People's Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

Amar Telidji University – Laghouat

Faculty of Technology

Department of Process Engineering

Specialty: Gas Engineering

Master's degree Thesis

Theme

Impact and performance of activator addition on the kinetics of CO_2 absorption into aqueous MDEA solutions using stopped-flow technique

Presented by

- Hadjer Boumediene
- Manal Ramlia Ziani

Supervisory and Examining Committee :

- Dr Ahmed abdelmouiz — Supervisor
- Dr Omar Mechraoui — Chair of Defense
- Dr Khaled Merigui — Examiner
- Dr Mouhoub Birane — Guest of Honor

Academic year: 2024/2025

Acknowledgements

All praise is due to Allah, by whose grace good deeds are accomplished. We thank Him for granting us the strength and perseverance to complete this work, and we ask that it brings benefit and goodness.

We extend our deepest gratitude and appreciation to our supervisor, Dr Ahmed Abdelmouiz, who has been a source of support and guidance. His valuable advice and encouragement made what once seemed difficult much more manageable and gave us the confidence to move forward.

We would also like to express our sincere thanks to the esteemed members of the examination committee, Dr Khaled Merigui, Dr Omar Mechraoui, and Dr Mouhoub Biran, for their time and efforts in evaluating our work and for contributing to our academic journey.

We extend our heartfelt gratitude to all the staff of Amar Telidji University, Laghouat, especially to the faculty and staff of the process Engineering Department.

Finally, we offer heartfelt thanks to everyone who joined us and shared this important moment, offering their support and encouragement.

Dedication

To my dear parents, your continuous support, unwavering encouragement, and your presence beside me every step of the way have been the greatest strength throughout my academic journey. Thank you from the bottom of my heart for providing me with everything I needed to reach this moment.

To my dear brother, Sadek, You have always been my pillar of strength and my companion, and having you by my side made everything feel less difficult.

To my sister-in-law, Thank you for being something precious and a beautiful addition to our family. I wish you both happiness and success always.

To my beloved grandmother, Thank you for your heartfelt prayers that have always accompanied me through every stage of my life.

To my uncles and aunts,Thank you for your encouragement and your prayers, which meant so much to me along the way.

To my dearest friends, (Fatima and Anfal) From you, I learned the true meaning of friendship, love, and sharing. And even though we sometimes disagree or go through moments of misunderstanding, the kindness in your hearts and the deep bond between us always bring us back together. Thank you for being my support.

To my research partner Manal, thank you for your contribution and cooperation throughout the project.

To the two wonderful friends whose friendship lit up my last two academic years Maroua and jamila, thank you for being the most beautiful part of these two years.

And finally, to all the professors who fulfilled their educational mission with sincerity and passion, my deepest gratitude for your efforts, dedication, and all the knowledge and values you instilled in us. A special thank you to Dr. Ahmed Abdelmouiz, whose guidance and support left a lasting impact on my academic journey.

This success is not mine alone… it belongs to everyone who stood by my side on this journey.

Hadjer

Dedication:

With the expression of my gratitude, I dedicate this modest work to those to whom, whatever the terms used, I will never be able to express my sincere love.

To man, my precious gift from God, to whom I owe my life, my success, and all my respect: my dear father, Ziani Hamadi.

To the woman who suffered without letting me suffer, who never said no to my demands, and who spared no effort to make me happy: my adorable mother, Touhami Fatoum.

To my dear sisters: Hana, Isra, and my dear brothers: Karim, Yacine, who never ceased to encourage and support me throughout my studies. May God protect them and grant them luck and happiness.

To my grandmothers, my uncles, and my aunts. May God grant them a long and happy life.

To all the cousins and friends I have known so far. Thank you for their love and encouragement.

And let's not forget my partner Boumediene Hadjer for his moral support, patience, and understanding throughout this project.

Manal

Abbreviations

AAD : Absolute Average Deviation

a-MDEA : Activated Methyldiethanolamine.

AGRU : Acid Gas Removal Unit.

AMP : 2-Amino-2-methyl-1-propanol.

DEA : Diethanolamine.

DGA : Diglycolamine.

DIPA : Diisopropanolamine.

MDEA : Methyldiethanolamine.

MEA : Monoethanolamine.

MMSCFD : Million Standard Cubic Feet per Day.

NMR : Nuclear Magnetic Resonance.

PSA : Pressure Swing Adsorption.

PZ : Piperazine.

Sul : Sulfolane

TEA : Triethanolamine.

TSA : Temperature Swing Adsorption.

List of Figures

Figure I. 1: Membrane separation technology in CO2 Capture 14
Figure I. 2: Acid gas removal using membrane 14
Figure I. 3: Simplified process diagram (AGRU) (Krechba, In Salah, Algeria) 19

Figure II. 1: Experimental equipment for measuring the CO2 absorption rate. (A) Stirred cell reactor; (B) wetted wall column; (C) laminar jet absorber; and (D) wetted sphere absorber. 24
Figure II. 2: Experimental equipment for measuring the CO2 absorption rate: stopped-flow apparatus.. 26
Figure II. 3: Zwitterion structure 28
Figure II. 4: Schematic drawing of single-step termolecular reaction mechanism (Crooks and Donnellan, 1989) 28

