gas flow and liquid flow. The  $\text{CO}_2$  diffuses through the membrane and is removed by the absorption liquid, which selectively removes certain components from a gas stream on the other side of the membrane. In contrast to gas separation membranes, it is the absorption liquid (not the membrane) that gives the process its selectivity (deMontigny, 2004; Gupta et al., 2003; Guha et al., 1990 and 1992; Chen et al., 1999).

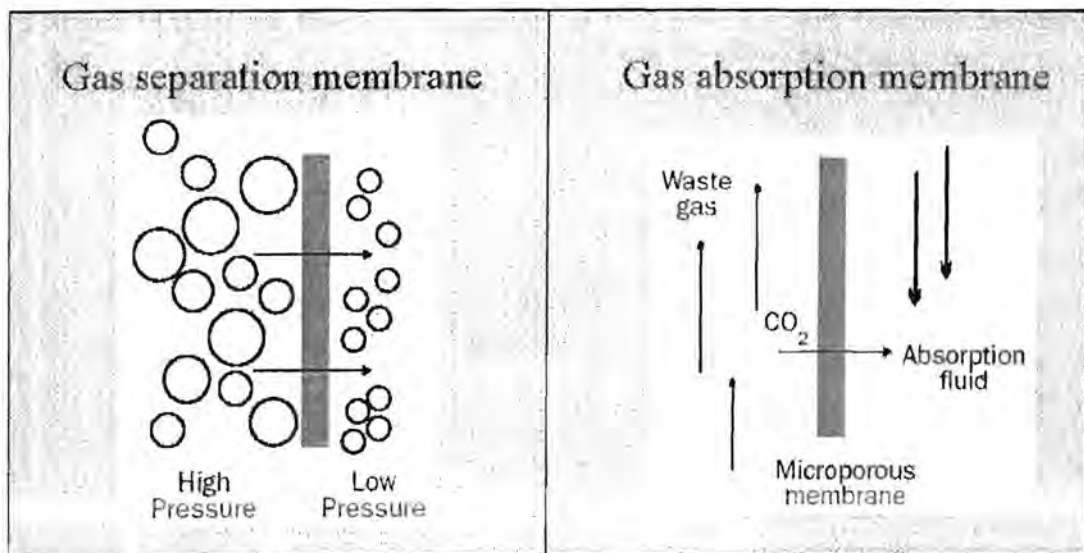


Figure 1.4 Principles of gas separation and gas absorption membranes (McKee, 2002)



Membranes could be used to separate CO<sub>2</sub> in power generation processes. However, with this application, membranes have not been optimized for the large volume of gas separation that is required for CO<sub>2</sub> capture. Membranes cannot usually achieve high degrees of separation, so multiple stages and/or recycling of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. Much development is required before membranes could be used on a large scale for capture of CO<sub>2</sub> in power stations (Gupta et al., 2003; McKee, 2002).

From these technologies, it can be concluded that absorption is a more economical and suitable process, and in fact, at present, it is the only commercially proven process for CO<sub>2</sub> capture from low CO<sub>2</sub> concentration streams such as flue gas from power plant (Astarita et al., 1983; Kohl and Neilsen, 1997; Fisher et al., 2002).

Furthermore, successes in the development of efficient chemicals used in the absorption process are very momentous. Today, alkanolamines such as Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA) are the effective solvents for CO<sub>2</sub> capture (Chakravarty et al., 1985). However, these chemicals also have disadvantages. Therefore, new solvents that are developed to improve on the absorption characteristics and enhance CO<sub>2</sub> removal efficiency are desirable. Development and testing of a potential new solvent are the objectives of this research, as discussed in the following section. The details of chemicals used in absorption processes as well as solvent development will be discussed comprehensively in the next chapter.

### 1.5 Objectives of This Research

The objective of this research is to study the performance of aqueous solution of 2-(Diethylamino)ethanol or DEAE as a new solvent to absorb CO<sub>2</sub> from fossil-fired power plant flue gas, in comparison with the current commercial solvents and processes.

In this work, relative performance of the chemical absorption of CO<sub>2</sub> is studied by comparing traditional solvent – MEA and MDEA and a new solvent system. These solvents are tested under similar conditions in order to evaluate their respective performance. Bench scale CO<sub>2</sub> absorption experiment is used under a variety of operating conditions to measure the solubility obtained in each system.

This work provides a number of contributions to carbon capture research. These are discussed in detail in the thesis. Some of the important contributions include:

1. Obtaining the fundamental knowledge of solubility of CO<sub>2</sub> in the aqueous solution of 2-(Diethylamino)ethanol or DEAE for the various conditions used in the fossil-fired power plants
2. Screening of an attractive solvent for use in CO<sub>2</sub> capture for chemical absorption process at the temperature from 30 to 80 °C and the CO<sub>2</sub> partial pressure ranging from 5 to 100 kPa which are the conditions used to remove CO<sub>2</sub> from the in power plants and compare the solubility performance with the traditional solvents, MEA and MDEA at the same conditions.

The remainder of this thesis presents the research in more detail. This includes a literature review of chemical selection and solvent development all of which are given in Chapter 2. Chapter 3 presents experiment on solubility studies with more detail on equipment, chemicals and procedure. The solubility results and a comparison of results between traditional solvents and the proposed new solvent are presented and discussed in Chapter 4. Finally, the report is summarized in Chapter 5 with conclusions and recommendations for the future work.

## CHAPTER TWO

### THEORIES AND LITERATURE REVIEWS

In Chapter 1, we concluded that chemical absorption is a highly suitable and commercially used process for CO<sub>2</sub> capture from power plant flue gas, which is a low pressure gas and has a low concentration of CO<sub>2</sub> (Astarita et al., 1983; Kohl and Nielsen, 1997; Fisher et al., 2002; McKee, 2002). Consequently, the basic knowledge of the absorption process is studied extensively and presented here.

#### 2.1 Absorption Process

##### 2.1.1 Basic concept of absorption

In absorption processes, as shown in Figure 2.1, the gas is brought into close contact with the liquid. The gas diffuses through a thin boundary layer on the gas side of the interface (gas film) and a thin boundary layer on the liquid side of the interface (liquid film.). Once the gas enters the liquid phase, it can simply dissolve or it can also react with other chemicals in the liquid.

In the case of simple dissolution, there may be a definite limit to mass transfer. Once the gas in the liquid phase has reached its solubility limit, there is no net transfer of gas across the gas-liquid interface. At this point, equilibrium has been reached whereby the amount of gaseous substance that continues to dissolve equals the amount coming out of the solution and reentering the gas phase.

In the case of chemical reaction, the chemicals in the liquid phase react with the dissolved gaseous substance. Through chemical reaction, the gaseous substance can change form and in effect reduce its concentration in the liquid phase, thereby allowing more gaseous molecules to enter the liquid through mass transfer until it reaches equilibrium. However, as long as there is a continual conversion of the pollutant species in the liquid phase to another substance, equilibrium cannot be reached.

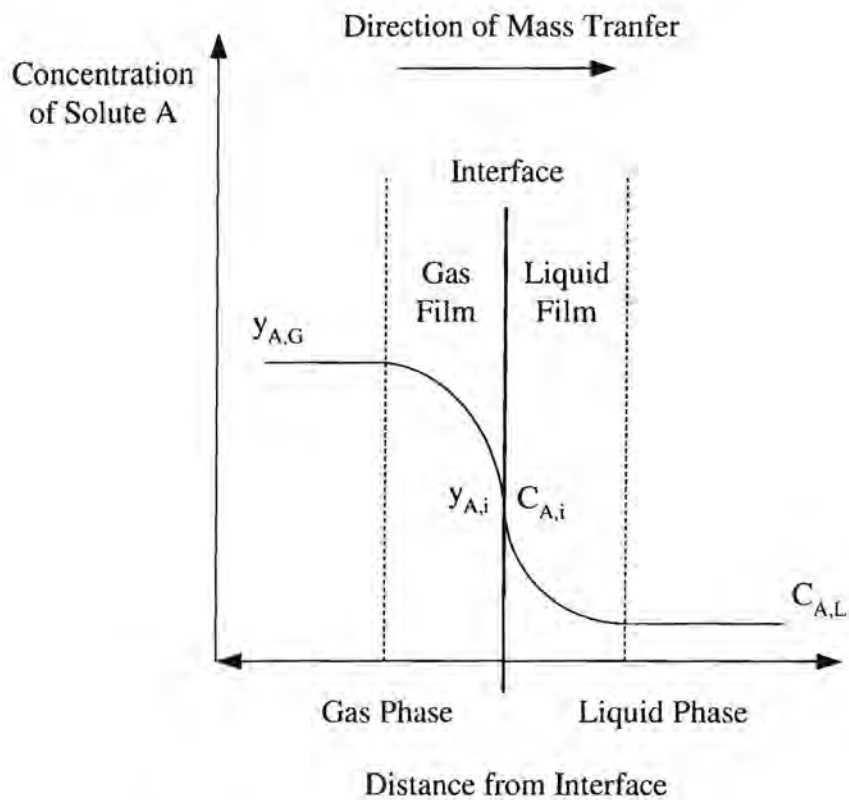


Figure 2.1 Film theory of mass transfer across the interface (deMontigny, 2004)

Where $C_{A,i}$	Concentration of solute A at the interface ( $\text{kgmol/m}^3$ )
$C_{A,L}$	Concentration of solute A in the bulk liquid ( $\text{kgmol/m}^3$ )
$y_{A,G}$	Mole fraction of solute A in the bulk gas-phase (mol/mol)
$y_{A,i}$	Mole fraction of solute A at the interface (mol/mol)

### 2.1.2 Type of absorption

Absorption can be categorized into 2 general classifications, physical and chemical absorption, based on the nature of the interaction between absorbate and absorbent.

#### 1. Physical absorption.

For physical absorption, the component being absorbed is soluble in the liquid absorbent but does not react chemically with the absorbent. The equilibrium concentration of the absorbate in the liquid phase is strongly dependent on the partial pressure of that

component in the gas phase. An example is the absorption of carbon dioxide in the dimethyl ether of polyethylene glycol (Selexol Process).

## 2. Chemical absorption

Chemical absorption involves a chemical reaction between the gaseous component being absorbed and a component of the liquid phase to form reaction products. This reaction is reversible and the process may be regarded as a reversible process (Kohl and Nielsen, 1997). An example is the absorption of carbon dioxide into a monoethanolamine (MEA) solution.

However, if the reaction product cannot readily be reversed to release the absorbate, the process is considered to be an irreversible reaction. An example of this reaction is the absorption of sulfur dioxide in a calcium carbonate solution to form a slurry of calcium sulfate particles.

### 2.1.3 Cyclic Capacity

The cyclic capacity is derived from the loading of chemical solvents for gas absorption, which is determined by considering vapor-liquid equilibrium (VLE) or gas solubility. Gas solubility is defined as the relationship between the concentration of acid gas in a solution and its partial pressure in the gas phase at equilibrium. Gas solubility is probably the most important data required for the design of treating plants (Kohl and Nielsen, 1997). The gas solubility in the liquid phase is normally reported as moles of acid gas per mole of amine. Solubility data varies with partial pressure of acid gas, temperature, type of solvent, solvent concentration, and the nature and concentration of other components in the solution.

Therefore, in practice, the cyclic capacity ( $C_C$ ) or the thermodynamic cyclic capacity or working cyclic capacity of the solvent can be calculated (Sartori and Leder, 1978a). The thermodynamic cyclic capacity for a given  $\text{CO}_2$  gas scrubbing process is the difference in the moles of  $\text{CO}_2$  absorbed in the solution per unit volume of the solution at the absorption step and the moles of  $\text{CO}_2$  absorbed in the solution per unit volume of the solution at the desorption step. In other words, it can be defined as the difference between the  $\text{CO}_2$  loading in solution under absorption conditions and the  $\text{CO}_2$  loading in solution

under regeneration conditions, each multiplied by the initial mole of solvent per unit volume in the scrubbing solution. Both conditions are measured at the point of equilibrium. Therefore, cyclic capacity can be expressed mathematically by:

$$C_C = (\text{mole of CO}_2_{\text{abs}} - \text{mole of CO}_2_{\text{regen}})/V_{\text{solution}} \quad (2.1)$$

$$C_C = (\text{loading of CO}_2_{\text{abs}} - \text{loading of CO}_2_{\text{regen}})(M) \quad (2.2)$$

where  $M$  = concentration of solution (mole /L).

