Experimental Investigation of CO_2 Absorption Capacity in Amine Blend of 2-Amino-2-methyl-1-propanol (AMP) and Tetraethylenepentamine (TEPA)

Dissertation submitted in partial fulfillment of the requirement

for the award of the degree of

Master of Technology

in

Chemical Engineering

Submitted By:

Babul Prasad
Roll No.: 601111006

Under the Guidance of:

Mr. Rakesh Kr. Gupta
Assistant Professor
Department of Chemical Engineering

Department of Chemical Engineering

Thapar University, Patiala
Patiala – 147004, Punjab, India

June 2013

CERTIFICATE

This is certified that the dissertation entitled **"Experimental investigation of CO_2 absorption capacity in amine blend of 2-amino-2-methyl-1-propanol (AMP) and tetraethylenepentamine (TEPA)"** is an authentic record of my own work carried out as requirements for the award of the degree of M. Tech. (Chemical engineering) at Thapar University, Patiala, under the guidance of **Mr. Rakesh Kr. Gupta** (Assistant Professor, ChED) during July 2012 to June 2013.

Date:- 12/06/2013

Prasad

Babul Prasad

Roll No. 601111006

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

RKGupta 12/06/13

Mr. Rakesh Kr. Gupta

Assistant Professor

Department of Chemical Engineering

Thapar University, Patiala

Counter signed by:

09/07/13

Dr. Rajeev Mehta

Head of the Department

Department of Chemical Engineering

Dr. S.K. Mohapatra

Dean of Academic Affairs

Thapar University, Patiala

ACKNOWLEDGEMENTS

At first, my sincere thanks to the Almighty for his abundant blessing showered on me throughout this endeavor to complete this successful work of mine. I am thankful to my parents for their great support throughout my life. I would cherish every moment where my parents were so keen and curious to know about the details and progress of my work which boosted my confidence. I express my deep sense of gratitude to them.

My honorable guide **Mr. Rakesh Kr. Gupta**, Assistant Professor, Department of Chemical Engineering, Thapar University**,** is a person to whom I will always remain grateful for his excellent guidance, valuable discussions, encouragement, constructive criticism and his ideas have strengthened this study significantly. He gave me a complete freedom to use my opinion, correcting whenever necessary in my dissertation.

I would like to thank my Head of Department **Dr. Rajiv Mehta,** who has at all times been very supportive and accommodating.

I thank **Dr. Raj Kumar Gupta,** my P.G. Coordinator for his terrific guidance regarding the thesis writing and sir has provided us much time to write thesis.

I would like to thank **all the faculty members** of the department of chemical engineering for encouraging me to write the seminar report.

I would like to thank the most senior person, **Dr. P.K. Bajpai** (Distinguished Professor) for his guidance and blessings.

I would like to thank all my **colleagues** at Thapar University, Patiala for their support and encouragement in carrying out my research smoothly.

ABSTRACT

In the light of increasing fears about climate change, greenhouse gas mitigation technologies have assumed growing importance. Carbon capture and sequestration (CCS) is one of the options that can enable the utilization of fossil fuels with lower CO_2 emissions. There are different technologies for CO_2 capture, but capture of CO_2 by chemical absorption is the technology that is closest to commercialization. A number of different solvents in chemical absorption for CO_2 capture have been proposed. The use of blended amines, a solution of two or more amines in varying compositions, shows considerable improvement in absorption and savings in energy requirements. This thesis focuses on developing a new solvent for an objective comparison of the performance with different solvents.

In this work, the results of an experimental investigation on the solubility of CO_2 in 2-amino-2-methyl-1-propanol (AMP), a primary sterically hindered amine and Tetraethylenepentamine (TEPA) having 5 amine sites (two primary and three secondary) as well as their mixtures are presented. It is observed, the ability of TEPA for CO_2 uptake is higher as compared to that of AMP. The addition of TEPA to AMP enhances the CO_2 loading capacity. Different mole ratio, CO_2 partial pressure and total concentration of AMP-TEPA have been studied. TEPA has been observed as an excellent CO_2 loading activator in aqueous AMP solution. CO_2 loading is observed to increase up to 150 % with addition of TEPA upto 50 mole % in 1 M AMP solution at normal temperature and CO_2 partial pressure of 10 kPa. 1 M AMP-TEPA removes 3 times more CO_2 than 1 M MEA, however working with AMP-TEPA blend at higher concentrations proved challenging.

CONTENTS

CONTENTS CONTINUED….

LIST OF FIGURES

LIST OF TABLES

ABBREVIATION

AMP	2-amino-2-methyl-1-propanol
MEA	Monoethanolamine
DEA	Diethanolamine
TEA	Triethanolamine
DETA	Diethylenetriamine
MDEA	N-methyldiethanolamine
PZ	Piperazine
DIPA	Di-isopeopanolamine
DGA	Diglycoamine
KIER-C3	1,8-diamino-p-menthane
TETA	Triethylenetetramine
TEPA	Tetraethylenepentamine
CO_2	Carbon dioxide
GHGs	Greenhouse gases
ppmv	Parts per million by volume
CCS	Carbon Capture and Storage
CLC	Chemical looping combustion method
r_1, r_2, r_3	Rota meters
LPH	Liter per hour
α	Absorption capacity, mol of CO_2/mol of amine
M	Molar or molarity, mol/l

Chapter 1

INTRODUCTION

It is scientifically evident that human activities have caused concentrations of greenhouse gases (GHGs) to rise significantly over the last 200 years contributing to the global warming problem. Global concentration of CO_2 in the atmosphere is increasing rapidly. CO_2 emissions have an impact on global climate change. The desire to alleviate this problem has resulted in serious environmental concerns deriving from the need to reduce CO_2 emissions from various sources.

Carbon dioxide (CO_2) accounts for the largest portion of the world's annual emissions of GHGs, its emissions from industrial waste gases, particularly flue gases from coal-fired power stations, have become a major target for reduction. Global concentrations of CO_2 in the atmosphere have increased from pre-industrialization levels of approximately 280 parts per million by volume (ppmv) in around 1860 to approximately 316 ppmv in 1958 and rapidly to approximately 369 ppmv. Global CO_2 concentration is predicted to rise to above 750 ppmv by 2100 if no action is taken to address the current situation (Wang et al., 2011). Power generation from fossil fuel-fired power plants (e.g. coal and natural gas) is the single largest source of CO_2 emissions. However, fossil fuel fired power plants play a vital role in meeting energy demands. For instance, coal-fired power plants could be operated flexibly in meeting with varying demand. With growing concerns over the increasing atmospheric concentration of greenhouse gases, effective CO_2 emission abatement strategies such as Carbon Capture and Storage (CCS) are required to prevent this trend. The removal of CO_2 from gas streams can be achieved by a number of separation techniques including absorption into a liquid solvent, adsorption onto a solid, permeation through membranes, and chemical conversion. Among these techniques, absorption into a liquid solvent is the most suiTable process for removing.

It should be noted that although capture and transportation of CO_2 is feasible and technically proven, further investigation regarding the reliability and safety of long-term storage remains necessary. Also, other concepts have been explored, including: the separation and capture of CO_2 from flue gas and fuel gas using wet scrubbing technologies, membranes separation technique etc. The use of CO_2 as a by-product would not only have economic benefits but also simultaneously reduces the global climate change concern. The specific goal is to develop a new technology that has advanced beyond the pilot scale and are ready for large scale field tests that can achieve more CO_2 capture with less cost of electricity. Capture and separation costs are significant portion of the cost to sequester CO_2. Transportation and storage are generally a minor fraction of the total cost. If CO_2 capture from power plants is to make less severe option, then research and development will be critical to achieve wide scale distribution with acceptable economic and environmental impacts.

Since CO_2 separation is the first and most energy intensive step of carbon capture and sequestration, many research have been done to improve the current technology or developing of new approaches of CO_2 separation and capture. There are many technologies are available for CO_2 capture but none of currently available CO_2 capture processes are economically feasible, since they consume large amount of power and electricity. Thus, improved CO_2 capture technologies are vital if the promise of reducing GHGs emission is to be realized.

Traditionally absorption via aqueous alkanoamines have been the most favored technology for removing CO_2 from process and waste gas stream. Numbers of different types of alkanoamines are available for CO_2 absorption but each alkanoamines have their own absorption capacity and own limitation like reaction rate, efficiency, high energy and cost intensive. Therefore, search is on for new improved absorbent with higher rate and high absorption capacity for CO_2, low corrosiveness and low energy use. Such solvent will decrease both capital and operating cost. The commonly used solvents are aqueous solutions of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA),

diisopropanolamine (DIPA), and methyldiethanolamine (MDEA). These alkanolamines have been competing with another class of acid gas treating solvents, the sterically hindered amines. One of the most recognized amine of this class is 2-amino-2-methyl-1-propanol (AMP).The work of this project is a further step towards in search of a new reliable CO_2 capture absorbent. In this work most classical CO_2 capture technology, CO_2 absorption by blend of amine, has been chosen for improvement of CO_2 capture. This work focus on CO_2 absorption in aqueous blend of a sterically hindered 2-amino-2-methyl-1-propanol (AMP) and tetraethylenepentamine (TEPA).

1.1 Worldwide greenhouse gases (GHGs) emission

In 2005 the latest year for which data are available the Southeast (Alabama, Florida, Georgia, Mississippi, North Carolina, South Carolina, Tennessee, Virginia) accounted for approximately 20 percent of national GHG emissions and approximately 4 percent of global GHG emissions (Larsen et al., 2007). Energy use is the largest driver of GHG emissions, primarily the burning of fossil fuels in the electricity generation, transportation, and industrial sectors. The largest share of GHG emissions by gas for the Midwest, the United States, and the world is carbon dioxide, principally from the combustion of fossil fuels in various forms as shown in the Figure 1.1. CO_2 accounts for approximately 89 percent of total emissions in both the Midwest and the nation as a whole, but only 72 percent of emissions globally.

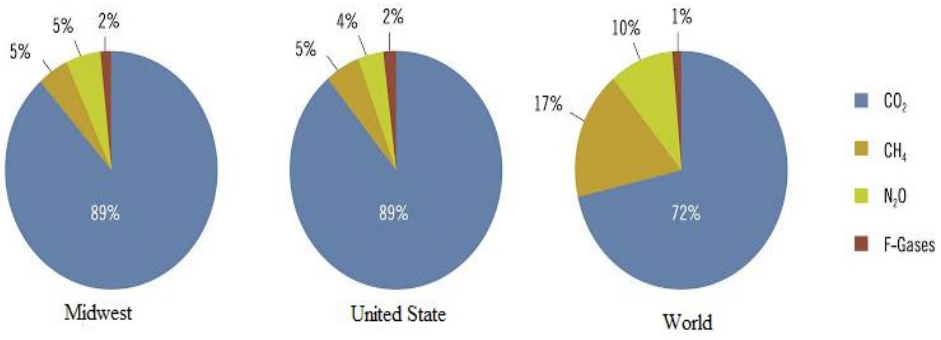

Figure 1.1: World GHGs emission profile by gas (Larsen et al., 2007).