Figure III.1: Chemical structure of the selected amines in this study 37
Figure III.2: Schematic diagram of stopped-flow equipment showing the major units 38
Figure III.3: A graphical plot of the stopped-flow experiment at a set temperature 41
Figure III.4: Comparison of k0 values for CO2 reaction with aqueous MEA with those published by Sodiq et al., (2014) at different temperatures and concentrations 42
Figure III.5: Plot of pseudo-first-order reaction rate constants K0 versus MDEA concentrations at different temperatures 47
Figure III.6: Arrhenius plots of aqueous (CO2-MDEA) rate constants using base catalysis mechanism. 48
Figure III.7: Comparison of Arrhenius plots of aqueous (CO2-MDEA) rate constants of this work and the literature 49
Figure III.8: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 10 mol/m3)] solutions at different concentrations and temperatures. 51
Figure III.9: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 10 mol/m3)] solutions at different concentrations and temperatures. 51
Figure III.10: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 30mol/m3)] solutions at different concentrations and temperatures. 52
Figure III.11: K0 values of the reaction between aqueous CO2 and aqueous [MDEA/ PZ (40mol/m3)] at different concentrations and temperatures. 52
Figure III.12: Parity plot for the experimental and predicted pseudo first-order rate constants for aqueous solutions of (MDEA+PZ) at different temperatures using Zwitterion mechanism. 54
Figure III.13: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 10 mol/m3] solutions at different concentrations and temperatures. 55
Figure III.14: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 50 mol/m3] solutions at different concentrations and temperatures. 55
Figure III.15: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 100 mol/m3] solutions at different concentrations and temperatures. 56

Figure III.16: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 150 mol/m3] solutions at different concentrations and temperatures. 56
Figure III.17: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 200 mol/m3] solutions at different concentrations and temperatures. 57
Figure III.18 : Variation of k2 as function of temperature for aqueous (CO2+MDEA) and aqueous (CO2+MDEA+Sulfolane) systems 59

List of tables

Table I. 1: Overall comparisons of natural gas purification technologies 17

Table III. 1: Experimental kinetic data for (CO_2-MDEA-Water) at different temperatures..................... 46
Table III. 2: Second-order rate constants (K_2) of MDEA with CO_2 at different temperatures 49
Table III. 3: Rate constants regressed using Equation III.10 for aqueous (MDEA+PZ) systems 53
Table III. 4: Reaction orders of aqueous (MDEA + Sulfolane) systems at different temperatures and Sulfolane concentrations 58
Table III. 5: Values of k_2 (m^3/mol·s) for the reaction between CO_2 and aqueous MDEA and (MDEA+ Sulfolane) solutions based on base catalyst mechanism 58

Table of Contents

Acknowledgements ii

Dedication iii

Abbreviations v

List of Figures ix

List of tables xi

General Introduction 1

Chapter I : Comprehensive Review of Different Processes Available and suitable for Removal of Acid Gas from Natural Gas

Introduction: 4

I.1) Acid gas removal technologies for natural gas purification: 4

I.2) Absorption process: 5

I.3) Physical absorption : 5

I.3.1) Basic separation principles for physical absorption process: 5

I.4) Chemical absorption : 6

I.4.1) Basic separation principles for chemical absorption process: 6

I.5) Adsorption process: 7

I.5.1) Basic separation principles for adsorption process : 7

I.5.2) Thermal swing adsorption: 9

I.5.3) Pressure swing adsorption: 9

I.5.4) Displacement desorption: 10

I.5.5) Limitation and challenges: 10

I.6.1) Basic separation principle for cryogenic process: 11

I.6.2) Limitation and challenges : 12

I.7) Membrane process : 12

I.7.1) Basic principle of membrane process: 12

I.7.2) Membrane selection for natural gas separation: 13

I.7.3) Polymeric membranes: 14

I.7.4) Inorganic Membranes: 15

I.7.5) Mixed matrix membranes: 15

I.7.6) Limitation and challenges : 16

I.8) Hybrid separation processes: 17

I.9) Amine Process: 18

I.10) Acid gas removal unit (AGRU): 18

I.10.1) Design basis: 18
I.10.2) Krechba AGRU description: 19
Conclusion : 20
Chapter II : General Literature Review of Reaction Kinetics of Acid Gas Absorption Into Reactive Amine Solutions
Introduction : 22
II.1) Stirred cell reactor: 22
II.2) Wetted wall column: 23
II.3) Laminar jet absorber: 23
II.4) Wetted sphere absorber: 24
II.5) String of disc contactor: 25
II.6) Stopped-flow apparatus: 25
II.7.1) Zwitterion Mechanism: 26
II.7.2) Base-catalyzed hydration mechanism: 29
II.8) Graphical method: 29
II.9) Simplified model based on reaction mechanism: 30
1) Primary & secondary amines: 30
2) Tertiary amine: 31
3) Primary sterically hindered amine: 32
4) Solvents containing polyamines: 32
5) Blended amine system: 33
Conclusion: 34
Chapter III : Kinetics of Absorption of Carbon Dioxide in Aqueous MDEA, Blended (MDEA+PZ), (MDEA+Sulfolane)
Introduction: 36
III.1) Experimental Section: 36
III.1.1) Chemicals: 36
III.1.2) Experimental Setup: 37
III.1.3) Experimental validation: 41
III.2) Kinetics of CO_2 absorption into aqueous amine solutions: 42
III.3) Reaction mechanisms: 43
III.3.1) Reaction kinetics of CO_2 in aqueous MDEA: 43
III.3.2) Reaction Kinetics of CO_2 in the Blended Aqueous MDEA-PZ System: 44
III.3.3) Reaction kinetics of CO_2 in blended Aqueous MDEA-Sulfolane system: 45
III.4) Results and discussion: 45

III.4.1) Absorption kinetics of CO_2 in aqueous MDEA: **45**
III.4.2) Absorption kinetics of CO_2 in aqueous blended (MDEA + PZ) system: **50**
III.4.3) Reaction of aqueous CO2 with aqueous MDEA + Sulfolane: **54**
General Conclusion **61**
Referances **63**

General Introduction

General Introduction

The presence of CO_2 in natural gas results in an increase in volume, reduces its heating value and enhances corrosion in pipelines and processing plants. Absorption rates are one of the most critical parameters that must be considered in screening chemical solvents for CO_2 removal operations. When the reaction kinetics of promising solvents are determined, they provide the necessary information for accurately modeling and designing both absorption and regeneration columns. The most conventional method of acid gas sweetening that has been widely used in industry is chemical absorption involving aqueous amine solutions. This technology allows for acid gas removal to very low levels even when the acid gas in the feed is at low partial pressures. Primary amines such as MEA and DGA, or secondary amines such as DEA and DIPA, and tertiary amines such as MDEA and TEA are examples of amines of industrial importance. Mixed amines such as (MDEA +PZ) have been widely used (Kohl and Riesenfeld, 1997).