The importance of the concept of cyclic capacity is demonstrated in Astarita et al., (1983). Given a certain gas-treating load ( $\Phi_T$ ) (i.e., the number of moles of  $\text{CO}_2$  to be removed from the gas stream per unit of time) the volumetric liquid circulation rate ( $L$ ) is subject to the following obvious condition:

$$L > (\Phi_T/C_C) \quad (2.3)$$

Equation 2.3 shows that a cyclic capacity as high as possible is desirable in order to minimize  $L$ .

As mentioned earlier, the solvent circulation rate is one of the most important factors in the economics of gas treating processes with chemical solvents (Astarita et al., 1983). The capital cost of gas treating plants depends on the desired solvent circulation rate, which influences the size of the pump, heat exchanger, and stripping column. Solvent rate also has a major influence on the energy requirement for solvent regeneration because the reboiler heat duty is associated directly with liquid circulation rate.

Solvent circulation rate can be reduced by increasing solvent capacity. This is achieved by increasing solution concentration or using solvents that have a higher cyclic capacity. In the favorable case, solvent circulation rate is reduced by over 50% relative to traditional processes, leading to a reduction of investment by nearly 50% (Astarita et al., 1983).

However, under any given conditions, the actual cyclic capacity of a solvent, which is measured under a non-equilibrium condition, can never be larger than the thermodynamic cyclic capacity of a solvent calculated from Eq.2.1 and 2.2. The actual capacity will, in fact, be smaller, owing to the need to provide finite driving forces for mass transfer and other limitations.

#### 2.1.4 Process description

The basic flow diagram for an acid-gas absorption process system is shown in Figure 2.2. Sour gas containing  $\text{CO}_2$  enters the bottom of the absorber and passes upwards through the absorber, countercurrent to a stream of solution entering at the top of the absorber. Inside the column, the gas and liquid phases contact each other and  $\text{CO}_2$  is absorbed in the solvent. The treated gas exits at the top of the absorber. The rich solution, loaded with  $\text{CO}_2$ , from the bottom of the absorber is heated by the heat exchanger with the lean solution from the regenerator and then is fed to the regenerator unit at the top.

The rich solution is boiled in the regeneration system, thus resulting in  $\text{CO}_2$  desorption from the solution. At the top of the regenerator, the vapor mixture is developed and fed into a condenser where the water and solvent are recovered and returned to the regenerator. The lean solution from the bottom of the regeneration system is cooled and fed into the top of the absorber to complete the cycle.

#### 2.2 Solvents for Acid Gas Absorption

One of the keys to the successful operation of a  $\text{CO}_2$  absorption process is the use of effective absorbing solutions. The principal desirable characteristics of an absorbing agent are: high solubility or cyclic capacity of acid gas, high reactivity (i.e., brief contact time), high water solubility (allowing the use of highly concentrated absorbing solutions), low vapor pressure, high thermal and chemical stability, minimum corrosion of materials of construction, low cost, and low environmental impact (Astarita, 1983; Kohl and Nielsen, 1997; Aroonwilas, 1996; Rinaldi, 1997). Practically, it is difficult to find a solvent that has all of these properties. Consequently, the solvent that is preferred for this application should possess a maximum number of desirable features and a minimum of undesirable characteristics.

In the previous section, we have shown that absorption can be classified into chemical and physical absorption. Each type has its own advantages and characteristics, and the chemicals used for each system are different as well. The chemicals used for each process will be discussed below. Table 2.1 lists the main solvents that are used for CO<sub>2</sub> capture.

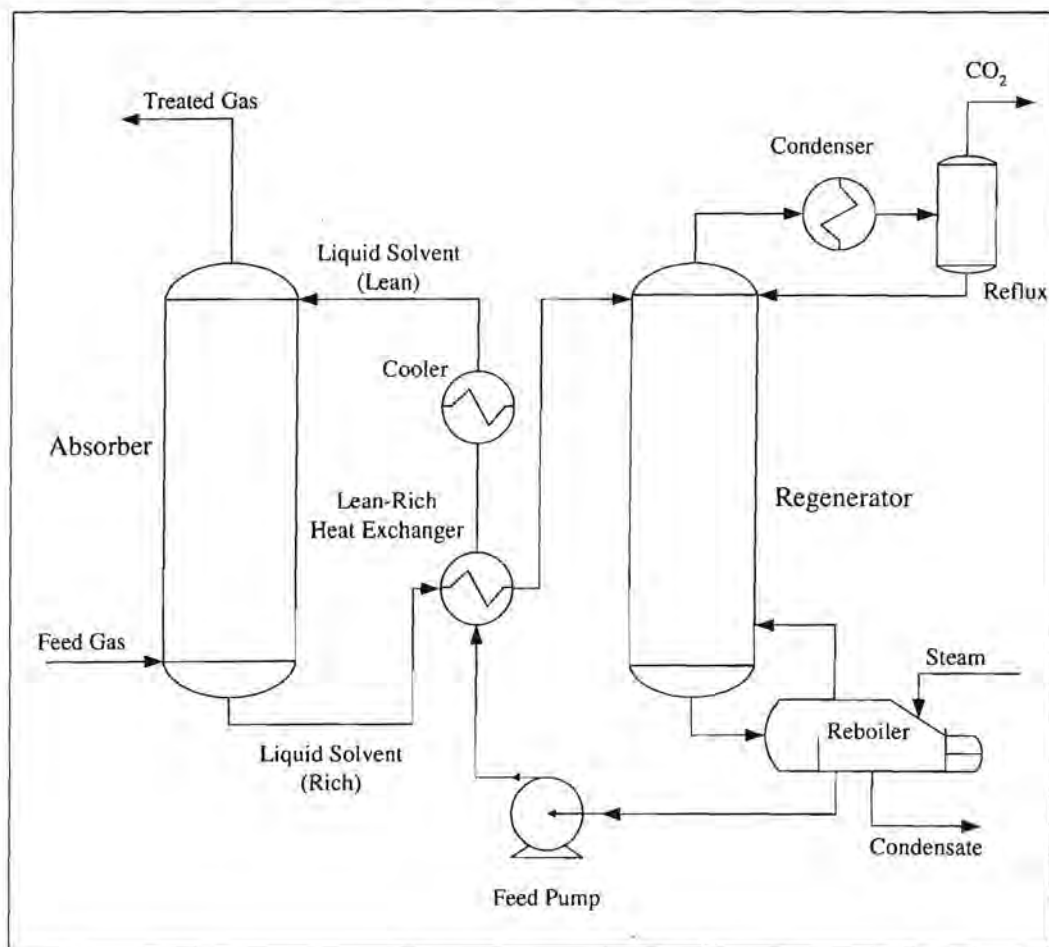


Figure 2.2 Schematic flow diagram of the absorption process



Table 2.1 Commercial CO<sub>2</sub> scrubbing solvents used in the industry (Gupta et al., 2003)

Absorption process	Solvent	Process conditions	Developer/ licensor
<b>Chemical Solvent</b>			
<i>Organic (Amine based)</i>			
MEA	2.5 M MEA and chemical inhibitors	40°C, ambient-intermediate pressures	Dow Chemical, USA
Amine Guard (MEA)	5 M MEA and chemical inhibitors	40°C, ambient-intermediate pressures	Union Carbide, USA
Econamine	6 M DGA	80-120°C, 6.3 MPa	SNEA version by Societe NationalElf Aquitaine, France
ADIP	2-4 M DIPA and 2 M MDEA	35-40°C, >0.1 MPa	Shell, Netherlands
MDEA	2 M MDEA		
Flexsorb/ KS-1, KS-2, KS-3	Hindered amine		Exxon, USA; M.H.I.
<i>Inorganic</i>			
Benfield and versions	K <sub>2</sub> CO <sub>3</sub> and catalysts Lurgi and Catarcab with arsenic trioxide	70-120°C, 2.2-7 MPa	Lurgi, Germany; Eickmeyer and Associates, USA;

Table 2.1 Commercial CO<sub>2</sub> scrubbing solvents used in the industry (Gupta et al., 2003) (continued)

Absorption process	Solvent	Process conditions	Developer/ licensor
<b>Physical solvent</b>			
Rectisol <sup>®</sup>	Methanol	-10/-70°C, >2 MPa	Lurgi and Linde, Germany; Lotepro Corporation, USA
Purisol <sup>®</sup>	N-methyl-2-pyrrolidone (NMP)	-20/+40°C, >2 MPa	Lurgi, Germany
Selexol <sup>®</sup>	dimethyl ethers of polyethylene glycol (DMPEG)	-40°C, 2-3 MPa	Union Carbide, USA
Fluor Solvent	Propylene carbonate	Below ambient temperature, 3.1-6.9 MPa	Fluor, El Paso, USA
<b>Mixed Physical-Chemical Solvents</b>			
Sulfinol-D <sup>®</sup> and Sulfinol-M <sup>®</sup>	Mixture of DIPA or MDEA, water and tetrahydrothiopene or diethylamine	>0.5 MPa	Shell, Netherlands
Amisol <sup>®</sup>	Mixture of methanol and MEA, DEA, diisopropylamine (DIPAM) or diethylamine	5/40°C, >1 MPa	Lurgi, Germany

### 2.2.1 Chemical solvents

The majority of chemical solvents are amine-base solvents. However, the limitations of this group, such as low absorption capacity, have led to the research and development of new amines that enhance the absorption capacity of the solvent. Furthermore, alternative inorganic solvent systems are carbonates and hydroxides of the potassium, sodium processes, and aqueous ammonia process.

#### 1. Alkanolamine process

Amine scrubbing technology has been established for over 60 years in the chemical and oil industries for the removal of hydrogen sulfide and CO<sub>2</sub> from gas streams. This technology has, for the most part, been used on natural gas streams, but, with other applications, amines are used to capture CO<sub>2</sub> from flue gas streams today.

The amines that have proven to be of principal commercial interest for gas treatment are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Among these, MEA is more effective and hence dominates the CO<sub>2</sub> capture market. Structural formulas for alkanolamines are presented in Table 2.2. Structurally, they contain at least one hydroxyl group, which helps to reduce their vapor pressures and increase their solubilities in an aqueous solution whereas the amino group provides for the necessary alkalinity for CO<sub>2</sub> absorption (Kohl and Riesenfeld, 1985).

According to their structures, amines such as MEA and DGA, which have two hydrogen atoms directly attached to a nitrogen atom, are called primary amines and are generally the most alkaline. DEA and DIPA are called secondary amines since they have one hydrogen atom directly attached to the nitrogen atom. TEA and MDEA represent a completely substituted ammonia molecule with no hydrogen atom attached to the nitrogen and are called tertiary amines.

