อิทธิพลของโครงสร้างของอะมิโนโพรพานอลต่อการดูดซึมของคาร์บอนไดออกไซด์

นางสาวรสสุคนธ์ นิ่มเจริญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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ปีการศึกษา 2560

EFFECT OF AMINO PROPANOL STRUCTURE ON CARBON DIOXIDE ABSORPTION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2017

Thesis Title	EFFECT OF AMINO PROPANOL STRUCTURE ON CARBON DIOXIDE ABSORPTION
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รสสุคนธ์ นิ่มเจริญ : อิทธิพลของโครงสร้างของอะมิโนโพรพานอลต่อการดูดซึมของคาร์บอนไดออกไซด์ (EFFECT OF AMINO PROPANOL STRUCTURE ON CARBON DIOXIDE ABSORPTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ธวัชชัย ชรินพาณิชกุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. เกรียงไกร มณีอินทร์, 109 หน้า.

ปัจจุบันภาวะโลกร้อนเป็นประเด็นหลักในด้านสิ่งแวดล้อมอันเนื่องมาจากปริมาณคาร์บอนไดออกไซด์ในบรรยากาศที่สูงขึ้นแหล่งที่มาของคาร์บอนไดออกไซด์ส่วนใหญ่มาจากอุตสาหกรรมต่างๆ เทคโนโลยีปัจจุบันที่ใช้กำจัดคาร์บอนไดออกไซด์คือการจับและเก็บคาร์บอนไดออกไซด์ โดยเฉพาะการดูดซึมด้วยสารละลายเอมีน สารละลายเอมีนที่ใช้ทั่วไปคือ โมโนเอทาโนลามีน จะมีข้อเสียเช่น ความจุต่ำและการใช้พลังงานสูง ดังนั้นจึงมีการศึกษาตัวทำละลายชนิดใหม่เพื่อชดเชยข้อบกพร่องดังกล่าว ตัวทำละลายตัวใหม่เช่น 3-อะมิโน-1-โพรพานอล, 3-ไดเมทิลอะมิโน-1-โพรพานอล และ 1-ไดเมทิลอะมิโน-2-โพรพานอล จะใช้เป็นตัวทำละลายสำหรับการกำจัดคาร์บอนไดออกไซด์ ในงานวิจัยนี้ความสามารถในการละลายของคาร์บอนไดออกไซด์ในตัวทำละลายใหม่ทำการศึกษาผลของความเข้มข้นของตัวทำละลายที่ความต่างกันในช่วง 3, 4 และ 5 ศึกษาผลกระทบของคาร์บอนไดออกไซด์ โดยจะมีการเปลี่ยนความดันบางส่วนของคาร์บอนไดออกไซด์ในช่วง 5 - 100 กิโลพาสคาล และที่อุณหภูมิ 30 ถึง 80 องศาเซลเซียส พบว่า 3-ไดเมทิลอะมิโน-1-โพรพานอล มีประสิทธิภาพที่เด่นในการจับคาร์บอนไดออกไซด์มากกว่า โมโนเอทาโนลามีนเอมีน นอกจากนี้ 3-ไดเมทิลอะมิโน-1-โพรพานอล ยังสามารถให้ความจุวัฏจักรเฉลี่ยมากกว่าของสารละลายโมโนเอทาโนลามีนเอมีนได้ถึง 279 เปอร์เซ็นต์และความจุวัฏจักรเฉลี่ยมากกว่า 3-อะมิโน-1-โพรพานอล เฉลี่ย 21 เปอร์เซ็นต์เมื่อเทียบกับโมโนเอทาโนลามีนเอมีน และศึกษาผลของเวลาต่อสมรรถนะของตัวทำละลายในการดูดซับคาร์บอนไดออกไซด์ โดยอัตราการเปลี่ยนของจับคาร์บอนไดออกไซด์เมื่อเทียบกับเวลาจะสูงมากที่จุดเริ่มต้นของปฏิกิริยาจนถึงสภาวะสมดุล ส่งผลให้การเพิ่มอัตราการเปลี่ยนแปลงคาร์บอนไดออกไซด์สำหรับแรงกดบางส่วนที่สูงขึ้นและอัตราการเปลี่ยนแปลงการโหลดอาจเพิ่มขึ้นเนื่องจากแรงขับเคลื่อนที่สูงขึ้นทำให้อัตราการเกิดปฏิกิริยาสูงขึ้นและหลังจากนั้นอัตราการเปลี่ยนแปลงคาร์บอนไดออกไซด์ค่อนข้างคงที่จนกว่าจะถึงจุดสมดุล จึงสรุปได้ว่า สารละลาย 3-ไดเมทิลอะมิโน-1-โพรพานอล มีสมรรถนะในการดูดซึมคาร์บอนไดออกไซด์ที่ดีกว่าสารละลายทั้งสองชนิด ช่วยลดการใช้พลังงานในการดูดซึมและการสามารถนำสารละลายกลับมาใช้ใหม่ ช่วยลดค่าใช้จ่ายของระบบได้

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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5870228421 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: CARBON DIOXIDE / ABSORPTION / SOLUBILITY

ROSSUKON NIMCHAROEN: EFFECT OF AMINO PROPANOL STRUCTURE ON CARBON DIOXIDE ABSORPTION. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., CO-ADVISOR: ASST. PROF. KREANGKRAI MANEEINTR, Ph.D., 109 pp.

Currently, global warming is the main issue on environmental concern due to the higher amount of carbon dioxide (CO_2) in the atmosphere.The current technology to remove CO_2 effectively is carbon capture and storage or CCS especially absorption with aqueous amine solutions. The commonly used amine solutions are monoethanolamine (MEA). They have some disadvantages like low capacity. Therefore, a new solvent such as 3-amino-1-propanol (3A1P), 3-dimethylamino-1-proapnol (3DMA1P) and 1-dimethylamino-2-proapnol (1DMA2P) have been designed to be used as alternative solvents for CO_2 removal. In this work, the solubility of carbon dioxide in a new promising solvents. The effect of solvents concentration is studied and varied in range of 3, 4 and 5 molars. The effect of carbon dioxide is examined by varying carbon dioxide partial pressure in a range of 5-100 kPa and at the temperature from 30°C to 80°C. Furthermore, 3DMA1P could provide the greater average cyclic capacity than that of MEA for 279 % and the greater average cyclic capacity than 3A1P for 21%. Time dependence of solvent performance in CO_2 absorption. The rates of CO_2 loading change versus time are very high at the beginning of the reaction until into a state of equilibrium. The increasing the rate of CO_2 change. For higher partial pressure, the rate of loading change can increase because of higher driving force leading to higher rate of reaction. Later, the rate is relatively stable until it reached equilibrium.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2017	Co-Advisor's Signature	....

ACKNOWLEDGEMENTS

I would like give my gratitude to my thesis advisor Assoc. Prof. Dr. Tawatchai Charinpanitkul and also to my thesis co-advisor Asst. Prof. Dr. Kreangkrai Maneeintr for giving me my encouragement to pursue this dissertation till the end and also academic knowledge.

My grateful appreciation also to Prof. Dr. Suttichai Assabumrungrat as a chairman, Dr. Chalida Klaysom and Dr. Winyu Tanthapanichakoon as an external examiner for their advice and comments.

Thanks to my friends in the Center of Excellence in Particle Technology (CEPT), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University and all of my friends for friendship, encouragement and their assistance all the time.

Finally, I would like to extremely express my highest gratitude to my parents and my family for their unconditional support.

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CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Greenhouse gases (GHGs) are the gases that are in the atmosphere and cause a greenhouse effect and global warming [1]. The main greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), vapor water (H_2O), ozone (O_3). In the past, greenhouse gases are essential and vital for keeping the global temperature balance. But, if the amount of gases are too high, the temperature will rise to the levels that can be harmful to living things [2].

After the industrial revolution, the amount of carbon dioxide (CO_2) has increased from 280 ppm to 400 ppm [2], which contributes to climate change and other impacts, such as ocean acidification, melting of snow and ice, sea level rising, ozone layer depletion and so on. The composition of carbon dioxide (CO_2) in approximately 76 % of GHGs as shown in Figure 1.1.

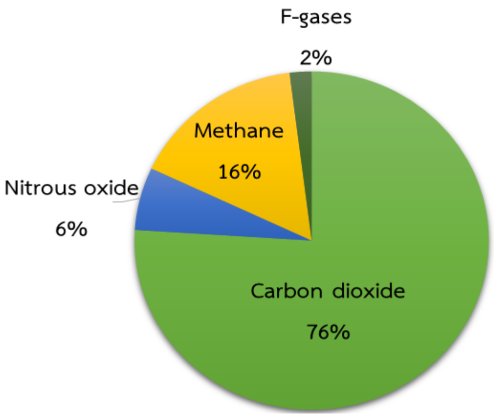


Figure 1.1 The composition of GHGs in world 2014 [2].

1.2 Carbon dioxide emission

According to Figure 1.2, the main sources of CO_2 emission come from a power generation and an industries. The electricity is produced by burning fossil fuels such as coal, natural gas and oil. By the sources, the amount of CO_2 emission can be categorized into 33 % from electricity generation, 24 % from argiculture and 21% from industry respectively. Furthermore, the use of coal to generate electricity is approximately 39% and natural gas is approximately 27% as shown in Figure 1.3.

CO_2 emission is released from power generation and heat production. Although fossil fuel-power plants produce a large amount of CO_2 that will impact to the environment, development of CO_2 capture process for power generation would be an effective method to reduce CO_2 emission [2].

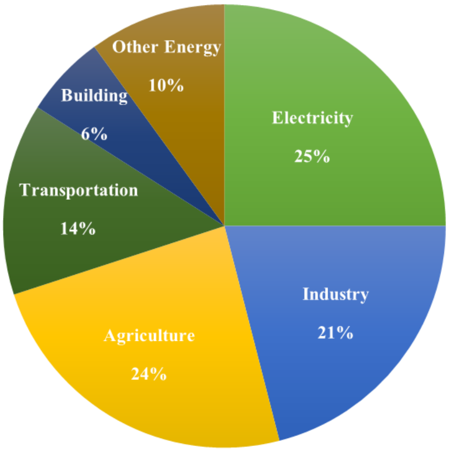


Figure 1.2 CO_2 emission by sectors in 2014 [2].

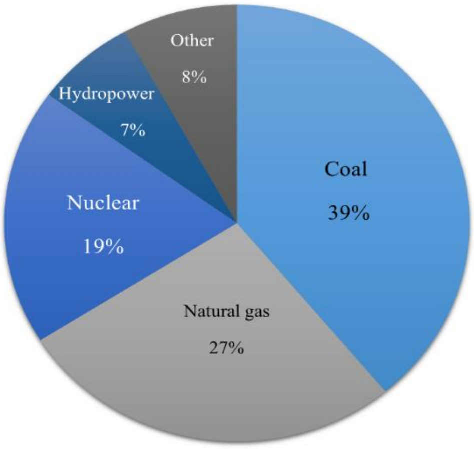


Figure 1.3 Type of Fuel in 2014 [2].

The flue gas from coal-fired power plant has the concentration of CO_2 is approximately 10-18 %, based on coal burning at atmospheric pressure [3].

1.3 Power Generation

Power generation is main source of CO_2 emission to environment. Therefore, there are 3 main technologies for power generation from fossil fuel usage as presented below:

1.3.1 Post-combustion

In this system, CO_2 is separated from the flue gas emitted from the combustion process between fuel and air. The product of combustion process is steam and flue gas. The steam from the process is then used in steam turbine to generate electricity. Flue gas containing N_2, water and CO_2 is separated by other appropriate capture methods. According to Figure 1.4, the concentration of CO_2 from the combustion process is low around 10-20 %, depending on fuel used and temperature in combustion (100-250 °C) for coal-fired power plants [4].

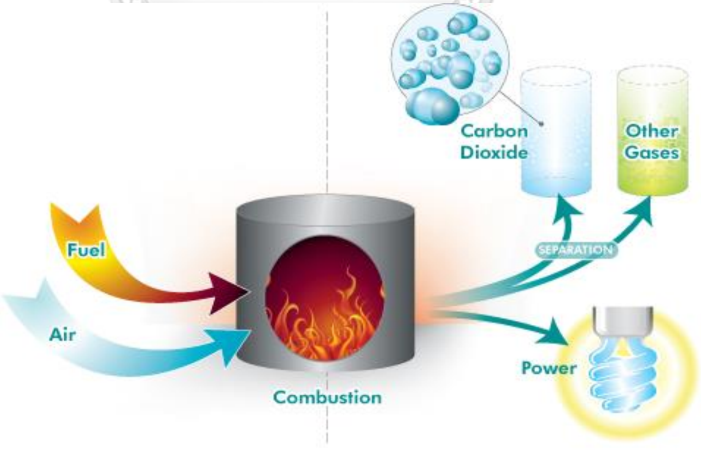


Figure 1. 4 Post-combustion capture (http://www.co2crc.com.au)

1.3.2 Oxyfuel combustion

The oxyfuel combustion process makes uses of oxygen instead of air for combustion. Fuel and oxygen is fed into the furnace at temperature of approximately

2500 °C and at atmospheric pressure. The product for this combustion is steam. The water vapor is then removed by cooling and compressing the gas stream and gap then used to spin turbine to generate electricity. According to Figure 1.5, the concentration of CO_2 is approximately 80–90%, depending on fuel used [4].

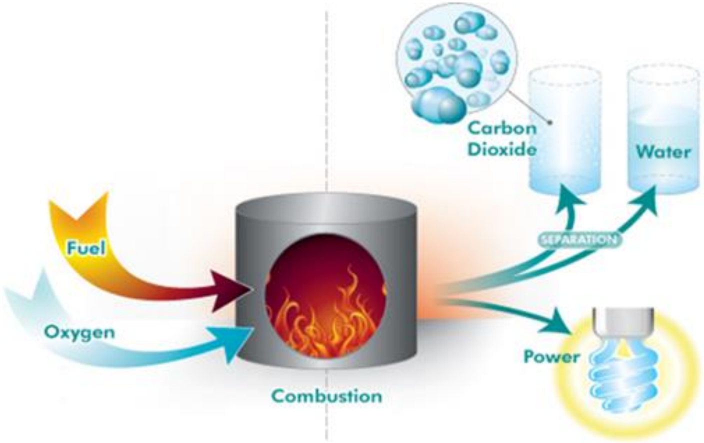


Figure 1.5 Oxyfuel combustion capture (http://www.co2crc.com.au)

1.3.3 Pre-combustion capture

Pre-combustion process comprises gasification of the fuel with oxygen or air to produce syngas consisting of H_2, CO_2, CO and water and mixed with steam H_2 and CO_2 are separated and sent to storage tank. H_2 is delivered to a gas turbine to generate electricity. According to Figure 1.6, the concentration of CO_2 is 25-40 % and pressure is in the range of 2-5 MPa [4].

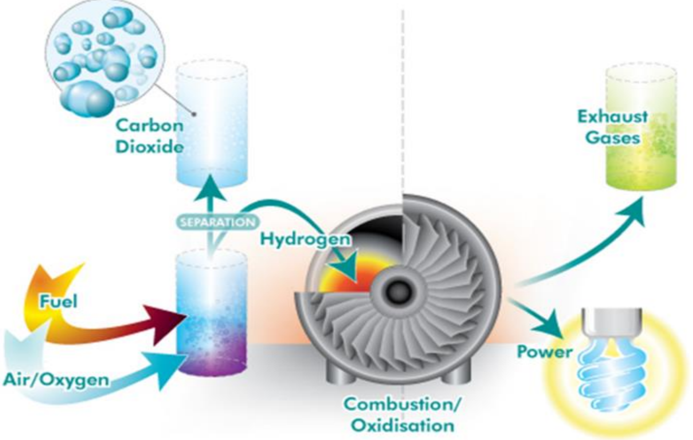


Figure 1. 6 Pre-combustion capture (http://www.co2crc.com.au)

1.4 CO_2 capture technology

Available technology for carbon dioxide capture is developed based on the characteristics of the properties of flue gas such as partial pressure of CO_2, pressure of flue gas, temperature and purity of CO_2. Also, there are many other factors such as capital and operating costs of the process. Such capture technologies can be broadly classified into 4 technologies as shown below.

1.4.1 Absorption process

Absorption technologies used for capturing carbon dioxide could be good used in power generation and industries. in two types, i.e., chemical absorption and physical absorption [4]. Physical absorption technology has chemicals such as Selexol process, Fluor process and Rectisol process. These are basically methanol, dimethyl ether of polyethylene glycol and propylene carbonate, respectively [5]. For chemical absorption, Typical absorbents used are Monoethanolamine (MEA), Diethanolamine (DEA) and Potassium carbonate [5].

Monoethanolamine (MEA) is the most commercially by used absorbent due to its high efficiency of CO_2 absorption of approximately 95 % and fast absorption rate. However, the disadvantages of MEA are low CO_2 loading capacity and high energy consumption for regeneration of absorbent [6].

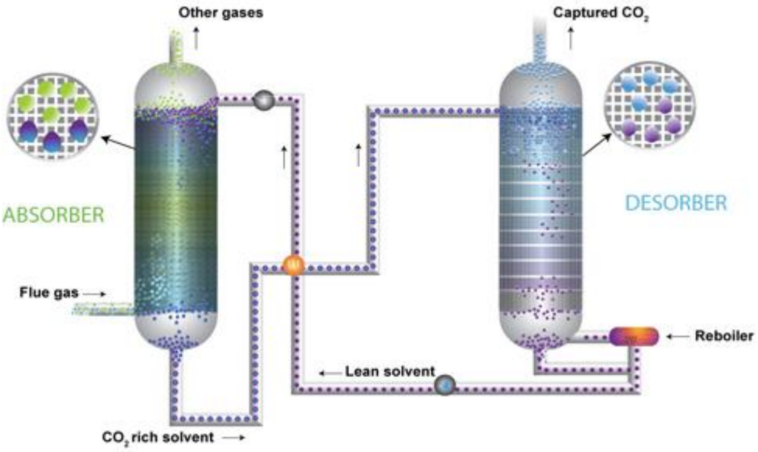


Figure 1.7 Absorption process (http://www.co2crc.com.au)

1.4.2 Adsorption process

Adsorption technology can be used to capture CO_2 from the flue gas [5]. In general, solid adsorbents such as activated carbon, zeolites, calcium oxides, hydro-.talcites and lithium zirconate can be used [4], whereas the types of regeneration are pressure swing adsorption (PSA), temperature swing adsorption (TSA) and an electrical swing adsorption technology. The adsorption process is cost effective and consumes less energy than the chemical absorption process. Adsorption is a suitable technique for high concentration of CO_2 in flue gas and high pressure process [4].

Figure 1. 8 Adsorption process (http://www.co2crc.com.au)

1.4.3 Cryogenic process

The cryogenic technology is a commercial process commonly used to purified carbon dioxide from the high carbon dioxide from relatively concentration of more than 90 % sources. This technology freezes carbon dioxide from the flue gas at temperature from -100 to –135 °C to liquid [4] so that the carbon dioxide can freeze-out / liquefy/ and separate. Cryogenic technology is the suitable technique for treating highly carbon dioxide natural gas. CO_2 removal methods can capture CO_2 in a liquid form thus it is necessary to storage carbon dioxide relatively easy underground. Coal fired power plant cannot use removal carbon dioxide form cryogenic technology. Typically, cryogenic technology is applied in oxy-fuel process because this process has high concentration of purified carbon dioxide of approximately 80-90%.

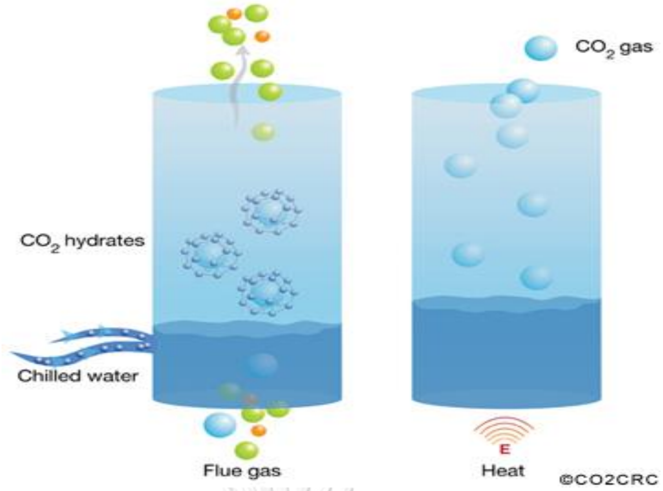


Figure 1. 9 Cryogenic Process (http://www.co2crc.com.au)

1.4.4 Membrane Process

Membrane technology is mass transfer between gas and liquid. Permeable that is selectively permeable under conditions suitable. The membrane technology for carbon dioxide capture are 2 types such as gas separation membranes and gas absorption membranes. [5].

1.4.4.1 Gas separation membranes

The polymeric membrane use for CO_2 separation from flue gas streams depends on diffusivity of each gas and membranes made from polymers such as polyamide or cellulose acetate, or from ceramic materials. The limit is CO_2 separation becomes very expensive. Membranes can be used for separating gas mixtures where they act as a permeable barrier through which different compounds move across at different rates. Polymeric membranes are economical and technologically useful, they are bounded by their performance. The gas molecules penetrate according to their size, diffusivity, or solubility as shown in Figure. 1.10.

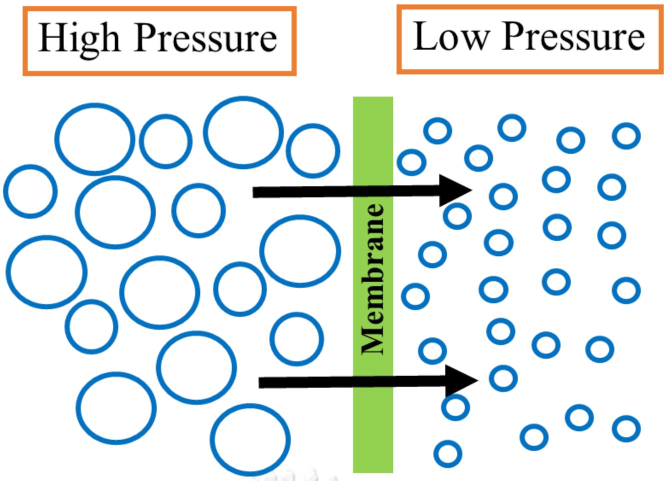


Figure 1. 10 Gas separation membranes [5]

1.4.4.2 Gas absorption membranes

Membrane gas absorption processes are absorption processes utilizing hollow fiber membranes as contact for gas flow and liquid flow. Membrane is used of a porous and hydrophobic membrane. As the membrane is porous, contact between the two flows is still despite of membrane barrier. The hydrophobic character of the membrane is keep an aqueous flow separated from the solvent relatively easy such as gas absorption by means of membranes. Membrane is made from polypropylene are currently available commercially as have been developed for micro filtration duties. In contrast to gas separation membrane, it is the absorption liquid that gives the process its selectivity as shown in Figure. 1.11

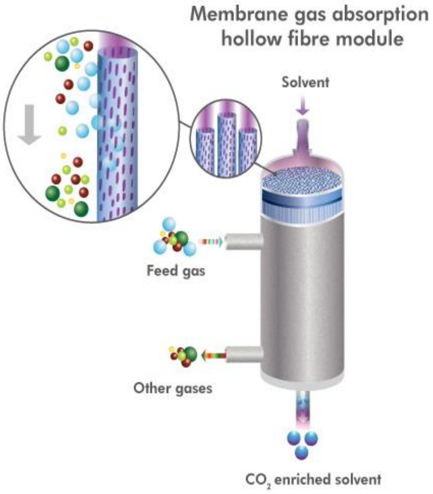


Figure 1.11 Gas absorption membranes (http://www.co2crc.com.au)

Membrane technology is not stable to capture carbon dioxide in coal-fired power plant, because membrane technology is not economically feasible for large scale separation of carbon dioxide and has low degrees of separation. Therefore, multiple stages can solve this problem at the expense of high energy consumption and cost.

The technology for carbon dioxide capture from power plant is chemical absorption technology due to conditions of the process. Current, alkanolamines such as monoethanolamine (MEA) is commercially available widely. Monoethanolamine (MEA) have advantages such as high reactivity and high alkalinity. However, these solvents have disadvantages such as low CO_2 loading capacity, corrosion and high heat of regeneration. Therefore, the novel solvent is developed and applied to increase the absorption performance and remove carbon dioxide efficiently.

MEA is chosen as a base case as a proven chemical for CO_2 capture process and data of equilibrium measurements are available in literature. The disadvantage of MEA is that it is highly corrosive and consumes high energy for solution regeneration.

Therefore, the development of new substances, i.e, 3-amino-1-propanol (3A1P), 3-Dimethylamino-1-propanol (3DMA1P) and 1-Dimethylamino-2-propanol (1DMA2P) to increases the efficiency of carbon capture.

1.5 The objectives of this work

1. To measure solubility of new solvents of 3-amino-1-propanol (3A1P), 3-Dimethylamino-1-propanol (3DMA1P) and 1-Dimethylamino-2-propanol (1DMA2P).

2. To investigate effect of temperature, partial pressure of CO_2 concentration and functional group attached to the backbone of amino propanol structure on solubility of CO_2.

1.6 Scope of this research

1.6.1. Types of solvents; MEA, 3A1P, 3DMA1P and 1DMA2P

1.6.2. Solvent concentration; 3, 4 and 5 M

1.6.3. Partial Pressure of CO_2; 5, 15, 30, 50, 75 and 100 kPa

1.6.4. Temperature; 30, 40, 60 and 80 °C

This thesis presents the research in detail. This includes the review of chemical selection and solvent development as well as the new solvent extraction for capture of carbon dioxide, all of which are given in Chapter 2. Chapter 3 shows solubility studies. Comparison between the original solvent and the proposed solvent. Discussion of theory and the experimental result is shown in Chapter 4. Finally, the thesis is summarized in Chapter 5, with conclusions and recommendations for future work.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1. Absorption Theory

The mass transfer of absorption processes, illustrated in Figure 2.1. the gas diffuses into with the liquid by pass thin boundary layer on the gas and a thin boundary layer on the liquid. When the gas enters boundary of the liquid, gas can simply dissolve and can react chemical in the liquid shown figure 2.1.