In an amine molecule, the basicity is provided by the amino group while the hydroxyl group enhances its solubility in water (Barvek and Alper, 1999).

The selection of a particular amine (single or mixed) principally relies on the absorption potential, reaction kinetics, regeneration energy, degradation, and possible drawbacks such as pipe corrosion, and high operating costs.

A full understanding of the reaction mechanism is fundamental in screening amines that are appropriate for removal of acid gases (Versteeg and swaaij, 1988).

The concept of combining the absorption characteristics of different amines, as in amine blends, has been proposed and applied in capture of acid gases (Chakravarty, 1985).

These blends were found to be desirable for bulk CO_2 removal, as these mixtures combine high absorption rates between CO2 and the primary or secondary amines with the lower regeneration energy and high absorption capacity of hindered or tertiary amines. The main objective of the present investigation is to report on the kinetic properties of CO_2 absorption using the stopped flow technique in a wide number of systems such as aqueous MDEA solutions, and MDEA mixed with PZ and Sulfolane at several concentrations by varying PZ and Sulfolane keeping MDEA concentration constant.

This study is divided into three chapters.

After a general introduction about the acid gas removal processes, the thesis is organized as follows:

Chapter one summarizes the most common technologies used in natural acid gas removal processes. Reaction kinetics of acid gas absorption into reactive amine solutions, kinetic apparatuses and procedures that have been used are presented in Chapter two.

All the experimental apparatuses procedures that have been used throughout this study, and the results and discussions, are presented in Chapter three.

Finally, the thesis includes overall conclusions .

Chapter I : Comprehensive Review of Different Processes Available and Suitable for Removal of Acid Gas from Natural Gas

Introduction:

Natural gas is formed through the decomposition of organic matter buried within the Earth's sedimentary layers, under high pressure and temperature over millions of years, a process known as thermogenic methane formation. It can also be generated near the Earth's surface by methane-producing microbes, referred to as biogenic methane. A third theory suggests that natural gas can form through a biogenic processes, where hydrogen-rich gases interact with underground minerals in oxygen-free environments deep within the Earth's crust.

The composition of natural gas varies depending on the depth and geological nature of the reservoir, and it is often found in association with crude oil. Methane (CH_4) is the primary component of natural gas, along with varying amounts of light hydrocarbons and impurities such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), mercury (Hg), and helium (He) etc. Thus, the impurities must be removed to meet the pipe-line quality standard specifications as a consumer fuel, enhance the calorific value of the natural gas, avoid pipelines and equipment corrosion and further overcome related process bottle necks.

I.1) Acid gas removal technologies for natural gas purification:

Carbon dioxide is one of the primary contaminants in natural gas feedstocks, and its effective removal is essential, as it lowers the energy content of the gas and negatively impacts its market value. In the presence of water, CO_2 becomes acidic and corrosive, posing risks to pipelines and equipment. Therefore, purifying natural gas to remove CO_2 is crucial for enhancing product quality (Dortmundt and Doshi, 1999). There is a wide range of technologies available for acid gas removal, each with its own strengths and limitations, making the selection of the most suitable process a critical decision.While general guidelines can simplify the selection process, several key factors must be carefully evaluated. These include the type and concentration of contaminants in the feed gas, the desired removal efficiency, the hydrocarbon content, pipeline specifications, capital and operational costs, gas throughput, selectivity requirements, and the feed gas conditions (Dortmundt and Doshi, 1999).

I.2) Absorption process:

The absorption process is one of the essential unit operations in natural gas purification, where selected gas components are dissolved in a liquid solvent based on their preferential solubility. It is typically performed in a countercurrent column, where the gas flows upward and the liquid flows downward. The column may be equipped with trays, packing, or other internals to increase the gas-liquid contact surface (Meyers, 2001).

A suitable absorbent should possess key properties such as high gas solubility, high selectivity, chemical stability, low viscosity, low freezing point, non-corrosiveness, non-flammability, environmental compatibility, and economic availability (Kohl & Nielsen, 1997).

At equilibrium, the partial pressure (fugacity) of a gas component in the gas phase equals its fugacity in the liquid phase, establishing the thermodynamic relationship between the two phases (Meyers, 2001). In physical absorption, the process is governed by solubility and mass transfer, whereas in chemical absorption, it is controlled by reaction kinetics and chemical equilibria (Meyers, 2001).

Desorption or regeneration is the reverse process, used to recover either the absorbed gas, the solvent, or both. Physical absorption regeneration typically involves pressure reduction, while chemical absorption regeneration involves thermal or chemical methods (Kohl & Nielsen, 1997; Scott, 1998).

I.3) Physical absorption :

I.3.1) Basic separation principles for physical absorption process:

Physical absorption processes are the type of absorption processes where the solvent interacts only physically with the dissolved gas. In this process, the solvent is used as an absorbent with thermodynamic properties such that the relative absorption of acid gas is more favored over the other components of the gas mixture. Mostly, physical solvent systems are used when the feed gas is characterized by high CO_2 partial pressure and low temperatures. Although heavy hydrocarbon restricts the wide use of physical solvent, its absorption capacity can be higher than chemical solvents. In addition, low CO_2 partial pressures as well as low outlet pressure of the product stream may also discourage the application of physical solvents (Ebenezer and Gudmunsson, 2005).