The principal reactions of CO<sub>2</sub> with amines occurring when solutions of a primary amine, such as MEA, are used to absorb CO<sub>2</sub> may be represented as (Kohl and Nielsen, 1997):



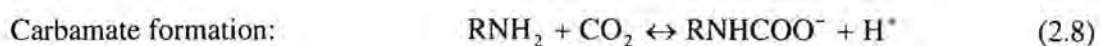
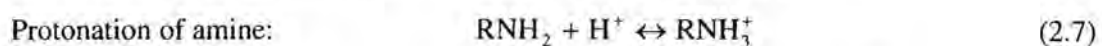
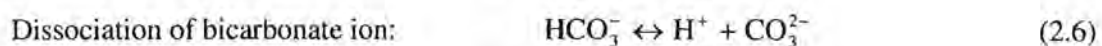
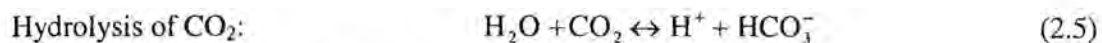

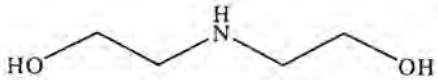
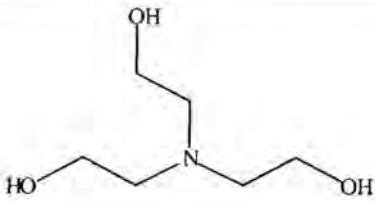
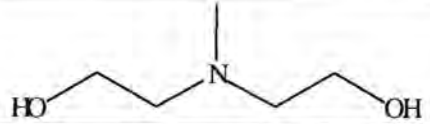
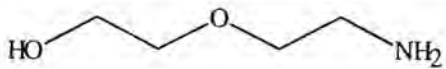

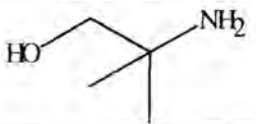


Table 2.2 Conventional alkanolamines (Kohl and Nielsen, 1997)

Name		Chemical Structure
Monoethanolamine	MEA	
Diethanolamine	DEA	
Triethanolamine	TEA	
Methyldiethanolamine	MDEA	
Diglycolamine	DGA	
Diisopropanolamine	DIPA	
2-Amino-2-Methyl-1-Propanol	AMP	

Although reactions 2.4-2.8 relate specifically to primary amines, they can also be applied to secondary amines by suitably modifying the amine formula. Tertiary amine solutions undergo reaction 2.4-2.7 but cannot react directly with  $\text{CO}_2$  to form a carbamate by reaction 2.8 because there is no H atom in the molecule attached to N atom. With a primary amine, theoretically, the capacity of the solution for  $\text{CO}_2$  is limited to approximately 0.5 mole  $\text{CO}_2$ /mole of amine, even at a relatively high partial pressure of  $\text{CO}_2$  in the gas to be treated. The reason for this limitation is the high stability of the carbamate and its low rate of hydrolysis to bicarbonate (Kohl and Nielsen, 1997). With tertiary amines, which are unable to form carbamates, a ratio of one mole of  $\text{CO}_2$  per mole of amine can theoretically be achieved. However, a  $\text{CO}_2$  reaction that does not produce carbamate is relatively slow. Recently, this problem is overcome for MDEA by adding another amine, such as MEA, which increases the rate of reaction with  $\text{CO}_2$  (Kohl and Nielsen, 1997).

The main concerns with MEA and other amine solvents are corrosion in the presence of oxygen and other impurities, high solvent degradation rates, and the large amount of energy required for regeneration. As much as 80% of the total energy consumption in an alkanolamine absorption process occurs during solvent regeneration (Chakravarty et al., 1985; White et al., 2003). These factors generally contribute to high solvent consumption, large energy losses, and a need for large equipment. New and improved solvents with higher  $\text{CO}_2$  absorption capacities, faster  $\text{CO}_2$  absorption rates, high degradation resistances, and low corrosion and energy usage for regeneration are needed to reduce equipment sizes and capital and operating costs in order to provide a greater opportunity and more alternatives for  $\text{CO}_2$  capture in the future.

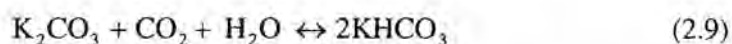
Recently, a mixed amine solution containing a variety of amines has become popular in the gas treating industry. These solutions provide a higher absorption performance when compared to the aqueous solutions of a single amine. For instance, the addition of primary or secondary amines, such as MEA or DEA in MDEA, has been implemented to increase the rate of  $\text{CO}_2$  absorption significantly (Chakravarty et al., 1985; McCullough et al., 1990; Shahi, 1993; Li and Mather, 1994; Chakravati and Gupta, 2000).

In addition to using a mixed alkanolamine such as MEA or DEA in MDEA, some researchers can synthesize the new absorbents, such as sterically hindered amine. An example of a well-recognized hindered amine is 2-amino-2-methyl-1-propanol (AMP). AMP has been receiving a great deal of attention because it has an excellent absorption capacity in comparison with the most commonly used conventional MEA. The details of new amines will be discussed extensively in the next section.

## 2. Alkali process

The inorganic based chemical solvents that are widely used are carbonates and hydroxides of potassium, sodium, and aqueous ammonia. Among these, potassium carbonate has the dominant market share. The potassium carbonate process can be used in various configurations. Generally, these process configurations are accompanied by minor changes in the solvent and catalytic additives used in the process.

The chemical reaction of absorbed CO<sub>2</sub> with an alkali carbonate solution takes place as shown below:



However, according to Astarita (1967), Benson et al. (1954) and Tosh et al. (1959), the reaction rate of CO<sub>2</sub> in carbonate-bicarbonate solutions is not fast enough at room temperature to enhance the absorption rate. The relatively low rate of absorption of CO<sub>2</sub> in these solutions has been an incentive for research on rate-increasing additives. Many such materials have been discovered and are usually referred to as promoters, activators, or catalysts.

The reaction of CO<sub>2</sub> in carbonate solutions can be catalyzed by a number of substances such as the anions of weak acids. The addition of potassium arsenite or arsenic trioxide (Gupta et al., 2003) can increase the rates of absorption and desorption of CO<sub>2</sub> and is widely used industrially. In addition to the anions of weak acids, a small level of an amine, such as a sterically hindered amine (Sartori, 1978a), DEA (Hesse, 2001) and piperazine (Cullinane and Rochelle, 2004), is included as an activator for the aqueous based alkali metal salt or alkali metal hydroxide used in the scrubbing solution. This type of process is generally used where the bulk removal of an acid gas, such as CO<sub>2</sub>, is

desired. This process also applies to situations where the  $\text{CO}_2$  and feed gas pressure are high.

In addition to activators, high temperatures can be used to increase the rate of reaction. At temperatures above about 318 K or 45°C, the reaction rate is sufficiently high to enhance the mass transfer rate, but even at temperatures as high as 105°C, the reaction rate is not high enough to be considered instantaneous (Kohl and Nielsen, 1997). This process, called the hot potash process, uses potassium carbonate as an absorbent (Danckwerts and Sharma, 1966). The overall process is usually run hot, typically 70–120°C, in order to speed up the chemical reactions.

Furthermore, the system can be operated with a relatively low incremental heat input for solvent regeneration. This feature normally eliminates the use of the heat exchangers used to cool the solvent flow between the regenerator and absorption column, thus making potash plants cheaper than amine plants for the same duty. This process is called the Benfield process and uses the basic potassium carbonate process with moderate gas pressures of around 2.2 MPa.

Moreover, alkali solutions can be used at ambient temperature as well. In the  $\text{CO}_2$ -recovery process, the alkaline carbonate was partially converted to bicarbonate in the absorber and back to the carbonate again in the regenerator that was heated by steam. However, this process had a low rate of  $\text{CO}_2$  absorption. The major drawbacks of this process were a low  $\text{CO}_2$  recovery efficiency and a high regeneration steam requirement. The majority of modern  $\text{CO}_2$  plants employ MEA to remove  $\text{CO}_2$  from flue gas.

Sodium hydroxide has also been used to remove traces of  $\text{CO}_2$  or to provide a high purity product from a gas stream containing trace quantities of  $\text{CO}_2$ . In this operation, no attempt was made to regenerate the solution, which is discarded or used elsewhere.

### 2.2.2 Physical solvents

The physical solvents are ideally suited for the removal of  $\text{CO}_2$  from fuel gases with high pressure. These physical solvents combine less strongly with  $\text{CO}_2$ . The advantage of using such solvents is that  $\text{CO}_2$  can be separated from them in the regenerator by reducing the pressure, resulting in much lower energy consumption. Table 2.1 shows the main physical solvents that could be used for  $\text{CO}_2$  capture. These are cold

methanol (Rectisol process), dimethyl ether of polyethylene glycol (Selexol process), propylene carbonate (Fluor process), and n-methyl-2-pyrrolidone or NMP (Purisol process). The majority of physical solvents are based on solvents with high boiling points and low vapor pressures. Other than methanol, most of these solvents can be used at ambient temperatures without appreciable vaporization losses.

Although many solvents appear to be suitable for use as physical solvents, their actual number is limited by certain criteria that must be fulfilled to make them acceptable for economic operation (Kohl and Nielsen, 1997). In general, physical solvents must have an equilibrium capacity for absorbing CO<sub>2</sub> several times than that of water and a lower capacity for removing other constituents of the gas stream. They may have low viscosity, low or moderate hygroscopicity, and low vapor pressure at ambient temperatures. They must be non-corrosive to common metals as well as non-reactive with other components in the gas stream. The technology development needs for physical solvents are similar in principle to those for chemical solvents. In particular, there is a need for higher efficiency gas-liquid contactors and solvents with lower energy requirements for regeneration.

### 2.2.3 Mixed physical-chemical solvents

Mixed physical-chemical absorption processes use a combination of chemical and physical solvents so that the bulk removal capabilities of the physical solvent are combined with the amine's ability to achieve acid-gas removal in a single treating step. Although this process resembles that of a conventional amine treating unit, the presence of the physical solvent enhances the solution capacity, especially when the gas stream to be treated is at a high pressure and the acidic components are present in high concentrations.

Two examples of this process are the Sulfinol process and Amisol process developed by Shell and Lurgi, respectively. In its original form, the Sulfinol process uses sulfolane (tetrahydrothiophene dioxide) as the physical solvent and an amine solvent, Diisopropanolamine (DIPA), with water. Instead of DIPA, Shell developed M-sulfinol, in which the amine solvent is MDEA. The main difference between a sulfinol unit and an alkanolamine unit is that a sulfinol unit tolerates a much higher acid gas loading before becoming corrosive (Gupta et al., 2003).



The Amisol process is based on a mixture of methanol and either MEA or DEA as the chemical component, and a small percentage of water (Kohl and Nielsen, 1997). Another version that is particularly suited for the removal of large quantities of CO<sub>2</sub> uses MDEA as the chemical solvent component.

From the above information, we can conclude that the suitable solvents used for CO<sub>2</sub> removal from low-pressure streams, such as flue gas from coal-fired power plant, are shown below.

Chemical absorption offers many advantages over physical absorption including an increased capacity, especially at a low partial pressure of acid gases, greater mass transfer coefficients, and a higher degree of solute removal. Furthermore, the chemical solvents can be chosen such that CO<sub>2</sub> will be selectively removed from the gas stream. Because of the nature of flue gas, as shown in Table 1.1, about 90% of CO<sub>2</sub> emissions are flue gas with a CO<sub>2</sub> concentration of 20% or less. In addition, based on the data presented previously, physical solvents tend to be preferred when the pressure of the feed gas and the partial pressure of the acid gas in the feed are high, whereas chemical solvents are preferred when feed acid gas partial pressure is low. Therefore, for the low-pressure stream of flue gas from a power plant, chemical solvents are more suitable and economical for CO<sub>2</sub> removal from the flue gas.

For amine process and alkali process, traditionally, carbonate solutions and alkanolamine solutions have been used in CO<sub>2</sub> absorption processes. These solvents can react reversibly or irreversibly with the CO<sub>2</sub>. Normally, chemical solvents that have reversible reaction kinetics are favored since they can be regenerated and reused in the process. Moreover, like physical solvents, the CO<sub>2</sub> absorption is more efficient in amine process than that in carbonate salt solutions because of higher mass transfer rates and a higher solubility for CO<sub>2</sub> (Nelson and Swift, 1997). As a result, amines have been a better choice for gas treating processes. Now, the majority of modern CO<sub>2</sub> plants employ amine solutions to remove CO<sub>2</sub> from flue gas (Kohl and Nielsen, 1997). Consequently, subsequent chapters of this thesis will focus only on the chemical absorption by alkanolamines and new solvents.