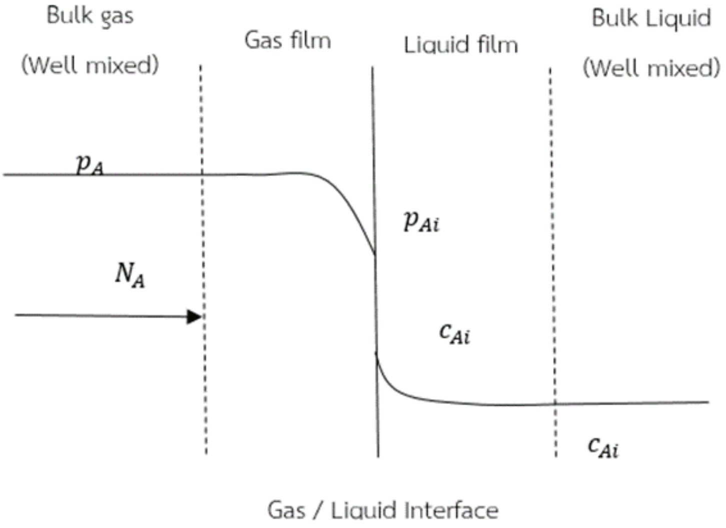


Figure 2.1 Mass transfer for a fluid-fluid interface into a liquid phase [5].

The bulk gas (well mixed) composition, P_A is partial pressure of gas, p_{Ai} is concentration of gas in bulk gas and c_{Ai} is a concentration in the bulk liquid phase. Solubility follows Henry's law, $c_{Ai} = H_A P_A$.

In the case of mass transfer may be a definite limit, when gaseous dissolve in solution into equilibrium gaseous reentering the gas phase. Through chemical reaction, the gaseous substance can change form in the liquid phase, thereby allowing more gaseous molecules to enter the liquid through mass transfer until it reaches equilibrium.

2.2. Types of absorption

Absorption can be categorized into 2 types, physical absorption and chemical absorption, based on the reaction of absorbent [5].

2.2.1 Physical absorption

Physical solvent processes or physical absorption technology use organic solvents to physically absorb carbon dioxide. In physical absorbent cannot react with the acid gas components. The main advantage of a technology is that physical solvent has more effective in high CO_2 partial pressure system.

2.2.2 Chemical absorption

The chemical absorption uses the chemical solvent to absorb carbon dioxide form flue gas stream. Chemical absorption involves a chemical reaction between the gaseous phase and liquid phase, the chemical product depends upon the absorbent used the solvent can be regenerated by the energy into the solvent. The examples of chemical solvent are monoethanolamine (MEA) and methyldiethanolamine (MDEA).

2.3. Process description

Figure 2.2. Indicates the flow diagram for acid gas absorption process system. In the absorption, typical gas treating operation which the flue gas is fed into the absorber at the bottom and alkanolamine solution is fed at the top. The reaction starts

between an alkanolamine solution and carbon dioxide when the flow gas through the column.

The gas stream containing CO_2 is contacted counter currently with the amine solution at 40 °C in absorption tower. The amine solution selectively absorbs the CO_2 is sent to the top of the stripper column through a heat recovery exchanger to increase the temperature before going to the stripper section. After, the amine solution will be steam-heated reboiler maintains 120 °C and sent into desorption tower by steam is used for the regeneration process. Finally, separated CO_2 leave the stripper at the top. The lean amine is recycled back through the heat exchanger to the top of the absorber unit.

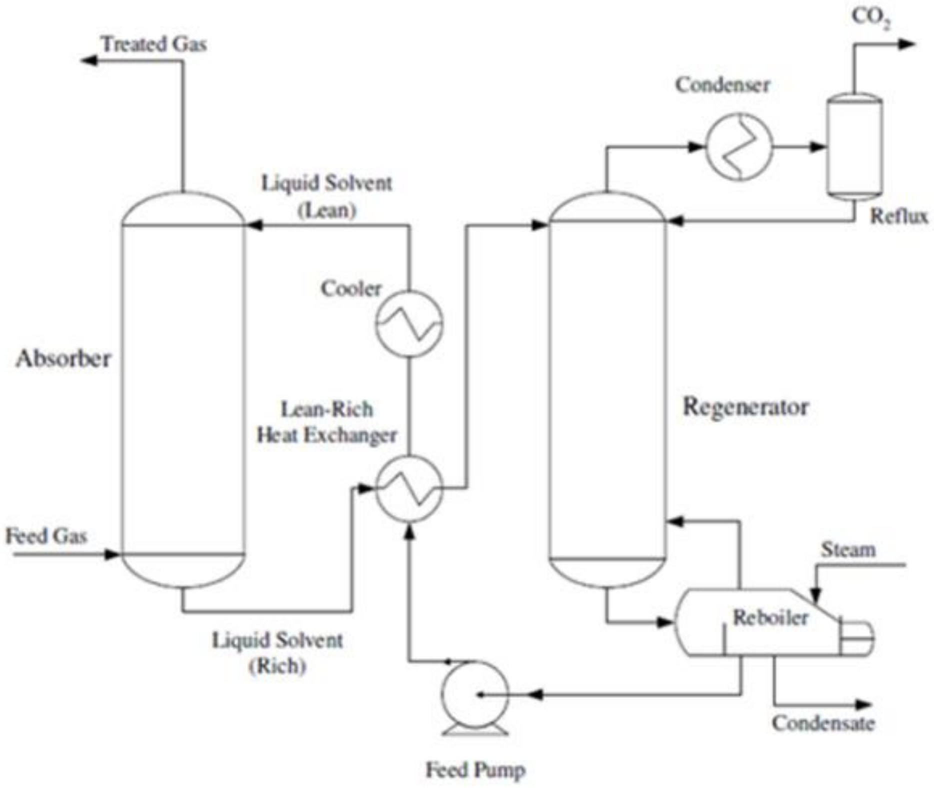


Figure 2.2 Basic flow scheme for alkanolamine acid gas removal processes [5].

2.4 Solvents used in absorption process

Carbon dioxide absorption process depends on effective absorbents. The absorbent has properties of high solubility of CO_2, huge water solubility, high rate of absorption, high chemical stability, low cost, low corrosion of material and low environmental effect [4]. The examples of chemical absorbents and physical absorbents are discussed below.

2.4.1 Solvents for chemical absorption

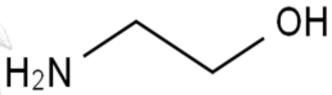
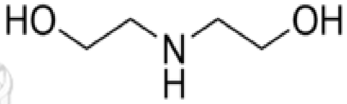
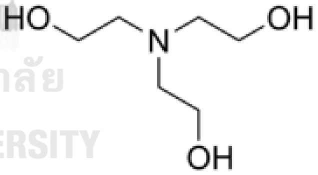
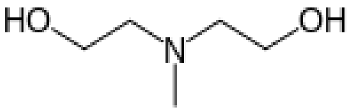
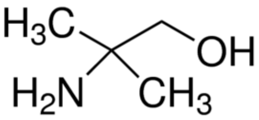
Chemical absorption is widely used in the natural gas, petroleum and chemical industries for separation of CO_2. The majority of chemical solvent are organic amine base. In chemical absorption depends on solvents. Organic absorbents such as monoethanolamine (MEA), methyldiethanolamine (MDEA) and diglycolamine (DGA) are alternative ways to absorb carbon dioxide. However, limitations of solvent, such as low absorption capacity and low absorption efficiency. This is the reason to develop the novel solvent to enhance the absorption performance.

2.4.1.1 Alkanolamine process

Amine scrubbing technology has been established for over 60 years in the chemical industries, for removal of hydrogen and CO_2 from gas streams. Amine solution has been widely used to carbon dioxide capture in the chemical and other industries. Nowadays, amine is used to capture CO_2 from the flue gas streams from the power plant. The amines widely are used three classes of amine, basically primary, secondary and tertiary amine, are generally used as organic chemical solvent.

Amine solutions at commercial applications are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). MEA is the best. These amines have amino group and hydroxyl group in their structures, which the hydroxyl group increases the water solubility and the amino group use for carbon dioxide capture [6]. The amines solution is shown in Table 2.1.

Table 2. 1 Conventional alkanolamine

Name	Acronym	Chemical structure
Monoethanolamine	MEA	
Diethanolamine	DEA	
Triethanolamine	TEA	
Methyldiethanolamine	MDEA	
2-Amino-2-Methyl-propanaol	AMP	

Amine can absorb carbon dioxide by mechanisms, as shown in the following equations [7].

As chemical solvent, the principal reactions between amine solution and CO_2 this mechanism can be described as follows [8].

Dissociation of water

$$H_2O \leftrightarrow H^+ + OH^- \tag{1}$$

Hydrolysis and ionization of dissolved CO_2

$$H_2O + CO_2 \leftrightarrow H^+ + HCO_3^- \tag{2}$$

Dissociation of bicarbonate ion

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{3}$$

Protonation of amine

$$RNH_2 + H^+ \leftrightarrow RNH_3^+ \tag{4}$$

Carbamate formation

$$RNH_2 + CO_2 \leftrightarrow RNHCOO^- + H^+ \tag{5}$$

Primary amine (1st)

$$2RNH_2 + CO_2 \leftrightarrow R_1NCOO^- + RNH_3^+ \tag{6}$$

Secondary amine (2nd)

$$2R_1R_2NH + CO_2 \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{7}$$

Tertiary amine (3th)

$$R_1R_2R_3N + CO_2 + H_2O \leftrightarrow R_1R_2R_3NH^+ + HCO_3^- \tag{8}$$

R_1 and R_2 are alkyl group.

In aqueous solutions of primary and secondary alkanolamines, the following from reactions 1-5. Primary and secondary amines can be in both forms. Amines is lone pair electrons at amino group which can be react direct carbon dioxide. The carbamate can be change to be bicarbonate form, depending on structure of amine. And in aqueous solutions of tertiary alkanolamines, the following from reactions 1-4, because tertiary amine cannot be carbamate form because carbon dioxide cannot react direct about amino group. [9]

The disadvantages of some anime are corrosion, high absorbent degradation and requirement of high energy to regenerate.More than 60% of total energy consumption in carbon dioxide capture by alkanolamine solvent process is the energy to regenerate the solvent [4]. That is the reason why the developer needs to increase carbon dioxide capture performance such as absorption capacity, absorption rate and degradation endurance.

2.4.1.2 Alkaline process

The widely used chemicals of alkaline absorbents are potassium carbonate, sodium carbonate and aqueous ammonia. In this group, absorbents potassium carbonate is more often used than other chemicals [10]. The mechanism of carbon dioxide capture by potassium carbonate follows the equation.

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3$$

Potassium carbonate process is a suitable technique for treating flue gas stream with low carbon dioxide concentration. It has fast reaction at high temperature and low carbon dioxide absorption rate at ambient temperature. That is the reason why alkaline process is not used to capture carbon dioxide from flue gas stream of industrial plants [5].

It can be concluded that the suitable type of chemicals for novel absorbent of carbon dioxide from industrial flue gas stream is the alkanolamine.

2.4.2 Solvents for physical absorption

There are several types of physical solvent that is utilized to capture CO_2 or H_2S. Various solvents are organic chemicals such as propylene carbonate (PC) used in Fluor Solvent process, methanol used in Rectisol process, dimethyl ether of polyethylene glycol (DMPEG) used in SELEXOL process and N-Methyl-2-pyrrolidone (NWP) used in Purisol. Chemical absorbents or physicochemical absorption have some restrictions, such as low viscosity and no reaction with gas stream [8].

2.5 Literature review on solubility

The chemical solvents that have been commercially used for CO_2 capture are categorized in the amine group. Generally, the structure of amine can be classified into primary, secondary and tertiary amines. Monoethanolamine (MEA) is the primary amine used for an effective removal of CO_2 in the power plants and natural gas plants. Furthermore, Table 2.2 also shows solubility of CO_2 removal from preview studies.

MEA is used in the existing CO_2 removal and published data of MEA are available. Nowadays, the problems of using MEA and other amines are limited absorption capacity of CO_2.

Table 2.2 Solubility for CO_2 in commercial aqueous amine solutions

Researcher	Year	solvent	Temperature (°C)	CO_2 partial Pressure
Yeh et al.[10]	1999	MEA	10-40	8-16 (kPa)
Jou et al.[6]	1995	MEA	0-150	200-2000 (kPa)
Yamada et al.[7]	2013	MEA	40-120	0.5 (kPa) -0.2 (MPa)
Aronu et al.[11]	2011	MEA	40-120	0-1000 (kPa)
Lee et al.[12]	1974	MEA	40,100	0.1-1000 (psia)
Shen et al.[13]	1992	MEA	40-100	1.0-2000 (kPa)
Tong et al.[14]	2012	MEA	40-100	23–983 (kPa)
Lee et al.[15]	1976	MEA	25-100	0.1-10000 (kPa)
Wook Rho et al.[16]	1997	MDEA	50-100	-
Addicks et al.[17]	2002	MDEA	40,80	200 (bar)

The problems of using commercial solvents or absorbents could be solved, by investigating the properties of the new solvent, such as CO_2 solubility. Beside using and studying of commercial amines such as MEA as absorbent, other new amines have also been studied, as shown in Table 2.3, for CO_2 capture.

Table 2.3 CO_2 capture data of new amine types.

Researcher	Year	Solvent	Temperature (°C)	CO_2 partial Pressure
Yamada et al.[7]	2013	IPAE	40-120	0.5 (kPa) -0.2 (MPa)
Yamada et al.[7]	2013	PAE	40-120	0.5 (kPa) -0.2 (MPa)
Chowdhury et al.[18]	2013	DMAE	40	20 (kPa)
Haider et al. [19]	2011	2(methylamino)ethanol	30-60	1-100 (kPa)
Luemunkong et al.[20]	2014	DMAE	40-100	5 – 100 (kPa)
Beak J.I et al.[21]	1998	2-amino-2-methyl-1,3-propanediol (AMPD)	30, 40, 60	0.5 - 3065 (kPa)

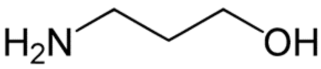
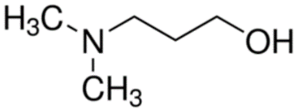
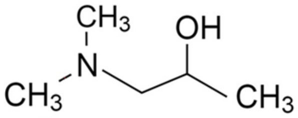
MEA solution is a chemical absorption technology. MEA has been commonly used as a solvent for CO_2 capture for many years. The advantages of MEA over other solvents are its high alkalinity, high reactivity and comparatively low cost. Although presently other solutions replace MEA for the CO_2 capture in high pressure gas streams, MEA is still preferred absorbent in systems with low concentrations of CO_2.

2.6 New solvents

The new amines for CO_2 removal are developed, based on the concept of molecular design, which places functional groups that promote CO_2 capture on solvent backbones. The new structures expected to capture carbon dioxide better than MEA are

3- Amino- 1- propanol (3A1P), 3- dimethylamino- 1- propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P). Their structures are shown in Table 2.4 and 2.5

Table 2.4 Basic in function of new solvent.

Name	Acronym	MW (g/mol)	Chemical structure
3-Amino-1-propanol	3A1P	75.11	
3-Dimethylamino-1-propanol	3DMA1P	103.16	
1-Dimethylamino-2-propanol	1DMA2P	103.16	

Relationships exist between the amine structure and capacity for CO_2 absorption [22].

Amine structure is depending on many factors such as the number of the chain lengths, an increase in the number of functional groups and performance of side chain at the α -carbon position. and the alkyl group position in amine etc.

Table 2.5 Some previous works on CO_2 capture, using new solvents.

Researcher	Year	solvent	Temperature (°C)	CO_2 partial Pressure
Dong et al. [23]	2010	3-Amino-1-propanol (3A1P)	40-120	2.5-700 (kPa)
Rodier et al. [24]	1996	3-dimethylamino-1-propanol (3DMA1P)	40-80	2 (MPa)
Liang et al. [25]	2015	1-dimethylamino-2-propanol (1DMA2P)	25-60	8-101 (kPa)
Rayer et al. [26]	2014	3-dimethylamino-1-propanol (3DMA1P) 1-dimethylamino-2-propanol (1DMA2P)	25,40 and 70	2 and 5 (MPa)
Kadiwala et al. [27]	2012	3-Amino-1-propanol (3A1P) 3-dimethylamino-1-propanol (3DMA1P) 1-dimethylamino-2-propanol (1DMA2P)	20-40	-

According to these literatures, alkanolamine solutions are still attractive solvents for CO_2 capture process. For this study, 3-amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P) are promising solvents for CO_2 absorption in both terms of high performance and good properties.

2.7 Molecular structure of solvent

Amines have many functional groups compounds such as hydroxyl group and amino group. Amino group contains at least one nitrogen atom bonded to hydrogen atoms or to alkyl or aryl groups. If the substituents (other than hydrogen atoms) are alkyl groups, the resulting compounds are termed alkyl amines. If one or more substituents is aryl groups, the compounds are termed aryl amines. Amines are commonly categorized as primary, secondary, or tertiary, depending on whether the nitrogen atom is bonded to one, two, or three alkyl or aryl groups, respectively [28]. The nitrogen atom is bonded to its hydrogen atoms and alkyl groups, but the nitrogen atom also bears a nonbonded electron pair. The three bonds and nonbonded electron pair are oriented around the nitrogen atom in a distorted tetrahedral geometry.

Amines are particularly valuable because of their ability to act as base, a property that is a consequence of the ability of amines to accept hydrogen atoms from acidic molecules.

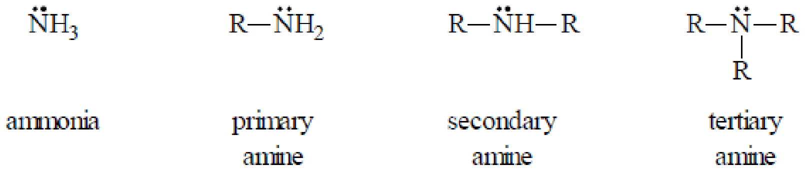


Figure 2.3 Types of amines.

In addition, hydroxyl groups can reduce vapor pressure and improve water solubility. While the amino group gives the necessary alkalinity in water to cause acid gas absorption, Amines are organic compounds that contain a nitrogen atom attached to at one alkyl substituent. Primary amines arise when one of three hydrogen atoms in ammonia is replaced by an organic substituent. Secondary amines have two organic substituents bound to nitrogen together with one hydrogen. Tertiary amines all three hydrogen atoms are replaced by organic substituents.

Physical properties of amines, boiling point of amines are greater than the boiling point of corresponding alkanes because of the presence of hydrogen bond between two amines as well as van der Waals dispersion forces and dipole-dipole interactions. The order of the boiling point of three types of amines- primary, secondary and tertiary are: Primary amine > Secondary amine > Tertiary amine. This is because of the more alkyl groups gets on the way of hydrogen bonding. Less hydrogen bonding and at least boiling point for tertiary amines [29].

The solubility amines are soluble in water due to the formation of hydrogen bonding between amine and water molecule. The solubility of amine decreases with the increase of longer chain of alkyl group or the number of alkyl groups attached to the amines, as the increased alkyl groups gets on the way of hydrogen bonding between water and amine molecule. Thus the order of the water solubility of amines is:

Primary amine > Secondary amine > Tertiary amine.

2.7.1 Primary Amines

In primary amines, the amine contains two hydrogen atoms attached to each nitrogen atom. This means that the formula of the primary amine will be RNH_2 where

R is an alkyl group such as monoethanolamine (MEA). Figure. 2.4 shows the molecular structure of all chemicals used.

Monoethanolamine (MEA) 3-Amino-1-propanol (3A1P)

Figure 2. 4 Molecular structure of primary amines used.

For primary amines, they can form hydrogen bonds with one another as well as Van der Waals forces and dipole-dipole interactions. Hydrogen bonds can form between the lone pair on the very electronegative nitrogen atom and the slightly positive hydrogen atom in another molecule [9].

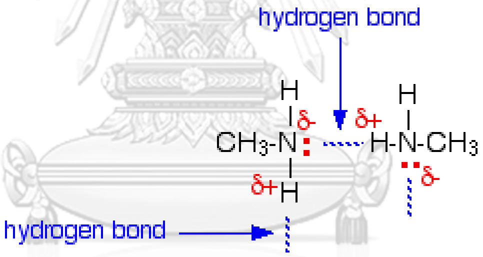
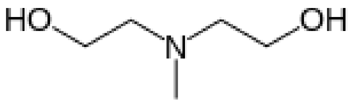


Figure 2. 5 Molecular structure of primary amines

2.7.2 Secondary Amine

In a secondary amine, two of the hydrogens in an ammonia molecule have been replaced by hydrocarbon groups. At this level, you are likely to come across simple ones where both of the hydrocarbon groups are alkyl groups. Diethanolamine (DEA) contains hydrogen atoms that are directly linked to nitrogen atoms and it is secondary amine. Figure. 2.6 shows the molecular structure of secondary amine used.



Diethanolamine (DEA)

Figure 2.6 Molecular structure of secondary amine used.

The secondary amine is a little lower than the corresponding primary amine with the same number of carbon atoms. Secondary amines still form hydrogen bonds, but having the nitrogen atom in the middle of the chain rather than at the end makes the permanent dipole on the molecule slightly less.

2.7.3 Tertiary Amine

In a tertiary amine, all of the hydrogens in an ammonia molecule have been replaced by hydrocarbon groups. There is not any hydrogen atom attached directly to the nitrogen. All three of the hydrocarbon groups are alkyl groups. That means hydrogen bonding between tertiary amine molecules. Figure. 2.7 show the molecular structure of tertiary amines chemicals and figure 2.8 Molecular structure of propanol amine all chemicals.

Triethanolamine (TEA)

Methyldiethanolamine (MDEA)

Figure 2.7 Molecular structure of tertiary amine.

3-Dimethylamino-1-propanol (3DMA1P) 1-Dimethylamino-2-propanol (1DMA2P)

Figure 2.8 Molecular structure of propanol amine all chemicals used.

3DMA1P and 1DMA2P in selected to study the partial pressure trends of CO_2 and the CO_2 loading relationship because both have a mutual molecular structure, which is the tertiary amine. Both indicated that 3DMA1P and 1DMA2P have a distinctive molecular structure which may advantage to CO_2 capture performance. 3A1P have a molecular structure, which is the primary amine. However, 3A1P has greater number of CO_2 loading than MEA but less than 3DMA1P and 1DMA2P which are the tertiary amine.

Amine is a polar molecule because of the singly isolated electrons on nitrogen atoms, amine bonds to hydrogen, but the bond N-H is weaker than O-H because nitrogen has less electron. Primary amines and secondary amines can form an N-H bond or a hydrogen bond between molecules. Tertiary amines cannot do because there is no hydrogen atom attached to the nitrogen atom. Primary and secondary amines have a lower boiling point than the boiling point of butanol, whereas tertiary amines do not have hydrogen bonds, so their boiling point is lower than the boiling point of the primary amine and secondary amine.

Amine is nucleotides (Lewis base) because it has an isolated pair of electrons that are not used in bonding. One atomic nitrogen can be bonded to the electrolyte. In addition, the amine exhibits properties as a base by accepting protons from acid. (Bronsted-Lowry base). The reaction of amines with alkyl halides is illustrated by the presence of amine as the nucleotide in Figure 2.9.

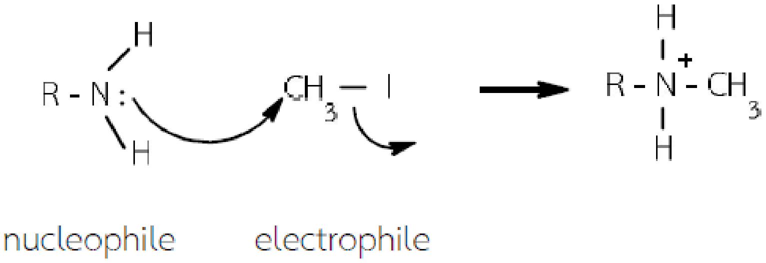


Figure 2. 9 The amine exhibits properties as a base by accepting protons from acid.

The reaction of amine when acting as a proton acceptor from acid is shown in Figure 2.10.

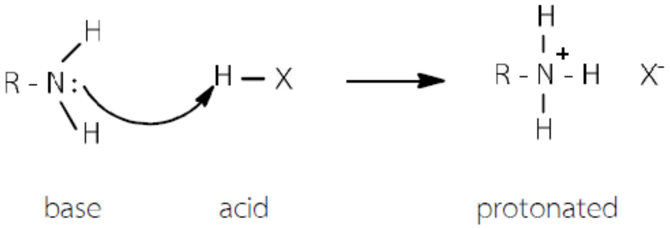


Figure 2. 10 The reaction of amine when acting as a proton acceptor from acid [30].

Primary and secondary amines react with carbon dioxide to form carbamate. The decomposition of carbon is in the form of bicarbonate, depending on many factors such as the chemical stability influenced by temperature. Tertiary amines group cannot react with carbon dioxide directly because these amines do not have free protons. Therefore, three types of amines produce hydration of carbon dioxide, which act as catalyst and cause the formation of protonated amine and bicarbonate [9]. The effect of molecular structures depends steric hindrance, which is an important parameter in reducing the stability of carbamates and also which affects the basicity of the solvent used. Amine (low to high) is dependent on the number of functional groups being replaced with α-carbon next to the amino group.

As a result of the breakdown of the amine, the electron pairs separate from the nitrogen atoms. The amine bonds with hydrogen from the molecular chain. Primary and secondary amine can form an N-H bond or a hydrogen bond between molecules. As a result, electrons of the nitrogen atoms fall out and get replaced by hydrogen atoms. The ability to capture more CO_2 and hydroxyl group breakdown will affect the solubility of the amine in water.

In this work, the new substances, 3-Amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P) are used to compensate for the disadvantages of MEA in solubility. These three new solvents have been subjected to different conditions. The difference in research and literature review is the temperature used in our work is 30 °C to 80 °C for other works. In comparison with the literature, the temperature is less than 80 °C and the partial pressure in the research and literature are similarly used this thesis.

CHAPTER 3

EXPERIMENTAL

This chapter highlights experimental works, which were conducted and reported in the thesis. It includes the chemicals, experimental apparatus and analysis method used in this study.

3.1 Materials and equipment

In this study, AALBORG GFM17 flow meters are used to measure the amount of N_2 and CO_2 which are fed into the system and calibrated by SUPELCO OPTIFLOW 520 with flow range of 0.5 to 500 mL/min and accuracy of ±3%. Reactor and saturation cell used hot plate, named IKA C-MAG HS7, for heating saturation cell. Temperature control is done by Thermo Fisher scientific.