Fluorinated gases (F-gases) which contributed 2 percent in Midwest and United State and contributed 1 percent of the world, are a family of man-made gases used in a range of industrial applications. Because they do not damage the atmospheric ozone layer, they are often used as substitutes for ozone-depleting substances. However, F-gases are powerful greenhouse gases, with a global warming effect greater than carbon dioxide (CO_2), and their emissions are rising strongly.

1.2 Global scenario of CO_2 emission

Since 1751 approximately 337 billion tons of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production (Boden et al., 2011). Half of these emissions have occurred since the mid 1970s. The 2007 global fossil-fuel carbon emission estimate, 8365 million metric tons of carbon, represents an all-time high and a 1.7% increase from 2006. Globally, liquid and solid fuels accounted for 76.3% of the emissions from fossil-fuel burning and cement production in 2007. Combustion of gas fuels (e.g., natural gas) accounted for 18.5% (1551 million metric tons of carbon) of the total emissions from fossil fuels in 2007 and reflects a gradually increasing global utilization of natural gas. Emissions from cement production (377 million metric tons of carbon in 2007) have more than doubled since the mid 1970s and now represent 4.5% of global CO_2 releases from fossil-fuel burning. Gas flaring, which accounted for roughly 2% of global emissions during the 1970s, now accounts for less than 1% of global fossil-fuel releases. Each of these scenarios are developed to illustrate one of a range of possible technological, economic and ecological futures. Every scenario imagines a world in which no explicit action is taken to reduce greenhouse gas emissions, but some scenarios explore worlds where "increased environmental awareness" lead independently to pollution controls and cleaner technology. The scenarios considered to be possible is one of the key factors contributing the large uncertainty in estimates of global warming effects during the 21st century. A set of scenarios was developed to represent the range of driving forces and emissions in the scenario so as to reflect current understanding and knowledge about underlying uncertainties. Any scenario necessarily includes subjective elements and is open to various interpretations. Emissions scenarios describe future releases

into the atmosphere of greenhouse gases, aerosols, and other pollutants and, along with information on land use and land cover, provide inputs to climate models (Table 1.1).

Table 1.1: Global fossil-fuel carbon emission estimation (Boden et al., 2011)

Year	total	Gas	Liquid	Solids	Cement Production	Gas Flaring	Per Capita
1990	6151	1020	2515	2419	157	40	1.16
1991	6239	1062	2624	2348	161	44	1.16
1992	6178	1094	2511	2372	167	35	1.13
1993	6172	1119	2541	2301	176	36	1.11
1994	6284	1133	2566	2361	186	38	1.12
1995	6422	1154	2588	2446	197	38	1.12
1996	6550	1208	2627	2473	203	39	1.13
1997	6663	1210	2703	2500	209	41	1.13
1998	6638	1243	2755	2395	209	37	1.11
1999	6584	1270	2703	2356	217	37	1.09
2000	6750	1288	2818	2370	226	48	1.10
2001	6916	1311	2827	2494	237	46	1.12
2002	6981	1346	2810	2525	252	48	1.11
2003	7397	1391	2935	2747	276	47	1.16
2004	7782	1431	3027	2971	298	55	1.21
2005	8086	1473	3071	3162	320	61	1.24
2006	8350	1519	3080	3333	355	62	1.27
2007	8543	1551	3074	3468	382	68	1.28
2008	8749	1616	3095	3578	386	73	1.30

1.2.1 Global fossil-fuel CO_2 emission

All fossil-fuel CO_2 emission estimates are expressed in million metric tons of carbon. To convert these estimates to units of carbon dioxide (CO_2), simply multiply these estimates by 3.667 Per capita emission estimates are expressed in metric tons of carbon. It is also to note that annual sums were tallied before each element (e.g., Gas) was rounded and differ slightly from the sum of the elements due to rounding. The graphs show recent and projected global emissions of carbon dioxide in Metric Tons in Figure 1.2 (Boden et al., 2011). Figure 1.3 shows per capita CO_2 emission current and projected for different countries and it is seen that CO_2 emission in India in 2030 will increase but in USA it will be decreased (Larsen et al., 2007).

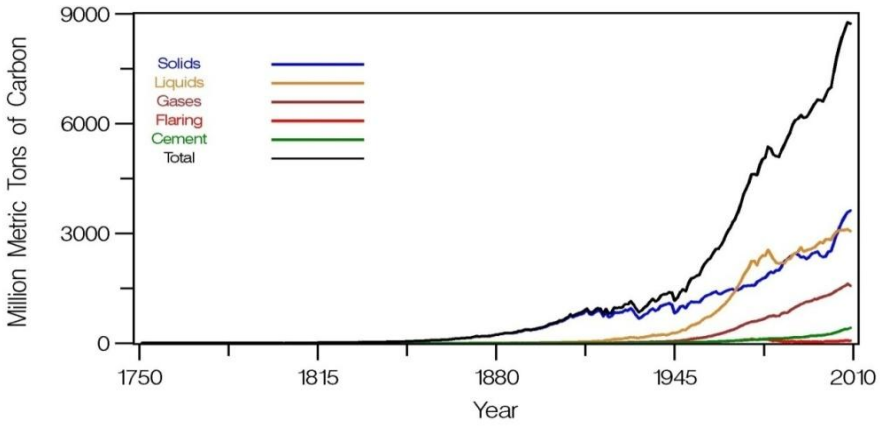

Figure 1.2: Fossil-fuel CO_2 emissions (Boden et al., 2011)

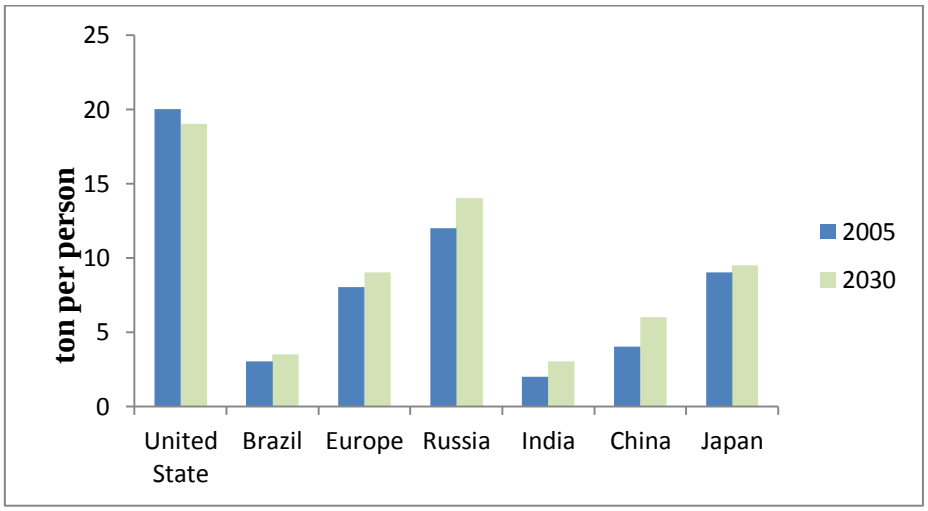

Figure 1.3: Per capita CO_2 emissions, current and projected (Larsen et al., 2007)

1.3 CO_2 capture technologies

There are several methods for CO_2 capture from gas streams such as the use of: chemical and physical solvents, membrane separation, etc. Equally, different plant configurations will require different CO_2 strategies such as:

1.3.1 Post-combustionCO_2 capture

As conventional approach is going through process improvements such as use of advanced solvent systems, new packing material, compact membranes and finally the use of electric swing absorption systems (Simmonds et al., 2003). Post-combustion capture is a downstream process that is analogous to flue gas desulfurization. It involves the removal of CO_2 from the flue gas produced after the combustion of the fuel. The oxidant used for combustion is typically air and hence, the flue gases are diluted significantly with nitrogen. In addition, since the flue gases are at atmospheric pressure, a large volume of gas has to be treated. A number of methods exist for the post-combustion capture of CO_2 from flue gases. These include:

- Chemical absorption
- Physical absorptions
- Membrane separation
- Adsorption
- Cryogenic separation

1.3.2 Pre-combustionCO_2 capture

In precombustion capture, the carbon content of the fuel is reduced prior to combustion, so that upon combustion, a stream of pure CO_2 is produced. Precombustion decarbonization can be used to produce hydrogen or generate electricity or both. A synthesis gas is produced in the first step of precombustion decarbonization. If natural gas is used as a fuel, this is obtained by either steam reforming or autothermal reforming. If coal is used as the fuel, synthesis gas is obtained by gasification. In the next step, the synthesis gas is subjected to the water gas shift reaction to produce carbon dioxide and hydrogen. The hydrogen

and carbon dioxide can be separated by absorption or physical absorption and the pure CO_2 stream is compressed and sent for storage

1.3.3 Oxy-fuel combustionCO_2 capture

Oxy-fuel combustion is a novel approach, uses recycled CO_2 to moderate the temperature of combustion of fuel with oxygen. This approach has been going through improvements in the use of air separation membrane systems and implementation of chemical looping combustion method (CLC). Oxy-fuel processes cover processes that employ oxygen instead of air as oxidizing agent and they are: (a) O_2/CO_2 combustion with oxygen from oxygen transport membranes, (b) advanced zero emission power concept, and (c) membrane reactor for end combustion. Practical oxy-coal combustion techniques have been developed in order to facilitate the conversion of coal-fired utility power plants so as to recover a CO_2 rich flue gas stream for use and sequestration (Chui et al., 2003).

1.3.4 Chemical looping combustionCO_2 capture

Chemical looping combustion (CLC) is an indirect combustion system that avoids the direct contact of fuel with the oxidant **(**Kothandaraman et al., 2010). Oxygen is transferred to the fuel via a solid oxygen carrier. The combustion system is split into two reactors. In the reduction reactor (also called the fuel reactor), the fuel reduces the solid oxide material which is then transported to the oxidation reactor where the reduced metal oxide is oxidized with air.

1.4 CO_2 capture by absorption

Chemical absorption systems at present are the preferred option for post-combustion capture of CO_2. Chemical absorption systems have been in use since the 1930s for the capture of CO_2 from ammonia plants for use in food applications and hence, are a commercially realized technology, though not at the scale required for power plants. CO_2 is separated from the flue gas by passing the flue gas through a continuous scrubbing system. Absorption processes utilize the

reversible chemical reaction of CO_2 with an aqueous alkaline solvent, usually an amine.

Although CO_2 capture can be technically implemented by a number of separation methods, yet gas absorption into liquid solvent is the most attractive because of its maturity in gas absorption in gas treating service. The technique has been proven to be effective in CO_2 absorption from stack gas in coal fired power plants, ammonia or hydrogen production, coal gasification, natural gas processing, synthesis gas processing and various refinery processes. Absorption of CO_2 is mass transfer phenomena in which CO_2 is transferred from gas phase to solvent (liquid) phase either by chemically or physically or both. The solvent can be regenerated reversibly from the absorbed mixture and gas will be available in pure form again. In physically or chemical absorption, the difference comes from chemical nature of solvent. In physical absorption process, the solvent capacity to absorb gas is a function of gas partial pressure in the absorption unit and depends on nature of solvent-gas pair. There is no reaction involved between gas and solvent. In physical absorption, the solvent capacity or loading, which initially follows Henry's law (for ideal non interacting gas mixture), assume an almost linear dependence on the gas partial pressure. The primary method of regeneration of solvent in physical absorption occurs by a simple pressure reduction in the system. This method of regeneration reduce the operating cost, but low absorption capacity of physical solvent may definitely a disadvantage for CO_2 removal process.