### 2.3 Literature Review of Solubility of CO<sub>2</sub> in MEA

Since MEA is the most widely used amine for gas treating processes (Jou et al., 1994; Baek and Yoon, 1998), a large amount of solubility data has been published. Much of the early work was conducted with dilute MEA solutions (2.0-2.5 M) because low concentration solutions were commonly used in commercial plants at the time since high concentrations were considered too corrosive (Kohl and Nielsen, 1997). However, with the arrival of corrosion inhibitors, more concentrated solutions have become popular. More information is provided for MEA than for any other amines because of its widespread and long-time commercial use. Furthermore, many of the conclusions based on the use of MEA, such as the effects of temperature and amine concentration, are also applicable to other amines.

Mason and Dodge (1936) investigated the solubility of CO<sub>2</sub> in the range of MEA concentrations from 0.5 to 12.5N at temperatures between 0°C and 75°C and partial pressures of CO<sub>2</sub> ranging from 10-760 mmHg. Lyudkovskaya and Leibush (1949) studied the solubility of CO<sub>2</sub> in 0.5, 2, and 5 MEA solutions at temperatures of 25, 50, and 75°C and partial pressures of CO<sub>2</sub> from 36.8-588 psia. Muhlbauer and Monaghan (1957) reported data on the solubility of CO<sub>2</sub> in 2.5 N MEA solutions at 25 and 100°C and partial pressures of about 0.5-1290 mmHg. Jones et al. (1959) investigated the solubility of CO<sub>2</sub> in a 2.5N MEA solution at temperatures of 40, 60, 80, 100, 120, and 140°C with partial pressures of CO<sub>2</sub> ranging from 0.5-7000 mmHg.

Lee et al. (1974) published the solubility data of CO<sub>2</sub> in 2.5 and 5.0N aqueous MEA solutions at 40 and 100°C and partial pressures of CO<sub>2</sub> between 0.1-1000 psia. An extensive literature review of the experimental determination of CO<sub>2</sub> in MEA was compiled by Lee et al. (1974).

Lee et al. (1976a) also determined the solubility of mixtures of CO<sub>2</sub> and H<sub>2</sub>S in a 2.5N MEA solution at 40 and 100°C and partial pressures of CO<sub>2</sub> ranging from 0.1-7000 psia. Lee et al. (1976b) published the solubility of CO<sub>2</sub> in 1.0 to 5.0N MEA solutions at temperatures from 25-120°C and CO<sub>2</sub> partial pressures from 0.1-10000 kPa. Similar data were presented by Lawson and Garst (1976) and Jou et al. (1995).

Nasir et al. (1977) measured the solubility of CO<sub>2</sub> in 2.5 and 5.0N solutions of MEA at 80 and 100°C and CO<sub>2</sub> partial pressures between 0.001-9 kPa. Isaccs et al. (1980)

determined the solubility of CO<sub>2</sub> in a 2.5N aqueous solution of MEA at 100°C and acid gas partial pressures between 0.003 and 3.36 kPa.

#### 2.4 Literature Review of New Solvents

CO<sub>2</sub> removal through the use of alkanolamines has long been used on a commercial scale for over 70 years (Gupta et al., 2003). Aqueous alkanolamine solutions have become the most widely used solvents for CO<sub>2</sub> absorption. The basic alkanolamine process has remained unchanged for many years, but current demands to reduce energy consumption, decrease solvent losses, and meet environmental concerns, such as concerns about air and water quality, are incentives for several modifications to upgrade the process. The most significant improvement is the introduction of specially formulated solvents. Depending on the process requirements (e.g., the selective removal of H<sub>2</sub>S and/or CO<sub>2</sub>-bulk removal), several options for alkanolamine based treating solvents are available.

A new solvent can be broadly defined as a solvent that has been specifically formulated to perform a specific task. For instance, solvents are designated for the selective separation of H<sub>2</sub>S from light hydrocarbons in the presence of CO<sub>2</sub>, the bulk separation of CO<sub>2</sub>, etc (Chakma, 1994; 1999). A new solvent can consist of a single solvent such as AMP or a solvent mixture such as a mixture of MEA and MDEA in an aqueous solution. Most of the proprietary solvents marketed by the major solvent manufacturers are based on new amines. Through the judicious selection of a new amine or amine mixture, the process efficiency of existing plants can be significantly enhanced beyond the efficiency related to the use of conventional amines (Chakma, 1999). Furthermore, some of the gas processing problems that cannot be dealt with using traditional technology in an economical manner can be easily handled with new amines (Chakma, 1994).

The advantage of new amines over alkanolamines is that new amines can absorb more CO<sub>2</sub> than alkanolamines. Therefore, with higher chemical solvent cyclic capacities, the thermal energy consumption for CO<sub>2</sub> regeneration is expected to be significantly less than that in the MEA process. Moreover, the solvent circulation rate, which is one of the

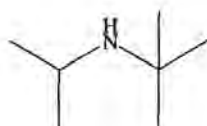
most important factors in the economics of gas treating with chemical solvents, is much lower, resulting in high capital cost savings (Astarita et al., 1983).

### 2.3.1 New solvents for acid gas removal

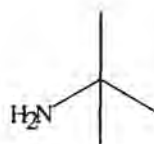
With the advantages of new amines, recently, many companies have developed proprietary hindered amines for use in removing acid gas from gas streams. These companies are Exxon, Mitsubishi, Kansai Electric, Siemens and so on. Exxon scientist Sartori and his group pioneered the idea of new amines in the last few decades as shown in the patents (Sartori and Leder, 1978a; 1978b; 1978c). One of the new amines that were developed by this group is AMP.

Furthermore, Sartori and his group invented many kinds of amines for use in many applications. Most of them are used for acid gas removal, especially carbon dioxide. These amines can work individually or work with other chemicals. For example, the absorbing solutions comprise the aqueous mixture containing the basic alkali metal salt, and sterically hindered amines are used as activators.

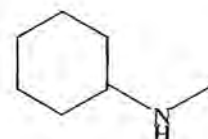
A huge number of sterically hindered amines (more than 100 chemicals) are presented in the patents. These are composed of, for example, diamine, cyclic, ring, diaminoalcohol, ether, and piperidine structure groups. However, it can be concluded that some sterically hindered amines shown in the patents contain structures as follows:



Sample 1.



Sample 2.



Sample 3.

Sample 1: at least one secondary amine group attached to either a secondary or tertiary carbon atom

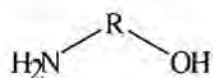
Sample 2: a primary amino group attached to a tertiary carbon atom

Sample 3: at least one secondary amino group that is part of a ring and is attached to either a secondary or tertiary carbon atom.

In addition to the new amines developed by Sartori, other researchers have developed new amines as well. Yoshida et al. (2002) proposed aqueous solutions of a hindered amine selected from the group consisting of the following (the general formulae of each group are presented below):

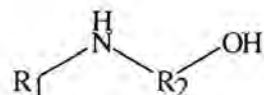
Sample A: a compound having an alcohol hydroxyl group and a primary amino group, i.e., the primary amino group is bonded to a tertiary carbon atom having two unsubstituted alkyl groups

General formula:



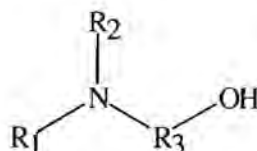
Sample B: a compound having an alcohol hydroxyl group and a secondary amino group, in other words, a secondary amino group having a nitrogen atom bonded to a group having a chain of 2 or more carbon atoms inclusive of a bonded carbon atom.

General formula:



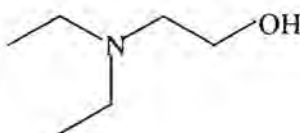
Sample C: a compound having an alcohol hydroxyl group and a tertiary amino group

General formula:

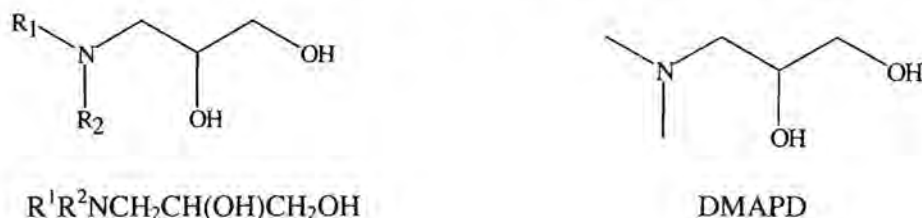


Sample D: a 2-substituted piperidine having a hydroxyl group substituted alkyl group at the 2-position

The example of this structure of group D is 2-(diethylamino)-ethanol (DEAE)

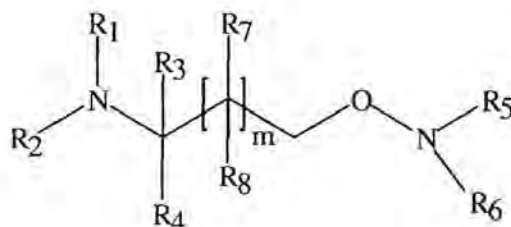


Mimura et al. (1997 and 2000) developed many hindered amines to apply to H<sub>2</sub>S absorption. Many of them are presented in Yoshida's work as well. Iijima and Mitsuoka (1998) developed an amine compound that has the general formula as shown below:



where  $R^1$  and  $R^2$  independently represent the lower alkyl group of 1 to 3 carbon atoms and the example of this structure is 3-(dimethylamino)-1,2-propanediol (DMAPD).

Suzuki et al. (2000) developed the amine compound that has a general formula as follows:



where  $R^1$  to  $R^8$  may be the same or different and each represent a hydrogen atom or alkyl group of 1 to 4 carbon atoms, and "m" is 0 or 1. An example of this structure is diethylaminoacetamide (DEAAA)

Besides the new amines presented in various patents, the new solvents are published in journal articles as well. Rinaldi (1997) and De Filippis et al. (2000) reported that the modified polyamines were prepared by reacting tetraethylenepentamine (TEPA) with formaldehyde (CH<sub>2</sub>O) and formaldehyde/phenol in various molar ratios. The products called polyalkylenepolyaminophenols (PAP.X) were tested with CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> for the absorption of these gases. These products were shown to be better than the alkanolamines, both in absorption and in desorption.

Another set of sterically hindered amines is KS-1 (commercial name). KS-1 has a lower circulation rate compared to MEA, a lower regenerative temperature, and a lower

heat of reaction with CO<sub>2</sub>. KS-1 has been used in a commercial gas scrubbing operations in Malaysia to produce a pure CO<sub>2</sub> stream for urea production (Gupta et al., 2003).

Maneeintr (2009) and Tontiwachwuthikul et al. (2007) developed the various new amines based on the concept of molecular design and the placement of functional groups that promote CO<sub>2</sub> capture on suitable solvent backbones. It is important to determine the effects of such placements on the performance of such amines for CO<sub>2</sub> capture.

According to the literature, alkanolamine solutions are still the attractive solvents for CO<sub>2</sub> removal process. In this study, DEAE is proposed to be a one of the promising candidates for removal since the structural molecule is expected to provide a high performance of the acid gas absorption and good properties of amine compound.