A schematic diagram of this equipment setup is shown in Fig. 3.1. CO_2 (99.9 % purity) and N_2 (99.5% purity) are purchased from Praxair (THAILAND) CO. Ltd. Monoethanolamine, MEA (99% purity) used in the experiment is purchased from Sigma-Aldrich CO. LLC. 3-Amino-1-propanol, 3A1P (99.6% purity)., 3-dimethylamino-1-propanol, 3DMA1P (purity 99.6%), 1- dimethylamino-2-propanol, 1DMA2P (purity 99.6%) are purchased from Merck Millipore CO. LLC. Methyl orange solution 0.1% concentration and hydrochloric acid (HCl) with purity of 99% are obtained from Fisher Scientific. De-ionized water from Purelab Classic is used for preparing aqueous solution of amines. The amine solutions were prepared to the desired concentrations of 3,4 and 5 M by mixing de-ionized water with the MEA, 3A1P, 3DMA1P and 1DMA2P.

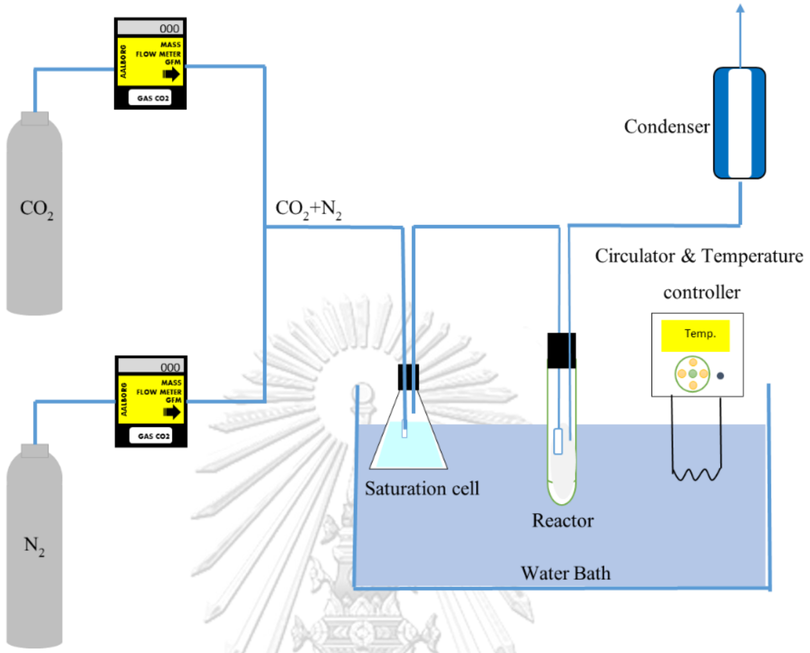


Figure 3.1 Schematic diagram of the experimental setup.

3.2 Procedure and conditions

To measure solubility of carbon dioxide in aqueous solution, operating variables which ware varied to investigate effect on CO_2 absorption loading are summarized in Table 3.1.

Table 3.1 Summary of operating conditions for solubility study.

Operating condition	Value
Solvent type	MEA, 3A1P, 3DMA1P and 1DMA2P
Solvent concentration (Molar)	3, 4 and 5
Partial pressure of CO_2 (kPa)	5, 15, 30, 50, 75 and 100
Absorption temperature (°C)	30, 40, 60 and 80

The CO_2 and N_2 are mixed until each compound meets the desired partial pressure. The moisture is added in the saturation cell to maintain the concentration of solution. After that, the humid gas is sent to reactor. In the reactor, CO_2 is absorbed in the solution and the gas is sent to the condenser to recover moisture in the gas stream before release to atmosphere. The operation is continued until the equilibrium is reached after approximately 10-20 hours

3.3 Analysis of solubility

3.3.1 Solubility

The addition of carbon dioxide in the amine solution was calculated by titration method using a CO_2 loading analyzer. The method includes with the molar determination of solvent and captured CO_2. At equilibrium, 2-3 ml sample is taken to analyze for CO_2 loading. The solution of 1.0 M HCl is then used to measure the concentration of liquid sample by titration method, and this measurement is repeated for 3 times. Figure 3.2., shows the equipment for CO_2 loading analysis. CO_2 loading will be calculated by the ratio of CO_2 mole per mole of amine sample for the CO_2 loading.

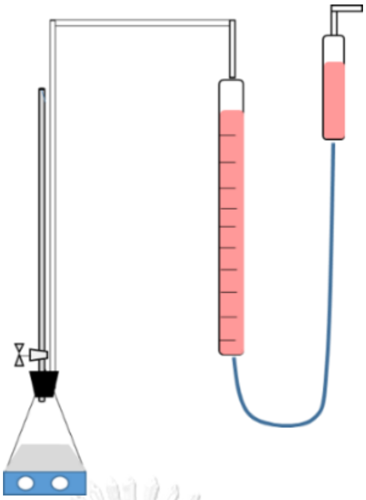


Figure 3.2 CO_2 loading analyzer

At the endpoint of the titration, the volume of HCl consumed is measured and used to calculate the solvent concentration by following equation 3.1.

$$C_{Amine} = \frac{C_{HCl} V_{HCl}}{V_{Amine}} \qquad (3.1)$$

C_{Amine}= Calculated amine concentration, molar

C_{HCl}= Standard HCl concentration, molar

V_{HCl}= Volume of HCl consumed, cm^3

V_{aminel}= Volume of sampled amine, cm^3

Mole of the solvent is determined from equation 3.2.

$$M_{Amine} = \frac{C_{Amine} V_{Amine}}{1000} \qquad (3.2)$$

Mole of carbon dioxide is measured by measuring the total volume of CO_2 emitted from the amine solvent while titrating. As an ideal gas, the mole of carbon dioxide can be calculated at standard temperature and pressures (STP) and converted to moles of carbon dioxide at room temperature (25 °C). Mole of captured CO_2 can be determined by equation 3.3.

$$M_{CO_2} = \left(\frac{V_{CO_2}}{V_{STP}}\right)\left(\frac{T}{T_{ref}}\right) \tag{3.3}$$

CO_2 loading is obtained from equation 3.4.

$$CO_2 \text{ loading or } \alpha = \frac{M_{CO_2}}{M_{Amine}} \tag{3.4}$$

3.3.2 Cyclic capacity

The cyclic capacity is defined as the difference between the carbon dioxide solubility in the liquid solvent at absorption temperature and carbon dioxide solubility at regeneration temperature. In this study, 40 °C and 80°C are set as absorption and regeneration temperatures, respectively. Cyclic capacity can be illustrated equation 3.5.

$$\text{Cyclic capacity} = \alpha_{Absorption} - \alpha_{Regeneration} \tag{3.5}$$

3.3.3 Time dependence of solvent performance in CO_2 absorption

The reaction takes place until it reaches equilibrium. To study the behavior of absorption, the rate of CO_2 loading with time will be measured. In the experiment, samples are collected every hour to analyze variation of CO_2 loading with time.

CHAPTER 4

RESULTS AND DISCUSSION

Method of CO_2 solubility study in an aqueous solution of 3-amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P) have been described in the previous chapter. In this chapter, measurement of carbon dioxide absorption and effects of each variable are discussed, and results and compared with that of commercial monoethanolamine (MEA). Moreover, equipment and procedure verification are also reported in this section.

4.1 Verification of solubility

Verification of the equipment and procedure of this study can be performed by comparing the solubility of carbon dioxide in 5M aqueous MEA solution at the temperatures of 40 °C and 80 °C and CO_2 partial pressure ranging from 5 to 100 kPa, which is the same partial pressure range as literatures [7, 13, 20]. These results are illustrated in Figure 4.1 and 4.2.

Figure 4.1 and 4.2 state the solubility of CO_2 at 40 °C and 80 °C, respectively. These the solubility data are reviewed from references. The average absolute deviation (%AAD) [31]. and the maximum absolute deviation when compared to Luemukong [20] measurement are 1.50% and 4.41%, respectively. This can be concluded that the equipment and methods used in this work are reliable enough to comply with others experimental conditions with acceptable deviations.

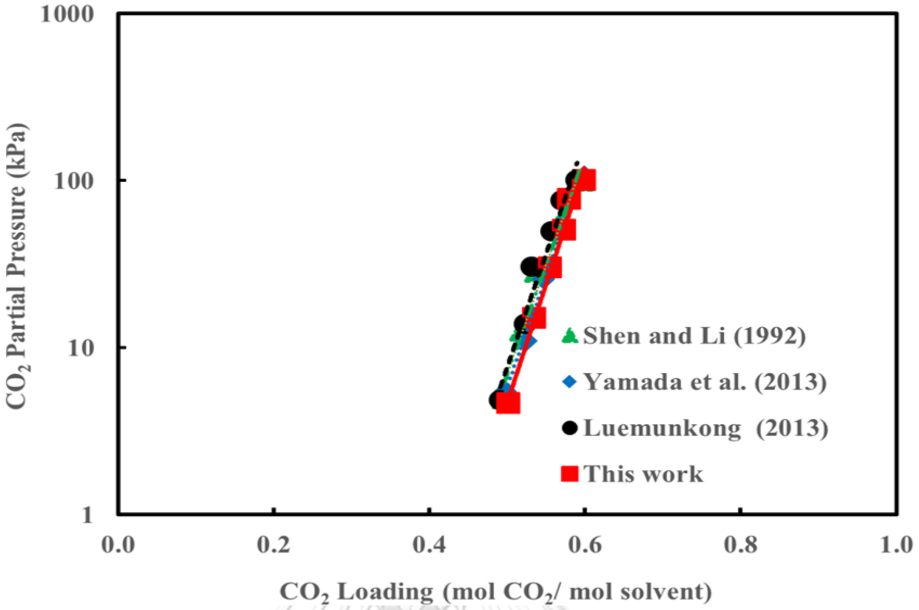


Figure 4.1 Solubility of CO_2 in MEA solution in comparison with the results from literature at 5M concentration and 40 °C

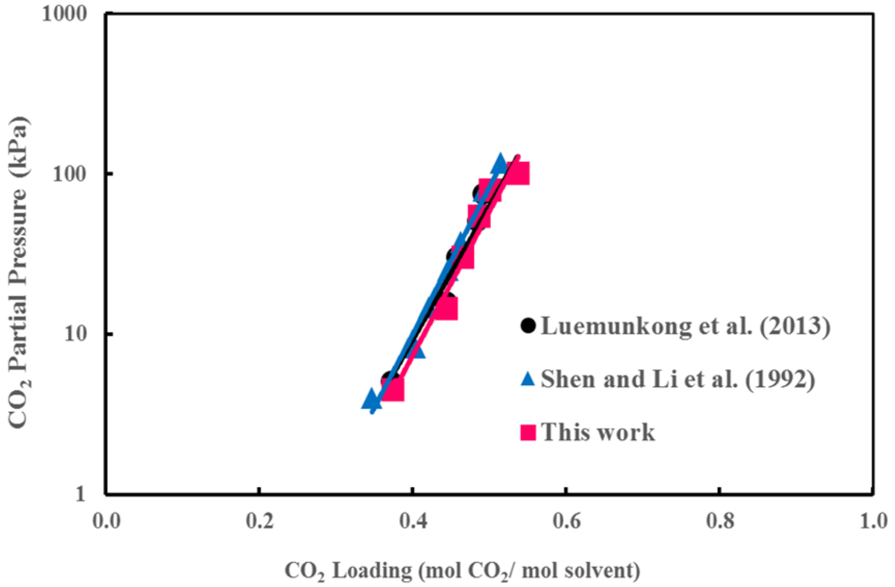


Figure 4.2 Solubility of CO_2 in MEA solution in comparison with the results from literature at 5M concentration and 80 °C

The deviation of this device is mainly due to an error in measuring the amount of carbon dioxide emitted. Sensitivity of the acid gas temperature, the difference of temperature between experimental conditions and determination of CO_2 loading are a major cause of error [31].

4.2 CO_2 solubility result

The effects of variables of interest to the CO_2 solubility are shown in this section.

4.2.1 Effect of type of solvents

The solvents investigated in this research are monoethanolamine (MEA), 3-Amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P). Figure 4.3 to Figure 4.4 show the performance on CO_2 removal of different solvent types at 3 M and 30 °C and 40 °C, respectively, 3DMA1P demonstrates the best ability to dissolve carbon dioxide in the range of 5-50 kPa of partial pressure of CO_2 while 1DMA2P shows the highest ability to dissolve carbon dioxide in the range of 75-100 kPa of partial pressure of CO_2 for absorption capacity[20]. Compared to MEA, CO_2 absorption in 3DMA1P is more sensitive at 30 °C and 40 °C. As to temperature between partial pressure of CO_2 increases, the amount of CO_2 captured by 3DMA1P will increase more rapidly than MEA.

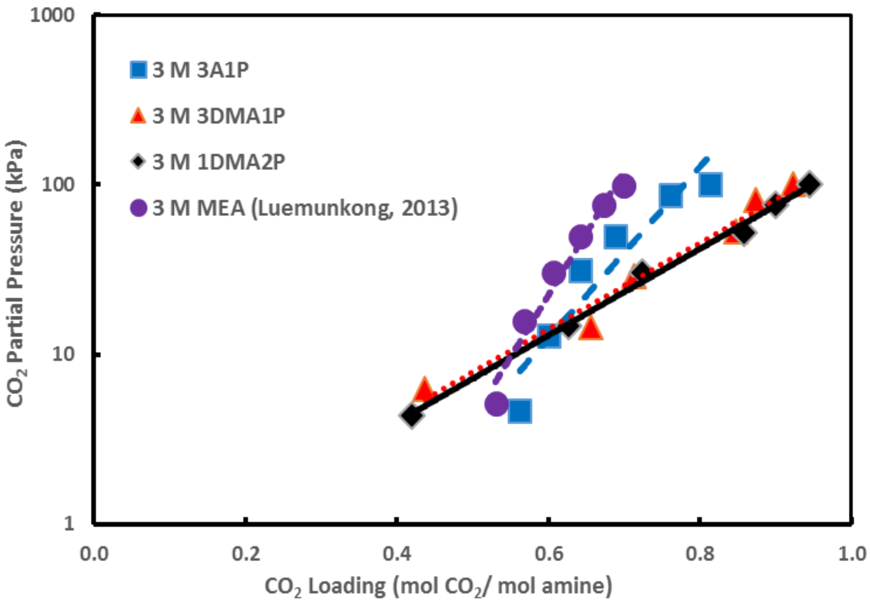


Figure 4. 3 Solubility of CO_2 in 3 M MEA, 3A1P, 3DMA1P and 1DMA2P at 30°C

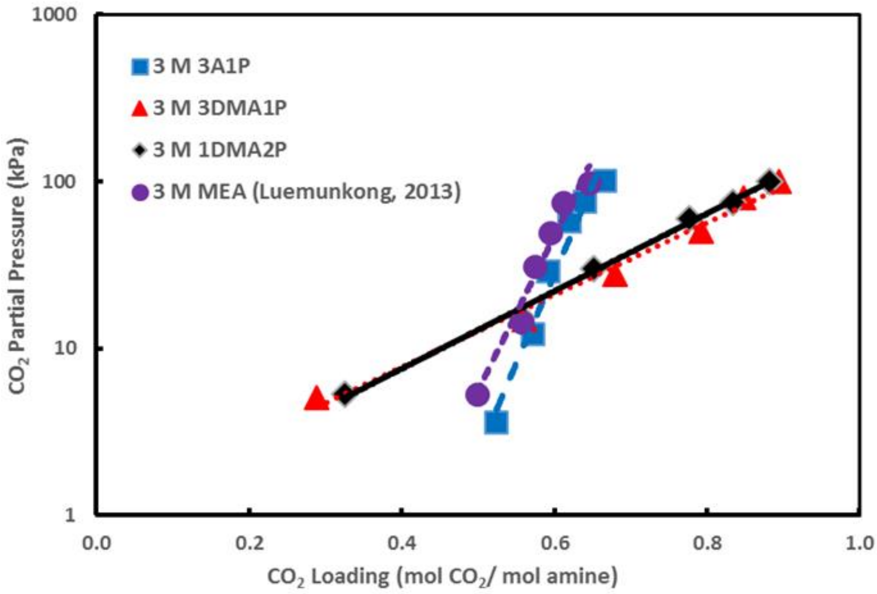


Figure 4. 4 Solubility of CO_2 in 3 M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

However, the results of temperature at 60 °C and 80 °C, as shown Figure 4.5 and Figure 4.6, respectively, show the performance on CO_2 removal of different solvent types at 3 M and 60 °C and 80 °C. Among these solutions, 3DMA1P demonstrates the ability to dissolve carbon dioxide best in the range of 30-100 kPa of partial pressure of CO_2 and at temperature of 60 °C. Compared to MEA, it is clear that CO_2 in 3DMA1P is more sensitive to carbon dioxide concentrations at 60 °C. As the partial pressure of CO_2 increases, the amount of CO_2 captured by 3DMA1P will increase more rapidly than the MEA. Figure 4.6 shows that 1DMA2P demonstrates the ability to dissolve carbon dioxide the best at 100 kPa of partial pressure of CO_2 and temperature of 80 °C. Compared with MEA at 80 °C and 5-75 kPa, 1DMA2P has a lower carbon solubility than MEA. The temperature at 80 °C is for regeneration.

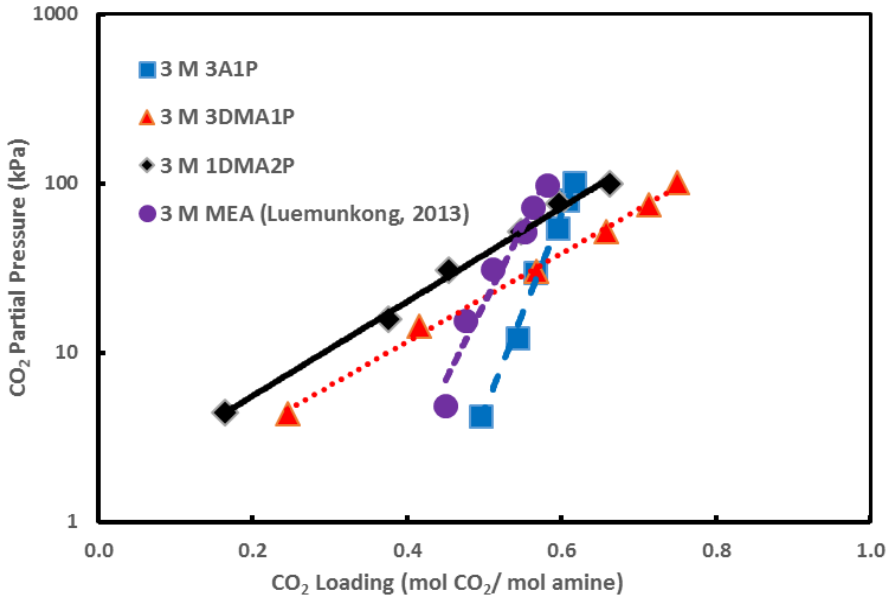


Figure 4.5 Solubility of CO_2 in 3M MEA, 3A1P, 3DMA1P and 1DMA2P at 60°C

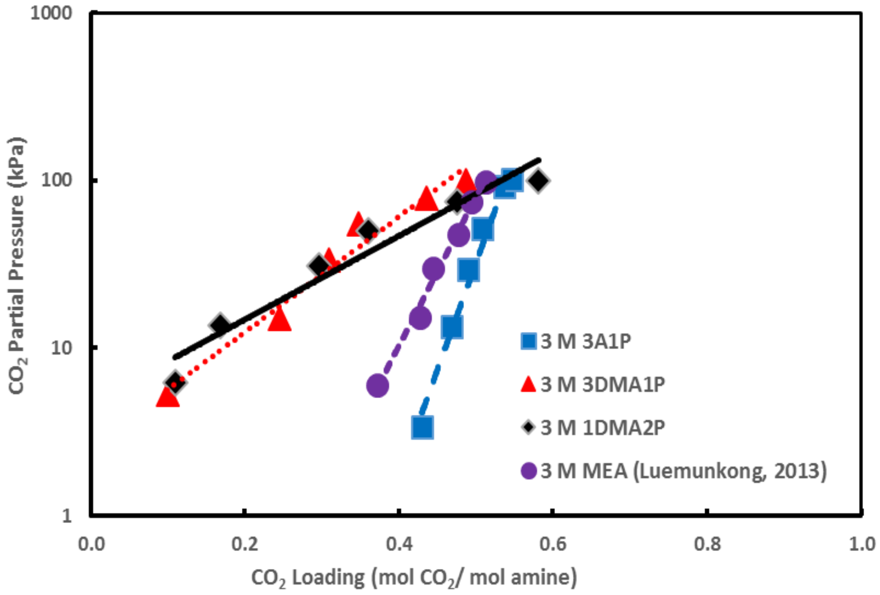


Figure 4.6 Solubility of CO_2 in 3M MEA, 3A1P, 3DMA1P and 1DMA2P at 80°C

For 4 M of solution concentration, the solvents investigated in this research are monoethanolamine(MEA), 3-Amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P). Figure 4.7 to Figure 4.10 show the performance of CO_2 removal of different solvent types at 4 M and 30 °C,40 °C, 60 °C and 80°C respectively, When temperature is in the range of 30 °C and 40 °C , the agility of CO_2 in the solvent 3DMA1P and 1DMA2P in tertiary amine shows the highest carbon dioxide solubility in ranges 50-100 kPa of partial pressure of CO_2 for absorption capacity [20] compared to MEA. In conclusion, when the partial pressure of CO_2 increases, the CO_2 content captured by 3DMA1P and 1DMA2P increases more rapidly than MEA and 3A1P.

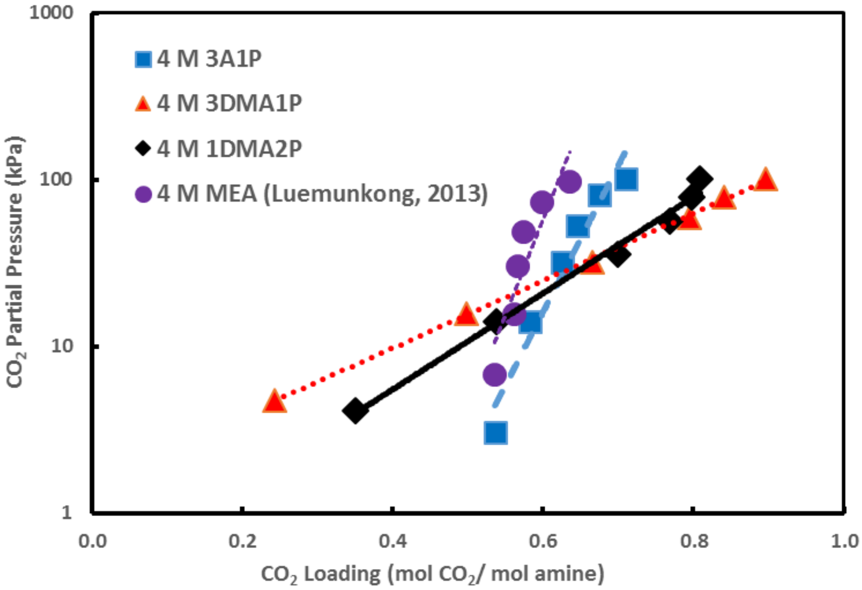


Figure 4.7 Solubility of CO_2 in 4M MEA, 3A1P, 3DMA1P and 1DMA2P at 30°C

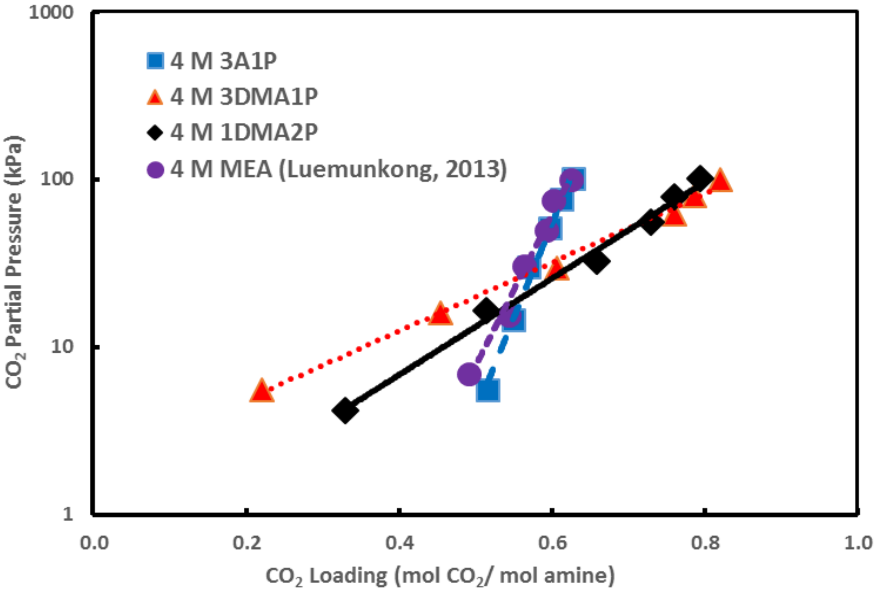


Figure 4.8 Solubility of CO_2 in 4M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

Solubility of CO_2 in 4M MEA, 3A1P, 3DMA1P and 1DMA2P at 60°C is 3A1P has shown in the figure 4.9 best ability to dissolve carbon dioxide in the range of 5-50 kPa of partial pressure of CO_2 compared to other solvents. At the range of 75-100 kPa of partial pressure of CO_2 is 3DMA1P best ability to dissolve carbon dioxide compared to other solvents.