Removal of acid gas from the feed gas by physical solvent absorption is based on the solubility of acid gas within the solvents. The partial pressure and the temperature of the feed gas are the two major factors that determine the solubility of the acid gas. In physical absorption, the interaction between CO_2 and the absorbent is weak relative to chemical solvents, decreasing the energy requirement for regeneration. Regeneration of solvents is assisted by either heating, pressure reduction or a combination of both. Mostly, physical solvent scrubbing of CO_2 is well established. Selexol, a liquid glycol-based solvent, has been used for decades to process natural gas, both for bulk CO_2 removal and H_2S removal (Davison, Freund et al., 2001). Glycol is effective for capturing both CO_2 and H_2S at higher concentration. However, the CO_2 is released at near atmospheric pressure, requiring recompression for transportation and geologic storage. The Rectisol process, based on low temperature methanol, is another physical solvent process that has been used for removing CO_2. Glycerol carbonate is interesting because of its high selectivity for CO2, but it has a relatively low capacity (Kovvali and Sirkar, 2002).

I.4) Chemical absorption :

I.4.1) Basic separation principles for chemical absorption process:

In natural gas purification plant, chemical absorption processes are used to remove acid gases such as CO_2 in the gas stream by the action of exothermic reaction of the solvent with the gases. Many alkanolamines are most widely used as the chemical solvent gas treating process for acid gas removal in the natural gas and petroleum processing industries. These processes use a solvent, either an alkanolamine or an alkali-salt (hot potassium carbonate processes) in an aqueous solution.

The common amine based solvents used for the absorption process are mono-ethanolamine (MEA), di-ethanolamine (DEA) and methyldiethanolamine (MDEA) that reacts with the acid gas to form a complex or bond. H_2S, CO_2 and SO_2 are termed as acid gases since they dissociate to form weak acidic solution when they come into contact with water or an aqueous medium. These amines are known as weak organic bases. The basicity is provided by the amine function, and it provides reactivity to remove the acid gases. The hydroxyl groups serve to increase the solubility of amine in water. This effect reduces the vapor pressure of the amines so that less is lost out the top of the absorber or stripper (Glasscock, 1990).

I.5) Adsorption process:

I.5.1) Basic separation principles for adsorption process :

In gas separation application, the process of adsorption is described as the adhesion or retention of selective components of feed gas stream brought into contact to the surface of certain solid adsorbent as the result of the force of field at the surface. As the surface of an adsorbing material may exhibit different affinities for the various components of a fluid, it offers a straightforward means of purification (removal of undesirable components from a fluid mixture) as well as a potentially useful method of bulk separation (separation of a mixture into two or more streams of enhanced value). Although adsorption process is rarely applied for bulk separation of CO_2 from CH_4, there are kinetics-based adsorption processes that have been implemented in USA for the recovery of methane from landfill gas. These gases mainly comprises of methane (50-65%), carbon dioxide (35-50%), a trace amount of nitrogen and sulfur compounds. In this process, carbon molecular sieve is used as the adsorbent. In use of this process, it can be possible to recover more than 90% methane with 87-89% purity (Yang, 1997). One of the successful applications for bulk separation of CO_2 from CH_4 is performed by using Engelhard molecular gate, a commercial brand name adsorbent developed by Engelhard Corporation. The first application of molecular gate CO_2 removal system is at the Tidelands Oil Production Company operated facility in Long Beach, California. The feed source for this unit is hydrocarbon rich associated gas from enhanced oil recovery section. The feed more typically operates at 30- 40% of CO_2 and the adsorbent able to reduce CO_2 level less than 2% (Ritter and Ebner, 2007).

Depending on the nature and strength of the surface forces, adsorptive gas separation process can be divided into two types: physical adsorption and chemisorption.

Chemisorption can be considered as the formation of a chemical bond between the sorbate and the solid surface (covalent interaction of CO_2 and the surface of the adsorbent) that gives scope for much larger increases in adsorption capacity. Such interactions are strong, highly specific, and often not easily reversible. Chemisorption systems are sometimes used for removing trace concentrations of contaminants, but the difficulty of regeneration makes such systems unsuitable for most process applications (Meyers, 2001).

In most operations, adsorption processes depend on physical adsorption. The forces of physical adsorption are weaker (a combination of Van der Waals forces and electrostatic forces) than the forces of chemisorption so the heats of physical adsorption are lower and the adsorbent is more easily regenerated as no covalent bonds are formed and heat is released upon adsorption. During capture, the chemical potential of the adsorbed CO_2 is lower than the chemical potential of CO_2 in the gas mixture.

Physical adsorption at a surface is so fast, and the kinetics of physical adsorption are usually controlled by mass or heat transfer rather than by the intrinsic rate of the surface process (Meyers, 2001). Most of the separation processes is based upon equilibrium mechanism and the separation is accomplished by the adsorption equilibrium capacity difference of the adsorbent among the adsorbate.

The main advantage of physical adsorption methods is its low energy requirement for the regeneration of the sorbent material with short period of time associated with the change in pressure. The widely used adsorption processes includes the metal oxide (metal organic frame works), molecular sieves (zeolites, activated carbon) and promoted hydrotalcites based processes. Zeolite systems can produce nearly pure streams of CO_2, but have high energy expenses due to vacuum pumps and dehumidification equipment. As most effective adsorbent, the use of hydrotalcites at high temperatures (177-327°C) is widely for adsorption of CO_2 in or near combustion or gasification chambers. However, more study is still required to decrease the pressure difference requirement and enhance the capacity of current adsorbents (Hermann, Bosshar et al., 2005).

Commercial adsorbents that show ultra-porosity have been used for the selective separation of gases, and included activated carbons, charcoal, activated clays, silica gel, activated alumina, and crystalline aluminosilicate zeolites.

The major advantages of using adsorption processes are simplicity of operation, the relative capability of the molecular sieve beds to withstand mechanical degradation and the possibility of simultaneous dehydration of gases and acid removal. Once saturation of the adsorbent is reached, regeneration is carried out by either applying heat or by lowering pressure (concentration).Based on regeneration methods, adsorption process is most commonly divided into temperature swing adsorption (TSA), pressure swing adsorption (PSA) and displacement desorption.