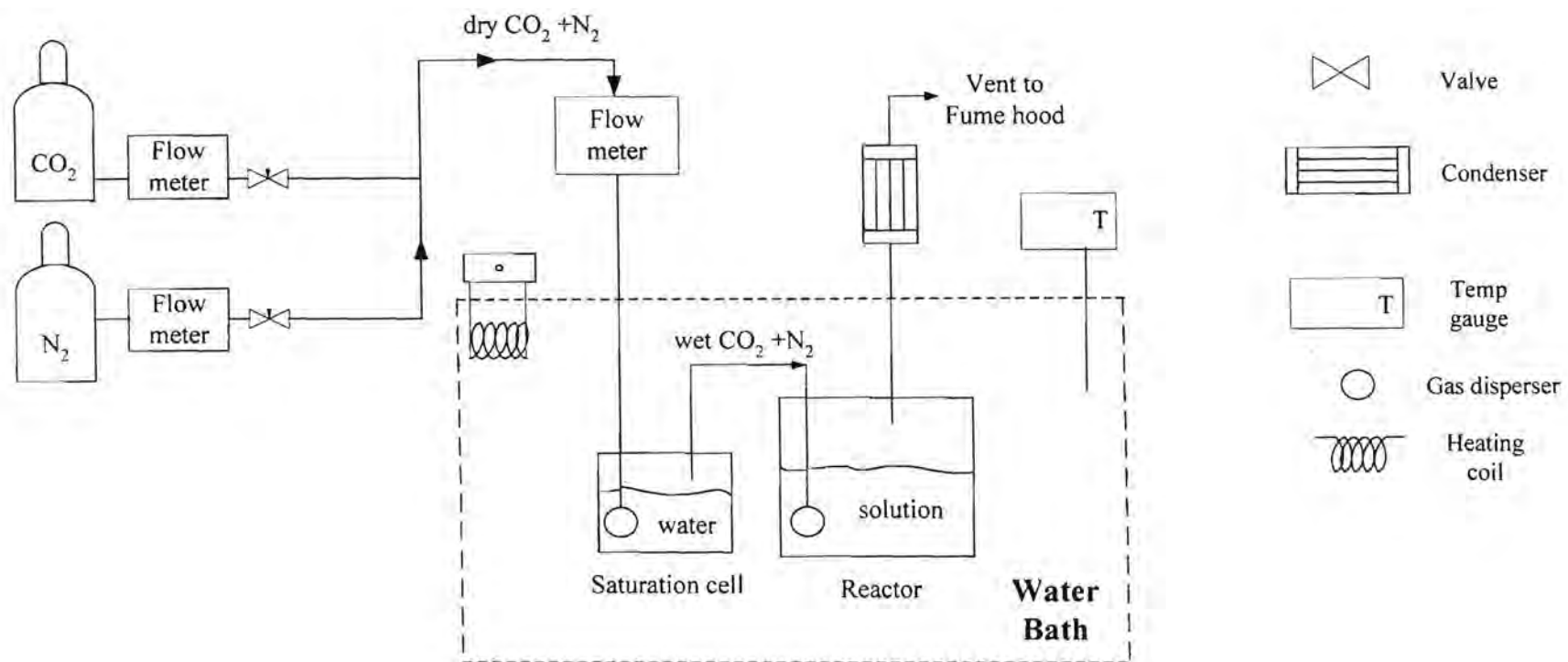


Figure 3.1 Schematic diagram of solubility apparatus (Maneeintr, 2009)



## CHAPTER THREE

### EXPERIMENT

This chapter highlights the experiment on solubility study of CO<sub>2</sub> in 2-(Diethylamino)ethanol (DEAE) and compares the results to MEA. Also, this section will include the chemicals, experimental apparatus used in this study, experimental procedure, operating conditions and analysis method for both gas and liquid samples.

#### 3.1 Chemicals and equipment

The MEA obtained from Sigma Aldrich has purity of 99%. DEAE is purchased from Merck with 99.9+% purity. The solutions are prepared to the desired concentration at 3-5M by mixing distilled water with the MEA and DEAE. Hydrochloric acid (HCl) used for CO<sub>2</sub> loading analysis is obtained from Fisher Scientific (99%). Laboratory grade nitrogen and CO<sub>2</sub> are supplied by Praxair Inc. with purities of 99.5% and 99.9%, respectively. All the materials are used without further purification.

The experiment is conducted in batch mode and included for both absorption and regeneration conditions represented at 40 and 80°C, respectively. The schematic diagram of the experimental setup to evaluate the performance of the CO<sub>2</sub> absorption capacity in DEAE is shown in Figure 3.1. As one can see in the figure, the experimental apparatus consisted of a saturation cell to control the concentration of solution. The cell connected to the reactor. Both the cell and the reactor are immersed in a constant temperature water bath. The water bath was maintained at desired temperatures by using a temperature controller which operated within the temperature ranging from -40 to 150°C with  $\pm 0.01^\circ\text{C}$  accuracy. The temperature in the system is measured using a J-type thermocouple ranging from -40 to 150°C with resolution of  $\pm 0.01^\circ\text{F}/^\circ\text{C}$  and  $\pm 0.03^\circ\text{C}$  accuracy and calibrated with thermometer with a resolution of  $\pm 0.1^\circ\text{F}/^\circ\text{C}$  and  $\pm 0.5^\circ\text{C}$  accuracy. Flow meters used in this system are electronic Aalborg GFM-17 gas flow meters with  $\pm 0.15\%$  / $^\circ\text{C}$  full scale accuracy which are calibrated by a digital flow meter (Agilent Technologies, model ADM-100) ranging from 0.5 mL to 1 L/min with accuracy  $\pm 3\%$  of reading.

### 3.2 Experimental procedure

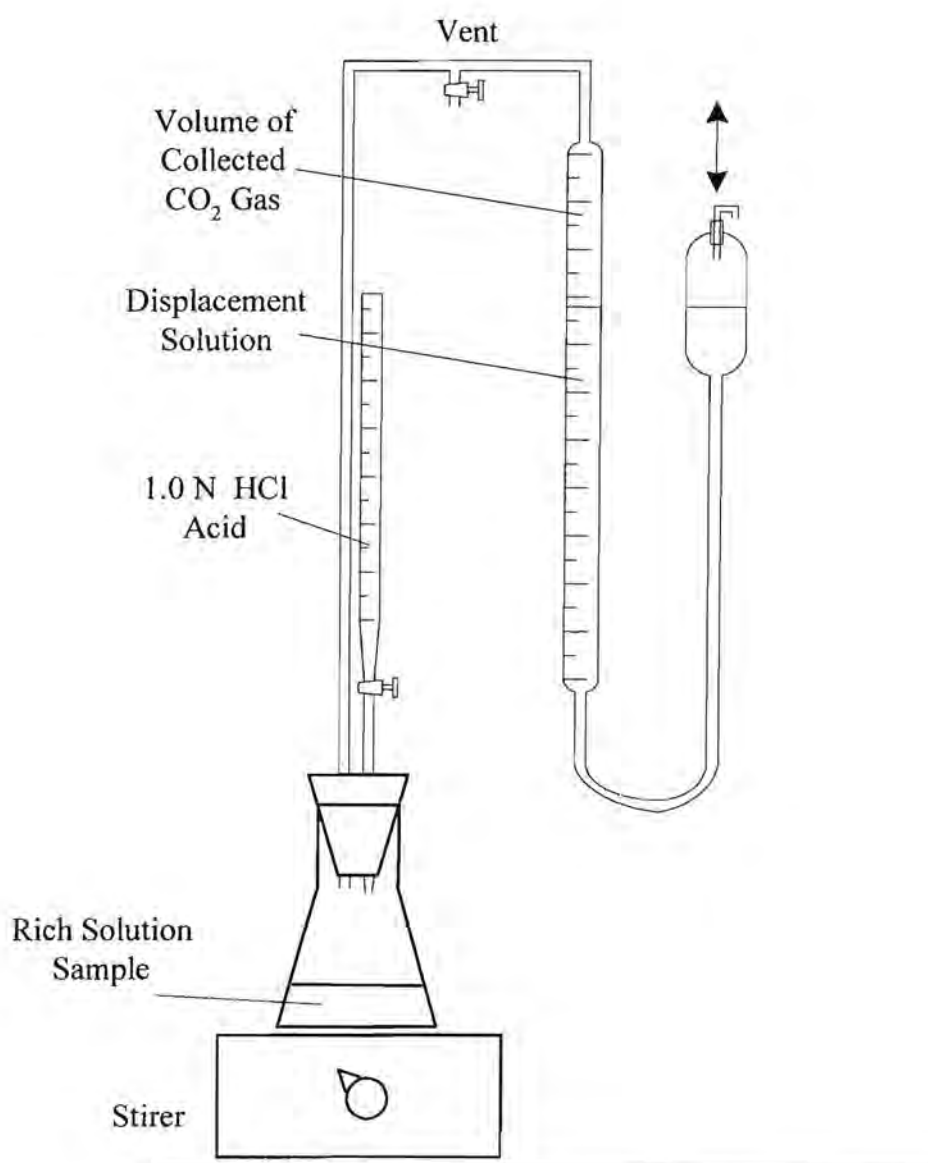
Initially, the 35-mL solution is fed into the system at the required temperature, and the gas mixture is generated by blending CO<sub>2</sub> with N<sub>2</sub> until the desired CO<sub>2</sub> partial pressure has been reached. The gas mixture is introduced to the system through the flow meters and saturated with moisture content in the saturation cell to maintain the solution concentration. The wetted gas mixture is then bubbled through the amine test solution and eventually exhausted. The gas is sent to the condenser used for recovering moisture in the gas stream before being vented to the fume hood. The process is operated under atmospheric pressure.

To ensure that equilibrium is reached, the system is kept in operation for 12-24 hours until the conditions such as temperature, partial pressure and solution concentration are constant. Then, the liquid sample is taken to analyze for the CO<sub>2</sub> loading. The CO<sub>2</sub> loading is evaluated many times by sampling every one or two hours until the CO<sub>2</sub> loading is constant or until two consecutive readings show only a slight difference ( $\leq \pm 0.05$  mol CO<sub>2</sub>/mol amine difference). The operating conditions for this evaluation are shown in Table 3. 2.

The CO<sub>2</sub> loading for each liquid sample is determined as follows: the sample is first withdrawn from the cell using a 2 or 3 mL pipette. Then, excess 1.0 N HCl acid is added to the 2-3 mL sample, and all of the CO<sub>2</sub> evolved is collected in a gas burette for measurement as seen in Figure 3.2. The amount of evolved CO<sub>2</sub> is calculated in g-mol. The sample solution concentration and the CO<sub>2</sub> loading are determined by using the procedure outlined by the Association of Official Analytical Chemists (Horwitz, 1975). From these results, the ratio of CO<sub>2</sub> to amine in the liquid phase is calculated. The CO<sub>2</sub> loading reported is the average of three equilibrium data points. For most of the system, the repeatability of the CO<sub>2</sub> loading is generally within  $\pm 7\%$  obtained from the repeated results of various operating conditions. The operating conditions used in this study is given in Table 3.1 which is factorial experimental design and the total number of experiment is 216 cases.

Table 3.1 Experimental operating conditions for solubility studies

Operating condition	Solubility Study
Type of solvents	MEA, MDEA and DEAE
Solvent concentration (molar)	3, 4 and 5
CO <sub>2</sub> partial pressure (kPa)	5, 15, 30, 50, 75 and 100
Temperature (°C)	30, 40, 60 and 80

Figure 3.2 CO<sub>2</sub> loading measurement equipment (Maneeintr, 2009)

## CHAPTER FOUR

### RESULTS AND DISCUSSION

The experimental data for the solubility of CO<sub>2</sub> in MEA, MDEA and 2-(Diethylamino)ethanol (DEAE) are determined at temperatures of 30, 40, 60, and 80°C at partial pressures ranging from 5 to 100 kPa.

#### 4.1 Verification of solubility study

To verify the applicability of the experimental setup and the procedure used in this study, the solubility of CO<sub>2</sub> in 5.0M MEA is measured at the same operating conditions and compared with the previously reported data in the literature (Lee et al., 1974; Shen and Li, 1992; Haider et al., 2011 and Yamada et al., 2013). The sources of error in this work are associated with the determination of the partial pressure of the acid gas and the measurement of the volume and composition of the gas evolved from the liquid sample. Other errors come from uncertainties in the temperature of the equilibrium cell and the container of the gas and error in the determination of the concentration of the solutions.