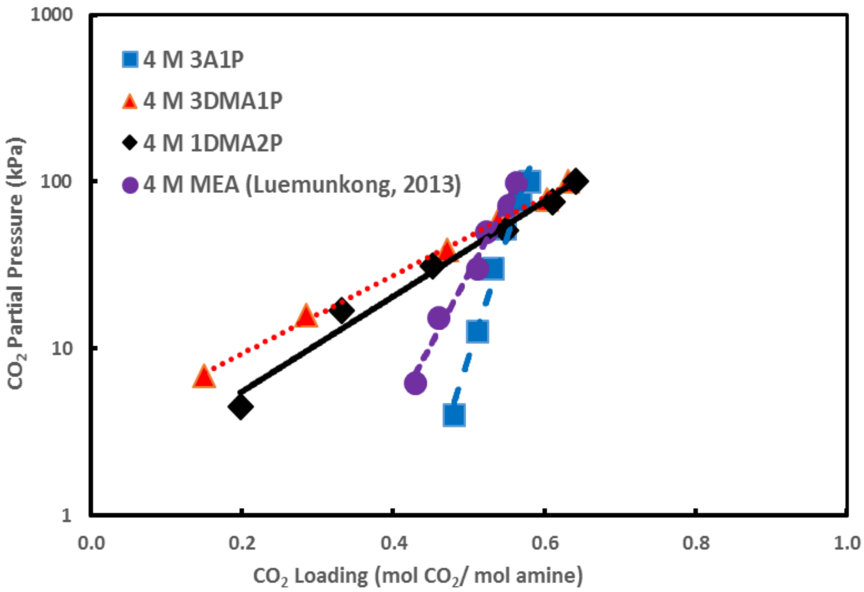


Figure 4.9 Solubility of CO_2 in 4M MEA, 3A1P, 3DMA1P and 1DMA2P at 60°C

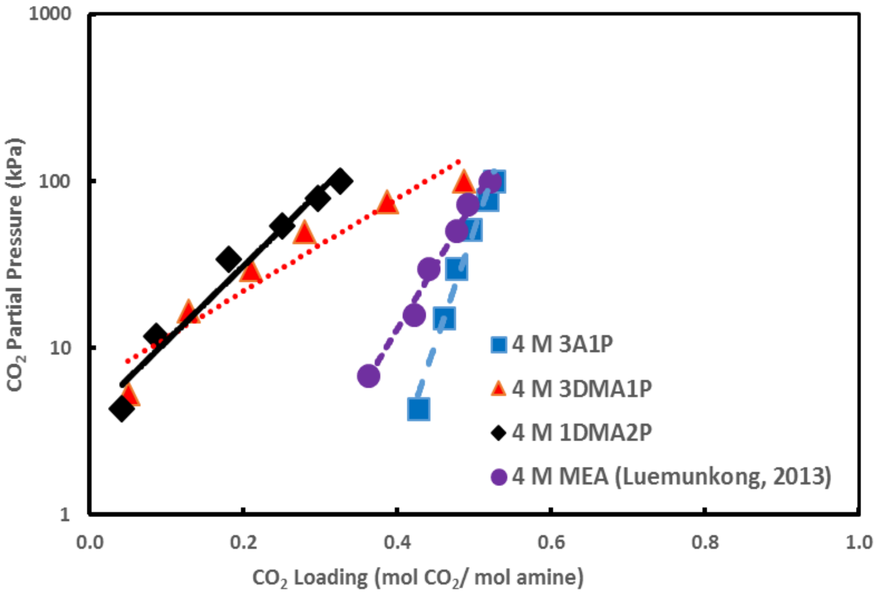


Figure 4.10 Solubility of CO_2 in 4 M MEA, 3A1P, 3DMA1P and 1DMA2P at 80°C

Solubility of CO_2 in 4 M MEA, 3A1P, 3DMA1P and 1DMA2P at 80 ° C is shown in Figure 4.10 1DMA2P solution is the least carbon dioxide solubility in the range of 5-100 kPa of partial pressure of CO_2 compared to other solvents. When the temperature is 80 ° C, it is the temperature used to regeneration the solvent, indicating that the lowest solubility of carbon dioxide at each partial pressure of CO_2 will be the best regeneration and reusability.

For 5 M of solution concentration, the solvents investigated in this research are monoethanolamine(MEA), 3-Amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P). Figure 4.11 to Figure 4.14 show the performance on CO_2 removal of different solvent types at 5 M and 30 °C,40 °C, 60 °C and 80°C, respectively. Figure 4.11 shows 3A1P has the best carbon dioxide solubility in the range of 5-50 kPa of partial pressure of CO_2 compared to other solvents. At the range of 75-100 kPa of partial pressure of CO_2 3DMA1P and 1DMA2P has the best ability carbon dioxide compared to MEA and 3A1P. At temperature of 40 °C and 60 °C carbon dioxide solubility of 3DMA1P and 1DMA2P in every of partial pressure of CO_2 is very similar. Shows in Figure 4.12 and Figure 4.13.

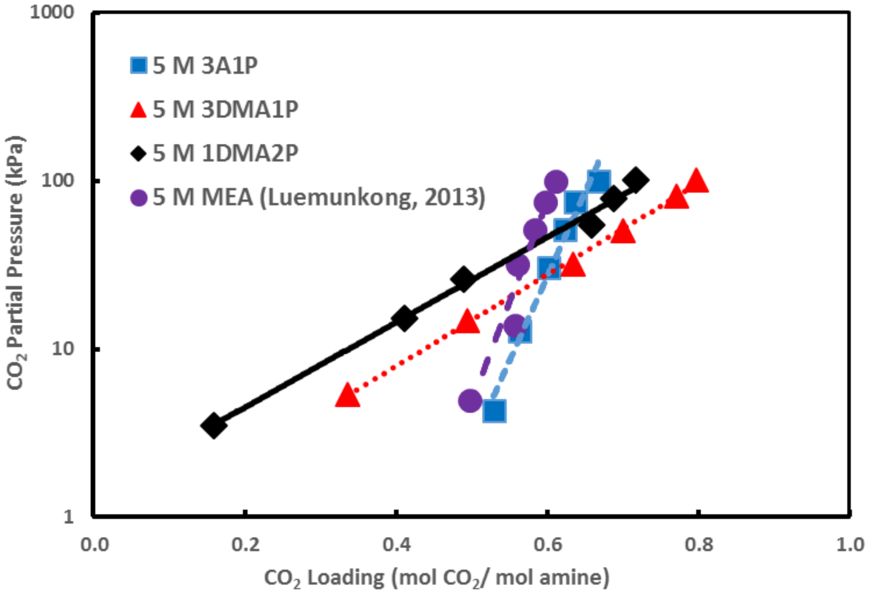


Figure 4. 11 Solubility of CO_2 in 5 M MEA, 3A1P, 3DMA1P and 1DMA2P at 30°C

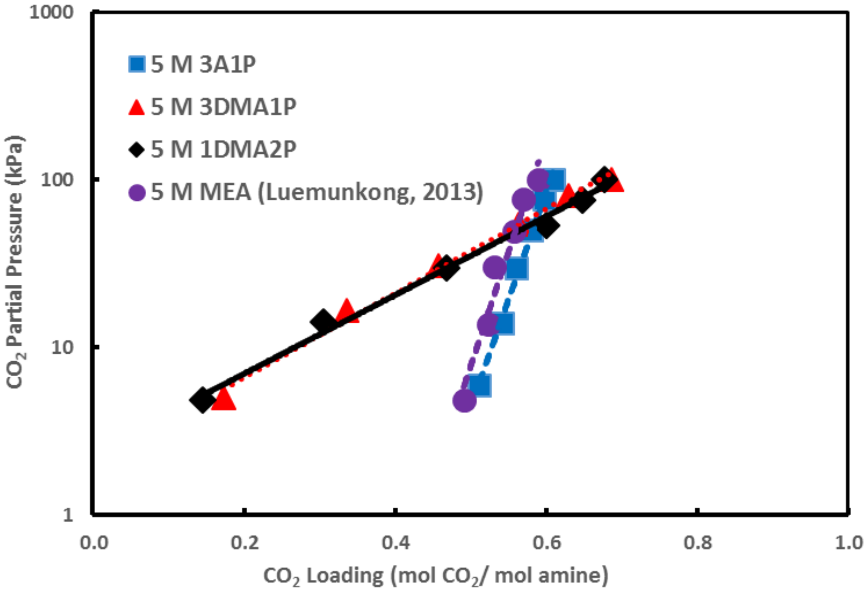


Figure 4. 12 Solubility of CO_2 in 5 M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

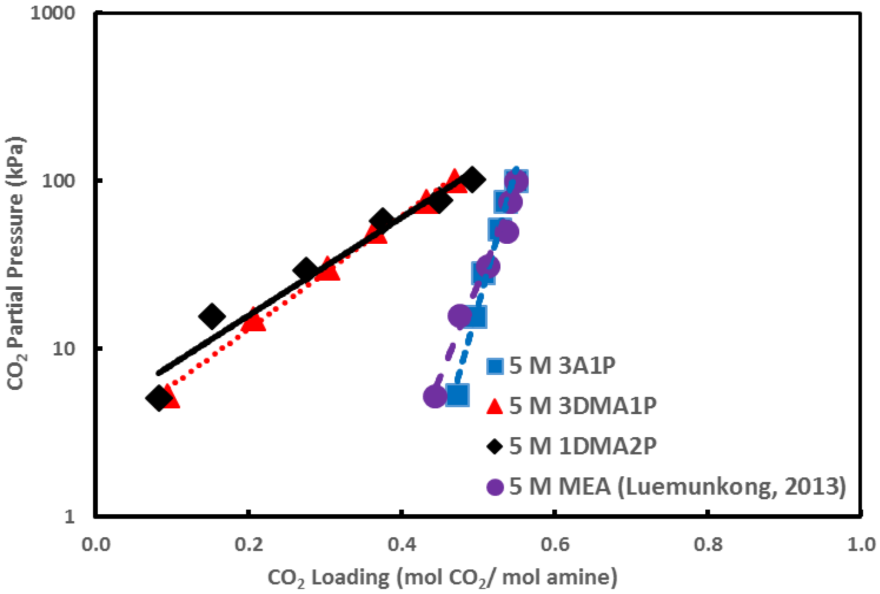


Figure 4.13 Solubility of CO_2 in 5M MEA, 3A1P, 3DMA1P and 1DMA2P at 60°C

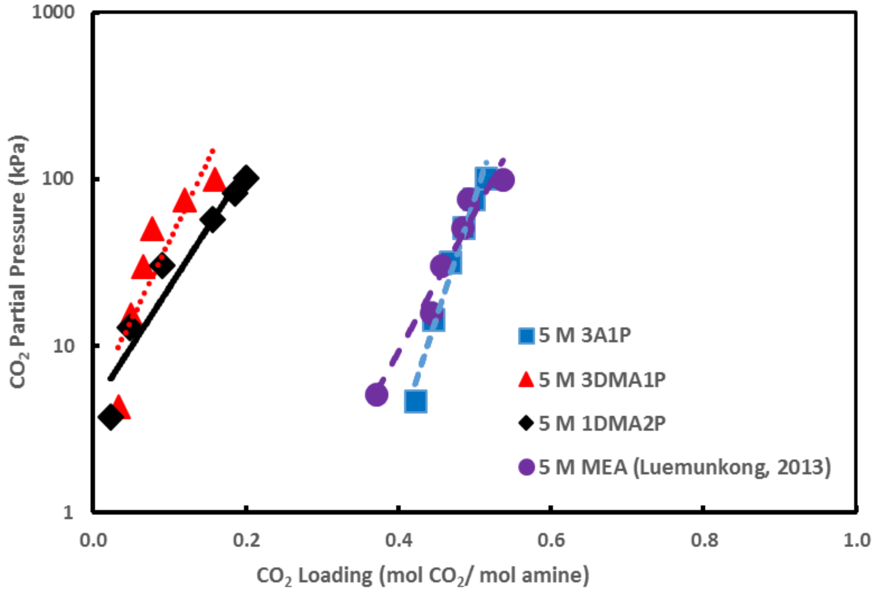


Figure 4.14 Solubility of CO_2 in 5M MEA, 3A1P, 3DMA1P and 1DMA2P at 80°C

However, the results of temperature at 80 °C, as shown Figure 4.14, show the performance on CO_2 removal of different solvent types at 5 M and 80 °C. Solution of 3DMA1P demonstrates the lowest solubility of carbon dioxide in ranges 15-100 kPa of partial pressure of CO_2 and at 80 °C. Compared with MEA at 80 °C, the3DMA1P has much lower carbon dioxide solubility than MEA. The temperature at 80 °C is considered as a regeneration condition.

In conclusion, the solubilities of CO_2 in various solvents, 3-Amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P), show that, in terms of solubility at absorption condition, the best performers are 3DMA1P and 1DMA2P, compared to MEA. However, for regeneration, the one with low solubility is preferred because lower CO_2 solubility at regeneration temperature means less energy required. The order from low to high solubility of each solvent at 80 °C is 3DMA1P, 1DMA2P, 3A1P, respectively.

It is possible that a mole carbon atom in the backbone can increase the performance of amine and position of OH group also affect the performance as well. The position of OH at the end of backbone can provide relatively higher that of with band. In case of primary amine, the ratio of dissolved CO_2: amine is 1: 2 in this case, bicarbonate is formed. And in case of tertiary amine the ratio of dissolved CO_2: amine is 1:1 will produce only bicarbonate not carbamate because CO_2 do not react direct about amine. 3A1P have a molecular structure, which is the primary amine. However, 3A1P has greater number of CO_2 loading than MEA but less than 3DMA1P which are the tertiary amine.

Therefore, the effects of molecular structures, such as types of amine, carbon chain lengths, position of functional groups attached to the backbone on the basis of various amines have been studied. It is found that the increase in the length of the carbon chain would affect the solubility in water and the molecular size. For these cases, 3DMA1P results is the highest solubility among the three amines.

4.2.2 Effect of CO_2 partial pressure

The effect of partial pressure of CO_2 studied in the range of typical carbon dioxide emissions from fossil-fueled power plants. CO_2 partial pressure used is ranged from 5 to 100 kPa, as shown Figure 4.15, the effect of CO_2 partial pressure to the CO_2 solubility.

For all solutions, the solubility of CO_2 is directly proportional to its partial pressure in equilibrium state. Increasing the CO_2 partial pressure will increase the carbon dioxide propulsion from the phase of the gas transferred to the liquid phase. Therefore, at higher CO_2 partial pressure in gas phase, the higher amount of CO_2 is captured. This corresponds of Henry's Law. In Figure 4.16 and 4.17 are similar Figure 4.15, when added to partial pressure of CO_2, CO_2 solubility increase according thermodynamic.

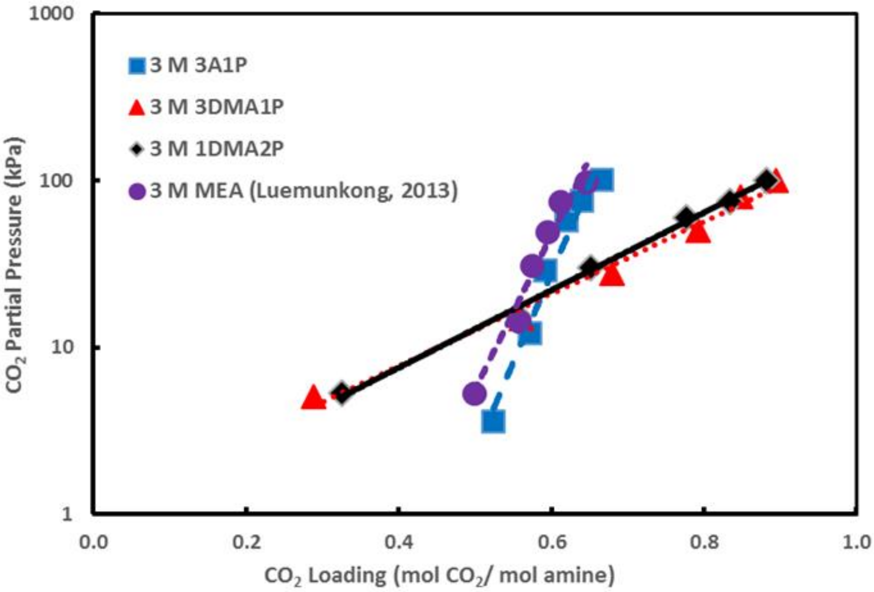


Figure 4. 15 Solubility of CO_2 in 3M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

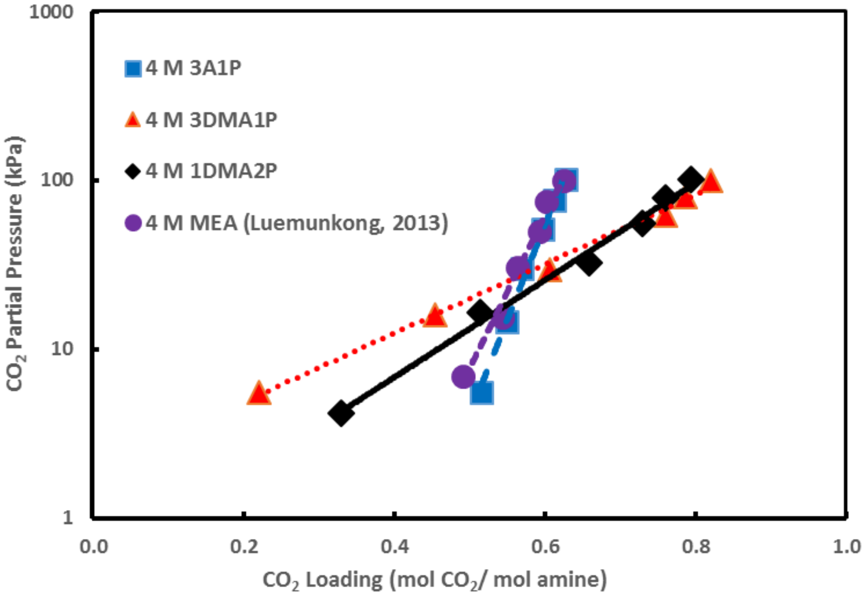


Figure 4. 16 Solubility of CO_2 in 4M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

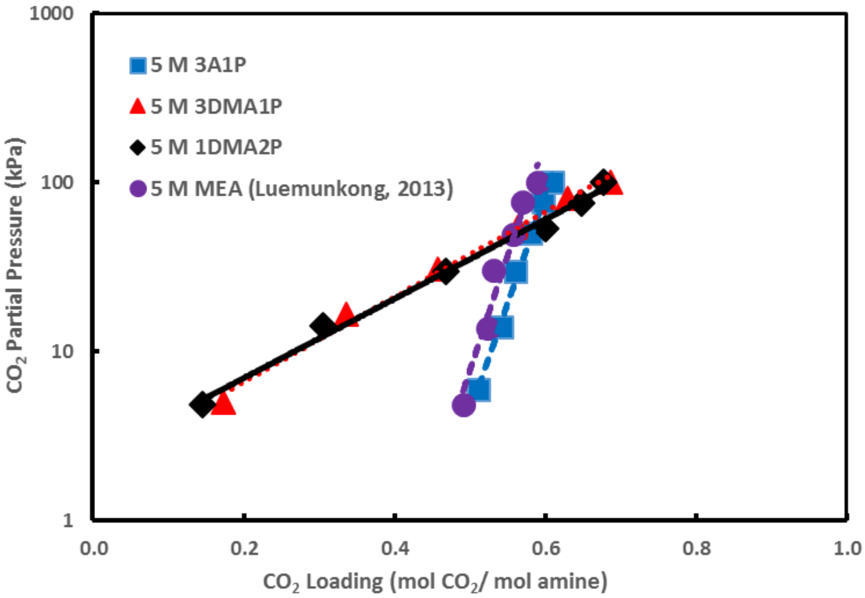


Figure 4. 17 Solubility of CO_2 in 5M MEA, 3A1P, 3DMA1P and 1DMA2P at 40°C

The CO_2 solubility in different partial pressure of CO_2 for each solvent is also illustrated. The slope of the trend line is an important the sensitivity of the solvents to the slope is greater in the solvent.

Partial pressure at high temperatures is less sensitive to partial pressure. Although the high temperature has the highest slope. At the temperature of 80 °C, the added Partial Pressure reaction is exothermic. The higher the temperature, the less gas will dissolve. At low temperatures, when added to Partial Pressure gas, it dissolves more. If the Partial Pressure is too much, the concentration of CO_2 dissolved in the liquid will have to be varied to match the Henry's constant [32].

Increase in CO_2 partial pressure from 5 to 100 kPa can enhance more capacity to capture CO_2 in MEA, 3A1P, 3DMA1P and 1DMA2P solutions, due to the increase of CO_2 driving force. In other words, CO_2 transports more from gas phase to liquid amine phase at higher partial pressure. Conclusion is that using 3DMA1P or 1DMA2P as a chemical solvent for CO_2 absorption is better than using MEA, especially, for CO_2 from power plants.

4.2.3. Effect of solvent concentration

Concentration of solvent is one of the most important factors that will be considered in the CO_2 capturing process. 3, 4 and 5 molar concentrations of 3A1P,3DMA1P and 1DMA2P are studied at 40°C for absorption temperature and 80°C for regeneration temperature

Figure 4.18 to 4.20 show the effect of solvent concentration to the CO_2 solubility. The experiments show that the carbon dioxide at 5 M has less CO_2 loading than those at 4 and 3 M concentrations. As the concentration of the solution increases, the CO_2 loading would be relatively reduced. Table 4.1 gives detailed information on the solubility of carbon dioxide at each point of CO_2 partial pressure.

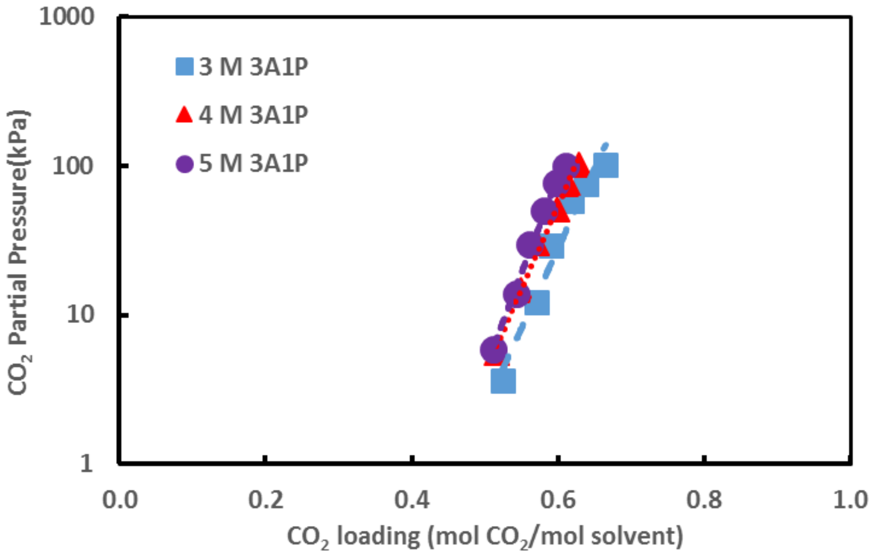


Figure 4. 18 CO_2 loading of 3, 4 and 5M 3A1P concentration at 40°C

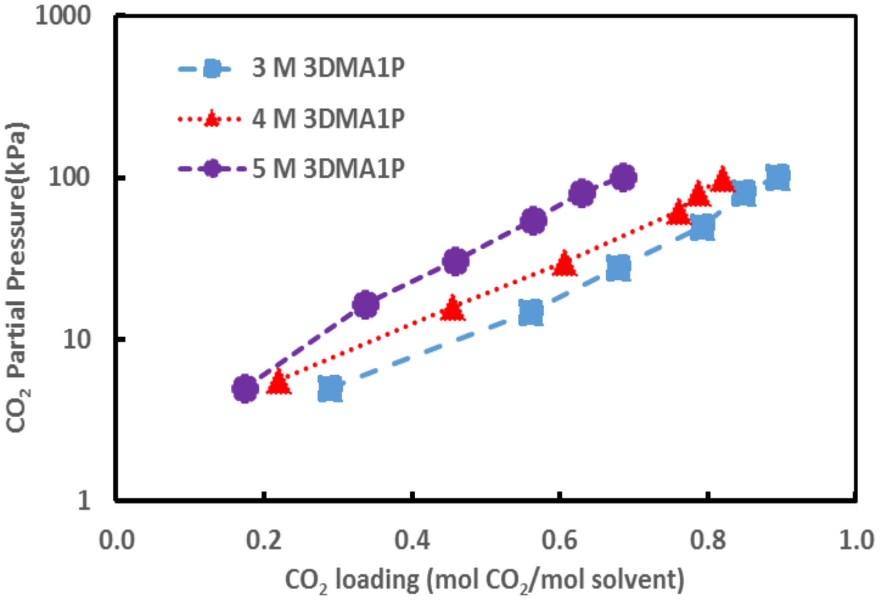


Figure 4.19 CO_2 loading of 3, 4 and 5M 3DMA1P concentration at 40°C

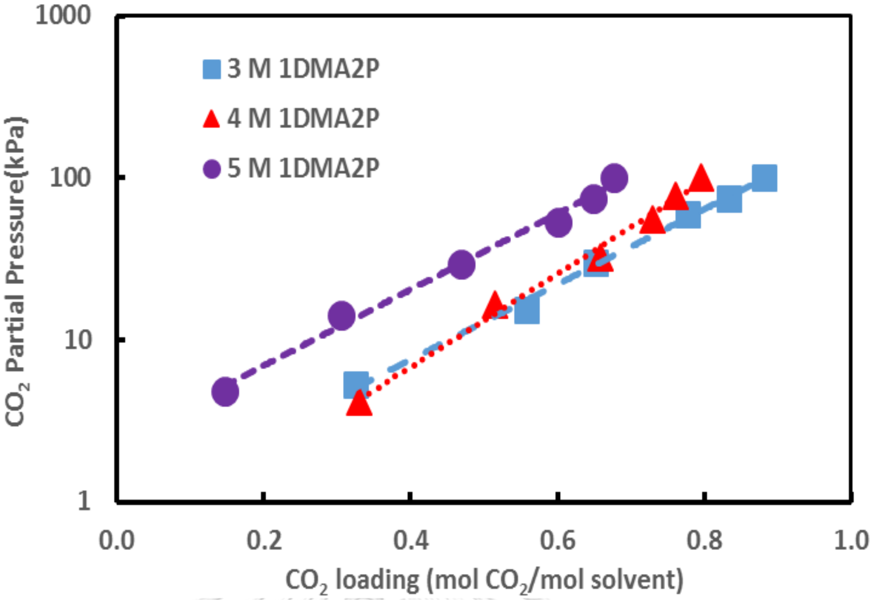


Figure 4.20 CO_2 loading of 3, 4 and 5M 1DMA2P concentration at 40°C

Theoretically, considered in an amine-based absorption process, increasing of solvent concentration results in increasing of the mole of unreacted amine or free amine per unit volume. In the theory of Henry's Laws, the increase in solvent concentration results in an increase of the mole of the non-reacted amine or free amine per unit volume. When the concentration of the solution increases, the rate of CO_2 absorption reaction decreases as expected. However, the absorbed CO_2 loading contradictory as shown in table 4.1. By phenomena, although there is an increase in the molar content of the carbon dioxide captured at a higher rate of reaction, the molar ratio of carbon dioxide per mole of amine or CO_2 loading, decreases as there is some extra amine concentration.