Energy costs play a significant role in the feasibility of any commercial CO_2 removal system. For amine based systems, the most significant energy demand is for the amine regeneration step. Primary amines typically have higher heats of absorption than secondary and tertiary amines. (Mohamed H. Al-Marzouqi et al., 2009).

In contrast to these single amine molecules, multi-amine molecules can contain more than one type of amine functionality, which suggests the possibility of

developing multifunctional amine sorbents that optimize their CO_2 capture behavior. In chemical absorption, CO_2 gas is physically absorbed in solvent as well as reaction between solvent and CO_2 is also observed. The solvent and CO_2 gas are reacted by a particular reaction of mechanism, may be complex one. These set of reaction are generally reversible. In chemical absorption, heating is necessary for solvent regeneration. Regeneration may be cost effective if process has large supply of low cost and sufficiently high temperature heat or steam available. However with much higher chemical solvent loading capacities, the solvent circulation rates are much lower, with high capital cost saving. Chemical absorption has been in use so much in commercial CO_2 removal application over six decades. A recent development in gas-treating processes is based on the use of aqueous solution of two amines in varying compositions. In this case, the high absorption capacity of one amine is combined with the high absorption rates of the other that lead to an improvement in the final CO_2 uptake.

1.4.1 Solvents for CO_2 chemical absorption

P. Greame et al., (2009) studied 76 different amines and screened their ability to absorb CO_2. These include primary, secondary, and tertiary amines, alkanolamines, polyamines of a mixed or single type, cyclic and aromatic amines, amino acids, and sterically hindered amines. The screening process involved an initial screening method using $BaCl_2$ to measure CO_2 absorption. Chemical solvent are basically classified into two categories, namely organic and inorganic. These amines can be used according to the cost, kinetics, corrosiveness. Recently the use of blended amines, a solution of two or more amines in varying compositions, shows considerable improvement in absorption and savings in energy requirements. Blended amines combine the absorption characteristics of the constituent amines such as a higher loading capacity and faster reaction rates. Blends of primary and tertiary amines, such as mixtures of AMP and TEPA, have been suggested for CO_2 removal. A comprehensive list of two types of chemical solvent is presented below:

a) Organic solvents

1. Monoethanolamine(MEA)
2. Diethanolamine(DEA)
3. 2-amino-2methyl-1propanol (AMP)
4. N-methyldiethanolamine(MDEA)
5. Piperazine(PZ)
6. Di-isopeopanolamine(DIPA)
7. Tetraethylenepentamine(TEPA)
8. Diglycoamine(DGA),etc.

b) Inorganic solvent

1. Ammonia
2. K_2CO_3/KOH
3. Na_2CO_3/NaOH

1.4.2 Reaction mechanism of amine with CO_2

Generally, primary and secondary amines (represented as R_1R_2NH) can react with dissolved CO_2 to form a carbamic acid (R_1R_2NCOOH) as in equation 1. Depending upon its acidity, it may then give up a proton to a second amine molecule forming a carbamate (R_1R_2NCOO) according to an overall stoichiometry as shown in equation 2. Via this pathway two moles of amine are consumed per mole of CO_2 if the carbamic acid is acidic, which is generally assumed to be the case. Kinetically and thermodynamically this reaction pathway is generally favored for primary and secondary amines (Puxty et al., 2009).The mechanism for the reaction can be represented by the following reactions.

$$CO_2 + R_1R_2NH \longleftrightarrow R_1R_2NCOOH \quad \ldots\ldots\ldots\ldots (1)$$

$$R_1R_2NCOO^- + H^+ \longleftrightarrow R_1R_2NCOOH \quad \ldots\ldots\ldots\ldots\ldots (2)$$

$$R_1R_2NH + H^+ \longleftrightarrow R_1R_2NH_2^+ \quad \ldots\ldots\ldots\ldots (3)$$

A second reaction pathway that also contributes to CO_2 absorption is CO_2 hydration to form bicarbonate. In this pathway an amine molecule (represented as

$R_1R_2R_3N$) simply acts as a proton accepting base, and possibly a catalyst, for the hydration of CO_2. The overall stoichiometry for this second pathway is given by equation 4 and 5. This pathway consumes one mole of amine per mole of CO_2, so in terms of capacity it is more efficient. For tertiary and some sterically hindered primary and secondary amines this is the only pathway contributing to absorption. However, this pathway is generally less favorable kinetically than carbamate formation (Puxty et al., 2009).

$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \text{.....} (4)$$

$$R_1R_2R_3N + H^+ \longrightarrow R_1R_2R_3NH^+ \text{.....} (5)$$

Assuming that either or both pathways can contribute to absorption for a given amine, the molar absorption capacity should vary between 0.5 and 1.0 if the reaction is driven to the products (which is the case if CO_2 (g) is constantly dosed). Both pathways depend on the availability of unprotonated base to accept a proton. The basic strength or pKa of a given amine will influence how far both of these reaction pathways can proceed to the products.

1.5 Properties of 2-amino-2methyl-1propanol (AMP)

AMP (2-amino-2-methyl-1-propanol) is Sterically hindered amine having molecular formula $C_4H_{11}NO$ and molecular weight 89.1362. Sterically hindered amines are amines in which a bulky alkyl group is attached on the amino group. As a consequences the reactivity is different from the alkanoamines. The advantages of this type of amine over alkanoamine is that only 1 mol of it required to react with 1 mol of CO_2 instead of 2 mol of alkanoamines. Steric hindrance occurs when the size of groups in a molecule prevents chemical reactions that are observed in related smaller molecules. Sterically hindered amines improve gas treating performance by modifying the reactions with CO_2. AMP is white crystals or viscous liquid used for the preparation of buffer solutions, suitable for the determination of alkaline phosphatase, CO_2 absorption etc. It is a clear light colored liquid. It is soluble in water and about the same density as water. Flash

point 172°F and used to make other chemicals. Common physical and chemical properties of AMP are given in Table 1.2.

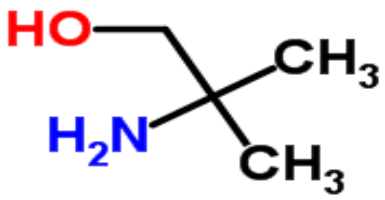

Figure 1.4: Structure of 2-Amino-2-Methyl-1-Propanol (AMP)

Table 1.2: Common physical and chemical properties of 2-Amino-2-methyl-1-propanol

Molecular Formula	$C_4H_{11}NO$
Vapor density	3 (vs air)
Molecular weight	89.14
Vapor pressure	<1 mmHg (25 °C)
Assay	≥95%
Impurities	≤0.005% Phosphorus (P)
Refractive index	1.4455
Useful pH range	9.0 - 10.5
pKa (25 °C)	9.7
Boiling point	165 °C
Melting point	24-28 °C
Solubility	H_2O: soluble 0.5 M at 20 °C, clear, colorless
Density	0.934 g/ml at 25 °C

1.5.1 Reaction mechanism of AMP with CO_2

The chemical equilibrium reaction takes place in the liquid phase when CO_2 is absorbed in an aqueous solution of AMP. It can be written with the following equations (Morteza et al., 2011).

$$2H_2O \longleftrightarrow H_3O^+ + OH^- \quad \textbf{……..……..... (6)}$$

$$2H_2O + CO_2 \longleftrightarrow H_3O^+ + HCO_3^- \quad \textbf{……..... (7)}$$

$$H_2O + HCO_3^- \longleftrightarrow H_3O^+ + CO_3^{-2} \quad \textbf{…… (8)}$$

$$H_2O + AMPH^+ \longleftrightarrow H_3O^+ + CO_3^{-2} \quad \textbf{…… (9)}$$

$$H_2O + AMPCOO^- \longleftrightarrow HCO_3^- + AMP \textbf{……... (10)}$$

The reaction between CO_2 and OH^- of the AMP group is negligible, so the only important reaction is between CO_2 and AMP which leads to the formation of bicarbonate ion. In this case, the stoichiometry between CO_2 and AMP is 1:1, as indicated by the reaction (11):

$$AMP + CO_2 + H_2O \longleftrightarrow AMPH^+ + HCO_3 \textbf{……..… (11)}$$

In this work, the following assumptions made for thermodynamic model: To simplify, we neglect the concentration of the ionic species CO_3^{-2}, OH^- in the aqueous liquid phase because of their very low concentration in comparison with the concentration of the other species.

1.6 Properties of Tetraethylenepentamine (TEPA)

The high performance of TEPA could be explained by its structural features where two primary and three secondary amine sites combine to enhance absorption rate and capacity. TEPA has shown outstanding CO_2 absorption potential. It maintained very high absorption rate and removes a large amount of CO_2. High viscosity of TEPA reduces the CO_2 absorption this could be explained by the higher viscosity of 2.0 M TEPA which led to reduced diffusivity resulting in reduced mass transfer rate thus absorption decreases. Presence of 5 amine sites

(two primary and three secondary) in TEPA (Figure 1.5) gives an indication of high absorption capacity. Common physical and chemical properties of TEPA are given in Table 1.3.

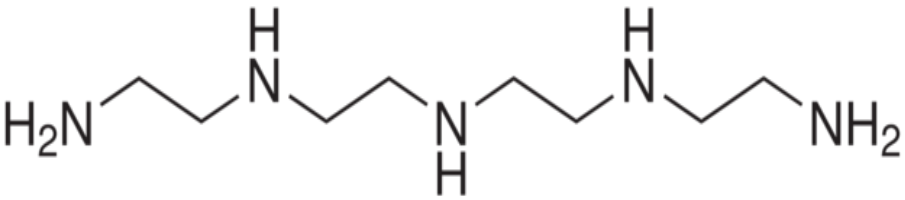

Figure 1.5: Molecular Structure of Tetraethylenepentamine (TEPA)

Table 1.3: Common physical and chemical properties of Tetraethylenepentamine

Vapor density	6.53 (vs air)
Vapor pressure	<0.01 mmHg (20 °C)
Autoignition temp.	610 °F
Refractive index	1.505
Boiling point	340 °C
Melting point	−40 °C
Density	0.998 g/mL at 25 °C

Chapter 2

LITRATURE REVIEW

A number of investigations have been made regarding CO_2 absorption from gas stream with use of different blends of amines. Use of aqueous blend of 2-amino-2-methyl-1 propanol (AMP) with other amine is quite popular since many years (Menghuiet et al., 1994, Kundu et al., 2006, Aroua et al., 2002, Kunihiko et al., 2009). Tetraethylenepentamine (TEPA) is also recognized as an effective absorbent for CO_2 absorption (Aronuet al., 2009, Singh et al., 2009, Al-Marzouqui et al., 2009). It is informative to study previous work of CO_2 removal applications with use of aqueous solution of 2-amino-2-methyl-1 propanol (AMP) and aqueous solution of Tetraethylenepentamine (TEPA). A brief summary of all CO_2 solubility related works carried out in above aqueous amine solutions are presented below for reference**.**

2.1 Experimental studies of CO_2 capture in 2-amino-2-methyl-1 propanol (AMP)/AMP blend

Menghui et al, (1994) observed the solubilities of carbon dioxide in water + Monoethanolamine (MEA) + (AMP). The solubilities of CO_2 in higher AMP mass fraction solutions were higher than those of solutions with a high MEA mass fraction.