However, as shown in Figure 4.1 and 4.2, which gives the experimental results at 40 and 80°C, respectively, these results are found to be in good agreement with the literature over the entire pressure range considered in this study. The average and maximum percent absolute deviations between this study and previous work obtained by Shen and Li (1992) are 2.75 and 11.05, respectively. It is considered that these percent absolute deviations are acceptable. Therefore, it is concluded that the equipment and procedures for this study are considered to be properly applicable for our solubility study.

#### 4.2 Solubility results

The solubility results of CO<sub>2</sub> in DEAE compared to conventional amines, MEA and MDEA, at various conditions in terms of absorption capacity are presented in Table 4.1 to 4.6. The cyclic capacities of each solvent from 30-80°C are also reported. Moreover, Table 4.2, 4.4 and 4.6 present the absorption capacity difference of DEAE compared with MEA and MDEA.

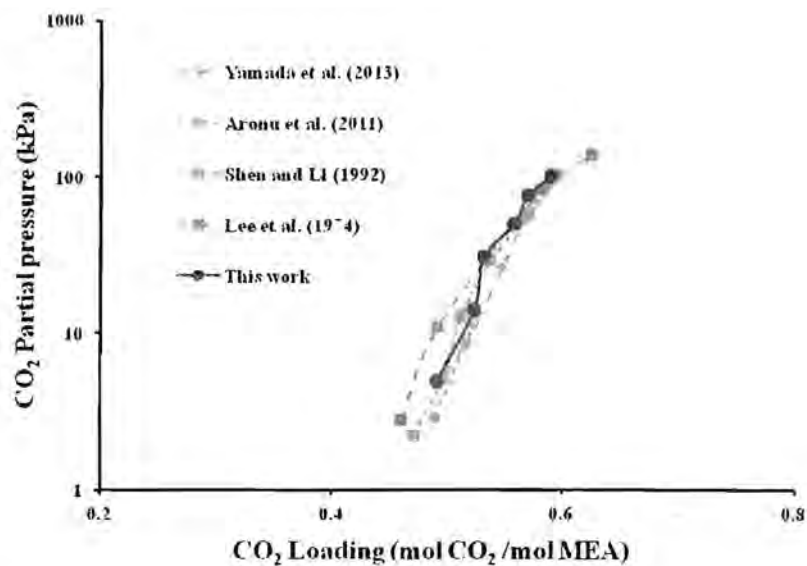


Figure 4.1 Comparison of solubility of CO<sub>2</sub> in 5.0M MEA solution at 40°C

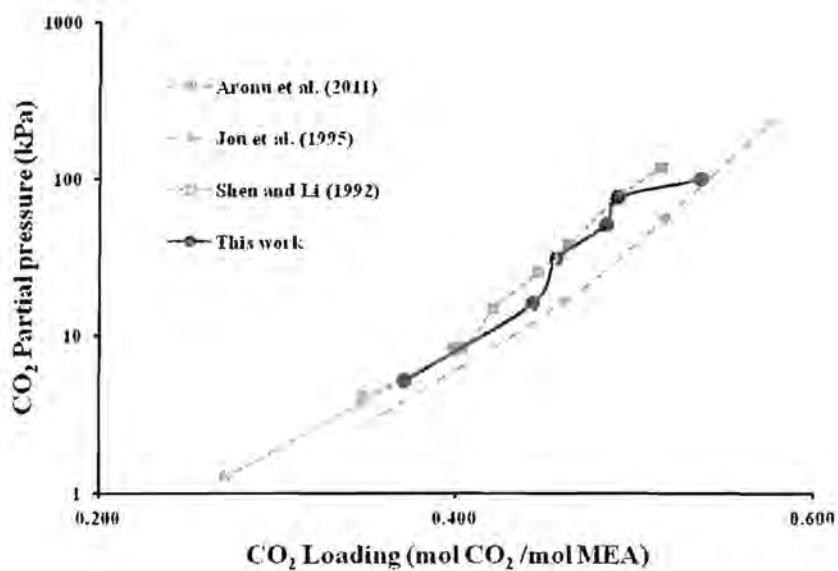


Figure 4.2 Comparison of solubility of CO<sub>2</sub> in 5.0M MEA solution at 80°C

Table 4.1 Solubility results of CO<sub>2</sub> in MEA, MDEA and DEAE at 3M concentration and 30-80°C

Temperature Solvent	30 °C		40 °C		60 °C		80 °C		Cyclic Capacity (mol/mol)
	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	
3.0 M MEA	5.12	0.530	5.32	0.498	4.87	0.450	6.06	0.372	0.126
	15.78	0.568	14.43	0.557	15.53	0.475	15.18	0.428	0.129
	30.59	0.606	31.21	0.575	31.36	0.510	29.93	0.445	0.130
	49.56	0.643	49.40	0.595	51.68	0.552	47.84	0.477	0.118
	76.00	0.673	74.77	0.611	73.00	0.563	74.38	0.494	0.118
	98.80	0.700	98.56	0.646	97.83	0.581	98.94	0.512	0.134
3.0 M MDEA	4.64	0.264	5.04	0.218	5.56	0.100	5.11	0.072	0.146
	13.87	0.464	16.08	0.398	13.14	0.166	14.47	0.090	0.308
	29.55	0.666	30.01	0.506	30.14	0.259	30.25	0.110	0.397
	49.68	0.725	49.87	0.588	48.02	0.312	50.62	0.146	0.442
	74.05	0.748	74.90	0.684	73.63	0.408	75.28	0.189	0.496
	99.06	0.815	99.78	0.735	97.67	0.478	99.93	0.230	0.505
3.0 M DEAE	5.60	0.710	5.32	0.626	5.16	0.408	4.72	0.105	0.521
	15.07	0.841	15.57	0.795	16.93	0.509	14.17	0.200	0.595
	30.07	0.870	30.07	0.814	32.97	0.651	28.61	0.262	0.552
	47.55	0.922	47.55	0.844	48.34	0.735	49.43	0.387	0.457
	73.60	0.969	74.08	0.880	73.43	0.758	74.35	0.467	0.413
	98.09	1.027	98.55	0.944	96.65	0.785	99.40	0.510	0.434

Note: Cyclic Capacity is calculated from the loading at 40 and 80 °C

Table 4.2 Absorption capacity difference of DEAE compared with MEA and MDEA at 3M concentration and 30-80°C

Temperature	Partial pressure (kPa)	Loading difference Compared to MEA	% Difference Compared to MEA	Loading difference Compared to MDEA	% Difference Compared to MDEA
30 °C	5.60	0.180	33.923	0.446	169.23
	15.07	0.273	48.128	0.377	81.06
	30.07	0.264	43.466	0.204	30.70
	47.55	0.279	43.462	0.197	27.19
	73.60	0.296	44.047	0.221	29.47
	98.09	0.327	46.789	0.212	25.98
40 °C	5.32	0.128	25.595	0.408	187.00
	15.57	0.238	42.747	0.397	99.71
	30.07	0.239	41.498	0.308	60.78
	47.55	0.249	41.780	0.256	43.52
	74.08	0.269	43.923	0.196	28.59
	98.55	0.298	46.123	0.209	28.47
60 °C	5.16	-0.042	-9.308	0.308	309.98
	16.93	0.034	7.100	0.343	206.04
	32.97	0.141	27.735	0.392	151.76
	48.34	0.183	33.124	0.423	135.92
	73.43	0.195	34.709	0.350	85.94
	96.65	0.204	35.105	0.307	64.20
80 °C	4.72	-0.267	-71.777	0.033	45.32
	14.17	-0.228	-53.278	0.110	122.94
	28.61	-0.183	-41.189	0.152	139.27
	49.43	-0.090	-18.892	0.241	164.27
	74.35	-0.027	-5.416	0.278	147.42
	99.40	-0.002	-0.321	0.280	121.73

Minus sign (-) means loading of DEAE is lower than that of MEA or MDEA.

Table 4.3 Solubility results of CO<sub>2</sub> in MEA, MDEA and DEAE at 4M concentration and 30-80°C

Temperature	30 °C		40 °C		60 °C		80 °C		Cyclic Capacity (mol/mol)
Solvent	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	
4.0 M MEA	6.78	0.535	6.98	0.492	6.22	0.429	6.85	0.362	0.130
	15.61	0.561	15.55	0.543	15.49	0.460	15.91	0.422	0.121
	30.52	0.565	30.62	0.563	30.38	0.511	30.09	0.441	0.122
	48.99	0.573	49.88	0.593	50.38	0.522	50.64	0.477	0.116
	73.63	0.598	74.64	0.602	72.73	0.552	73.28	0.491	0.111
	97.67	0.635	99.65	0.625	98.57	0.562	99.30	0.520	0.105
4.0 M MDEA	6.33	0.324	6.26	0.156	6.01	0.064	6.59	0.024	0.132
	15.91	0.416	15.75	0.314	15.33	0.165	14.59	0.052	0.262
	30.01	0.549	29.77	0.405	31.34	0.184	29.41	0.069	0.336
	50.17	0.654	49.40	0.525	49.02	0.221	50.30	0.099	0.426
	75.61	0.700	76.27	0.582	74.85	0.275	75.28	0.125	0.457
	97.83	0.736	99.97	0.642	98.86	0.292	99.22	0.155	0.487
4.0 M DEAE	4.91	0.576	3.96	0.411	5.36	0.157	4.44	0.063	0.348
	15.40	0.749	14.71	0.712	15.52	0.350	15.10	0.165	0.547
	34.63	0.858	30.01	0.753	29.70	0.389	30.14	0.173	0.580
	50.14	0.911	49.76	0.837	49.60	0.494	47.60	0.218	0.619
	74.05	0.916	74.05	0.870	73.86	0.630	74.90	0.294	0.576
	99.06	1.022	99.06	0.920	99.09	0.776	99.78	0.347	0.573

Note: Cyclic Capacity is calculated from the loading at 40 and 80 °C



Table 4.4 Absorption capacity difference of DEAE compared with MEA and MDEA at 4M concentration and 30-80°C

Temperature	Partial pressure (kPa)	Loading difference Compared to MEA	% Difference Compared to MEA	Loading difference Compared to MDEA	% Difference Compared to MDEA
30 °C	4.91	0.041	7.664	0.252	77.72
	15.40	0.188	33.512	0.333	79.99
	34.63	0.293	51.858	0.309	56.27
	50.14	0.338	58.988	0.257	39.22
	74.05	0.318	53.177	0.216	30.79
	99.06	0.387	60.945	0.286	38.83
40 °C	3.96	-0.081	-16.463	0.255	163.04
	14.71	0.169	31.123	0.398	126.60
	30.01	0.190	33.748	0.348	86.03
	49.76	0.244	41.147	0.312	59.31
	74.05	0.268	44.518	0.288	49.54
	99.06	0.295	47.200	0.278	43.35
60 °C	5.36	-0.272	-63.403	0.093	144.29
	15.52	-0.110	-23.913	0.185	112.39
	29.70	-0.122	-23.875	0.205	111.94
	49.60	-0.028	-5.364	0.273	123.31
	73.86	0.078	14.130	0.355	128.98
	99.09	0.214	38.078	0.484	165.37
80 °C	4.44	-0.299	-82.597	0.039	158.79
	15.10	-0.257	-60.900	0.113	218.10
	30.14	-0.268	-60.771	0.104	152.54
	47.60	-0.259	-54.298	0.119	119.49
	74.90	-0.197	-40.122	0.169	135.77
	99.78	-0.173	-33.269	0.192	124.43

Minus sign (-) means loading of DEAE is lower than that of MEA or MDEA.