Table 4.1 Solubility data of 3A1P, 3DMA1P and 1DMA2P at 40 °C and 3, 4 and 5 M concentration

Solvent Type	**3 M**		**4 M**		**5 M**	
	P_{CO2}	**α**	**P_{CO2}**	**α**	**P_{CO2}**	**α**
3A1P	3.61	0.524	5.52	0.516	5.90	0.512
	12.20	0.571	14.60	0.549	13.99	0.542
	29.30	0.591	30.26	0.570	29.81	0.560
	58.15	0.619	51.27	0.598	50.15	0.580
	76.06	0.639	75.91	0.613	76.90	0.597
	101.05	0.665	101.05	0.628	100.59	0.610
3DMA1P	5.06	0.289	5.584	0.22	5.038	0.173
	14.85	0.561	15.993	0.455	16.495	0.336
	27.76	0.679	29.827	0.606	30.749	0.458
	50.17	0.793	61.915	0.761	54.176	0.563
	80.42	0.848	80.298	0.787	80.239	0.629
	100.64	0.894	100.181	0.820	100.620	0.686
1DMA2P	5.348	0.325	4.18	0.330	4.81	0.146
	15.327	0.558	16.55	0.515	14.12	0.306
	30.245	0.652	32.60	0.659	29.64	0.468
	60.248	0.777	55.78	0.730	53.29	0.600
	75.014	0.834	78.20	0.760	75.25	0.648
	100.541	0.882	100.59	0.795	100.61	0.677

As another explanation, the difference in water content of each of the amine solvents is the mechanism. When the concentration of amine is high, the amount of water in the solution decreases and the molar amount of water per mole of amine decreases according to equations (2) - (5). Since formation of bicarbonate requires water, this leads to a reduced rate of reaction high solvent concentrations. (Low water content)

In summary, for the highest performance of CO_2 removal, the concentration of 3 M solvent is the best concentration. If the solvent is used at high concentration, it might encounter some physical problems. In addition, by economics, when higher concentrations are used, higher capital and operating cost will be required.

4.2.4 Effect of temperature

ln terms of thermodynamics, temperature is a major parameter that affects the equilibrium of carbon dioxide capture. The effect of temperature on the carbon dioxide solubility obtained from the experimental conditions of 30, 40, 60 and 80 °C, solvent concentration of 3 M, 4 M and 5 M and types of solution of 3A1P, 3DMA1P and 1DMA2P, respectively.

The solubility of carbon dioxide is proportional to the absorption temperature of all solvents. It is observed that low temperature results in higher dissolved carbon dioxide levels compared to higher temperatures. The decreased CO_2 loading when increasing the temperature of the system can be explained that, the reaction of CO_2 and amine solution is exothermic reaction. Therefore, when the acid gas dissolved in the solution yields high kinetic energy at high temperature, the amount of gas released from the liquid phase increases and the amount of carbon dioxide in the solvent decreases.

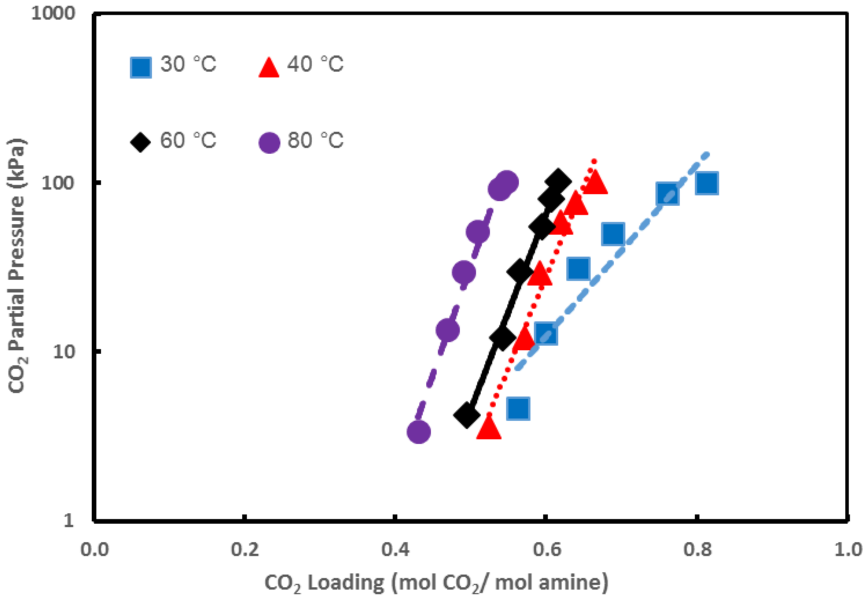


Figure 4. 21 Effect of temperature at 3M 3A1P concentration.

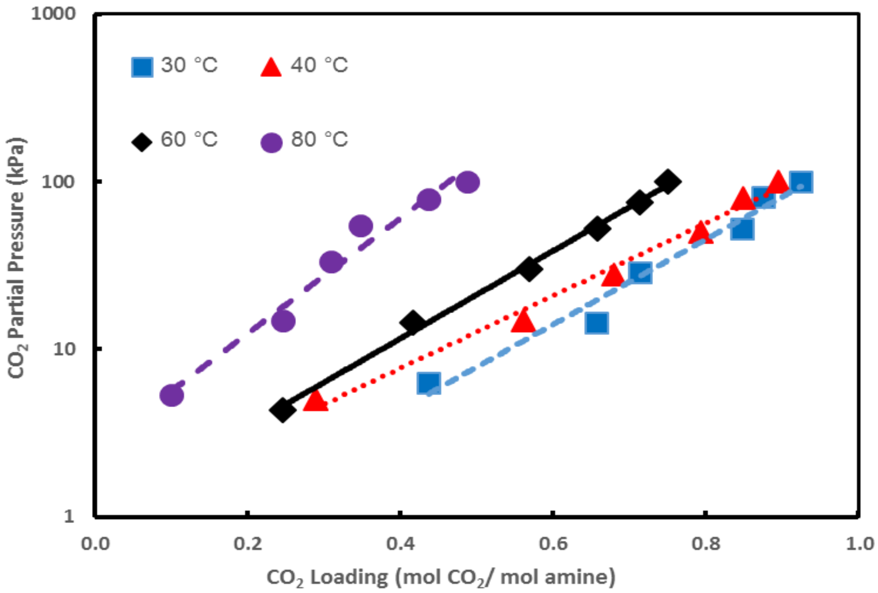


Figure 4. 22 Effect of temperature at 3M 3DMA1P concentration.

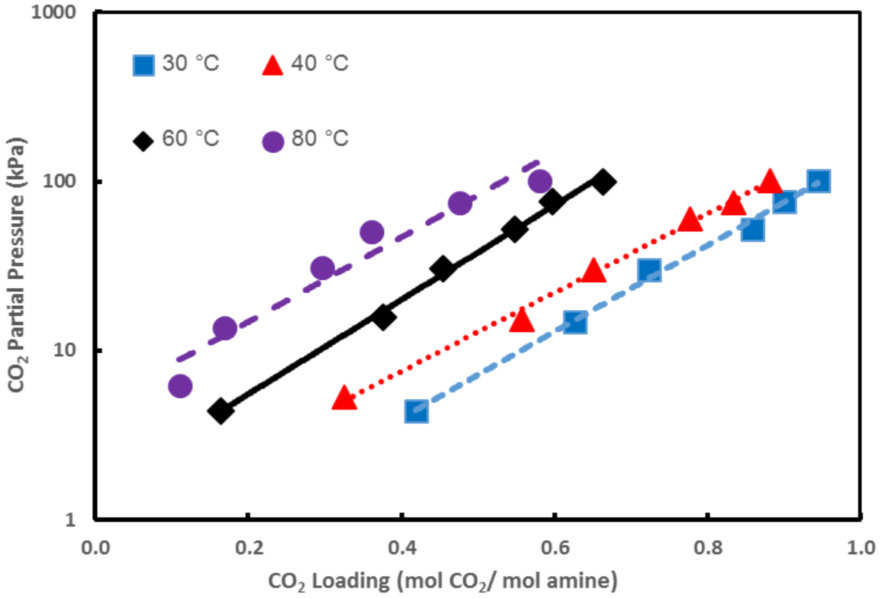


Figure 4.23 Effect of temperature at 3M 1DMA2P concentration.

For 3,.4 and 5 M, Figure 4.21 to 4.29 demonstrate the different carbon dioxide capture behavior of each solvent at different operating conditions. For 3A1P, in Figure 4.21, Figure 4.24 and Figure 4.27, the solubility of carbon dioxide at various temperatures is closest to that of two other solvents. When the primary amine solutions, such as MEA or 3A1P reacts with a carbon dioxide solution, the complex is called a carbamate ion, which is relatively stable although the temperature is increased. In case of tertiary amines such as 3DMA1P and 1DMA2P at 3,4 and 5 M shown in Figures 4.22 to 4.23, Figures 4.25 to 4.26 and Figures 4.28 to 4.29., the solutions of tertiary amines cannot create carbamate while capturing CO_2. This leads to easier CO_2 release in the amine molecule. It can be concluded, tertiary amines benefit over MEA and 3A1P. in terms of greater in the cyclic capacity, which is discussed in the next section.

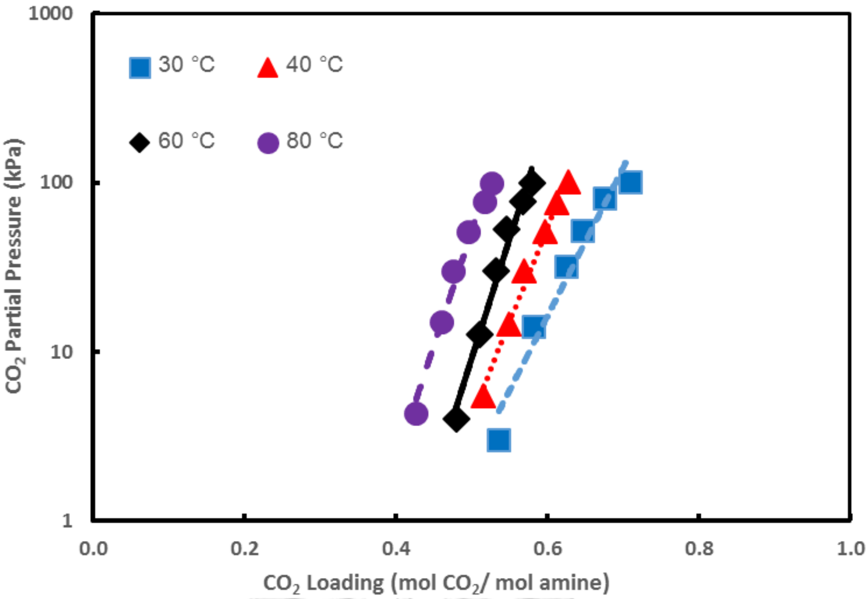


Figure 4. 24 Effect of temperature at 4M 3A1P concentration.

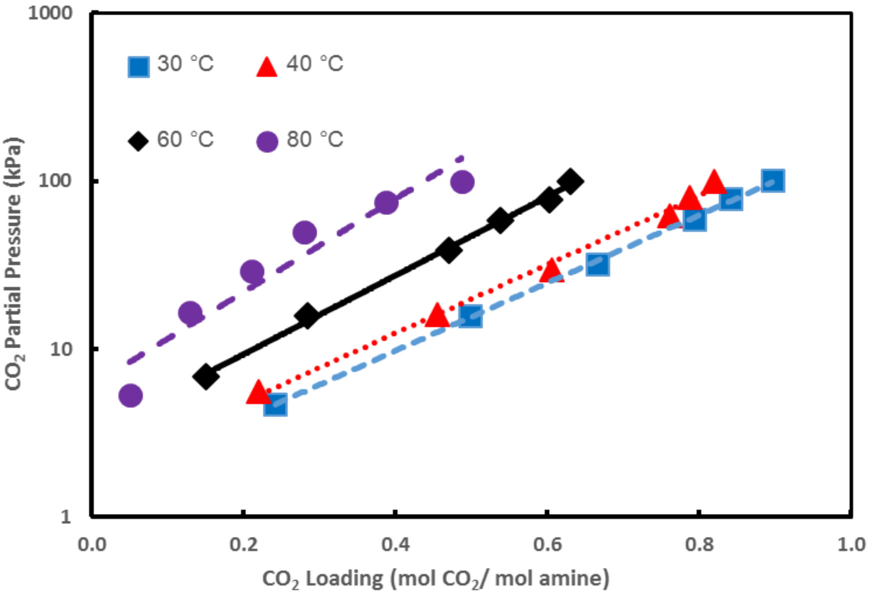


Figure 4. 25 Effect of temperature at 4M 3DMA1P concentration.

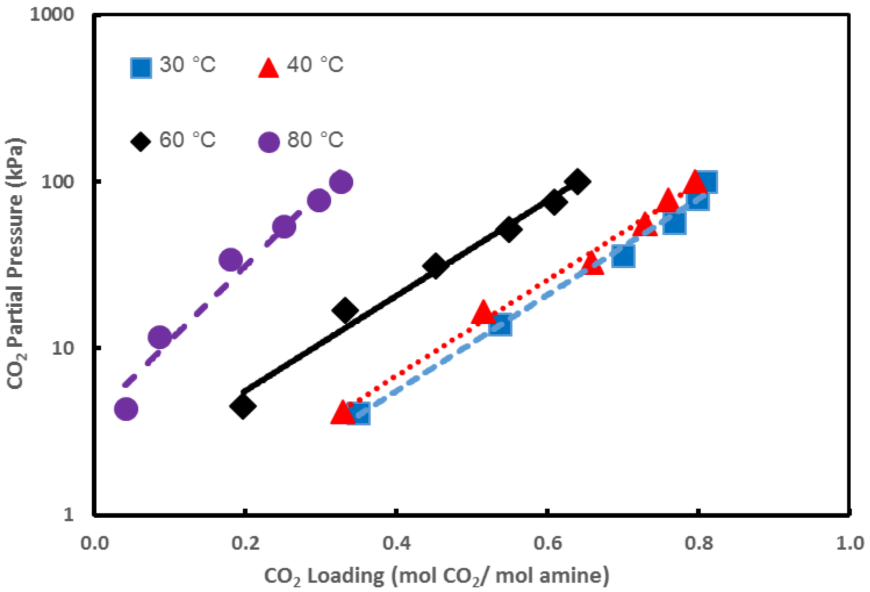


Figure 4. 26 Effect of temperature at 4M 1DMA2P concentration.

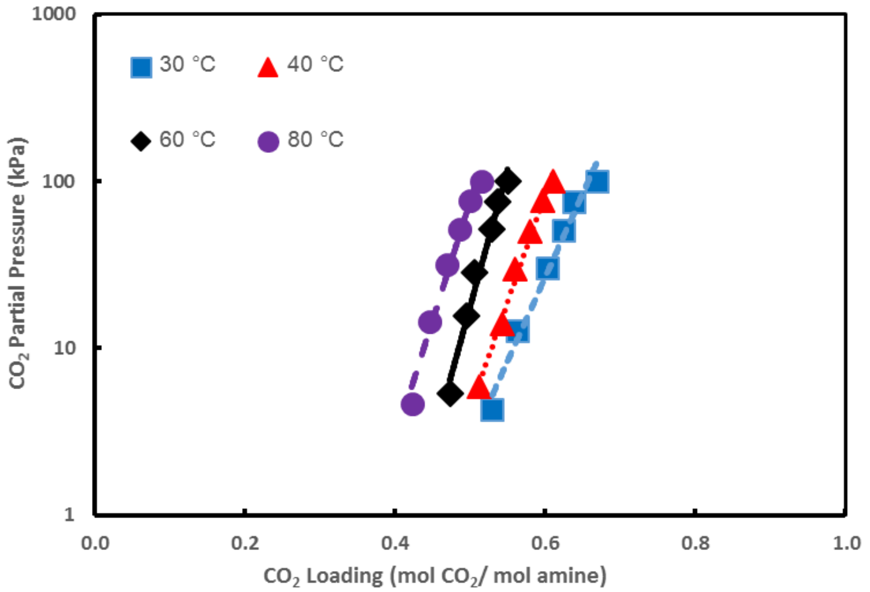


Figure 4. 27 Effect of temperature at 5M 3A1P concentration.

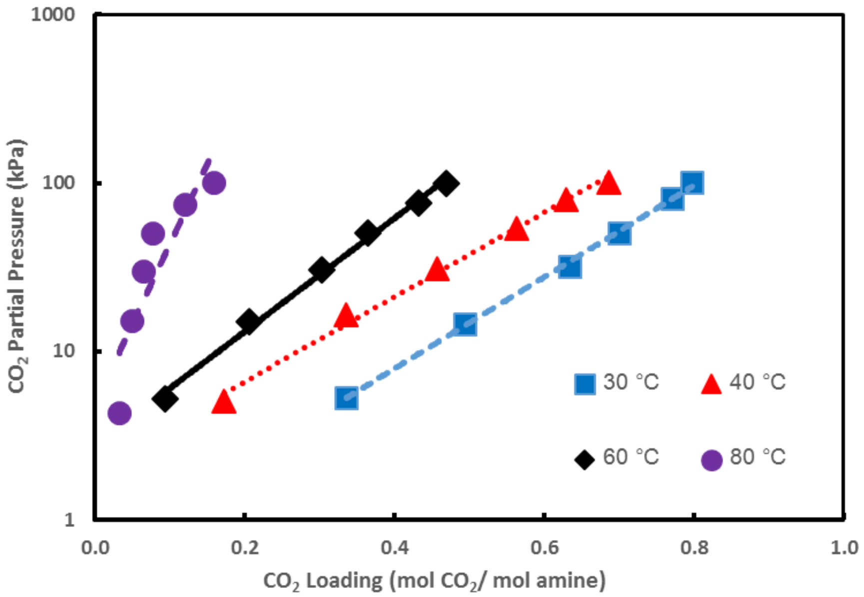


Figure 4. 28 Effect of temperature at 5M 3DMA1P concentration.

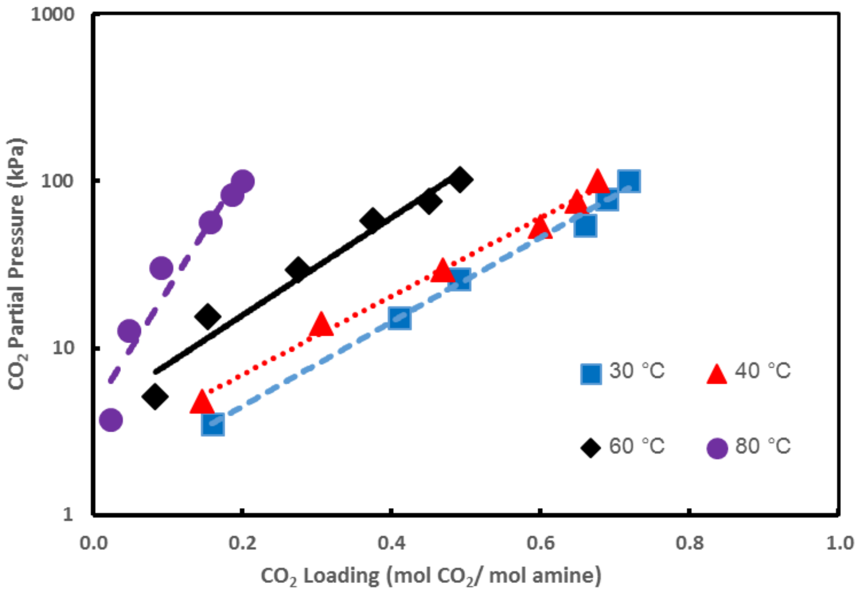


Figure 4. 29 Effect of temperature at 5M 1DMA2P concentration.

In general, the reaction between the solvent used in the chemical absorption process and the CO_2 absorbed for this study is reversible, which means that the absorbed CO_2 can be regenerated. Then, these free solutions will be able to absorb again. In order to release the carbon dioxide trapped in the solvent, steam heaters are used generally.

This mechanism is often referred to as desorption or stripping. In other words, absorption and stripping use the principle of temperature that affects the amount of carbon dioxide captured in the carbon capture system. The temperature in Thailand is 30 ° C. This temperature is used for experimental instead of 25 ° C. However, at present, the power plant will use the temperature of absorption at 40 °C because it is the temperature used in the absorption tower. Especially for MEA, a temperature of 60 ° C is also used to indicate the trend of temperature change between 40 °C to 80 °C. Finally, a temperature of 80 °C is indicated as the solvent regeneration temperature. The reason for choosing this temperature is that if the new solvent dissolves carbon dioxide at this temperature it is better to use lower temperatures even though the solvent regeneration temperature in the original factory will be at 120 °C. The dissolution of CO_2 in the amine solution is exothermic. At low temperatures, the dissolution of carbon dioxide is greater than at higher temperatures because the gas dissolves more than at elevated temperatures. If we increase the temperature of the system, it will cause less CO_2. The system tries to cool down. The reaction is a reverse reaction. Therefore, the dissolution of CO_2 is lower, but if the temperature is lower, the reaction is more likely to occur. Consequently, the solubility of CO_2 at low temperature is higher than the solubility of CO_2 at high temperature [32].

4.3 Cyclic capacity study

The cyclic capacity is defined as the difference of equilibrium CO_2 loading of carbon dioxide at the absorption condition and the loading at the regeneration condition.

CO_2 loading is defined from mole of absorbed CO_2 per mole of solvent. The absorption and regeneration conditions are indicated by operating temperatures, which are used at 40 and 80 °C for absorption and regeneration, respectively.

The results of cyclic capacity study are obtained at 3M solvent concentration and at temperature of 40 and 80 °C. The comparison of cyclic capacity between MEA, 3A1P, 3DMA1P and 1DMA2P are shown in Table 4.2 to Table 4.4

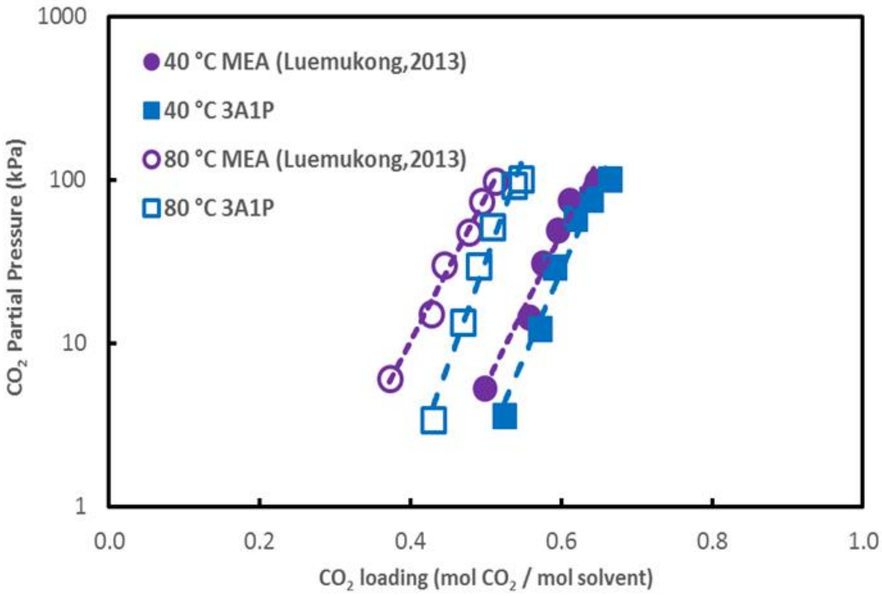


Figure 4.30 Comparison of cyclic capacity between 3M MEA [20] and 3A1P

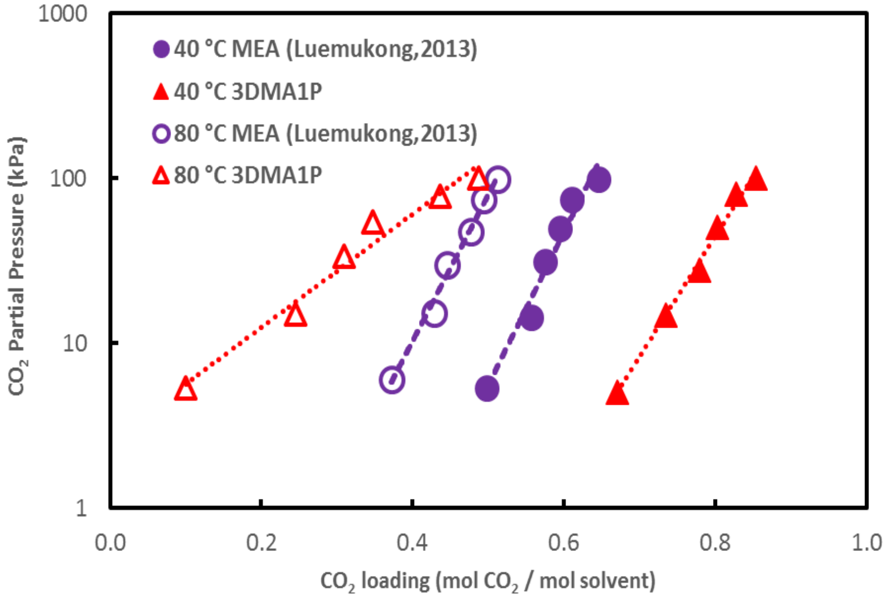


Figure 4. 31 Cyclic capacity between 3M MEA [20] and 3DMA1P.

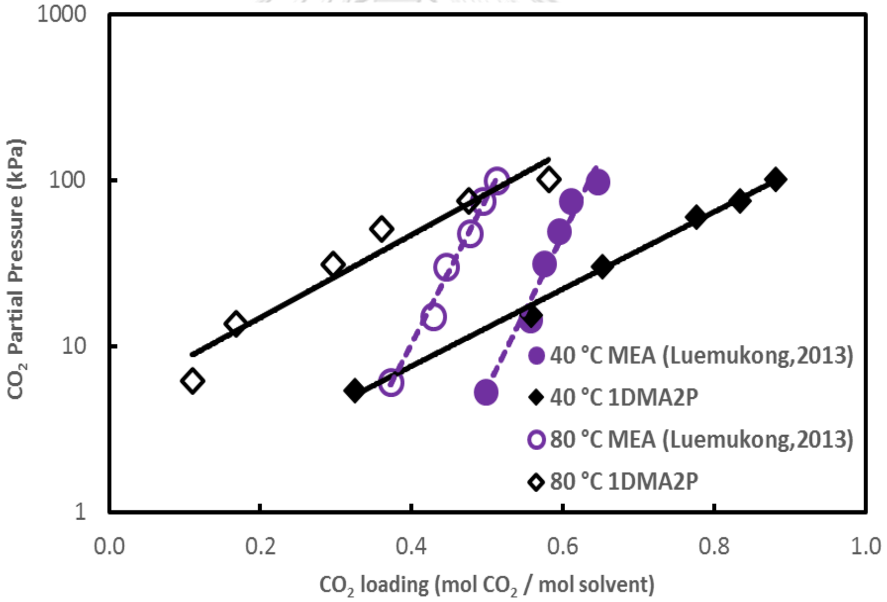


Figure 4. 32 Cyclic capacity between 3M MEA [20]and 1DMA2P.