Aroua et al., (2002) proposed the use of a sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP), for CO_2 capture applications. In his study, 2.0 M AMP solution showed the effect of both temperature and CO_2 partial pressure, the CO_2 loading increases with the CO_2 partial pressure and with decreasing temperature. Maximum loading capacity was achieved at 30^0C which is considered to be normal temperature. The addition of AMP to MDEA at the same total amine concentration (2 M) showed an improvement in CO_2 loading over the entire range of CO_2 partial pressure.

Kundu et al., (2006) Proposed that (AMP + MEA + H_2O) and (AMP + DEA + H_2O) appear to be attractive new blended amine solvents in addition to (MDEA + MEA + H_2O) and (MDEA + DEA + H_2O) blends for the gas-treating processes. They presented new experimental results for the CO_2 solubility in aqueous blends of diethanolamine (DEA) + 2-amino-2-methyl-1 propanol (AMP) in the temperature range of 303K to 323K and CO_2 partial pressure of 1 to 100 kPa. Solubility of CO_2 in aqueous solutions of mass fractions 1.5 % DEA and 28.5 % AMP at Temperature 303K and partial pressure 6.25 kPa was found as 0.648. As temperature increased absorption capacity decreased for this kind of blends. They also observed if mass fraction of DEA increased the loading capacity decreased.

Kunihiko et al., (2009) mentioned a patented a method for CO_2 absorption and cited that AMP promoted with piperazine (PZ) is the preferred solvent blend for Kansai Electric Power Company (KEPCO) and Mitsubishi Heavy Industries (MHI) Ltd in Japan under US Patent No: US6500397 (December 31, 2002). It is found that 2.5 M AMP maintained a significantly lower absorption rate than MEA, but achieved higher loading of 0.6 Promoting 2.5M AMP with 0.5M PZ resulted in a significant increase in rate as well as improved loading.

Zhu et al., (2012) found that cyclic capacity of AMP in mol CO_2/mol amine was found to be 70% higher than that of 5 M MEA. Aqueous 1,8-diamino-*p*-menthane (KIER-C3) and commercially available amine solutions were tested for CO_2 absorption. A 2-amino-2-methyl-1-propanol (AMP) solution with an addition of (1,8-diamino-*p*-menthane) KIER-C3 showed 9.3% and 31.6% higher absorption rate for CO_2 than the AMP solution with an addition of monoethanolamine (MEA) and ammonia (NH_3), respectively. A CO_2loading ratio of the AMP/KIER-C3 solution was also 2 and 3.4-times higher than that of the AMP/NH_3 solution and the AMP/MEA solution, respectively. Based on the experimental results, KIER-C3 may be used as an excellent additive to increase CO_2 absorption capability of AMP.

2.2 Experimental studies of Tetraethylenepentamine (TEPA)

To achieve high CO_2 capture Aronu et al.,(2009) observed tetraethylenepentamine (TEPA) as a solvent with high absorption capacity and fast kinetics. Their observation was based on absorption rate and capacity with different alkanoamines and alkanoamines mixture with different concentration. To provide a broad basis for comparison, different concentrations of MEA (e.g. 1.0 M, 2.5 M, 5.0 M and 10.0 M) were analyzed.

They observed the absorption rates versus loading (mol CO_2/mol solvent) curves at 40^0C for various systems tested. It was observed that 1.0 M and 2.0 M TEPA maintained consistently the highest absorption rates and reached the highest CO_2 loadings of 1.92 and 1.85 respectively when compared with other systems. It is however observed that the rates for 2.0 M TEPA were slightly lower than those for 1.0 M TEPA. 1 M TEPA removes 3 times more CO_2 per cycle than 1 M MEA.

Singh et al., (2009) studied to determine the structure and activity relationships of various amine-based CO_2 absorbents. They observed that an increase in the number of amine groups increased the capacity from 1.83 to 3.03 mol CO_2/mol amine.

Al-Marzouqui et al., (2009) also found that the CO_2 absorbance capacity of TEPA is far better than many other amines. The data presented showed that the removal rate of the amines increases with increasing the number of nitrogen atoms: tetraethylenepentamine (TEPA)> triethylenetetramine (TETA)> diethylenetriamine (DETA). The solvent with higher number of amino groups showed better performance in term of CO_2 removal. The CO_2 capacity for TEPA was observed upto 3 moles of CO_2 per mole of amine.

Furthermore, when the total absorption capacity of these absorbents was compared in unit of kg of CO_2 absorbed per mole of amine, results show that the absorption capacity did not increase with increase in number of amine group in the structure, for example ethylenediamine (where two amine groups are present)

could absorb up to 17.93 moles CO_2/kg amine, whereas tetraethylenepentamine (in which 5 amine groups are present) could absorb up to 15.98 moles CO_2/kg amine **(**Singh et al**.,** 2009).

1.0 M tetraethylenepentamine (TEPA) and 5.0 M MEA showed the best performance in terms of absorption rate. 1.5 M Bis-(3-dimethylaminopropyl) amine was easy to desorb, has high absorption capacity; and when promoted it showed the best performance in terms of CO_2 carrying capacity (Hoff et al., 2011).

2.3 Absorption Capacity of various amine and amine blends

The absorption rates versus loading (kilograms of CO_2 per kilogram of solute) curves for various systems tested are shown in Table 2.1. It can be observed that the 20% MEA + 10% DETA system maintained the highest average absorption rate and reached the highest CO_2 loading of 0.556 kg of CO_2/kg of solute when compared to other systems. The high performance of MEA solution with DETA additives could be explained by the structural feature of DETA, where two primary and one secondary amine sites combine to enhance the absorption rate and capacity in DETA. The 15% MEA + 15% MDEA system maintained the lowest average absorption rate and reached the lowest loading of 0.260 kg of CO_2/kg of solute. This phenomenon is quite easy to understand because MDEA usually maintains a lower absorption rate and lower capacity relative to MEA because of the secondary amine site and molecular-weight difference. Furthermore, for the additives of the same mass concentration, the enhancement effects on the absorption rate caused by the additives.

2.4 Absorbent selection

Generally, a good solvent must be characterized by high cyclic capacity, low reaction energy, low stripping energy, fast kinetics, low degradation rate, and easy operation. However, these characteristics should be confirmed by experiment only. Some general guidelines for choosing the additives of blends had been proposed to save time and efforts for experimental research. A two-level screening

method is applied to select the appropriate chemical agent and evaluate the performance of blends. As for this method, the parameters are classified into two categories, primary parameters and validation parameters. The primary parameters, which are based on molecular weight, boiling point, freezing point, density, viscosity, saturation vapor pressure, selectivity, corrosive characteristics, foaming behavior, price, etc. Validation parameters refer to the parameters deserved by experimental tests, such as removal efficiency, mass-transfer rate, cyclic capacity, absorption capacity, absorption rate, regeneration extent, stripping energy, degradation rate, irreversible reaction, and toxicity. Though all these properties are important in solvent selection, our main focus of selection is highly dependable upon absorption capacity and cost of the materials for this work.

Table 2.1: Absorption performance summary for different solvents (Zhu et al., 2012)

S. No.	Absorbent	Maximum loading(kg/kg)
1	10% MEA	0.403
2	20% MEA	0.373
3	30% MEA	0.364
4	25% MEA + 5% AEEA	0.409
5	20% MEA + 10% AEEA	0.520
6	25% MEA + 5% AMP	0.344
7	20% MEA + 10% AMP	0.301
8	25% MEA + 5% DETA	0.462
9	20% MEA + 10% DETA	0.556
10	25% MEA + 5% MDEA	0.331
11	20% MEA + 10% MDEA	0.302
12	15% MEA + 15% MDEA	0.260
13	20% MEA + 5% PZ	0.488
14	20% MEA + 10% PZ	0.428
15	20% MEA + 5% TETA	0.437
16	20% MEA + 10% TETA	0.452

Ouimet et al., (2009) reported the polyamines that include diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) or mixtures is currently using by Cansolv Technologies Ltd. But from the literature review (Singh et al., 2009), TEPA has shown best absorption capacity among TEPA, TETA, DETA and EDA. As from the literature it is clear that absorption capacity of TEPA is much better than other amines or blends of amines. Also absorption rate is quite high. AMP and TEPA both are low volatility and very less corrosion problems. Main focus of the project is to make blend of AMP + TEPA and study the loading capacity by changing different parameter like mole ratio, partial pressure, mole concentration, etc. The reason behind selection of the blend (AMP + TEPA) is their absorption capacity and use of various blend of AMP, as AMP + other amine is currently use by different industry for CO_2 absorption.

2.5 Literature gaps

From the literature survey 2-amino-2-methyl-1-propanol (AMP) is recognize as a amine with high CO_2 absorption capacity. Therefore, 2-amino-2-methyl-1-propanol (AMP) has proven promising constituents in different blends viz. AMP + KIERC3 and AMP + MEA for CO_2 loading capacities. Similarly tetraethylenepentamine (TEPA) has high loading capacity, high rate of reaction towards CO_2 removal from gas stream.

New or improved solvent with higher CO_2 absorption capacities, faster CO_2 absorption rate, high degradation resistance and low energy use for regeneration are always needed to reduce equipment size, capital cost and operating cost. The aqueous blend of AMP and TEPA has not been studied yet. In literature, there is no reference concerning the solubility of CO_2 in aqueous AMP + TEPA. On the basis of their specific properties towards CO_2 absorption, aqueous blend of AMP and TEPA is chosen for study of CO_2 absorption capacity. The scope of this work is to produce a new CO_2 aqueous blend with high absorption capacity with moderate cost.

Chapter 3

OBJECTIVE

The present work has been under taken with an objective to study CO_2 loading capacity in aqueous blend of 2-amino-2-methyl-1-propanol (AMP) and tetraethylenepentamine (TEPA). The CO_2 loading has been measured in packed column on a laboratory scale at atmospheric pressure. Experimental investigation of CO_2 absorption capacity is measured with variation in following parameters:

- Mole ratio of AMP and TEPA in blend
- Partial pressure of CO_2 in gas stream
- Total concentration of blend
- Comparison with literature values of different single or mixed amine solutions

Chapter 4

EXPERIMENTAL WORK

4.1Experimental Setup

For absorption of CO_2 into AMP-TEPA blend, absorption experiments are carried out in packed bed column at atmospheric conditions as shown in Figure 4.1. This apparatus therefore enables us to acquire first hand knowledge on the behaviour of solvent systems in carbon dioxide absorption process. The main units of the set up are

1. Packed column
2. Solvent cylinder
3. Compressor
4. CO_2 cylinder
5. Gas mixing chamber
6. Rotameters

4.1.1 Packed Column

It is vertical borosilicate glass tube of 5 cm internal diameter and 53 cm long. Packed bed column is a cylindrical column packed with cylindrical rings packing material. These packing enhance the surface area available for transfer operations. CO_2 gas mixture flows from bottom to top and solvent flows from top to bottom in a counter current manner.