I.5.2) Thermal swing adsorption:

The use of cyclic thermal swing processes (TSA) is widely applicable for the purification operations such as removal of CO_2 from natural gas or drying. In TSA, desorption is achieved by increasing the temperature of the adsorption bed by applying heat to the bed or more commonly by purging with a hot purge gas. At higher temperatures the adsorption equilibrium constant is reduced so that even quite strongly adsorbed species can be removed with a comparatively small purge gas volume. TSA is generally used for purification of the process such as drying or removal of CO_2 from natural gas (Meyers, 2001). Thermal swing adsorption is very reliable to remove minor component. The limitation in thermal swing adsorption process is the adsorption cycle time that is required to cool down the bed. Other obstacles are the high energy requirements and large heat loss (Mersmann, Kind et al., 2011).

I.5.3) Pressure swing adsorption:

Pressure swing adsorption (PSA) is one of the most known industrial processes for gas separation. PSA is well known a technology for the removal of CO_2 from gaseous streams containing methane In such process, the removal of CO_2 from natural gas streams by adsorption processes are based on materials with selective adsorption to CO_2 by different equilibrium capacities or by differences in uptake rates (Cavenati, Carlos et al., 2006). In PSA, regeneration is carried out by lowering the operating partial pressure to desorb the adsorbate (Kerry, 2007). This can be obtained either by depressurization or by evacuation or by both. PSA is more suitable for bulk separation. Moreover, PSA is also used for drying of air and industrial gases. Air pre-purification (purification of air prior to cryogenic distillation by removal of CO_2, water, and hydrocarbons) is also at developing stage for PSA (Yang and Wiley, 2003). As the most important decision in any adsorption-based technology is the adsorbent selection, zeolites as microporous materials that adsorb CO_2 strongly, are mostly used in PSA processes. Zeolites have good records for separation of CO_2 than activated carbons in the PSA (Cavenati, Carlos et al., 2006). The major advantages of PSA system are low capital and maintenance costs, high purity product, rapid shutdown and start-up characteristics, lack of corrosions problems, absence of heat requirement and pipe insulation and comparative straight forward operation.

I.5.4) Displacement desorption:

Displacement desorption, is similar to purge gas stripping as the temperature and pressure are maintained constant, but instead of an inert purge, an adsorbable species is used to displace the adsorbed component from the bed similar to displacement chromatography. Displacement desorption is usually used when desorption by pressure swing or thermal swing fails to be practical. Steam stripping process can be considered as a combination of thermal swing and displacement desorption as it is mostly used in the regeneration of solvent recovery system using an activated carbon adsorbent. In a typical displacement desorption, the displacing component should be adsorbed somewhat less strongly than the preferentially adsorbed species so that the adsorption desorption equilibrium can be shifted by varying the concentration of the desorbent. Such processes run more or less isothermally and offer a useful alternative to thermal swing processes for strongly adsorbed species when thermal swing would require temperatures high enough to cause cracking, coking, or rapid aging of the adsorbent (Meyers, 2001).

I.5.5) Limitation and challenges:

As compared to other methods, for adsorption to be economical, ideal adsorbents should have high transfer rates, high regenerability and high capacity that allow for thermal swing adsorption (TSA) or low pressure swing adsorption (PSA). At the adsorption equilibria, the loading usually decreases with increasing temperature for a given partial pressure or concentration of the adsorptive in the fluid. In an isothermal system, the loading decreases with decreasing partial pressure or concentration. A further regeneration process is based on the replacement of the adsorbate by another adsorptive with a greater affinity to the adsorbent (Mersmann, Kind et al.,2011).

I.6) Cryogenic process:

I.6.1) Basic separation principle for cryogenic process:

Cryogenic separation (also known as low temperature distillation) uses a very low temperature (-73.30°C) for purifying gas mixtures in the separation process (Ebenezer and Gudmunsson, 2005).The major industrial application of low-temperature processes involves the separation and purification of gases. Much of the commercial oxygen and nitrogen, and all the neon, argon, krypton, and xenon, are obtained by the distillation of liquid air (Meyers, 2001). Commercial helium is separated from helium-bearing natural gas by a well-established low temperature process. Cryogenics has also been used commercially to separate hydrogen from various sources of impure hydrogen (Meyers, 2001).

The cryogenic method is better at extraction of the lighter liquids, such as ethane, than is the alternative absorption method. Essentially, cryogenic processing consists of lowering the temperature of the gas stream to around (-84.44 °C). While there are several ways to perform this function the turbo expander process is most effective, using external refrigerants to chill the gas stream. The quick drop in temperature that the expander is capable of producing condenses the hydrocarbons in the gas stream, but maintains methane in its gaseous form (Tobin J., Shambaugh P. Et al., 2006). While cryogenic separation is used commercially to liquefy and purify CO_2 from streams that have high CO_2 concentrations (typically greater than (50-70 percent), it has not been applied to large scale CO_2 capture from flue gas due to the low concentration of CO_2 that makes the application of this technique not economical. Cryogenic separation can separate CO_2 from other gases using pressure and temperature control resulting in solid or liquid CO_2 particulate matter and other contaminants are also removed in the process. Cryogenics use condensation of gases as the main principle. When CO_2 is cooled below its boiling point, it begins to condense and separate and turns into a liquid state. Differences in boiling points cause the gases to separate because each gas will turn to a liquid at a different point, but separation into pure components can also be influenced by the composition of the gas being cooled (Tobin , Shambaugh et al., 2006). The advantages of this process are the suitability to liquefy and purify the feed gas with high concentration of CO_2 and for producing a liquid CO_2 ready for transportation by pipeline and does not require compression since there is no additional chemicals used.

I.6.2) Limitation and challenges :

The main disadvantage of cryogenic separation is that the process is highly energy intensive for regeneration and can significantly decrease the overall plant efficiency when applied to streams with low CO_2 concentration. Moreover, tendency for blockage of process equipment is high and some cryogenic fluids are flammable and toxic such as (acetylene, ethane) (Ebenezer and Gudmunsson, 2005).