Table 4.5 Solubility results of CO<sub>2</sub> in MEA, MDEA and DEAE at 5M concentration and 30-80°C

Temperature Solvent	30 °C		40 °C		60 °C		80 °C		Cyclic Capacity (mol/mol)
	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	Partial pressure (kPa)	Loading (mol/mol)	
5.0 M MEA	4.98	0.498	4.87	0.491	5.22	0.444	5.11	0.371	0.120
	13.89	0.557	13.82	0.523	15.78	0.475	15.97	0.443	0.080
	31.71	0.560	30.44	0.532	31.02	0.513	30.43	0.456	0.075
	51.42	0.583	49.52	0.557	49.89	0.537	50.90	0.484	0.073
	74.32	0.597	76.14	0.570	76.11	0.532	75.80	0.491	0.079
	99.64	0.611	100.33	0.590	101.05	0.549	99.46	0.537	0.053
5.0 M MDEA	5.08	0.126	5.94	0.096	4.51	0.050	5.00	0.018	0.078
	16.59	0.323	15.22	0.179	15.76	0.088	15.01	0.033	0.146
	29.37	0.427	32.94	0.290	30.91	0.119	31.38	0.048	0.241
	50.79	0.570	50.03	0.379	49.44	0.146	49.55	0.061	0.317
	74.28	0.632	76.02	0.456	74.80	0.181	76.30	0.086	0.370
	98.89	0.706	97.50	0.526	98.89	0.246	99.19	0.099	0.427
5.0 M DEAE	5.07	0.309	4.89	0.222	5.10	0.151	5.12	0.061	0.161
	15.60	0.612	15.11	0.516	18.79	0.307	14.97	0.149	0.367
	30.28	0.758	31.32	0.562	29.97	0.465	29.89	0.167	0.395
	50.55	0.832	51.01	0.702	49.87	0.499	50.06	0.202	0.500
	74.82	0.872	75.41	0.775	75.43	0.626	75.13	0.241	0.534
	98.24	0.912	100.70	0.808	99.72	0.761	99.96	0.301	0.507

Note: Cyclic Capacity is calculated from the loading at 40 and 80 °C

Table 4.6 Absorption capacity difference of DEAE compared with MEA and MDEA at 5M concentration and 30-80°C

Temperature	Partial pressure (kPa)	Loading difference Compared to MEA	% Difference Compared to MEA	Loading difference Compared to MDEA	% Difference Compared to MDEA
30 °C	5.07	-0.189	-37.925	0.183	145.62
	15.60	0.055	9.888	0.289	89.47
	30.28	0.198	35.420	0.331	77.35
	50.55	0.249	42.792	0.262	45.99
	74.82	0.275	46.106	0.241	38.09
	98.24	0.301	49.348	0.206	29.19
40 °C	4.89	-0.269	-54.765	0.126	131.97
	15.11	-0.007	-1.346	0.337	188.06
	31.32	0.030	5.705	0.272	94.09
	51.01	0.145	25.947	0.323	85.37
	75.41	0.205	36.077	0.319	70.11
	100.70	0.218	37.063	0.282	53.63
60 °C	5.10	-0.293	-66.064	0.101	201.89
	18.79	-0.168	-35.378	0.220	251.05
	29.97	-0.048	-9.447	0.345	288.99
	49.87	-0.038	-6.989	0.353	241.15
	75.43	0.094	17.670	0.446	246.79
	99.72	0.211	38.488	0.515	208.99
80 °C	5.12	-0.310	-83.554	0.043	245.76
	14.97	-0.294	-66.387	0.116	351.07
	29.89	-0.289	-63.403	0.119	247.09
	50.06	-0.282	-58.300	0.141	229.28
	75.13	-0.250	-50.916	0.155	180.87
	99.96	-0.236	-43.925	0.202	202.70

Minus sign (-) means loading of DEAE is lower than that of MEA or MDEA.

#### 4.2.1 Effect of types of solvents

Solvents that are investigated in this study are MEA, MDEA and DEAE. The results are presented in Table 4.1 to 4.6 and Figure 4.3 to 4.5 illustrating the performance of this solvent in terms of solubility and cyclic capacity on CO<sub>2</sub> removal of difference types of solvent at 5M and 40 and 80°C. Among them, DEAE shows the most preferable in CO<sub>2</sub> solubility at almost entire range of CO<sub>2</sub> partial pressure especially at higher CO<sub>2</sub> partial pressure.

According to the Figure 4.3 and 4.4, the result shows that at 40°C and 15 kPa CO<sub>2</sub> partial pressure which is represented the range of flue gas emitted from fossil-fired power

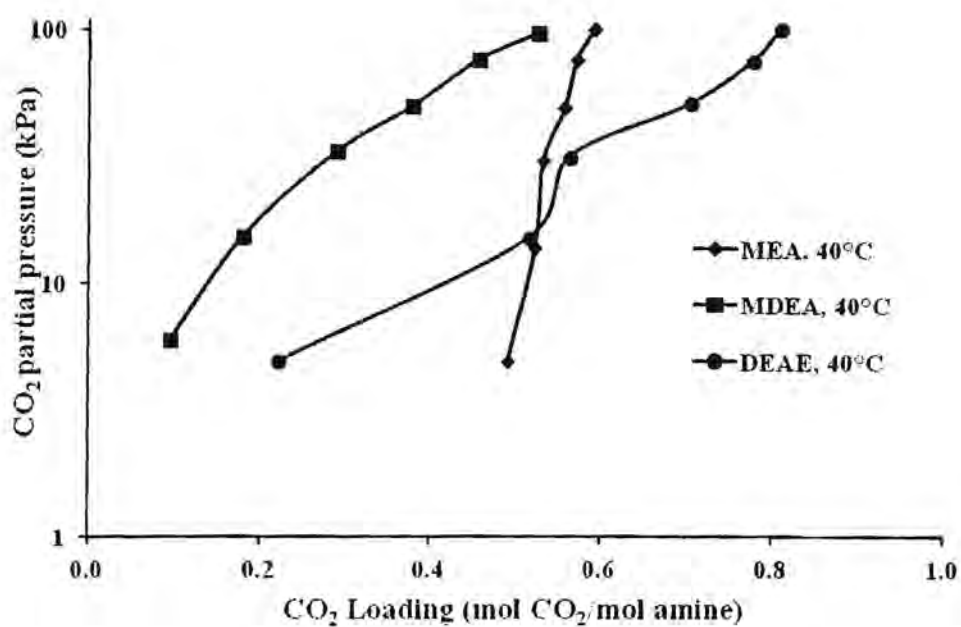


Figure 4.3 Solubility of CO<sub>2</sub> in 5.0M MEA, MDEA and DEAE at 40°C

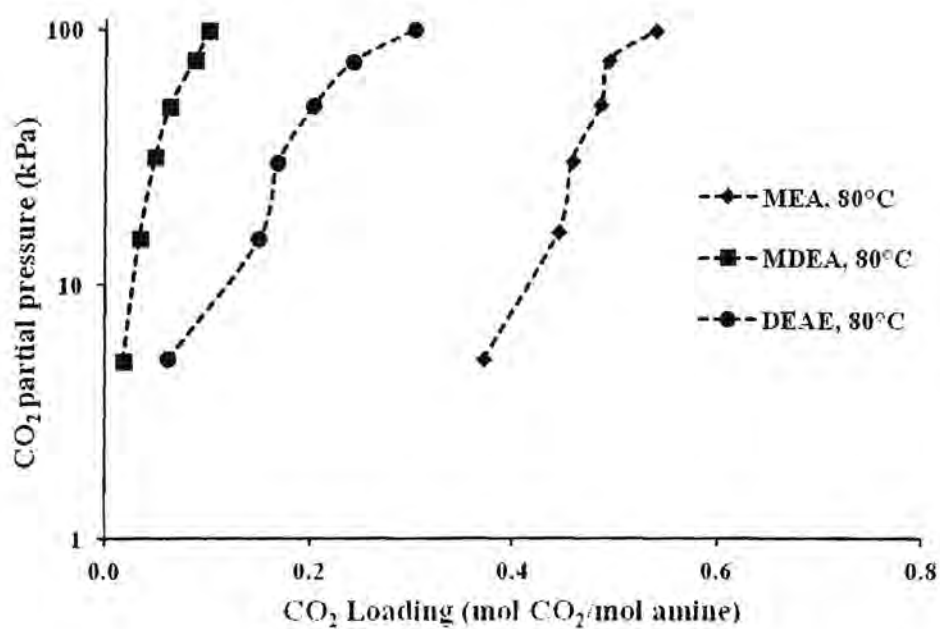


Figure 4.4 Solubility of CO<sub>2</sub> in 5.0M MEA, MDEA and DEAE at 80°C

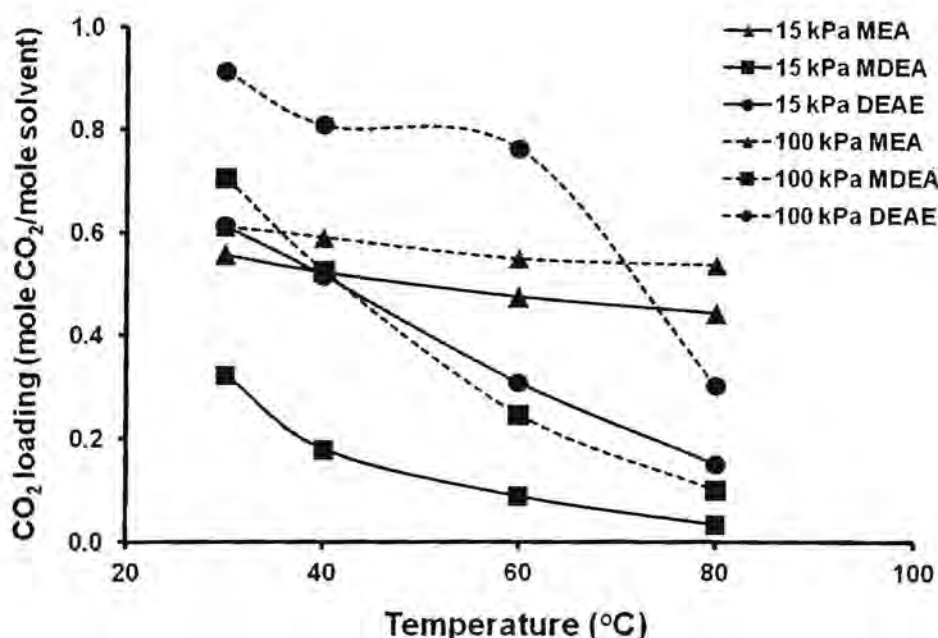


Figure 4.5 Cyclic capacities of CO<sub>2</sub> in 5.0M MEA, MDEA and DEAE at 15 and 100 kPa

plants, DEAE provides a slightly lower CO<sub>2</sub> absorption capacity than that of MEA for 1.3%. On the other hand, at 80°C, DEAE provides much lower CO<sub>2</sub> absorption capacity for the whole range of CO<sub>2</sub> partial pressure than those of MEA up to 84%. This means that DEAE can absorb less at regeneration condition. At partial pressure lower than 15 kPa, DEAE provides less absorption capacity than MEA especially at higher temperature.

From the Table, one can see that at 5M, low temperature and partial pressure above 15 kPa, the tendency of the absorption capacity of CO<sub>2</sub> in DEAE solution is found to be superior to that in MEA. The absorption capacity differences for DEAE at 40°C compared with MEA are -54 to 37% higher. However, at a partial pressure below 15 kPa, the absorption capacity of DEAE is lower than that of MEA. Furthermore, at high temperature, the solubility of CO<sub>2</sub> in DEAE is much lower than that in MEA.

In term of cyclic capacity as shown in Figure 4.5, DEAE provides a much higher cyclic capacity than that of MEA and slightly higher than MDEA. Figure 4.5 presents the cyclic capacity of these solvents using 15 and 100 kPa CO<sub>2</sub> from 30-80°C. It is shown that DEAE has a cyclic capacity that is 360% and 856% greater than MEA at 15 and 100 kPa,

respectively. Therefore, when using conditions above 15 kPa CO<sub>2</sub> and 40°C, or at the flue gas absorption conditions, DEAE has higher absorption capacity as well as cyclic capacity than that in MEA.