4.1.2 Solvent cylinder

Solvent cylinder contain aqueous amine blend. Solvent will flow through a rotameter where flow rate is maintained and the outlet of the rotameter will flow from top to bottom of the column**.**

4.1.3 Compressor

It provides compressed air to the whole set-up. Air provide by compressor is used for mixing purpose and also to provide pressure to the solvent tank.

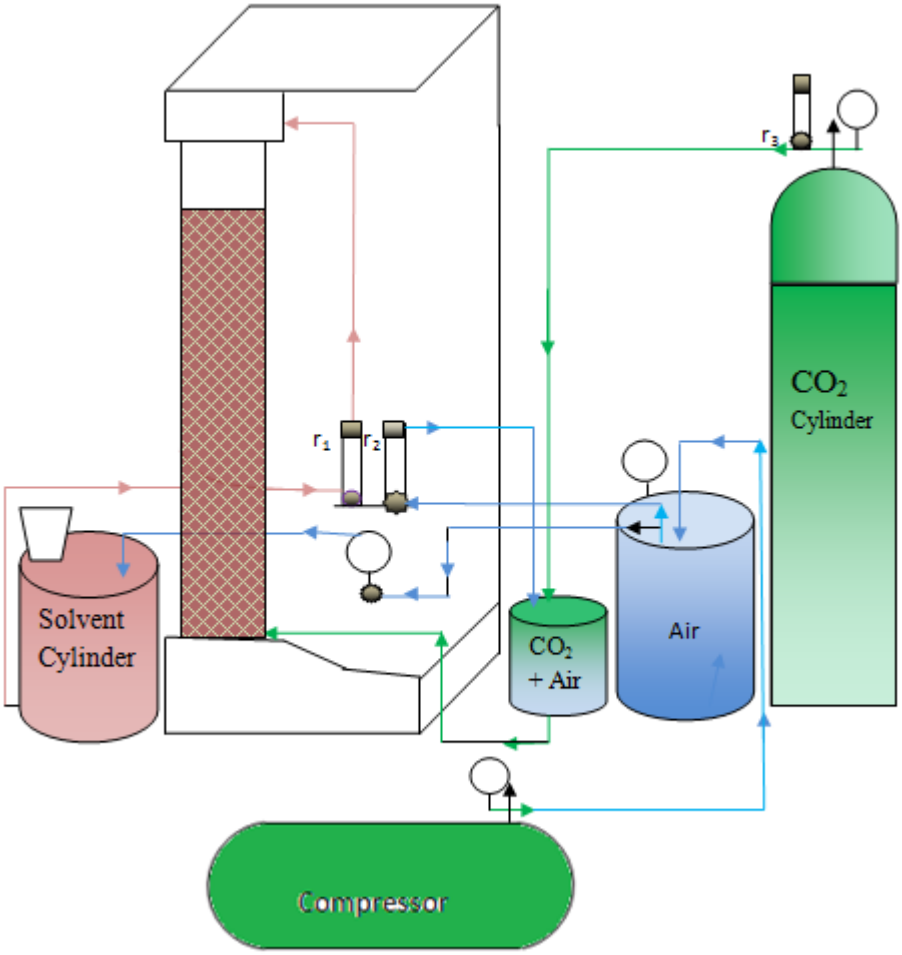

Figure 4.1: Experimental set-up of packed bed absorption column (r_1, r_2, r_3: rotameters)

4.1.4 CO_2 cylinder

CO_2 cylinder contains pure CO_2 with 99.99% purity. Firstly it mixes with air following compressor in mixing chamber and then flow bottom to top of the column.

4.1.5 Gas mixing chamber

Compressed air and CO_2 are supplied to the mixing tank mixed gas is sent to column.

4.1.6 Rotameters

Rotameter measures the flow rate of air, solvent, and CO_2 from the CO_2 cylinder.

In the Figure 4.1 there are three rotameters (R_1, R_2, R_3) present. Rotameter R_1 controls the absorbent flow rate, R_2 is used for gas flow rate and R_3 is connected to the CO_2 cylinder for measuring the flow rate of CO_2.

4.2 Chemicals used in present work

Following chemicals are used in present experimental work are given in Table 4.1:

Table 4.1: List of chemicals used in present work

Sr. no	Name of the chemical	Company name	Purity
1.	2-amino-2-methyl-1-propanol(AMP)	Loba Chemical	>95%
2.	Tetraethylenepentamine (TEPA).	TCI Chemical	>95%
3.	Barium Chloride Extrapure ($BaCl_2.2H_2O$)	Loba Chemical	99%
4.	Sodium Hydroxide (NaOH)	Loba Chemical	99%
5.	Hydrochloric Acid (HCl)	Loba Chemical	38% (12N)
6.	Methyl Red	Loba Chemical	99%

4.3 Experimental procedure

4.3.1 Preparations.

Sodium hydroxide solution (NaOH)

0.1 M Sodium hydroxide solution (NaOH) was prepared by dissolving 4 g of NaOH in deionized-distilled water and then made up volume to 1000 ml in volumetric flask.

Hydrochloric Acid (HCl)

1 M hydrochloric acid (HCl) was prepared by pipeting 83.33 ml of concentrated HCl (38% v/v) and made volume up to 1000 ml in a volumetric flask which was

again confirmed its molarity by taking 2 ml of HCl which was titrated by 0.1 M NaOH solution using phenolphthalein indicator.

Barium chloride solution

0.5 M Barium chloride ($BaCl_2$) was prepared by dissolving 122.13 g of barium chloride in deionized-distilled water and then made up to 1000 ml in a volumetric flask.

Methyl red indicator

Methyl red of 0.100 g was dissolved in 50.0 ml methanol and made up volume to 100.0 ml in a volumetric flask with deionized-water.

Glassware cleaning

All glassware, pipette tips, vials and other materials were carefully cleaned by washing with liquid detergent to remove dust or particulate remaining, after that, glasswares were rinsed with DI water and dried in an oven at 60^0C at least 24 h before use.

4.3.2 Measurement of CO_2 solubility data

1.2 litre of AMP-TEPA blend solutions is prepared in distilled water and pH the solution is measured as 11.22 (as shown in Table 5) and put into the solution tank. The solvent flows at a flow rate of 10 LPH with CO_2 partial pressure 10 kPa. After running few minutes the solution in the tank becomes empty (some solution still left in the tank) at that time the setup is made stopped and pH measure of outlet sample which absorb some amount of CO_2. After completing 1^{st} cycle pH of the blend is measured and found decreases to 10.44. Solution is again put to the solvent tank and mixed with solvent which are left in the solvent tank and then again setup is started to run. pH of the blend decreases as CO_2 is acidic in nature.

This procedure is continuously repeated unless and until the AMP-TEPA blend reached to saturation pH. Saturation pH means no further CO_2 absorption will take

place. 1 M AMP-TEPA (9:1) blend reached saturation after 17th cycle as shown in Figure 4.2. After reaching saturation analysis method is done.

Table 4.2: No. of cycles and corresponding pH for AMP-TEPA

No. of Cycles	pH
0	11.22
1	10.44
2	10.36
3	10.26
4	10.2
5	10.13
6	10.05
7	10
8	9.95
9	9.88
10	9.81
11	9.77
12	9.71
13	9.64
14	9.61
15	9.59
16	9.57
17	9.56
18	9.56
19	9.56

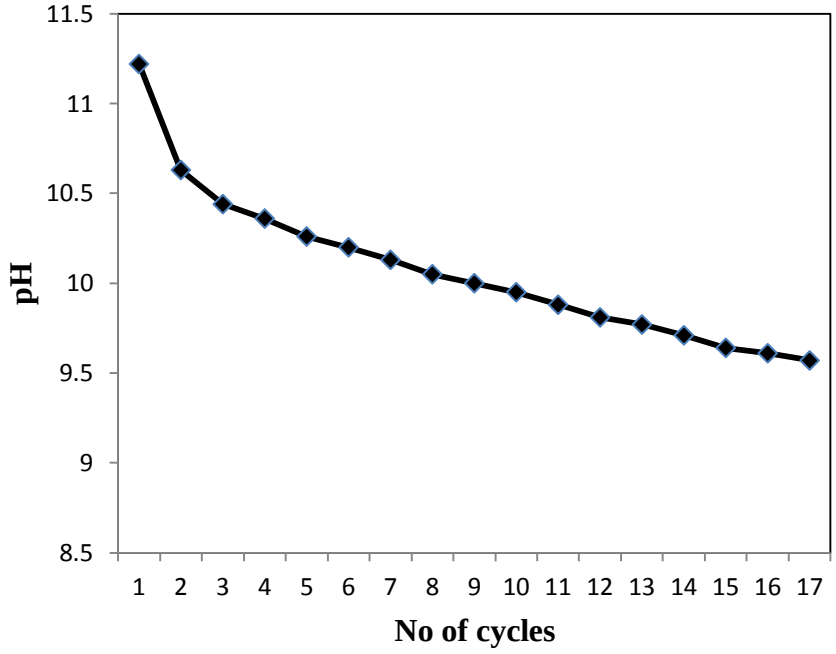

Figure 4.2: AMP-TEPA solutions pH Vs no. of cycles

When AMP (1 M) or AMP-TEPA (1 M) blend is prepared, colour of the blend is transparent. But during the absorption process when pH of the solution starts decreases or number of cycles increases, colour of the solution changes. In case of AMP colour of the solution is transparent at pH range 11.25 to 10.25, but becomes pink in the pH range10 to 9.25 as shown in the Figure 4.3. Similarly 1 M AMP-TEPA changes its colour to blue when reached saturation as shown in Figure 4.4.