I.7) Membrane process :

I.7.1) Basic principle of membrane process:

In essence, gas separation membranes are thin films that selectively transport gases through the membrane based on differences in permeabilities of the species flowing through the membrane. The permeability of gases in a membrane is related as a function of membrane properties (physical and chemical structure), the nature of the permeant species (size, shape, and polarity), and the interaction between membrane and permeant species (Stern 1994; Burggraaf 1996; Shekhawat, Luebke et al., 2003). The membrane properties and the nature of the permeant species determine the diffusional characteristics of a penetrant gas through a given membrane. The interaction between membrane and permeant, refers to the sorptivity or solubility of the gas in the membrane. The permeability coefficient (or permeability) of a penetrant is the product of the solubility coefficient or the sorptivity (thermodynamic parameter) and the diffusion coefficient (kinetic parameter). The permeability coefficient denotes the rate at which a penetrant crosses a membrane. The solubility (sorptivity coefficient) is a measurement of the amount of gas sorbed by the membrane when equilibrated with a given pressure of gas at a given temperature. The diffusion coefficient indicates how fast a penetrant is transported through the membrane in the absence of obstructive sorption. The selectivity of the membrane to specific gas or liquid molecules is subject to the ability of the molecules to diffuse through the membrane. The permselectivity or ideal separation factor is simply the ratio of the pure gas permeability of the gases being separated.

Membranes utilized in separations need to possess both high selectivity and high permeation. The higher the permeability, the less membrane area is required for a given separation and therefore the lower the membrane cost. The higher the selectivity is the lower the losses of methane and therefore the higher the volume of the product that can be recovered (Porter 1990; Shekhawat, Luebke et al., 2003). Gas transport through porous membranes takes place through a number of mechanisms, such as molecular sieving, Knudsen diffusion, surface diffusion, capillary condensation and micropore diffusion. Brief descriptions of these mechanisms are provided as follows.

I.7.2) Membrane selection for natural gas separation:

Membranes have been widely used in natural gas processing, particularly for CO_2 removal, with capacities ranging up to 250 MMSCFD and new designs targeting up to 500 MMSCFD (Sridhar, Smitha et al., 2007). Key factors in membrane material selection include intrinsic permselectivity, resistance to plasticization and chemical degradation, and the ability to form strong asymmetric structures. Effective separation also depends on molecular structure, chemical group arrangement, molecular weight distribution, and polarity. For acid gas removal (CO_2, H_2S) from methane-rich streams, membrane performance relies on a combination of material choice, synthesis, and system design. Proper membrane chemistry and material selection are crucial for achieving both high selectivity and permeability.

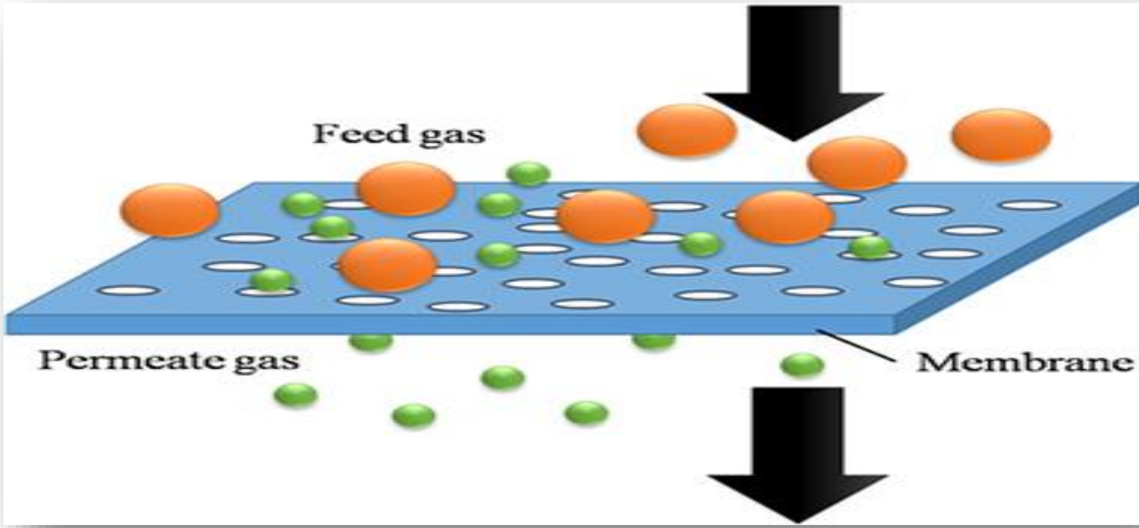

Figure I. 1: Membrane separation technology in CO2 Capture

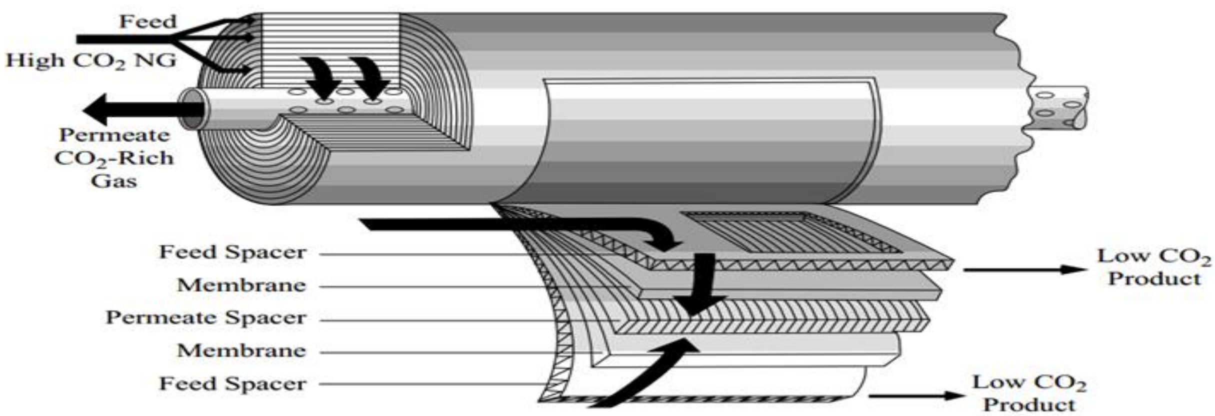

Figure I. 2: Acid gas removal using membrane

I.7.3) Polymeric membranes:

Polymeric membranes are widely used in commercial gas separation applications, including nitrogen recovery, oxygen/nitrogen separation, hydrocarbon processing, and natural gas purification. In CO_2/CH_4 separation for natural gas sweetening, these membranes selectively allow CO_2 to permeate due to a pressure gradient across the membrane, requiring feed gas compression.