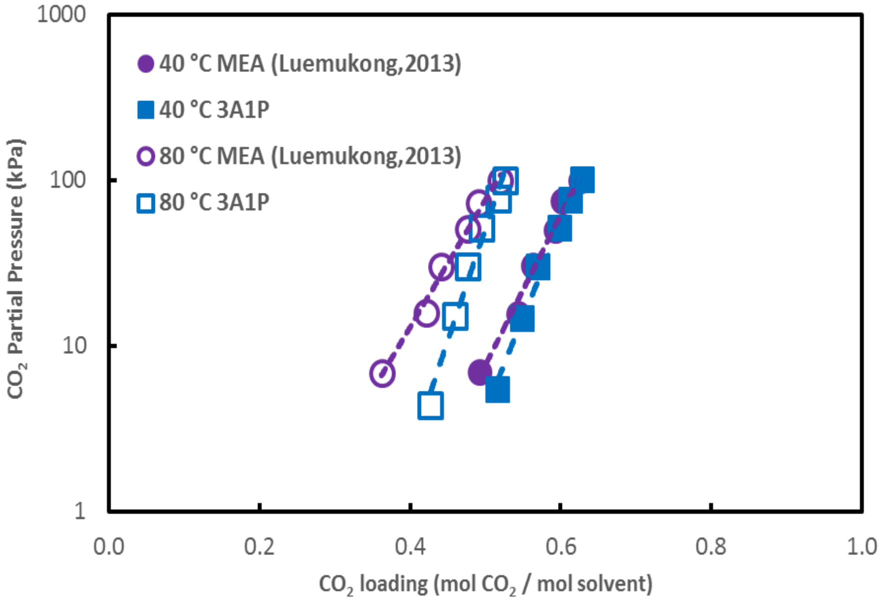


Figure 4. 33 Cyclic capacity between 4M MEA [20] and 3A1P.

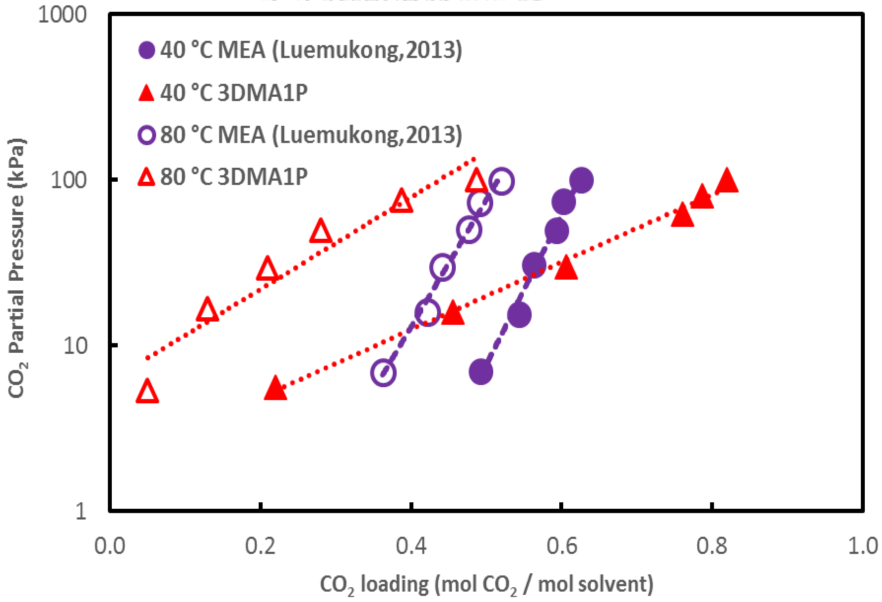


Figure 4. 34 Cyclic capacity between 4M MEA [20] and 3DMA1P.

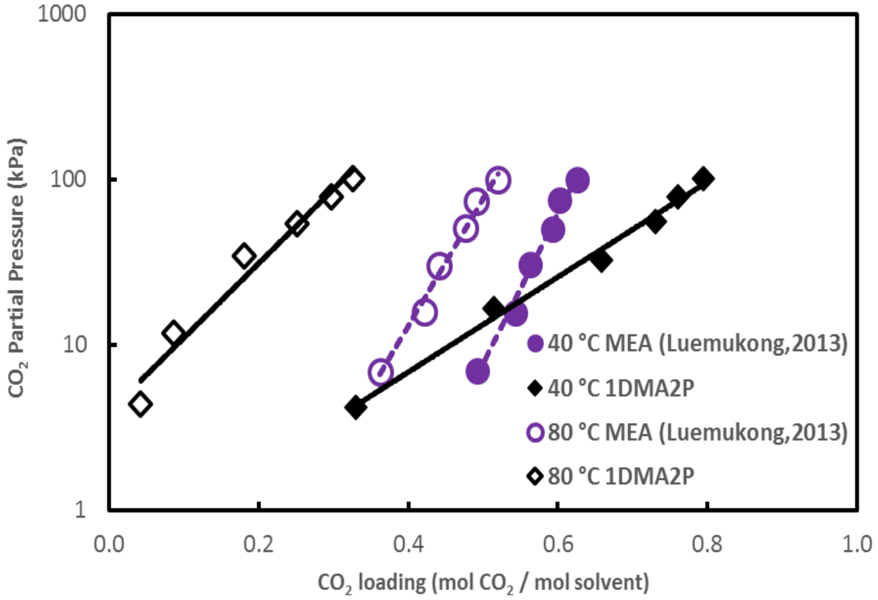


Figure 4. 35 Cyclic capacity between 4M MEA [20] and 1DMA2P.

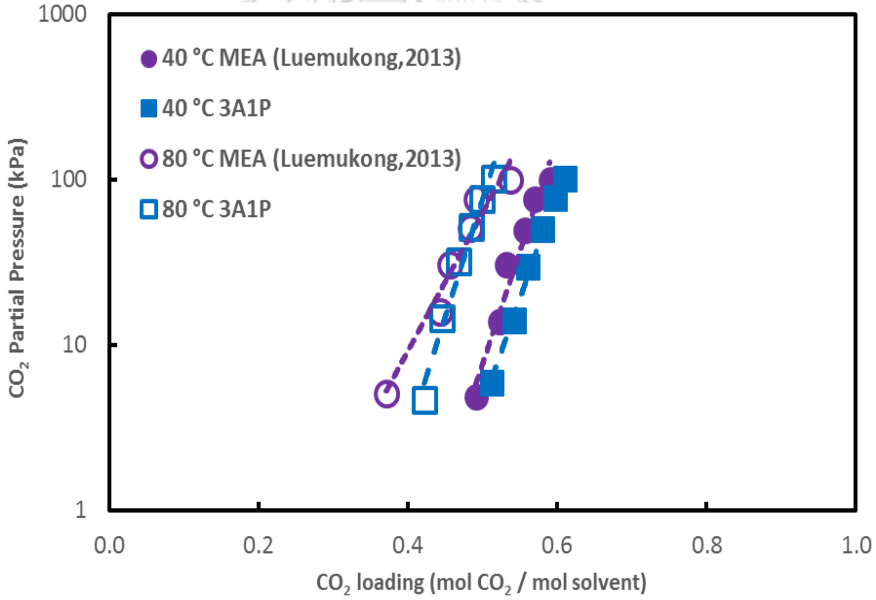


Figure 4. 36 Cyclic capacity between 5M MEA [20] and 3A1P.

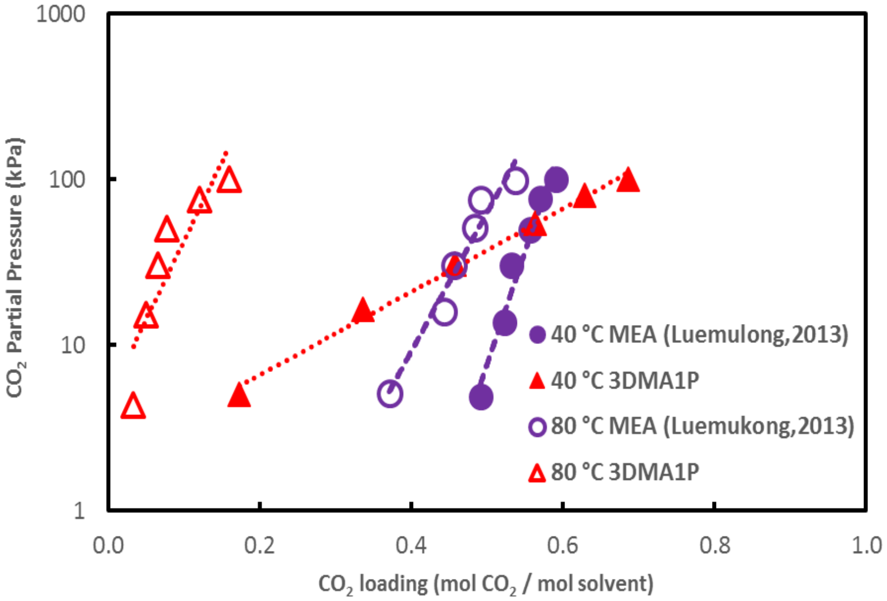


Figure 4.37 Cyclic capacity between 5M MEA [20] and 3DMA1P.

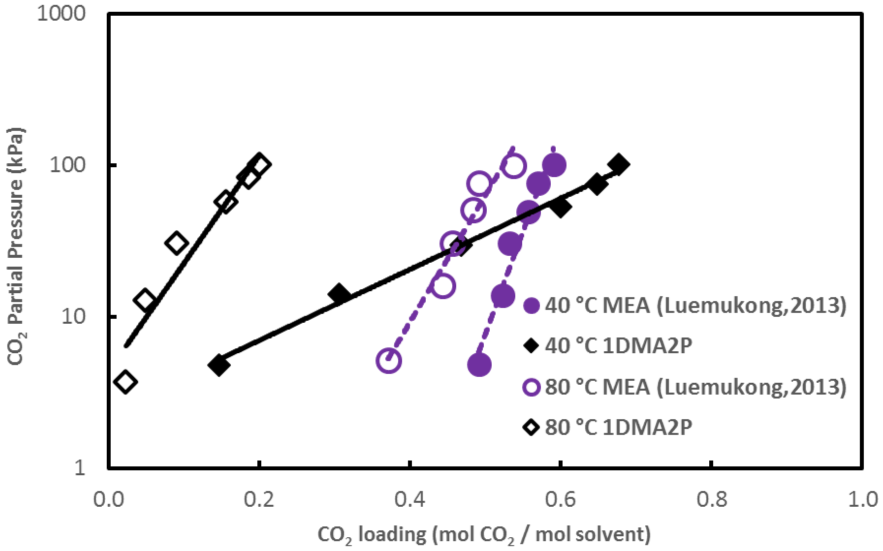


Figure 4.38 Cyclic capacity between 5M MEA [20] and 1DMA2P.

According to Figure 4.30 to Figure 4.38 and Table 4.2 to Table 4.4, the results show that, at 40 °C and 100 kPa, 3A1P, 3DAM1P and 1DMA2P can provide higher CO_2 loading than MEA. Although, at 40 °C and low partial pressure range, CO_2 loading is lower than MEA, CO_2 loading is higher than MEA in high partial pressure region.

Furthermore, at high temperatures of 80 °C, CO_2 loading obtained from 3A1P, 3DAM1P and 1DMA2P are lower than of MEA. It can be concluded that 3A1P, 3DAM1P and 1DMA2P has regeneration capacity compared to MEA. This can be concluded that 3DMA1P has a greater cyclical capacity compared to MEA, In addition, 3DMA1P can be regenerated at lower CO_2 loading than that of MEA and the lower energy consumption for regeneration. However, the large cycle capacity of 3DMA1P also reduce lowers the solvent in the process due to its high capacity, it can be concluded that the efficiency of 3DMA1P, 3A1P and 1DMA2P over MEA can enhance the overall efficiency of the absorption process and will result in lower overall cost.

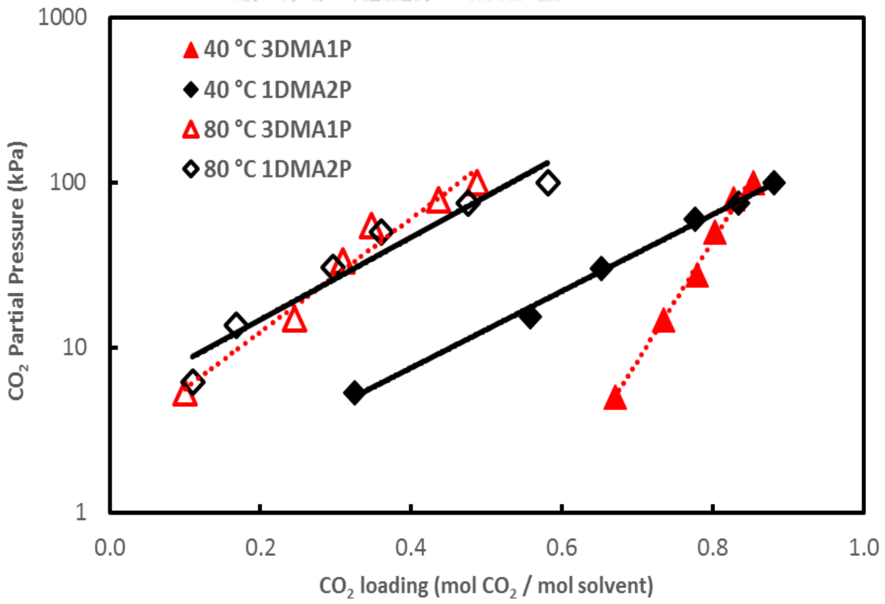


Figure 4.39 Cyclic capacity between 3M 3DMA1P and 1DMA2P.

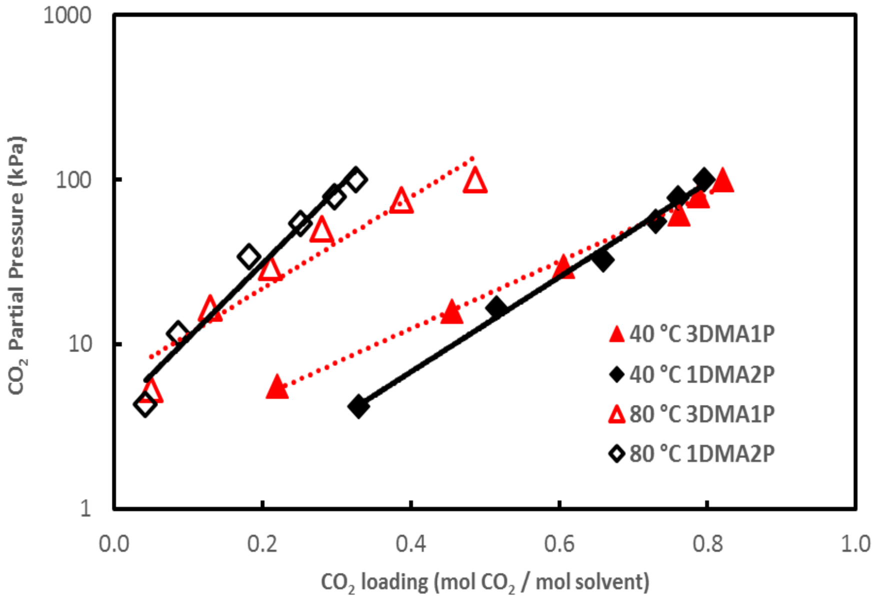


Figure 4.40 Cyclic capacity between 4M 3DMA1P and 1DMA2P.

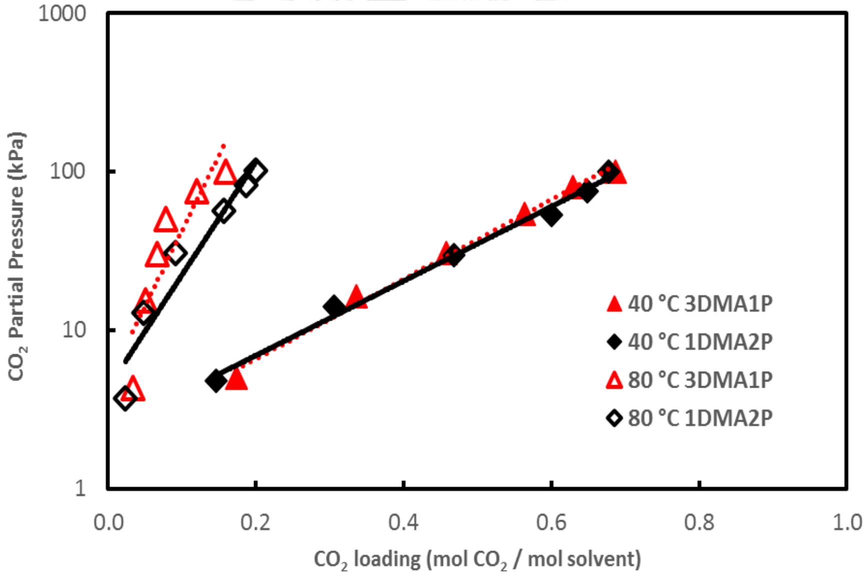


Figure 4.41 Cyclic capacity between 5M 3DMA1P and 1DMA2P.

The comparison of the cyclic capacity between 3DMA1P and 1DMA2P is shown in Fig. 4.39 to Figure.4.41. The results show that at absorption, 3DMA1P shows higher ability in CO_2 loading than 1DMA2P for range of CO_2 partial pressure. However, 1DMA2P provides lower CO_2 solubility in regeneration conditions. Considering the cyclic capacity of both solvent, 3DMA1P presents an advantage over 1DMA2P for average cyclic capacity over of 34.76% for concentrations 3 M, 19.18% for concentrations 4 M and 9.17% for concentrations 5 M. Although,3DMA1P gives lower performance in regeneration 1DMA2P, it can use benefit over 3DMA1P for both absorption and cyclic capacity conditions.

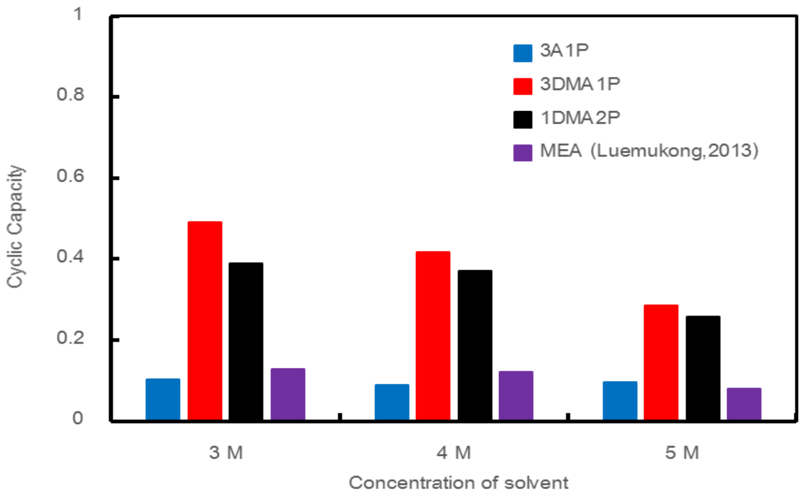


Figure 4.42 Cyclic capacity between concentration.

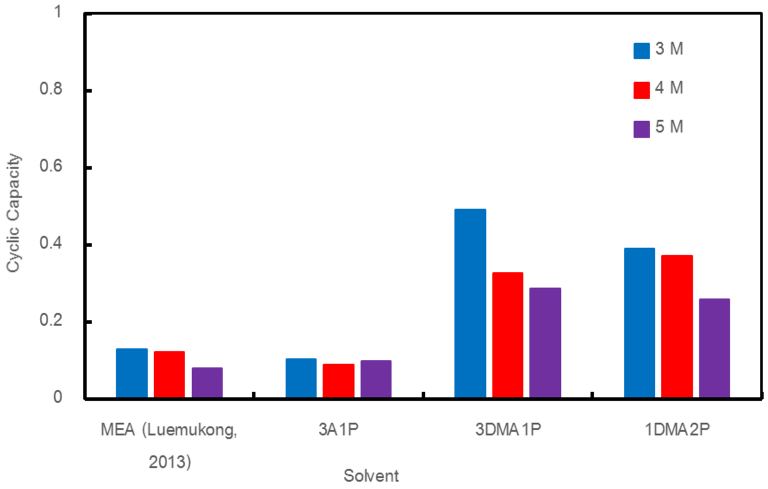


Figure 4.43 Cyclic capacity between solvent.

Finally, the experimental results and conclusions, from Figure.4.42 and Figure 4.43 3DMA1P demonstrates the preferable ability to more carbon dioxide capture than the MEA. And 1DMA2P as proposed in many aspects, such as outstanding absorption capacity, to partial pressure sensitivity and temperature. Therefore, 3DMA1P can be used or developed in the larger scale and potentially in hopefully reduce the operating cost and makes the carbon dioxide capture becomes more attractive.

Table 4.2 Details of cyclic capacity between 3M MEA,3A1P, 3DMA1P and 1DMA2P.

Solvent Type	**40 °C**		**80 °C**		**Cyclic Capacity**
	P_{CO2}	**α**	**P_{CO3}**	**α**	
MEA (Luemukong,2014)	5.32	0.498	6.06	0.372	0.126
	14.43	0.557	15.18	0.428	0.129
	31.21	0.575	29.93	0.445	0.130
	49.40	0.595	47.84	0.477	0.118
	74.77	0.611	74.38	0.494	0.117
	98.56	0.646	98.94	0.512	0.134
3A1P	3.61	0.524	3.38	0.430	0.094
	12.20	0.571	13.49	0.469	0.102
	29.30	0.591	29.75	0.490	0.101
	58.15	0.619	51.44	0.509	0.110
	76.06	0.639	91.96	0.537	0.102
	101.05	0.665	101.05	0.547	0.118
3DMA1P	5.06	0.289	5.32	0.100	0.189
	14.85	0.561	14.96	0.245	0.316
	27.76	0.793	33.54	0.309	0.484
	50.17	0.848	54.73	0.347	0.501
	80.42	0.894	78.36	0.436	0.458
	100.64	0.854	100.57	0.487	0.367
1DMA2P	5.348	0.325	6.189	0.110	0.215
	15.327	0.558	13.679	0.168	0.390
	30.245	0.652	30.874	0.296	0.356
	60.248	0.777	50.369	0.360	0.417
	75.014	0.834	75.125	0.476	0.358
	100.541	0.882	100.195	0.581	0.301

Table 4.3 Details of cyclic capacity between 4M MEA, 3A1P, 3DMA1P and 1DMA2P.

Solvent Type	40 °C		80 °C		Cyclic Capacity
	P_{CO2}	α	P_{CO3}	α	
MEA	6.98	0.492	6.85	0.362	0.130
	15.55	0.543	15.91	0.422	0.121
MEA (Luemukong,2014)	30.62	0.563	30.09	0.441	0.122
	49.88	0.593	50.64	0.477	0.116
	74.64	0.602	73.28	0.491	0.111
	99.65	0.625	99.30	0.520	0.105
3A1P	5.52	0.516	4.36	0.427	0.089
	14.60	0.549	15.20	0.460	0.089
	30.26	0.570	30.15	0.476	0.094
	51.27	0.598	51.74	0.495	0.103
	75.91	0.613	77.21	0.517	0.096
	101.05	0.628	100.07	0.526	0.102
3DMA1P	5.584	0.22	5.341	0.05	0.170
	15.993	0.545	16.595	0.129	0.416
	29.827	0.606	29.340	0.210	0.396
	61.915	0.761	50.003	0.280	0.481
	80.298	0.787	75.354	0.387	0.400
	100.181	0.820	100.135	0.487	0.333
1DMA2P	4.18	0.330	4.35	0.042	0.288
	16.55	0.457	11.70	0.086	0.371
	32.60	0.659	34.23	0.181	0.478
	55.78	0.730	54.20	0.251	0.479
	78.20	0.760	78.32	0.297	0.463
	100.59	0.795	100.60	0.326	0.469

Table 4.4 Details of cyclic capacity between 5M MEA, 3A1P, 3DMA1P and 1DMA2P.

Solvent Type	**40 °C**		**80 °C**		**Cyclic Capacity**
	P_{CO2}	α	P_{CO3}	α	
MEA (Luemukong, 2014)	4.87	0.491	5.11	0.371	0.120
	13.82	0.523	15.97	0.443	0.080
	30.44	0.532	30.43	0.456	0.076
	49.52	0.557	50.90	0.484	0.073
	76.14	0.570	75.80	0.491	0.079
	100.33	0.590	99.46	0.537	0.053
3A1P	5.90	0.512	4.67	0.422	0.090
	13.99	0.542	14.44	0.445	0.097
	29.81	0.560	31.81	0.468	0.092
	50.15	0.580	51.58	0.485	0.095
	76.90	0.597	76.18	0.499	0.098
	100.59	0.610	100.62	0.515	0.095
3DMA1P	5.038	0.173	4.325	0.033	0.140
	16.495	0.336	15.327	0.050	0.286
	30.749	0.458	30.124	0.066	0.392
	54.176	0.563	50.669	0.078	0.485
	80.239	0.629	75.024	0.120	0.509
	100.620	0.686	100.365	0.159	0.527
1DMA2P	4.81	0.146	3.73	0.023	0.123
	14.12	0.306	12.89	0.048	0.258
	29.64	0.468	30.50	0.091	0.377
	53.29	0.600	57.04	0.156	0.444
	75.25	0.648	83.03	0.186	0.462
	100.61	0.677	101.06	0.200	0.477

4.4 Time dependence of solvent performance in CO_2 absorption

The change on the rate of CO_2 loading in solvent. Rates of CO_2 loading change are very high at the beginning of the reaction until into a state of equilibrium. It is considering the advantage of using new solvents for capturing carbon dioxide from gas mixtures. The rate of CO_2 uptake using new different solvents is compared with that of absorption by MEA.