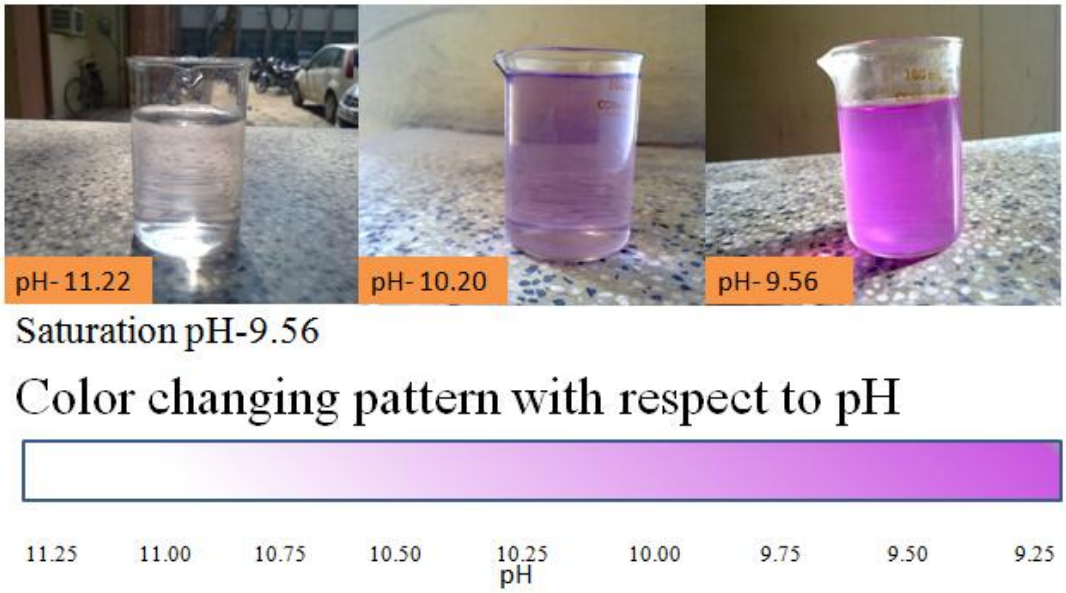

Figure 4.3: Colour changing pattern with respect to pH for 1 M AMP

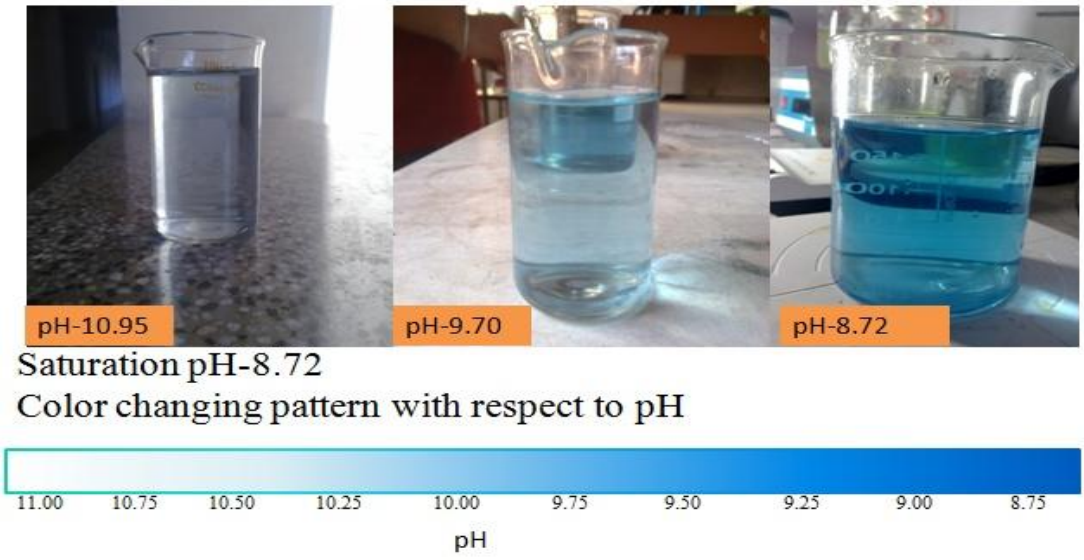

Figure 4.4: Colour changing pattern with respect to pH for 1 M AMP-TEPA

The experiments are carried out in a packed column with different molar ratio of aqueous blend of AMP-TEPA. For absorption of CO_2 into AMP-TEPA blend in packed column, column essentially operates at atmospheric pressure (101.325kPa). The CO_2 partial pressure in inlet gas stream is varied in a range of

10 kPa-40 kPa for observing the variation of CO_2 partial pressure. Initially, flow rate of the solvent is taken at 10 LPH and throughout the experiment the flow rate is kept constant.

CO_2 absorbent enters from the top of the absorber through a spray nozzle to ensure good initial liquid distribution to the packing material. The spray nozzle, which delivers fine mists, is placed 2.5 cm above the packing. Gases enter from the bottom of the absorber and gas flow rate is controlled by a rotameter. Before entering to the column CO_2 (99.99% pure) is mixed with compressed air and mixing ratio is maintained such that flue gas composition can be achieved. Gas flow rate was kept constant at 45 LPH. The baseline gas composition is 10% CO_2 and 90% air. Coal-fired flue gas nominally consists of 10-12% CO_2 on a dry basis. The temperature in packed column is normal (25°C to 32°C) during CO_2 absorption and during this series of tests, the temperature variations along the height of the packing have not been measured.

AMP reacts with CO_2 at a slower rate than TEPA. Though AMP reacts with CO_2 at a slower rate, less energy is required to drive out CO_2 from its CO_2 rich solution. The total concentration of AMP-TEPA blend is varied from 0.5 M to 3 M during experiment and AMP-TEPA molar ratio from 9:1 to 5:5.

Initially, 1.2 litre solution of 9:1 (AMP-TEPA) ratio is prepared in distilled water and its pH has been measured. After measuring its pH solution is fed into the solvent tank and run the setup. After completing one cycle pH of the outlet sample is measured and again fed to the solvent tank. During each process pH of the solution decrease as CO_2 is acidic in nature and absorbent is basic in nature. This process is repeatedly performed unless and until pH of the outlet solution has become constant. Here, constant pH represents that no more CO_2 will absorb further by the absorbent. When constant pH is achieved then analysis is done.

4.3.3 Analysis Method

AMP-TEPA reacts with CO_2 to form bicarbonate. Liquid samples containing all bound CO_2 for the experiments are analyzed by the barium chloride ($BaCl_2$) method. $BaCl_2$ concentration up to 0.5 M can precipitate the carbonate completely. $BaCl_2$ concentration in this range has high efficiency to precipitate carbonate completely. For this reason, an excess $BaCl_2$ concentration of 0.5 M is chosen. When $BaCl_2$ react with CO_2, it forms barium carbonate ($BaCO_3$). 0.5 M $BaCl_2$ solution has been added in excess to the 30 ml outlet sample taken from the packed column. Absorbed CO_2 has been precipitated as $BaCO_3$ and then the precipitation is filtered with the help of filter paper and allowed it to dry in oven at 80^0C. After drying 1.0 M HCl solution is added to complete dissolve the precipitation. The amount of hydrogen chloride (HCl) not used to dissolve $BaCO_3$ is titrated with 0.1 mol/l sodium hydroxide (NaOH) by using methyl red as a indicator with an end point of pH 5.0. Following reaction takes place during the titration method.

$$CO_2 + RNH_2 \longrightarrow RNHCOO^- + H^+ \quad \ldots\ldots\ldots (12)$$

$$RNHCOO^- + H_2O \longrightarrow RNH_2 + HCO_3^- \quad \ldots\ldots\ldots (13)$$

$$HCO_3^- + BaCl_2 \longrightarrow BaCO_3 + HCl \quad \ldots\ldots\ldots (14)$$

$$BaCO_3 + 2HCl \longrightarrow BaCl_2 + CO_2 + H_2O \quad \ldots\ldots\ldots (15)$$

The amount of HCl left can be determined by the titration with NaOH and we can find the total HCl reacted with $BaCO_3$. It can be seen from the equation (15) that for 1 mole $BaCO_3$ requires 2 mole of HCl and from the same equation it is also clear that 1mole CO_2 is formed from 1 mole of $BaCO_3$. The calculation procedure is shown with help of an example as following.

Calculations

Suppose,

Sample taken from column	=30 ml
Volume of HCL (1N) added	=65 ml
Volume of NaOH (0.1) Consumed	=130 ml

Total HCl Reacted with $BaCO_3$ = 1.0*65-(130*0.1)

=52 millimole (mmol)

$BaCO_3$formed during the reaction = 52/2

=26 mmol (from equation 9)

Moles of CO_2 absorbed/mole of amine = 26/30

=0.86 mol CO_2/mol amine

Chapter 5

RESULT AND DISCUSSION

5.1 Effect of mole ratio of 2-amino-2-methyl-1-propanol (AMP) and tetraethylenepentamine (TEPA) in CO_2 absorption

Effect of mole ratio of 2-amino-2-methyl-1-propanol (AMP) and tetraethylenepentamine (TEPA) on CO_2 loading has been determined in 5 different mole ratio of AMP-TEPA. The mechanism of CO_2 absorption into blended amine solution is very complex because the reaction of CO_2 takes place not only with one particular amine but with every amine in the blend. The exact kinetics of CO_2 absorption in the blended amine system is yet debatable and not entirely understood. The mole ratio of AMP-TEPA is chosen in a way such that total concentration becomes 1 M as shown in the Table 5.1. CO_2 partial pressure has been taken as 10 kPa at normal temperature. CO_2 loading capacity of 1 M AMP is 0.4 mol CO_2/mol amine at 10 kPa and in normal temperature.

The Figure 5.1 shows that the performance of an amine mixture (AMP-TEPA) and is characterized by a value of gas loading is higher than the values obtained from single amines (AMP). The addition of AMP to TEPA at the same total amine concentration shows an improvement in CO_2 loading over the entire range mole ration at a fixed temperature and partial pressure.

From the Figure 5.1 it is clearly shown the increase in the CO_2 absorption capacity with increasing the TEPA concentration at the same condition. Initially CO_2 absorption at 9:1 ratio is 0.51 mole CO_2/mol amine. Similarly, absorption capacity of ratio 9:2, 9:3 and 5:5 is 0.63, 0.75 and 1.00 respectively. It should be noted that in Figure 5.1 showing CO_2 absorption 0.4 mol CO_2/mol amine when TEPA is 0, it means data is for pure AMP. The nonlinear behavior of the blended AMP-TEPA solution is consistent with the behavior found in other blended system, such as MEA-AMP as reported by Sakwattanapong et al., (2009). Table 5.1 shown that mixing ratio 7:3 (AMP : TEPA) gives highest loading capacity than any other mixing ratio. In this experiment mixing is not exceeded below 5:5 ratios because

our main focus is to use TEPA as low as possible due higher cost of TEPA. The AMP-TEPA blend with the ratio 7:3 has the highest mass transfer while the blend with the ratio of 9:1 has the lowest transfer compared to other mixing ratios tested. This is because the addition of TEPA to AMP results in higher CO_2 absorption capacity due to an increase in diffusivity, solubility, enhancement factor and overall rate constant.