However, the separated CO_2 is obtained at low pressure and must be recompressed to meet pipeline standards (Pandey & Chauhan, 2001; Sridhar, Smitha et al., 2007; Bernardo, Drioli et al., 2009).

Two main types of polymeric membranes exist: glassy and rubbery. Glassy membranes are rigid, operate below their glass transition temperature, and offer high selectivity but lower permeability. Rubbery membranes, which operate above their glass transition temperature,

Are more permeable but less selective. Despite this, glassy membranes are more commonly used in industry due to their balance of selectivity and mechanical stability. Overall, polymeric membranes are valued for their good transport properties, ease of processing, and low cost.

I.7.4) Inorganic Membranes:

Inorganic (ceramic) membranes are known for their excellent thermal, mechanical, and chemical stability, along with good erosion resistance, bacterial insensitivity, and long operational life (Caro, Noack et al., 2000). These membranes are divided into microporous and dense types, both

suitable for high-temperature gas separation. Dense inorganic membranes, made from materials like perovskites, palladium, silver, and zirconia, are primarily used for selective separation of gases

such as hydrogen (via Pd) and oxygen (via perovskites). However, their low permeability due to thick membrane structure limits their practical use in separation processes (Ismail & David, 2001; Baker, 2004). Microporous inorganic membranes, made from materials like glass, metal, alumina, and zeolite, are commercially used for gas separations. These membranes typically consist of a ceramic support, intermediate layers, and a selective top layer. Despite being more expensive than polymeric membranes, inorganic membranes offer better temperature and wear resistance, stable pore structures, and higher selectivity. However, high production costs, brittleness, and the inability to form continuous, defect-free membranes limit their commercial use. For instance, the cost of a zeolite membrane module is around US\$ 3000/m^2, compared to US\$ 20/m^2 for polymeric hollow-fiber membranes (Vu, 2001; Baker, 2004).

I.7.5) Mixed matrix membranes:

Molecular-sieve fillers such as zeolite and carbon molecular sieve (CMS) are used in mixed matrix membranes (MMMs) to differentiate molecules based on size and shape (Pal, 2007; Shimekit, Mukhtar et al., 2009). Gas transport through MMMs is complex due to their heterogeneous structure, and several theoretical models have been developed to predict gas permeability based on the permeabilities of both the continuous and dispersed phases (Hashemifard, Ismail et al., 2010). Permeation occurs through both the polymer matrix and the filler particles, with the relative rates determined by the intrinsic permeabilities of each phase (Baker, 2004). Detailed models for gas permeability in MMMs can be found in Shimekit, Mukhtar et al. (2011). The membrane market for acid gas separation is divided as follows:

Very small systems (<5 MMSCFD): These are simple, effective units where the permeate gas is often used as fuel or flared.

Small systems (5–40 MMSCFD): Two-stage membrane systems are used to reduce methane loss, and they compete with amine systems depending on site-specific conditions.

Medium to large systems (>40 MMSCFD): Membranes are generally more costly than amine systems at large scales, but are preferred in specific cases such as offshore platforms or CO_2 flood operations (Baker, 2004).

I.7.6) Limitation and challenges :

The application of membranes today for CO_2 separation in natural gas processing is mainly used for moderate-volume gas streams. For large-volume gas streams, membrane separation today cannot yet compete with the standard amine absorption as the flux and selectivity of the membranes are too low for processing large gas volumes.

Membranes are used in situations where the produced gas contains high levels of CO_2. However, a key sensitivity with these current membranes is that they must be protected from the heavier C^{5+} hydrocarbons present in wet natural gas streams. Exposure to these compounds immediately degrades performance and can cause irreversible damage to the membranes. Thus, in order to fully exploit the use of membranes in natural gas purification, development of more selective, higher-flux and cost effective new membranes are still critical concerns. And hence, the outcome will make membrane processes much more competitive with other technologies such as amine absorption for large scale systems (Baker, 2004).

Table I. 1: Overall comparisons of natural gas purification technologies

Process	Advantages	Disadvantages
Absorption	-Widely used technology for efficient (50-100) % removal of acid gases (CO_2 and H_2S)	-Not economical as high partial pressure is needed while using physical solvents absorption -Long-time requirement for purifying acid gas as low partial pressure is needed while using chemical solvents.
Adsorption	-High purity of products can be achieved. -Ease of adsorbent relocation to remote fields when equipment size becomes a concern.	-Recovery of products is lower - Relatively single pure product
Membrane	-Simplicity, versatility, low capital investment and operation. – Stability at high pressure - High recovery of products - Good weight and space efficiency - Less environmental impact	- Recompression of permeate - Moderate purity
Cryogenic	-Relatively higher recovery compared to other process -Relatively high purity products	-Highly energy intensive for regeneration -Not economical to scale down to very small size. -Unease of operation under different feed stream as it consists of highly integrated, enclosed system.

I.8) Hybrid separation processes:

In hybrid separation processes, an integration of one process is used with other separation process or processes in which the basic functioning of one process is joined with another physical or chemical process in a single unit operation (Bernardo, Drioli et al., 2009).