Therefore, it is clear that the DEAE has a much higher cyclic capacity than MEA and slightly higher than MDEA under the same operating conditions. This can lead to a lower liquid circulation rate for an absorption-regeneration system and indicate an advantage from the viewpoint of energy efficiency in the regeneration of solvent. This advantage can result in lower both operating and capital costs for gas treating process.

#### 4.2.2 Effect of CO<sub>2</sub> partial pressure

The partial pressure of CO<sub>2</sub> studied in this work covers the range of typical amount of CO<sub>2</sub> emitted from fossil-fired power plants and can be extended to natural gas processing plants. Figure 4.6 demonstrates the effect of the partial pressure of CO<sub>2</sub> on the solubility of CO<sub>2</sub> in 5M DEAE from 30 to 80°C. Solubility increases as partial pressure increases because gas can absorb more at higher partial pressure. For every solution, the solubility of CO<sub>2</sub> is a direct proportional to the partial pressure of itself at equilibrium state. In the other words, increasing the CO<sub>2</sub> partial pressure is likely to enlarge the driving force of CO<sub>2</sub> in gas phase transferring to liquid phase. Thus, the higher of CO<sub>2</sub> partial pressure in gas phase is applied, the higher amount of CO<sub>2</sub> is to be captured.

#### 4.2.3 Effect of temperature

In terms of thermodynamics, temperature is the main role that affects the equilibrium CO<sub>2</sub> capture capacity of the solvent. The effect of temperature to the CO<sub>2</sub> solubility derived from the experimental conditions of 30, 40 60 and 80°C temperature and 5M solvent concentration is shown in Figure 4.6

The results from Figure 4.6 clearly illustrate that the solubility of CO<sub>2</sub> is conversely proportional to the absorption temperature for all solution types. It can be observed that the isotherm of lower temperature has higher CO<sub>2</sub> loading when comparing to the higher temperature isotherm. The decreasing in CO<sub>2</sub> loading while increasing the system

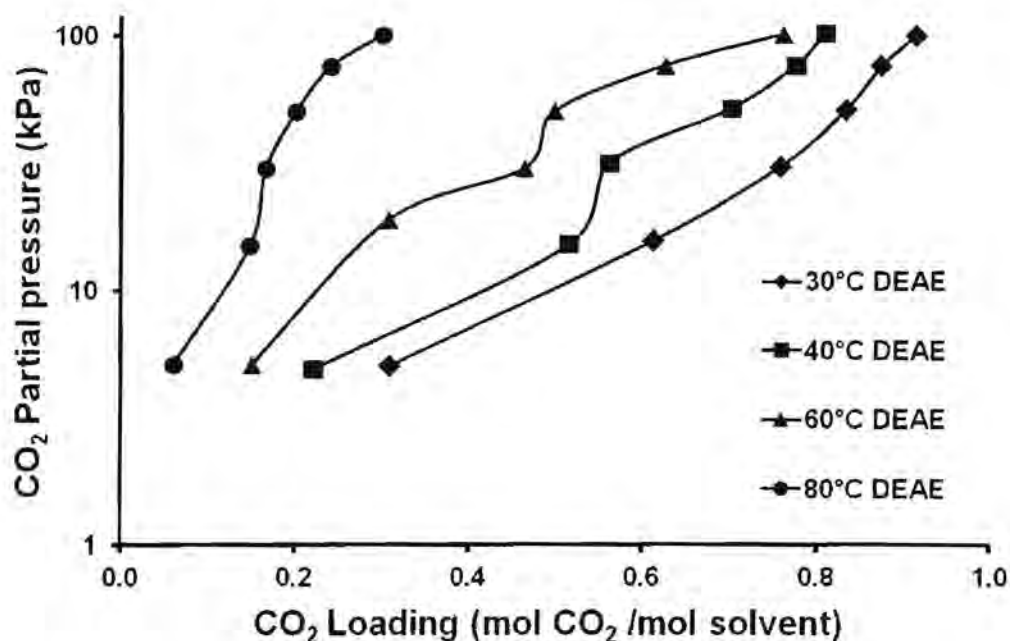


Figure 4.6 Solubility of CO<sub>2</sub> in 5.0M DMAE from 30 to 80°C and CO<sub>2</sub> partial pressure from 5-100 kPa

temperature can be explained that for exothermic reaction, the acid gas dissolving in the solution gains a large amount of kinetic energy at high temperature and results in the increasing amount of the escaping gas from liquid phase and eventually reduces the CO<sub>2</sub> content in the solvent.

#### 4.2.4 Effect of solvent concentration

Concentration of solvent is one of the most essential factors which are considered in acid gas capturing process design. Figure 4.7 shows the effect of solution concentration of 3, 4 and 5M on CO<sub>2</sub> solubility at 40 and 80°C. The results illustrate that the performance of CO<sub>2</sub> loading or mole of CO<sub>2</sub> per mole of amine at 5M is less than that at 3M concentration because at 5M mole of amine, the denominator is higher. In the other words, as the solution concentration increases, the CO<sub>2</sub> loading is decreased. Table 4.1 to 4.3 also shows details of the CO<sub>2</sub> solubility at any points of CO<sub>2</sub> partial pressure.

Theoretically, in an amine-based absorption process, increasing of solvent concentration results in the increase of the amount of un-reacted amine or free amine per unit volume. Therefore, the higher amount of acid gas is captured but at a certain level. Although the mole of captured  $\text{CO}_2$  is increased as well as the solvent concentration, the mole of solution is also developed at a higher rate. Consequently, from the definition of  $\text{CO}_2$  loading, this affects to the mole of  $\text{CO}_2$  per mole of solvent ratio, or  $\text{CO}_2$  loading, that it will be decreased when the solution concentration is increased.

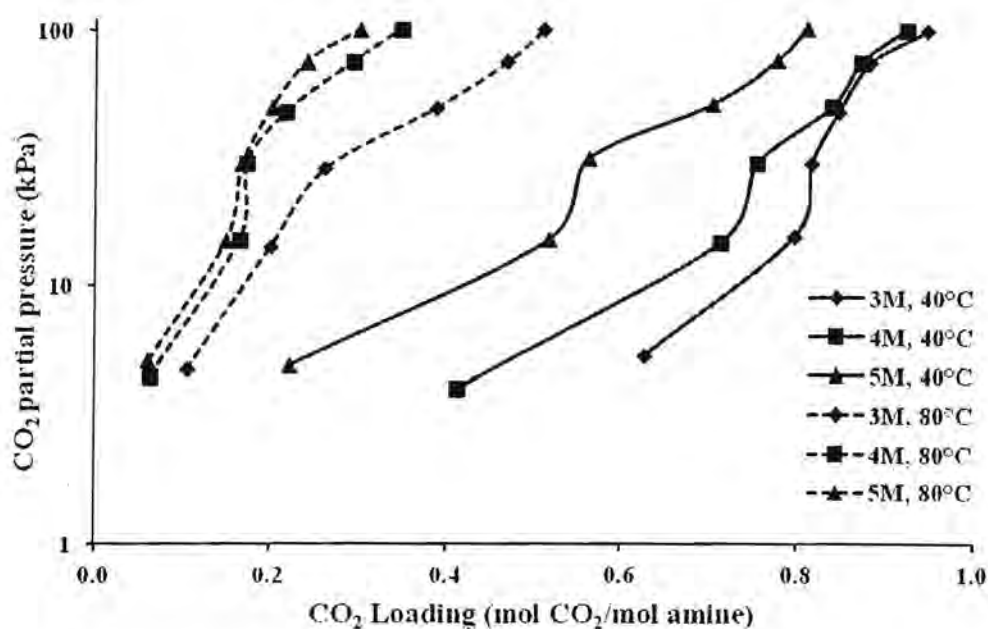


Figure 4.7 Effects of solution concentration on solubility of  $\text{CO}_2$  in DEAE from 30 to 80°C

Consequently, it can be concluded that, in terms of absorption and cyclic capacities, the new solvent, 2-(Diethylamino)ethanol, is an effective reagent for capturing  $\text{CO}_2$  from gas streams and it can be considered as a new promising solvent for acid gas treating processes. The desirable characteristics of this solvent relative to MEA and MDEA include its capacity to absorb a larger amount of  $\text{CO}_2$  per unit mole and to permit



## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

The study of new solvents requires the fundamental knowledge of gas separation processes. The research carried out here dealt with many aspects. This report has introduced the research topic and the scope for the project. The review of absorption systems and solubility studies are presented in this report as shown in Chapters 2 to 4. From the results, it was found that the new solvent, DEAE has the potential to play an important role in CO<sub>2</sub> absorption in the future, especially with respect to capturing CO<sub>2</sub> from flue gas or combustion gas from the sources like flair or power plants.

#### 5.1 Conclusions

In this work, the chemical absorption of CO<sub>2</sub> was studied using traditional solvent, MEA, MDEA and a new solvent, DEAE systems. The three solvents were operated under similar conditions in order to evaluate their performance with respect to each other. Bench scale CO<sub>2</sub> absorption experiments were conducted under a variety of operating conditions to measure the solubility obtained in each system.

In terms of solubility data and cyclic capacity, compared to MEA and MDEA, the results have shown that DEAE offered superior performance for CO<sub>2</sub> absorption. With the higher absorption capacity and cyclic capacity, DEAE has presented better results for CO<sub>2</sub> capture compared to MEA and MDEA. Its excellent absorption capacity and cyclic capacity can allow the reduction of the solvent circulating rate in the CO<sub>2</sub> absorption processes, which will thereby increase the potential to reduce both capital and operating costs for CO<sub>2</sub> capture processes. Therefore, DEAE has been demonstrated to have strong potential feasibility as a promising solvent for CO<sub>2</sub> capture.

#### 5.2 Recommendations for Future Work

The results of this thesis have proven that this new solvent, DEAE, is a promising solvent for CO<sub>2</sub> capture from flue gas in term of solubility and cyclic capacity. However, for industrial application, more research on DEAE is needed, especially with respect to understanding its physical and transport properties, mass transfer, kinetics, corrosion, as a component of a formulated solvent, solvent

degradation as well as the mathematical modeling of its solubility. Proposed future work includes the following:

1. Physical and transport properties, the properties studied are density, viscosity, and refractive index, playing a significant role in the rational design and operation of a gas treating process plant in addition to their use for estimating the other properties, such as reaction rate constant, in the future.
2. A comparative mass transfer study is needed in terms of the overall mass transfer coefficient,  $K_{Ga_v}$  to calculate for the height of the absorption column as well as the process design.
3. The kinetics of the new solvent needs to be studied to identify the speed of the new solvent's reaction with  $CO_2$  by measuring diffusivity and kinetics rate constant. This will lead to studies aimed at elucidating the reaction mechanisms of the new solvent.
4. One of the main problems of  $CO_2$  capture in industry is corrosion. Therefore, the corrosion characteristics of the new solvent and methods to overcome them need to be identified before this solvent can be used for any industrial application.
5. In terms of commercial economics, the solvent's degradation characteristics are needed. A basic understanding of degradation is required in order to determine how to reclaim the lean solution.
6. In addition to  $CO_2$  capture, it will be useful to know if the new solvent can be applied to work with other acid gases such as  $SO_2$  and  $H_2S$  for flue gas and natural gas applications because these are also the components in flue gas and natural gas, respectively. In order to capture acid gas at a lower cost, simultaneous removal of  $CO_2$  and other pollutants may be an interesting option.
7. Mathematical modeling of solubility studies of the new solvent is recommended in order to predict the solubility of  $CO_2$  with the new solvent.
8. Environmental concern on this new solvent need to be proven before using this chemical.
9. Heat or energy consumption for solution regeneration is one of the most important issues for carbon capture. Therefore, heat duty for solvent recovery is needed to study in the future as well as the life cycle assessment for this new solvent.

All recommendations are required to investigate further to prove the application for the new solvent and make it a new promising solvent in the future.

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