Table 5.1: CO_2 loading with mole ratio of AMP-TEPA at P_{CO_2}=10kPa

Mole ratio (AMP:TEPA)	Concentration of TEPA in mol%	Absorption capacity (α)
10:0	0	0.40
9:1	10	0.51
8:2	20	0.63
7:3	30	0.85
5:5	50	1.00
0:10	100	1.52

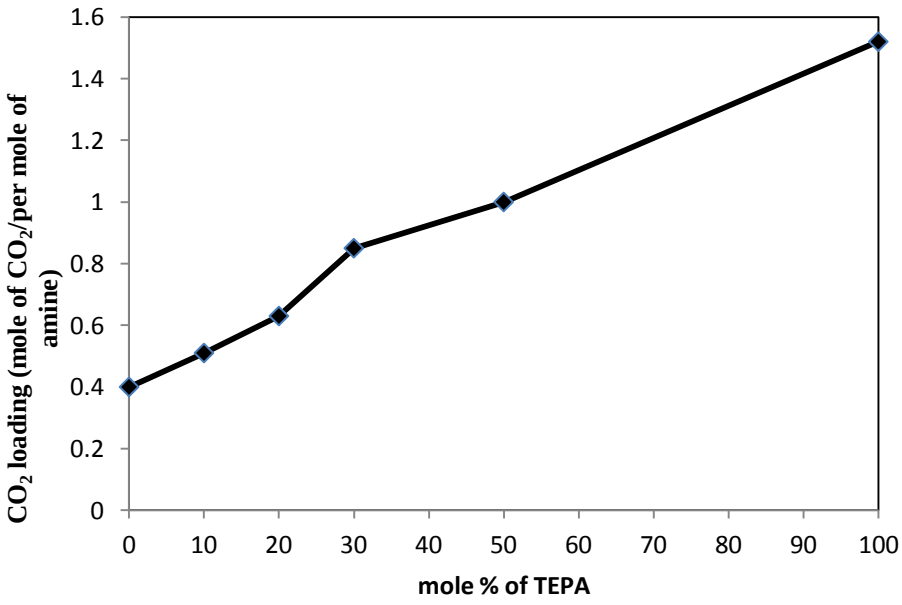

Figure 5.1: CO_2 loading with different mole percentage of TEPA (1 M)

5.2 Effect of CO_2 partial pressure in inlet gas stream

Table 5.3 shows the effect of CO_2 partial pressure on the ultimate CO_2 uptake of a 1.0 M AMP-TEPA blend with ratio7:3. Only 7:3 ratio is chosen because this ratio gives cost-effective high loading capacity than any other AMP-TEPA ratio. As expected, the loading increases with the CO_2 partial pressure at a fixed temperature (Figure 5.2). Despite being a primary amine, AMP-TEPA showed a loading of 1.03 (mol CO_2/mol amine). This result can be explained by the absence of carbamate in the system. The structure of AMP induces steric hindrance that is unfavorable for carbamate formation.

The inlet CO_2 partial pressure has been taken in range of 10 kPa-40 kPa. Effect in CO_2 absorption by changing partial pressure from 10 kPa-40 kPa is observed from 0.85-1.03 mole CO_2/mol amine and increase of value 0.18 mole CO_2/mol. Further increasing in CO_2 partial pressure does not affect much in absorption capacity as seen in Table 5.2 as 30 kPa gives loading capacity to 1 by increasing 0.90 from its previous value of 0.91, but at 40 kPa loading capacity approaches to 1.03 and increases very less from its previous value of 1.0 as shown in Table 5.2.

Table 5.2: CO_2 loading with partial pressure in inlet gas stream at normal temperature and 1.0 M AMP-TEPA (7:3) blend

Flow rate of CO_2 (LPH)	Flow rate of air (LPH)	Partial Pressure of CO_2 (P_{CO2})	CO_2 absorption capacity (α) (mol/mol)
5	45	10	0.85
10	40	20	0.91
15	35	30	1.00
20	30	40	1.03

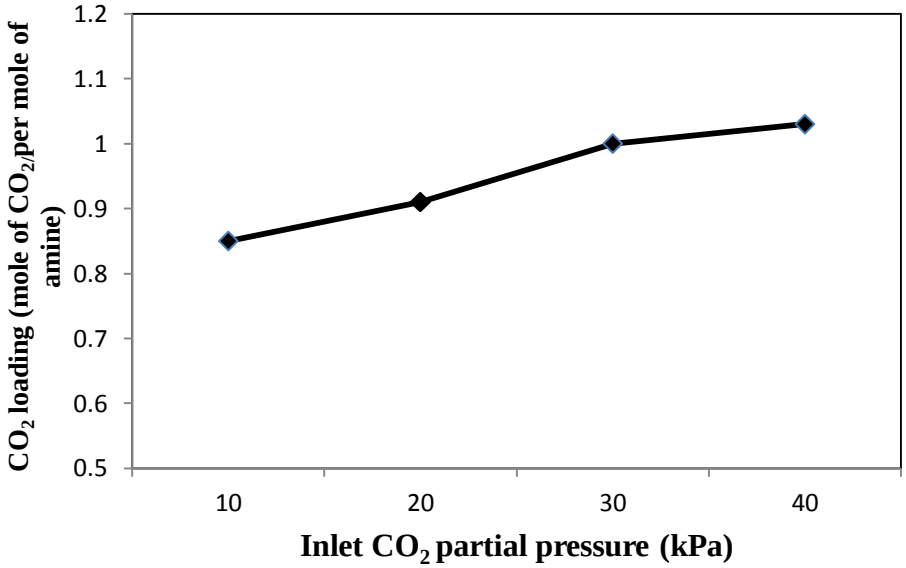

Figure 5.2: CO_2 loading with partial pressure for 1.0 M AMP-TEPA (7:3)

5.3 Effect of different mole concentration of AMP-TEPA blend

5.3.1 Effect of 1 M and 2 M with different moles ratio of blend

Loading capacity of 2 M AMP-TEPA blend is higher than 1 M blend with different mole ratio as mentioned in Table 5.3(a). Loading capacity (α=1.00) of 2 M blend with mole ratio 9:1 is nearly double than 1 M amine blend (α=0.51). It is also clear from the Figure 5.3(a) that loading capacity of 2 M AMP-TEPA blend increases than 1 M in all ratio. AMP-TEPA blend having 5:5 ratio gives higher value in both the cases shown Table 5.3(a) but amine blend having ratio 7:3 gives economically higher value because only 30 % TEPA is being used which is cost

Table 5.3(a): CO_2 loading capacity for 1 M and 2 M AMP-TEPA blend with different mole ratio at P_{CO_2}=10 kPa

Mole ratio (AMP:TEPA)	Concentration of TEPA in mol%	CO_2 loading (α) (mol/mol)	
		1M	2M
9:1	10	0.51	1.00
8:2	20	0.63	1.18
7:3	30	0.85	1.58
5:5	50	1.00	1.72

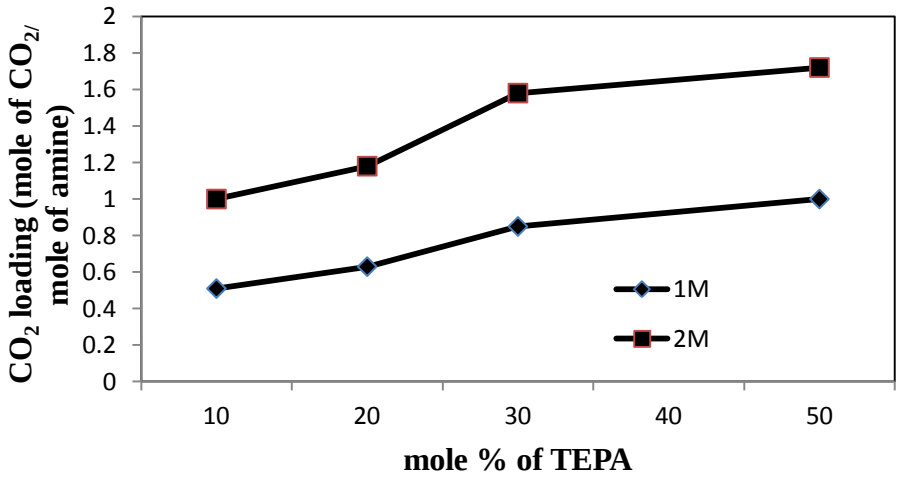

Figure 5.3(a): CO_2 loading capacity for 1 M and 2 M AMP -TEPA with different mole percent of TEPA at P_{CO2}=10 kPa**.**

effective rather than 50 % TEPA in case of 5:5 ratio. The effect of total concentration of AMP-TEPA blend on CO_2 loading has been observed at 10 kPa and at normal temperature and flow rate of 10 LPH. It is found that CO_2 absorption is economically maximum at 2 M of AMP-TEPA blend having mole ratio 7:3. The observed CO_2 loading are tabulated in Table 5.3(a) and these CO_2 loading are also plotted in Figure 5.3(a).

5.3.2 Effect of different mole with mole ratio 7:3 in CO_2 absorption.

CO_2 loading for fresh AMP-TEPA blends increases with total amine concentration. This is because more active TEPA and AMP molecules have ability to absorb high CO_2. From the Figure 5.3(b) it is clear that CO_2 loading in AMP-TEPA (7:3) blend continuously increased upto 2 M and showing highest absorption capacity of 1.57 mole of CO_2/per mole of amine. It is however observed that the CO_2 loading for 3.0M AMP-TEPA were slightly lower than those of 2.0 M AMP-TEPA blend. 3 M AMP-TEPA blend shows CO_2 loading of 1.48, (Table 5.3b) exhibited a decreasing nature. This could be explain by the higher viscosity of 3.0 M AMP-TEPA which led to reduced diffusivity resulting in reduced mass transfer rate thus, slight decreased in rate. The same behavior of

decreasing CO_2 capacity for TEPA at higher moles was observed by aronu et al., (2009).

Table 5.3(b): Effect of different mole with mole ratio 7:3 in CO_2 absorption

Moles of AMP-TEPA(7:3)	CO_2 absorption capacity (mol/mol)
0.5	0.40
1	0.85
2	1.57
3	1.48

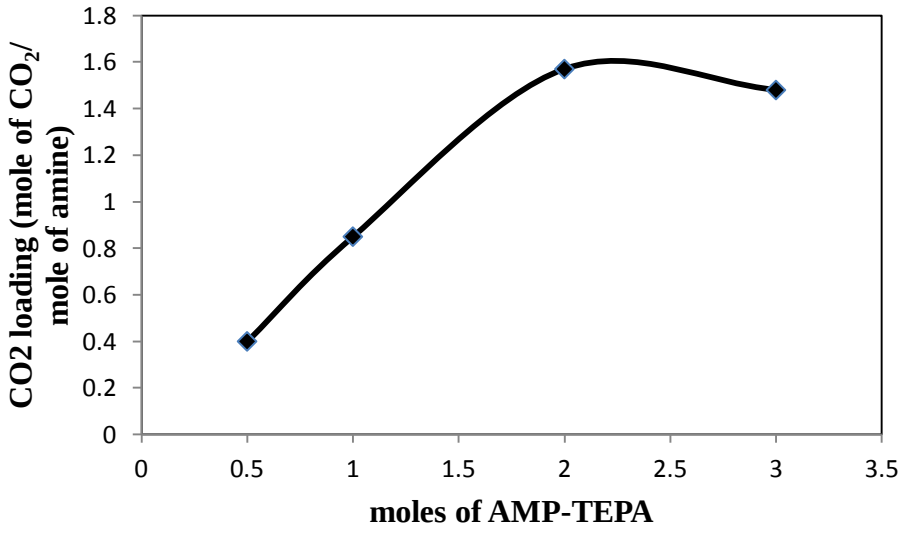

Figure 5.3(b): Effect of different mole concentration of AMP-TEPA blend (7:3)

5.4 Comparison of present work with literature values

A comparison of present work's CO_2 loading capacity with other blend's maximum CO_2 loading capacity available in literature are given in Table 5.4. This comparison shows AMP-TEPA blend is one of the best blend.