4.4.1 Effect of solvent on CO_2 solubility

The effect of solvent on CO_2 solubility. For the solvent efficiency, the solvent primary amine comparison is 3A1P and MEA. Figure 4.44 to Figure. 4.61 shown time dependence of solvent between 3A1P and MEA at 3,4 and 5 M,15 and 100 kPa in CO_2 absorption.

Figure 4.44 and Figure 4.45 at 3 M show that in the first 15 minutes, MEA had an effective react rapidly per carbon dioxide absorption compared to 3A1P. After 15 minutes, 3A1P can react faster compared to MEA. However, one mole of CO_2 reacts with one moles of amine, as required by to afford carbamates formation as equation. Therefore, the amount of CO_2 taken up by the 3A1P at 40 °C and 80 °C and partial pressures at 15 and 100 kPa increased when over time the amount of CO_2 constant up to equilibrium.

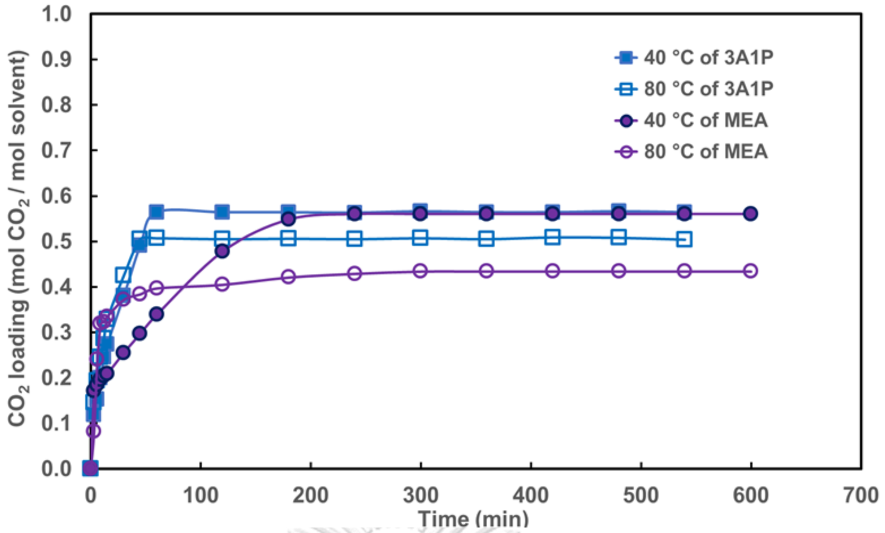


Figure 4. 44 Time dependence of solvent between 3A1P and MEA at 3 M,15 kPa.

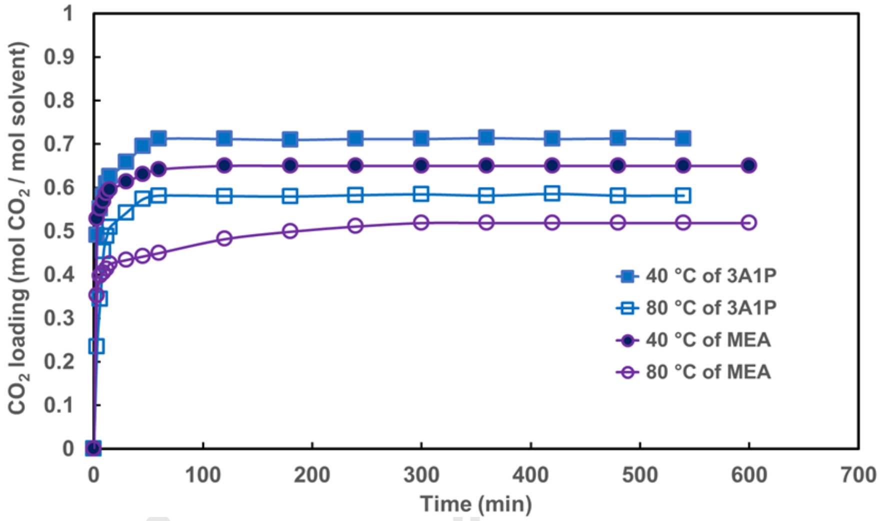


Figure 4. 45 Time dependence of solvent between 3A1P and MEA at 3 M,100 kPa.

Figure 4.46 and Figure 4.47 in 4 M at temperature 40 °C partial pressures 15 and 100 kPa show that, at temperature 40 °C in the first 15 minutes MEA absorb faster comparison with 3A1P. After that, 3A1P can absorb CO_2 more to equilibrium. However, at 40 °C, CO_2 loading of solubility is similar between MEA and 3A1P. At temperature of 80 °C partial pressures at 15 and 100 kPa it is show that in the range first 15 minutes the result is similar with 40 °C. After that 3A1P can absorption CO_2 increased compared to MEA.

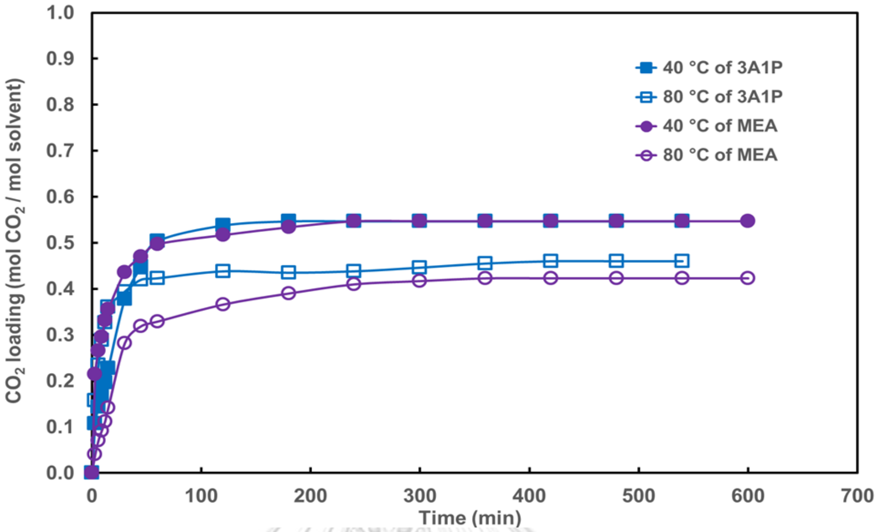


Figure 4. 46 Time dependence of solvent between 3A1P and MEA at 4 M,15 kPa.

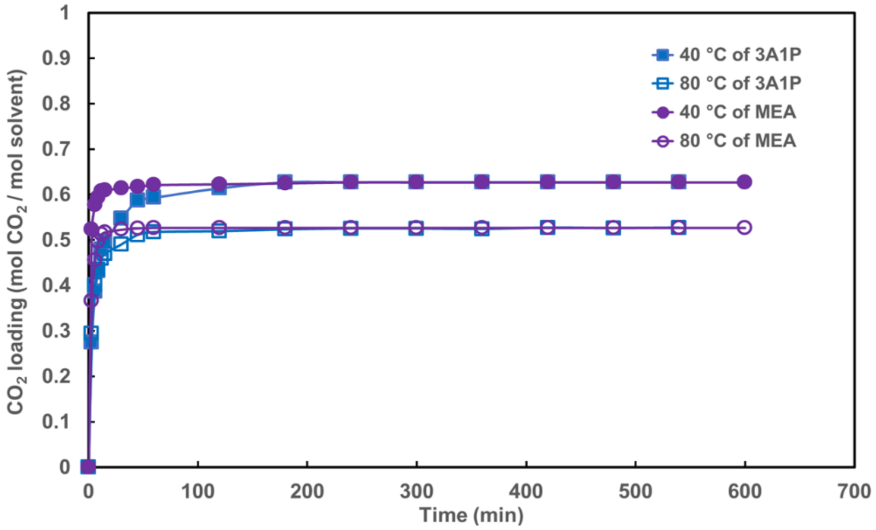


Figure 4. 47 Time dependence of solvent between 3A1P and MEA at 4 M,100 kPa.

Figure 4.48 and Figure 4.49 in 5 M at temperature 40 °C and 80 °C partial pressure 15 and 100 kPa show that, the concentration of 5 M is similar to that of 3 and 4 M as described previously.

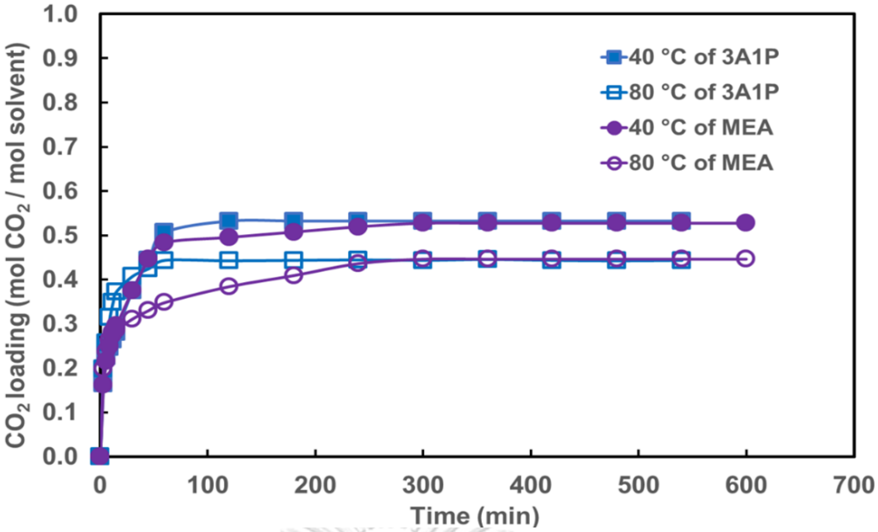


Figure 4.48 Time dependence of solvent between 3A1P and MEA at 5 M,15 kPa.

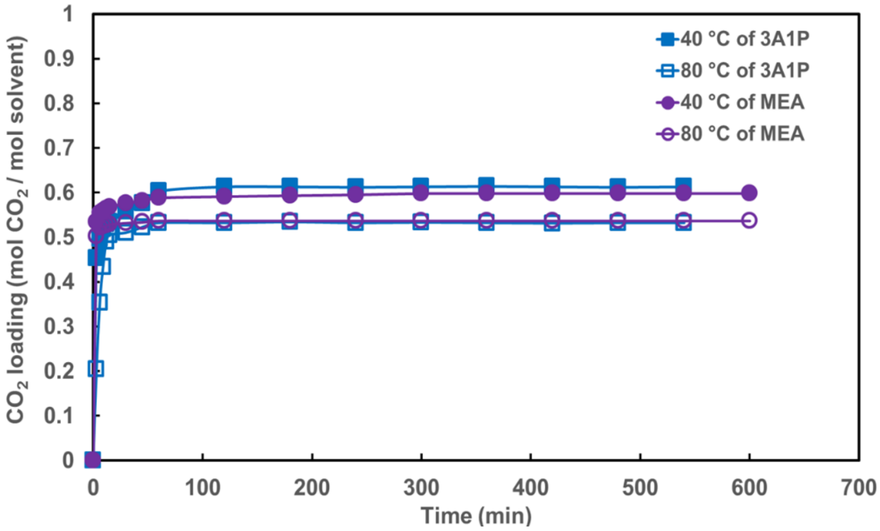


Figure 4.49 Time dependence of solvent between 3A1P and MEA at 5 M,100 kPa.

The effect of solvent on CO_2 solubility. For the solvent efficiency, the solvents of tertiary amine comparison as 3DMA1P and MEA. Figure 4.50 to Figure. 4.55 show time dependence of solvent between 3DMA1P and MEA at 3,4 and 5 M,15 and 100 kPa in CO_2 absorption.

Figure 4.50 and Figure 4.51 in 3 M at temperature 40 °C partial pressure 15 and 100 kPa show that, at temperature 40 °C in the first 15 minutes MEA can be absorption

CO_2 react rapidly comparison with 3DMA1P. After that, 3DMA1P is absorption CO_2 increased according time and the amount of CO_2 constant up to equilibrium. And part at temperature 80 °C partial pressures 15 and 100 kPa show that in the range first 15 minutes is absorption CO_2 decreased compared to MEA. The reaction quickly takes place also in absence of solvent. The resulting carbamates have been characterized. 3DMA1P are thus by far more efficient than MEA for CO_2 capturing and regeneration solvent.

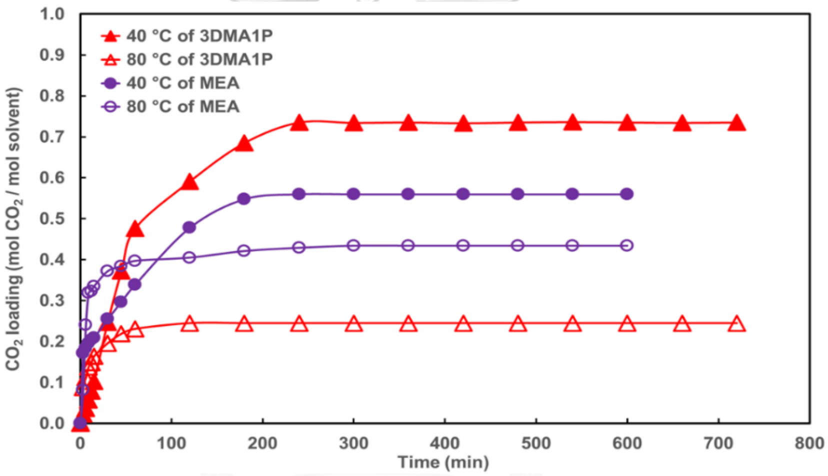


Figure 4.50 Time dependence of solvent between 3DMA1P and MEA at 3 M,15 kPa.

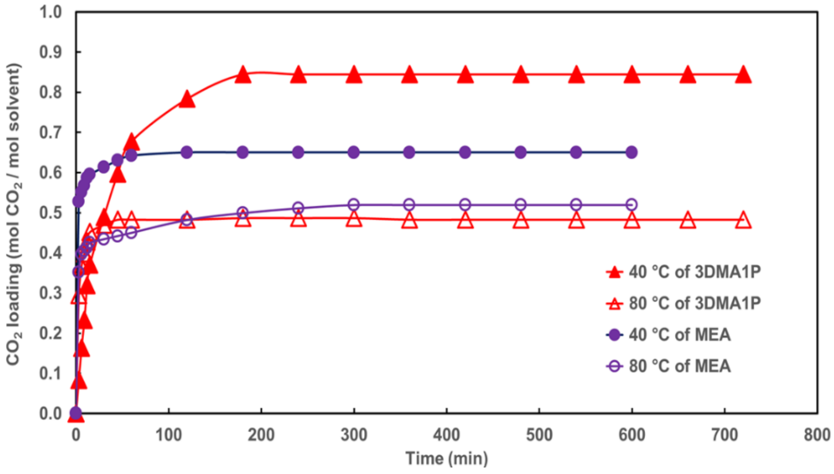


Figure 4.51 Time dependence of solvent between 3DMA1P and MEA at 3 M,100 kPa.

Figure 4.52 and Figure 4.53 at 4 M show that in the first 15 minutes, MEA had an effective react rapidly per carbon dioxide absorption compared to 3DMA1P. After that, 3DMA1P can be compared to MEA at temperature 40 °C partial pressure 15 and 100 kPa show that the amount CO_2 absorption a great increase compared MEA. And at temperature 80 °C partial pressure 15 and 100 kPa show that in the range first is absorption CO_2 decreased compared to MEA. After a while, the reaction quickly takes. Resulting in the CO_2 loading decrease compared MEA. so, suitable with regeneration solvent.

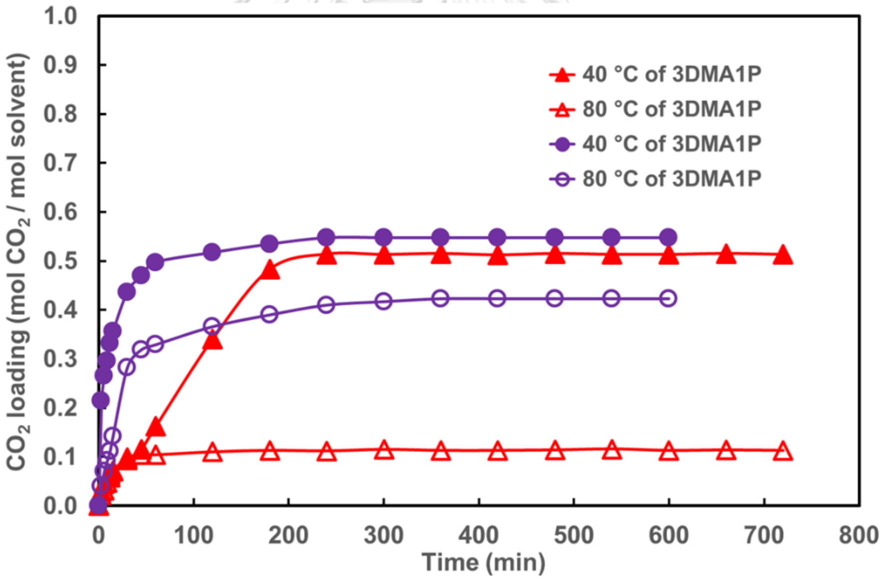


Figure 4.52 Time dependence of solvent between 3DMA1P and MEA at 4 M,15 kPa.

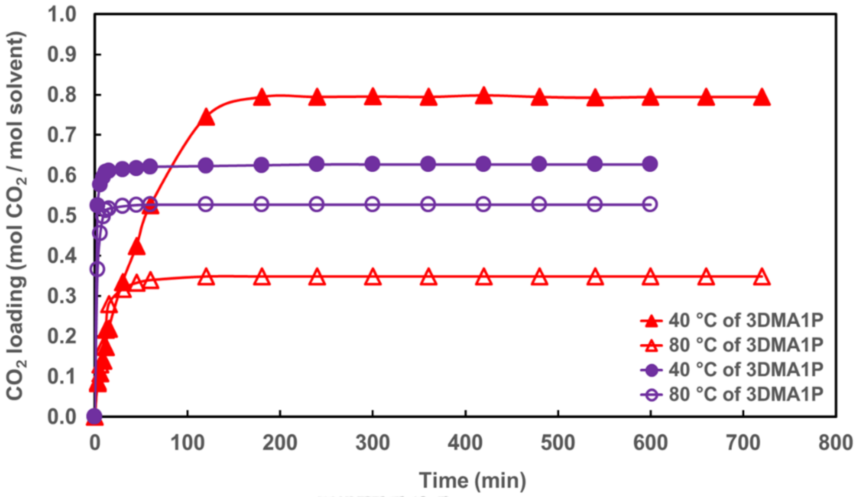


Figure 4.53 Time dependence of solvent between 3DMA1P and MEA at 4 M,100 kPa.

Figure 4.54 and Figure 4.55 in 5 M at temperature 40 °C and 80 °C partial pressure 15 and 100 kPa show that, the concentration of 5 M is similar to that of 3 and 4 M described previously. Conclusion, in the first 15 minutes, MEA had an effective react rapidly per carbon dioxide absorption compared to 3DMA1P. After that, 3DMA1P can be compared to MEA at temperature 40 °C show that the amount CO_2 absorption a great increase compared MEA. And at temperature 80 °C can absorption CO_2 decreased compared to MEA. So, suitable to return new used to the solvent.

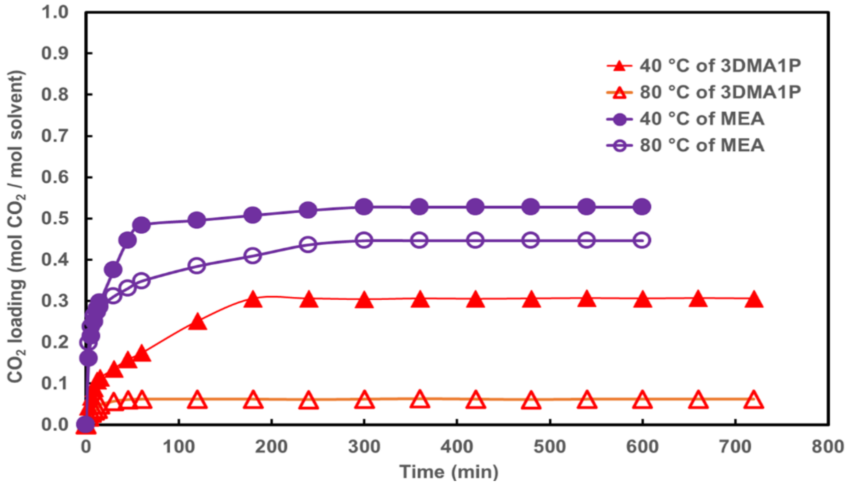


Figure 4.54 Time dependence of solvent between 3DMA1P and MEA at 5 M,15 kPa.

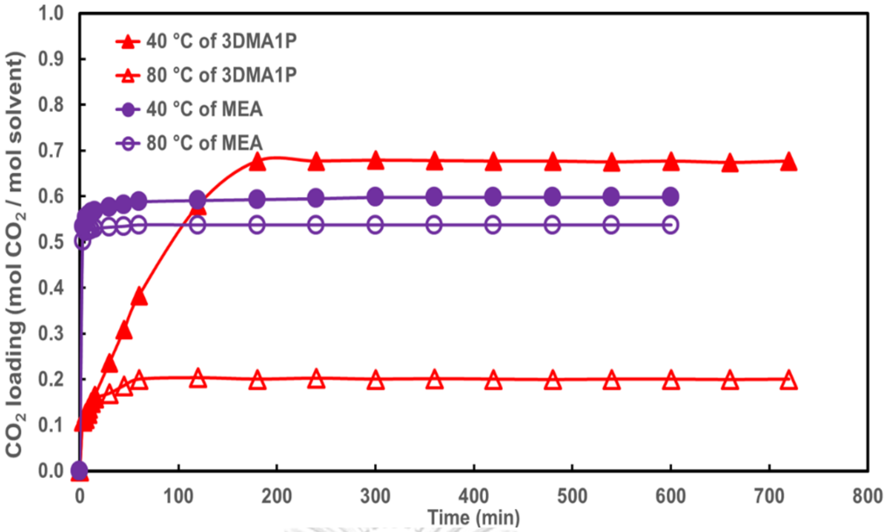


Figure 4.55 Time dependence of solvent between 3DMA1P and MEA at 5 M,100 kPa.

The effect of solvent on CO_2 solubility. In study the solvent efficiency, the solvent tertiary amine comparison was 1DMA2P and MEA. Figure 4.56 to Figure. 4.61 shown time dependence of solvent between 1DMA2P and MEA at 3,4 and 5 M,15 and 100 kPa in CO_2 absorption.

Figure 4.56 and Figure 4.57 in 3 M at temperature 40 °C and 80 °C partial pressure 15 and 100 kPa show that, in the first 15 minutes, MEA had an effective react rapidly per carbon dioxide absorption compared to 1DMA2P. After that, 1DMA2P is absorption CO_2 increased according time and the amount of CO_2 constant up to equilibrium. Thus, 1DMA2P is as performing as MEA. And at temperature 80 °C can absorption CO_2 decreased compared to MEA. So, suitable with regeneration.

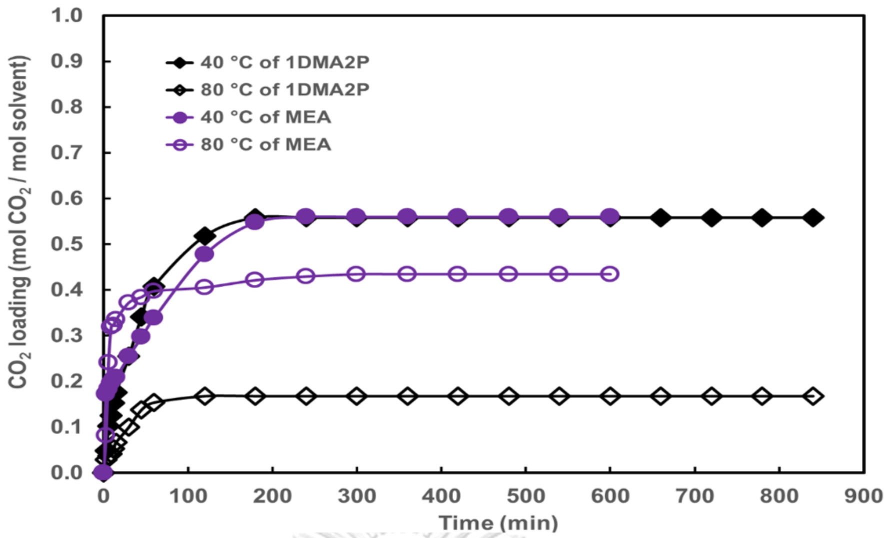


Figure 4.56 Time dependence of solvent between 1DMA2P and MEA at 3 M,15 kPa.

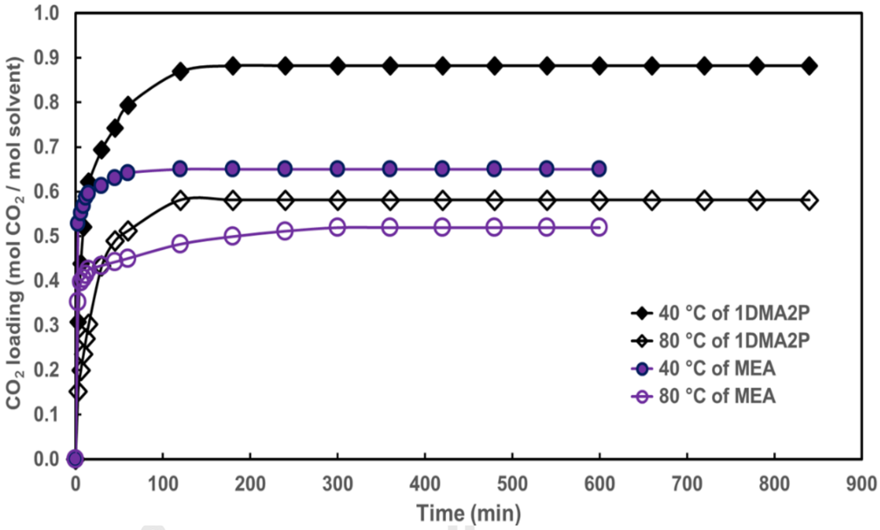


Figure 4.57 Time dependence of solvent between 1DMA2P and MEA at 3 M,100 kPa.

For Figure 4.58 and Figure 4.59 in 4 M at temperature 40 °C and 80 °C partial pressure 15 and 100 kPa show that, in the first 15 minutes, MEA had an effective rapidly per carbon dioxide absorption compared. After that, about 120 minutes 1DMA2P is absorption CO_2 increased according time and the amount of CO_2 constant up to equilibrium. Therefore, 1DMA2P is as performing absorption a great than MEA.