Table 5.4: Comparison of maximum CO_2 loading of AMP-TEPA (7:3) blend with other blends available in literature

S. No	Amine Blend, total Concentration of blend	CO_2 loading (mole of CO_2/mole of amine)	References
1.	AMP + TEPA (1M)	0.85	Present work
2.	AMP + TEPA (2M)	1.58	Present work
3.	MDEA + PZ	0.75	Ali and Aroua (2004)
4.	AMP + MDEA	0.71	Aroua et al., (2002)
5.	DEA+ MDEA	0.706	Benamor and Aroua (2005)
6.	DEA + MDEA	0.690	Kundu and Bandyopadhyay (2006)
7.	DEA + PZ .	0.662	Mondal et al., (2009)
8.	AMP + TEG	0.611	Zheng et al., (2012)
9.	DEA + AMP	0.614	Seo and Hong (1996)
10.	7 DEA + MDEA	0.585	Murrieta-Guevara et al., (1998)
11.	MDEA + PZ .	0.561	Jenab et al., (2005)
12.	MDEA + PZ	0.500	Liu et al., (1999)
13.	DEA + MDEA	0.492	Austgen et al., (1991)
14.	TIPA + PZ	0.271	Daneshvar et al., (2004)

Chapter 6

CONCLUSIONS

On the basis of experimental study, following conclusions have been made:

1. TEPA has been observed as an excellent CO_2 loading activator in aqueous AMP solution. CO_2 loading is observed to increase upto 150% with addition of TEPA upto 50 mole % in 1 M AMP (9:1) solution at normal temperature and CO_2 partial pressure of 10 kPa.

2. CO_2 loading capacity of AMP-TEPA blend (7:3) is increased (from 0.4 to 1.58) in total concentration range of 0.5-2.0 M and decreased (1.58 to 1.47) after total concentration of 2 M. Decrease in CO_2 loading can be explained by high viscosity of solution at higher concentration of AMP-TEPA blend.

3. It is also concluded that AMP-TEPA blend (1 M) gives the best economic loading capacity 0.85 mol/mol at molar ratio of 7:3.

4. CO_2 loading in 1 M blend has increased with CO_2 partial pressure in range 10 kPa to 30 kPa, but with further increase in the CO_2 partial pressure has shown very less increase in the CO_2 loading.

5. CO_2 loading in AMP-TEPA blend (1 M-2 M) has been found to be a superior to other blends viz. DEA-AMP, MDEA-PZ, MDEA-AMP available in literature at normal temperature and pressure.

References

Ali, B. S.; Aroua, M. K. Effect of Piperazine on CO_2 Loading in Aqueous Solutions of MDEA at Low Pressure. *Int. J. Thermophys*. **2004**, 25, 1863–1870.

Al-Marzouqui, H. M.; Marzouk, M. S.; El-Naas, H. M.; Abdullatif, N. CO_2 Removal from CO_2-CH_4 Gas Mixture Using Different Solvents and Hollow Fiber Membranes: Ind. *Eng. Chem. Res*., **2009**, 48, 3600–3605.

Aronua, U.E.; Svendsena, H.F.; Hoffb, K.A.; Juliussenb,O. Solvent Selection for Carbon Dioxide Absorption. *Energy Procedia*, **2009**, 1, 1051–1057.

Aroua, K. M.; Sulaiman, H. Z. M.; Ramasamy, K. Modelling of Carbon Dioxide Absorption in Aqueous Solutions of AMP and MDEA and Their Blends Using Aspenplus. *Separation and Purification Technology*, **2002**, 29, 153–162.

Austgen, D. M.; Rochelle, G. T.; Chen, C. Model of Vapor-Liquid Equilibria for Aqueous Acid Gas-Alkanolamine Systems. 2. Representation of H_2S and CO_2 Solubility in Aqueous MDEA and CO_2 Solubility in Aqueous Mixtures of MDEA with MEA or DEA. *Ind. Eng. Chem. Res*. **1991**, 30, 543–555.

Benamor, A.; Aroua, M. K. Modeling of CO_2 Solubility and Carbamate Concentration in DEA, MDEA, and Their Mixtures Using the Deshmukh_Mather Model. *Fluid Phase Equilib*. **2005**, 231, 150–162.

Boden, Tom; M. Gregg; B. Andres, Global CO_2 Emissions from Fossil-Fuel Burning,Cement Manufacture, and Gas Flaring: 2011,1751-2008.

Chui, E. H., M. A. Douglas, and Y. Tan .Modeling Of Oxy-Fuel Combustion for A Western Canadian Sub-Bituminous Coal. *Fuel,* **2003**, 82, 1201-1210.

Daneshvar, N.; Moattar, M. T. Z.; Abdi, M. A.; Aber, S. Carbon Dioxide Equilibrium Absorption in the Multicomponent Systems of CO_2+TIPA+MEA+H_2O, CO_2+TIPA+PZ+H_2O,and CO_2+TIPA+H_2O at Low CO_2 Partial Pressures: Experimental Solubility Data, Corrosion Study, and Modeling with Artificial Neural Network. *Sep. Purif. Technol*. **2004**, 37, 135–147.

Hoff, K. A.; Aronua,U.E; Hallvard F. Svendsen. CO_2 Capture Solvent Selection by Combined Absorption–Desorption Analysis. *Chemical Engineering Research and Design* **2011**, 89, 1197–1203.

Jenab, M. H.; Abdi, M. A.; Najibi, S. H.; Vahidi, M.; Matin, N. S. Solubility of Carbon Dioxide in Aqueous Mixtures of N-Methyldiethanolamine + Piperazine + Sulfolane. *J. Chem. Eng. Data* **2005**, 50, 583–586.

Kundu, M.; Bandyopadhyay, S. S. Solubility of CO_2 in Water + Diethanolamine + 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data*, **2006**, 51, 398-405.

Kundu, M.; Bandyopadhyay, S. S. Solubility of CO2 in Water + Diethanolamine + N-methyldiethanolamine. *Fluid Phase Equilib*. **2006a**, 248, 158–167.

Kunihiko, Y.; Tomio, M.; Shigeru, S.; Mutsunori, M.; Masaki,J.; Touru, S.; Mitsuoka,S.; Shigeaki. Method for Removing Carbon Dioxide from Combustion Exhaust Gas; *Patent No: US6500397*, **2002**.

Larsen, J.; Thomas, D.; and Ryan L. Charting the Midwest: An Inventory and Analysis of Greenhouse Gas Emissions in America's Heartland. Washington, DC: **2007**.

Lee, S. S.; Mun, M. S.; Choi, J. W.; Min, M. B.; Cho, W. S.; Oh, J. K. Absorption Characteristics of New Solvent Based on a Blend of AMP And 1,8-Diamino-P-Menthane for CO_2 Absorption. *Journal of Environmental Sciences*, **2012**, 24, 897-902.

Li, H. M.; Chang, C. B. Solubilities of Carbon Dioxide in Water + Monoethanolamine + 2 -Amino -2-methyl-1-propanol. *J. Chem. Eng. Data*, **1994**, 39, 448-452.

Liu, H.; Zhang, C.; Xu, G. A Study on Equilibrium Solubility for Carbon Dioxide in Methyldiethanolamine_Piperazine_Water Solution. *Ind. Eng. Chem. Res*. **1999**, 38, 4032–4036.

Ma'mun, S.; Nilsen, R.; Svendsen, F. H. Solubility of Carbon Dioxide in 30 mass % Monoethanolamine and 50 mass % Methyldiethanolamine Solutions. *J. Chem. Eng. Data*, **2005**, 50, 630-634.

Mazen, M.; Khader, A.; Recent Progress in CO_2 Capture /Sequestration:A Review. *Energy Sources*, **2006**, Part A, 28:1261–1279.

Mondal, M. K. Solubility of Carbon Dioxide in an Aqueous Blend of Diethanolamine and Piperazine. *J. Chem. Eng. Data*, **2009**, 54, 2381–2385.

Murrieta-Guevara, F.; Rebolledo-Libreros, M. E.; Romero- Martinez, A.; Trejo, A. Solubility of CO_2 in Aqueous Mixtures of Diethanolamine with Methyldiethanolamine and 2-Amino-2-methyl-1- propanol. *Fluid Phase Equilib*. **1998**, 150-151, 721–729.

Mohamed H. Al-Marzouqi,; Sayed A. M. Marzouk,; Muftah H. El-Naas,; Nadia Abdullatif. CO_2 Removal from CO_2-CH4 Gas Mixture Using Different Solvents and Hollow Fiber Membranes. *Ind. Eng. Chem. Res*., **2009**, 48, 3600–3605.

Ouimet, A. M. Process for The Recovery of Carbon Dioxide from a Gas Stream. Patent number: US7601315, **2009**.

Puangploy, P. Detrminartion of Microbial Biomass Gases Using Titration and Headspace Gas Chromatography. A thesis report, applied analytical and organic chemistry, Mahidol University; **2007**.

Puxty, G.; Rowland, R.; Allport, A.; Yang, Q. I.; Bown, M.; Burns, R.; Maeder, M.; Attalla, M. Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines. *Environ. Sci. Technol*, **(2009),** 43, 6427–6433.

Robinson, K.; McCluskey, A.; Attalla, M. I. The Effect Molecular Structural Variations Has on the CO_2 Absorption Characteristics of Heterocyclic Amines. ACS Symposium Series; *American Chemical Society*: Washington, DC,10.1021, **2012**, bk-2012-1097.ch001.

Sakwattanapong, R.; Aroonwilas, A.; Veawab, A. Reaction Rate of CO_2 in Aqueous MEA-AMP Solution: Experiment and Modeling. *Energy Procedia*, **2009**, 1, 217-214.

Seo, D.; Hong, W. Solubilities of Carbon Dioxide in Aqueous Mixtures of Diethanolamine and 2-Amino-2-methyl-1-propanol. *J. Chem. Eng. Data* **1996**, 41, 258–260.

Simmonds, M., Hurst, P., Wilkinson, M. B., Watt, C., and Roberts, C. A. A Study of Very Large Scale Post Combustion CO_2 Capture at a Refining & Petrochemical Complex. *Greenhouse Gas Control Technologies, Vols. I and II, Proceedings*, **2003**, 39–44.

Singh, P.; Niederer, J.P.M.; Versteeg, G.F. Structure and Activity Relationships for Amine-Based CO_2 Absorbents-II, *Chemical Engineering Research and Design*, **2009**, 87, 135–144.

Wang, M.; Lawal, A.; Stephenson, P.; Sidders, J.; Ramshaw, C.; Yeung, H. Post-combustion CO_2 Capture with Chemical Absorption: A State-of-the-art Review. *Chemical Engineering Research and Design*, **2011,** 89, 1609-1624.

Yoshida Kunihiko, Mimura Tomio, Shimojo Shigeru, Karasaki Mutsunori, Iijima Masaki, Seto Touru, Mitsuoka Shigeaki; Method for Removing Carbon Dioxide from Combustion Exhaust Gas; Patent No: US6500397, **2002**.

Zhu, D.; Fang, M.; Lv, Z.; Wang, Z.; Luo, Z. Selection of Blended Solvents for CO2 Absorption from Coal-Fired Flue Gas. Part 1: Monoethanolamine (MEA)-Based Solvents. *Energy Fuels* , **2012**, 26, 147–153.