And at temperature 80 °C can absorption CO_2 decreased compared to MEA. Consequently, suitable with regeneration.

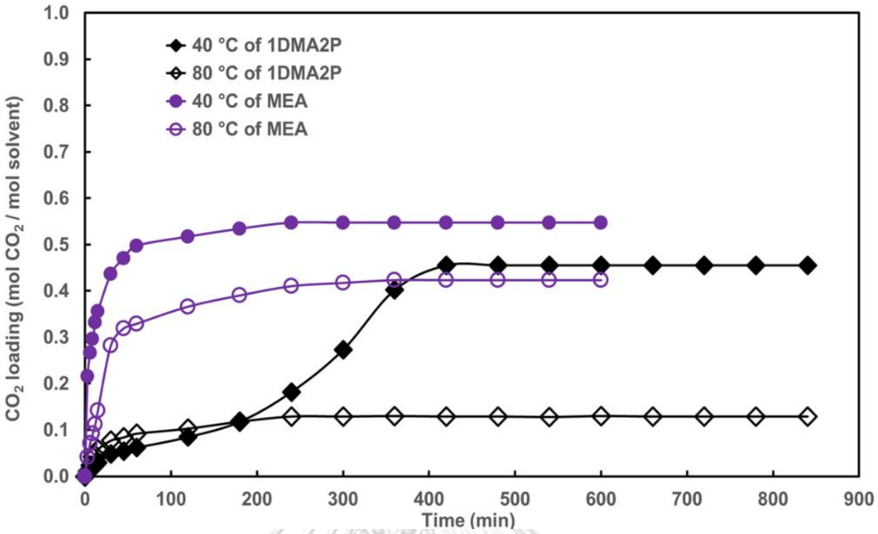


Figure 4. 58 Time dependence of solvent between 1DMA2P and MEA at 4 M,15 kPa.

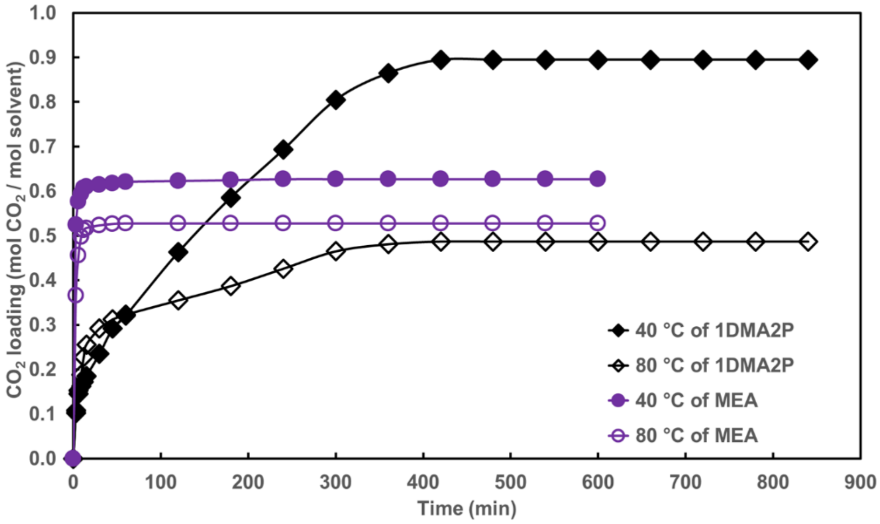


Figure 4. 59 Time dependence of solvent between 1DMA2P and MEA at 4 M,100 kPa.

For Figure 4.60 and Figure 4.61 in 5 M at temperature 40 °C and 80 °C partial pressure 15 and 100 kPa show that, in the first 15 minutes, MEA had an effective rapidly per carbon dioxide absorption compared 1DMA2P. At 15 kPa of partial pressure It has been shown that at 40 °C, 1DMA2P has a lower CO_2 loading than MEA, as it may be due to the concentration of the substance that results in less carbon dioxide dissolution and may be due to the viscosity of the substance. Part at 100 kPa of partial pressure 1DMA2P are absorption CO_2 increased according time and the amount of CO_2 constant up to equilibrium. While at temperature 80 °C can absorption CO_2 decreased compared to MEA. Consequently, suitable to return new used to the solvent and suitable with regeneration.

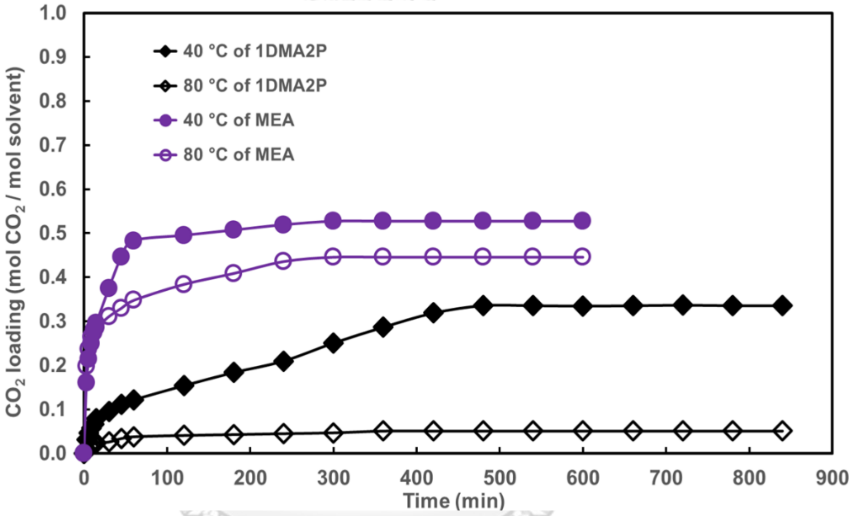


Figure 4. 60 Time dependence of solvent between 1DMA2P and MEA at 5 M,15 kPa.

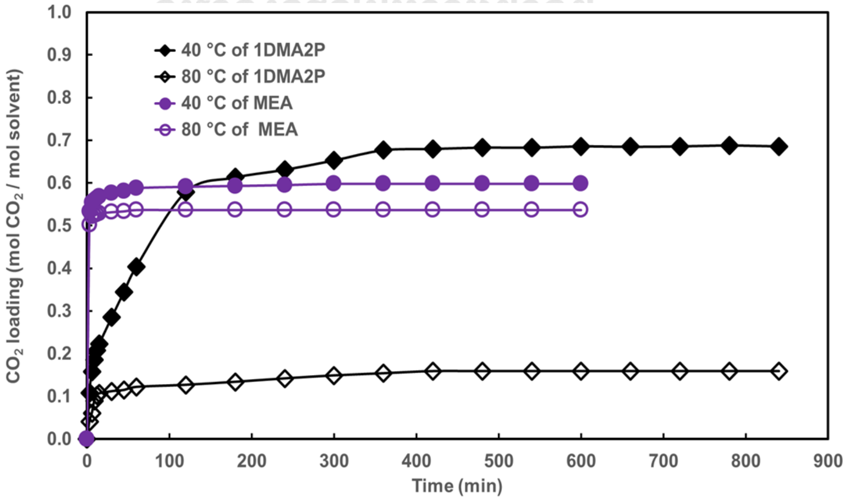


Figure 4. 61 Time dependence of solvent between 1DMA2P and MEA at 5 M,100 kPa.

For the time dependence of 3A1P it is conclusion that, in the first 15 minutes, MEA has an effective react rapidly per carbon dioxide absorption compared to 3A1P. After that, 3A1P can react with CO_2 with higher rate to equilibrium. Thus, 3A1P is better perform were MEA. Temperature results in faster reactions at the beginning, so that the graph accelerates until it reaches equilibrium.

For 3DMA1P and 1DMA2P, in the first 15 minutes, the MEA will resemble the 3A1P described earlier. After that, 3DMA1P and 1DMA2P can be compared to MEA at temperature 40 °C show that the amount CO_2 absorption a great increase compared MEA. And at temperature 80 °C can absorption CO_2 decreased compared to MEA. The slope of the graph causes the reaction to accelerate in the early stages. The higher the CO_2 loading, the greater the effect on the absorption and regeneration.

Eventually, according to the experimental results and the conclusions above, 3DMA1P demonstrates the ability to capture more carbon dioxide than the MEA. In section of 3A1P and 1DMA2P, as originally proposed in such various aspects as the amount of absorption, great sensitivity the temperature and the partial pressure and larger cyclic capacity and time dependence of solvent performance in CO_2 absorption. In conclusion, 3DMA1P may be used or developed in large scale and is expected to reduce operating costs and make the process of carbon dioxide capture more attractive and 3DMA1P

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, the solubilities of CO_2 into the new solvents, 3-amino-1-propanol (3A1P), 3-dimethylamino-1-propanol (3DMA1P) and 1-dimethylamino-2-propanol (1DMA2P). for chemical absorption have been studied. The operating conditions used are the solvent concentration at 3, 4 and 5 M partial pressure of CO_2 5, 15, 30, 50, 75 and 100 kPa the temperature at 30, 40, 60 and 80 °C

From the solubility results, it is clear that 3DMA1P and 1DMA2P can capture more CO_2 than MEA solutions. CO_2 loading data are higher in both 40 °C and 80 °C. In term of absorption capacity, 3DMA1P has a better absorption performance than MEA. As the partial pressure of CO_2 increases, the amount of CO_2 captured by 3DMA1P will increase more than that of MEA. 3DMA1P and 1DMA2P illustrate the partial pressure trends of CO_2 and the CO_2 loading relationship because both have a mutual molecular structure, which is the tertiary amine. Both indicated that 3DMA1P and 1DMA2P have a distinctive molecular structure which may advantage to CO_2 capture performance. And 3A1P have a molecular structure, which is the primary amine. However, 3A1P has greater number of CO_2 loading than that of MEA but less than 3DMA1P and 1DMA2P which are the tertiary amines. However, 3DMA1P and 1DMA2P solution could have a potential as an alternative absorbent. There are also other criteria to consider in many aspects to conclude the performance of this new solvent. The effects of molecular structures, such as types of amine carbon chain lengths, position of functional groups attached to the backbone on the basis of various amines have been studied. It is found that the increase in the length of the carbon chain would affect the solubility in water and the size of molecular. But for these case all solvents 3DMA1P solubility results in the highest solubility among the three amines solvents.

The effects of partial pressure of CO_2 on the solubility of carbon dioxide are directly proportional to their partial pressures in equilibrium and changing of CO_2 for each solvent. For partial pressure, the increase in CO_2 partial pressure from 5 to 100 kPa can enhance the capacity to capture more CO_2 for each solvent. At some pressure in the range of 5 to 100 kPa CO_2, the 3DMA1P and 1DMA2P solutions are more soluble in carbon dioxide than the MEA solution. For the effect of concentration, the greater the concentration, the greater the carbon dioxide absorbed in the 3DMA1P and 1DMA2P solutions. So, the conclusion is that using 3DMA1P and 1DMA2P as a chemical solvent for CO_2 absorption is better than MEA especially for CO_2 from power plants. For the effect of solvent concentration on the CO_2 solubility. The experiment shows that the carbon dioxide concentration at 5 M is less than the 4 and 3 M concentration, respectively. As the concentration of the solution increases, the CO_2 loading would be noticeably lower than that of the previous results.

The effect of temperature shows that the solubility of carbon dioxide is directly dependent on temperature. The solubility of carbon dioxide at various temperatures can be observed that the solubility at lower temperatures has a higher carbon dioxide content compared to that at higher temperatures. At present, the absorption process uses an absorption temperature of 40 °C the reaction between CO_2 and amines is reversible and exothermic. When the temperature increases, it results in the lower CO_2 loading capacity. At high temperature, it is considered as a regeneration condition since the gas is removed from the solvent.

The cyclic capacity is defined as the difference between the CO_2 solubility in the liquid solvent at absorption condition and that of at regeneration condition. In this study, 40 °C and 80 °C are set as absorption and regeneration conditions, respectively. Meanwhile, 3DMA1P demonstrates the preferable ability to have more carbon dioxide capture than that of the MEA for 279 %. 3A1P could provide the greater average cyclic capacity than that of MEA for 21 %. Therefore, 3DMA1P can be used or developed in the larger scale and potentially in hopefully reduce the operating cost and makes the carbon dioxide capture becomes more attractive.

Furthermore, time dependence of solvent performance in CO_2 absorption. The rates of CO_2 loading change versus time are very high at the beginning of the reaction until into a state of equilibrium. At higher temperature, the rate of loading change is higher because the higher energy can enhance the rate of reaction; thus, increasing the rate of CO_2 change. For higher partial pressure, the rate of loading change can increase because of higher driving force leading to higher rate of reaction. Later, the rate is relatively stable until it reached equilibrium. It is the same for both temperature and partial pressure.

Eventually, 3DMA1P exhibited outstanding performance on carbon dioxide loading over both 3A1P and 1DMA2P. 3DMA1P is suitable for use in natural gas power plants rather than coal-fired power plants. CO_2 emissions are in the range of 5-10 %, resulting in 3DMA1P for CO_2 capture. Some of the higher partial pressures are better than the lower partial pressures, and the efficiency of regeneration is improved. The cause is reduced energy consumption in re-usable and re-usable solutions as well as reduce overall system costs.

5.2 Recommendations

The solubility of carbon dioxide is one of the properties of the solvent that should be monitored. However, for this new solvents, 3A1P, 3DMA1P and 1DMA2P solutions other properties should be investigated. There properties are kinetics, mass transfer coefficient, physical properties such as density and viscosity. The kinetics reaction between the solution and the carbon dioxide, can be analyzed by using a Nuclear magnetic resonance spectroscopy or ion chromatography. Study investigate of heat absorption of new solvents, 3A1P, 3DMA1P and 1DMA2P solutions in CO_2 solubility.

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APPENDIX

APPENDIX A: FLOWMETER CALIBRATION

AALBORG GFM17 flow meters are used to measure the amount of N_2 and CO_2 which are fed into the system and calibrated by SUPELCO OPTIFLOW 520. The examples of calibration curve are illustrated in Figure A.1 through A.4

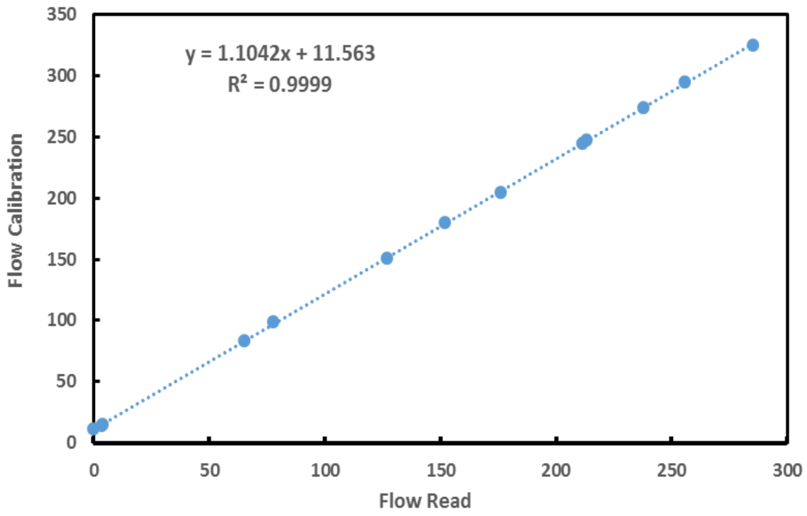

Figure A.1 Calibration curve of N_2 flowmeter line 1.

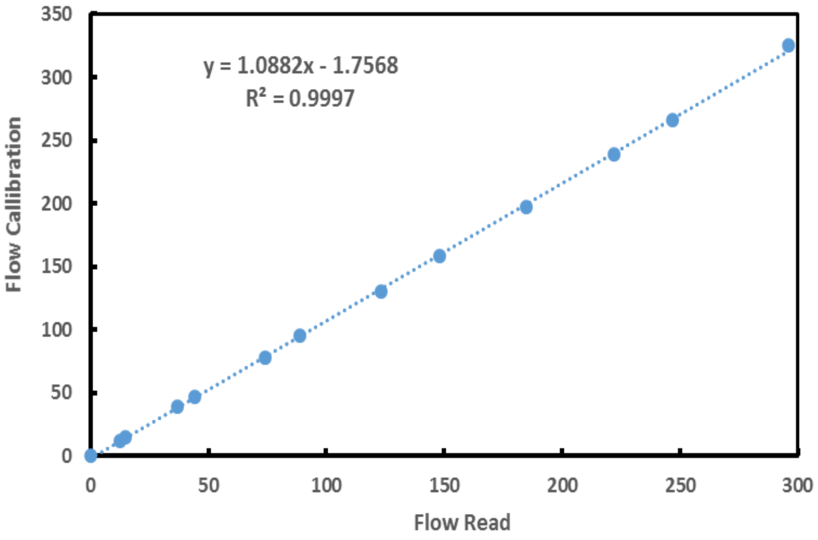

Figure A.2 Calibration curve of CO_2 flowmeter line 1.

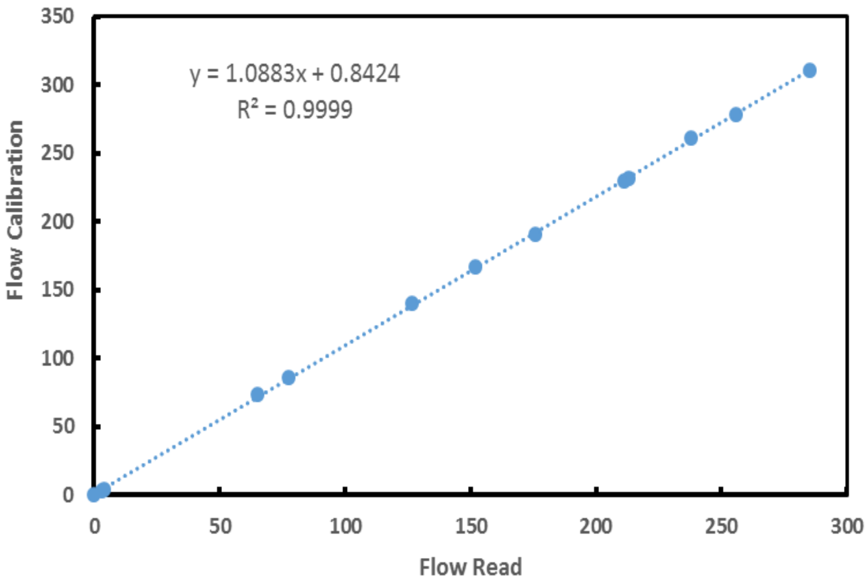

Figure A.3 Calibration curve of N_2 flowmeter line 2.

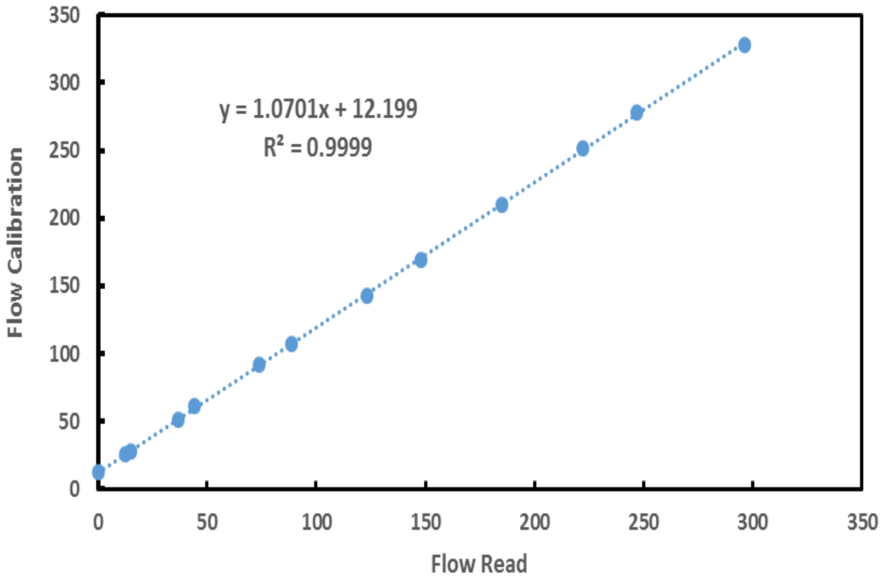

Figure A.4 Calibration curve of CO_2 flowmeter line 2.

APPENDIX B: SOLUBILITY DATA

Table B.1 Solubility data of 3A1P, 3DMA1P and 1DMA2P at 30 °C and 3, 4 and 5 M concentration

Solvent Type	**3 M**		**4 M**		**5 M**	
	P_{CO2}	**α**	**P_{CO2}**	**α**	**P_{CO2}**	**α**
3A1P	4.68	0.562	3.04	0.536	4.33	0.529
	12.89	0.600	14.16	0.582	12.74	0.563
	31.24	0.642	32.15	0.625	30.31	0.602
	50.05	0.688	52.70	0.646	51.21	0.624
	86.19	0.761	81.17	0.675	74.96	0.638
	100.59	0.831	100.59	0.710	100.07	0.668
3DMA1P	6.28	0.437	4.71	0.382	5.35	0.336
	14.51	0.656	15.85	0.498	14.66	0.495
	28.78	0.713	32.05	0.666	31.78	0.634
	52.75	0.847	58.90	0.794	50.36	0.700
	81.26	0.874	78.50	0.841	80.88	0.771
	100.67	0.924	100.58	0.896	100.22	0.798
1DMA2P	4.38	0.419	4.09	0.350	3.52	0.159
	14.73	0.626	14.03	0.538	15.14	0.411
	30.22	0.724	35.75	0.700	25.99	0.490
	52.32	0.859	56.52	0.768	54.20	0.659
	76.37	0.900	78.56	0.798	78.55	0.688
	100.71	0.945	100.59	0.809	101.06	0.718

Table B.2 Solubility data of 3A1P, 3DMA1P and 1DMA2P at 40 °C and 3, 4 and 5 M concentration

Solvent Type	**3 M**		**4 M**		**5 M**	
	P_{CO_2}	**α**	**P_{CO_2}**	**α**	**P_{CO_2}**	**α**
3A1P	3.61	0.524	5.52	0.516	5.90	0.512
	12.20	0.571	14.60	0.549	13.99	0.542
	29.30	0.591	30.26	0.570	29.81	0.560
	58.15	0.619	51.27	0.598	50.15	0.580
	76.06	0.639	75.91	0.613	76.90	0.597
	101.05	0.665	101.05	0.628	100.59	0.610
3DMA1P	5.06	0.289	5.584	0.220	5.038	0.173
	14.85	0.561	15.993	0.455	16.495	0.336
	27.76	0.679	29.827	0.606	30.749	0.458
	50.17	0.793	61.915	0.761	54.176	0.563
	80.42	0.848	80.298	0.787	80.239	0.629
	100.64	0.894	100.181	0.820	100.620	0.686
1DMA2P	5.348	0.325	4.18	0.330	4.81	0.146
	15.327	0.558	16.55	0.515	14.12	0.306
	30.245	0.652	32.60	0.659	29.64	0.468
	60.248	0.777	55.78	0.730	53.29	0.600
	75.014	0.834	78.20	0.760	75.25	0.648
	100.541	0.882	100.59	0.795	100.61	0.677

Table B.3 Solubility data of 3A1P, 3DMA1P and 1DMA2P at 60 °C and 3, 4 and 5 M concentration

Solvent Type	**3 M**		**4 M**		**5 M**	
	P_{CO_2}	**α**	**P_{CO_2}**	**α**	**P_{CO_2}**	**α**
3A1P	4.24	0.495	4.05	0.480	5.36	0.473
	12.19	0.543	12.76	0.511	15.57	0.495
	29.69	0.566	30.33	0.532	28.51	0.506
	54.90	0.595	52.75	0.547	51.33	0.528
	80.38	0.607	77.58	0.568	75.41	0.536
	101.05	0.616	100.16	0.580	100.18	0.550
3DMA1P	4.36	0.245	6.85	0.150	5.24	0.095
	14.35	0.416	15.85	0.285	14.99	0.206
	30.32	0.\568	38.80	0.471	30.38	0.304
	52.20	0.658	58.71	0.538	50.35	0.365
	75.24	0.713	77.78	0.603	75.69	0.433
	100.54	0.750	100.18	0.631	100.06	0.470
1DMA2P	4.41	0.198	4.52	0.164	5.12	0.083
	15.83	0.376	16.89	0.332	15.50	0.153
	30.65	0.454	31.40	0.425	29.29	0.275
	51.75	0.548	51.32	0.549	57.63	0.375
	76.32	0.597	75.48	0.610	76.25	0.450
	99.74	0.663	100.62	0.641	101.50	0.492

Table B.4 Solubility data of 3A1P, 3DMA1P and 1DMA2P at 80 °C and 3, 4 and 5 M concentration

Solvent Type	**3 M**		**4 M**		**5 M**	
	P_{CO2}	**α**	**P_{CO2}**	**α**	**P_{CO2}**	**α**
3A1P	3.38	0.430	4.36	0.427	4.67	0.422
	13.49	0.469	15.20	0.460	14.44	0.445
	29.75	0.490	30.15	0.476	31.81	0.468
	51.44	0.509	51.74	0.495	51.58	0.485
	91.96	0.537	77.21	0.517	76.18	0.499
	101.05	0.547	100.07	0.526	100.62	0.515
3DMA1P	5.32	0.100	5.34	0.05	4.32	0.033
	14.96	0.245	16.59	0.129	15.32	0.050
	33.54	0.309	29.34	0.210	30.12	0.066
	54.73	0.347	50.03	0.280	50.66	0.078
	78.36	0.436	75.35	0.387	75.02	0.120
	100.57	0.487	100.13	0.487	100.36	0.159
1DMA2P	6.19	0.110	4.35	0.042	3.73	0.023
	13.67	0.168	11.70	0.086	12.89	0.048
	30.87	0.296	34.23	0.181	30.50	0.091
	50.36	0.360	54.20	0.251	57.04	0.156
	75.12	0.476	78.32	0.297	83.03	0.186
	100.19	0.581	100.60	0.326	101.06	0.200

VITA

Miss Rossukon Nimcharoen was born on 23 November 1991. In 2009, she graduated from high school at Rayong Witthayakom Paknam, Rayong. In 2012, she graduated from High Vocational Certificate, Rayong Technical College, Rayong. In 2015 she received bachelor of Engineering in Chemical Engineering, Rangsit University.