The hybrid separation processes combines the properties of physical and chemical solvent for effective and selective removal of acid gas from natural gas. One of the well acclaimed successful hybrid separation process uses in the oil and gas industry is Sulfinol process licensed by shell E&P (energy and petrochemical companies). Sulfinol is a mixture of sulfolane (tetrahydrothiophene1-1 dioxide a physical solvent), water and either di-isopropanol-amine (DIPA) or Methyl-di-ethanol-amine (MDEA) (both chemical solvent). The dual functionality and capacity of physical and chemical solvents mixture of sulfinol make the solvent more efficient. The physical solvent for instance provides the system for bulk removal of acid gas and also allows much greater solution loading of acid gas than most pure base solvents.

I.9) Amine Process:

In the gas processing industry absorption with chemical solvents has been used commercially for the removal of acid gas impurities from natural gas. The currently preferred chemical solvent technology for acid gas removal is chemical absorption of acid gases by amine-based absorbents. Alkanolamines are the most commonly used category of amine chemical solvents used for acid Gas removal. Chemical absorption of CO_2 with alkanolamines as solvent has been used in a large variety of industries over years. It is notable that MDEA is advantageous over other amines due to selective removal of H_2S from its mixture with CO_2. The selectivity of absorption is due to the higher rate of the reaction of MDEA with H2S than the reaction of MDEA with CO_2 (Anufrikov et al., 2007). H2S has H+ that can give directly to MDEA; the proton transfer reaction is always fast and spontaneous. Moreover, comparing to other amines, MDEA is more stable, less volatile and less corrosive, it has lower heat of reaction and higher absorption capacity (Anufrikov et al., 2007).

I.10) Acid gas removal unit (AGRU):

I.10.1) Design basis: A single phase absorption process of Activated Methyldiethanolamine (a-MDEA) (activated by the piperazine) is used for the treatment of the export gas to meet the product gas specifications and which must be less than or equal to 0.3 mol% CO_2 and 2.0 mg / cm3 in H2S. The table below summarizes the design case defining the operating conditions of the AGRU.

The AGRU acid gas removal unit is designed for an overall feed gas flow rate of 1,338,416 (Cm^3 / h) and theoretical dry gas concentrations for CO_2 and H_2S of 6.6 mole% and 15 ppmv, respectively. The CO_2 concentration of 6.6 mole% (dry basis) including the design margin of approximately 0.1 mole% is the maximum threshold expected in the gas at a design flow rate.

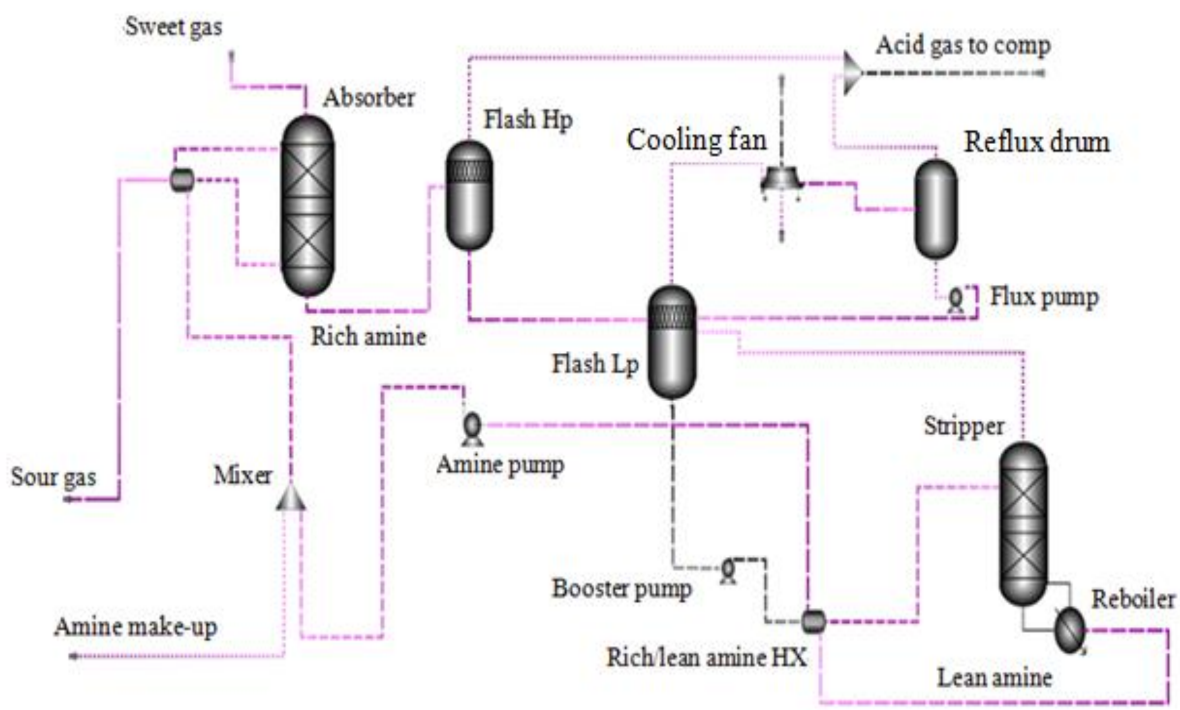

Figure I. 3: Simplified process diagram (AGRU) (Krechba, In Salah, Algeria)

I.10.2) Krechba AGRU description:

The raw gas enters the two CO_2 extraction trains at Krechba treatment plant at about 72.3 bar and a temperature between 25°C and 35°C. It is preheated to 55°C to enhance absorption efficiency. The gas flows upward through the absorber column, contacting a downward flow of lean a-MDEA solution, which absorbs CO_2 and H_2S. Treated gas exits the top of the column, while the rich amine solution is sent to high and low-pressure flash drums for partial acid gas separation.

The separated acid gas is either sent for reinjection or flared if the reinjection system is unavailable. The rich amine is then heated and sent to the CO_2 stripper, where CO_2 is released using heat from reboilers. The regenerated lean amine is cooled, pressurized, and recycled back to the absorber to complete the cycle.

Conclusion :

The removal of acid gases from natural gas has been an essential and important unit operation for many decades. Traditionally, the motivation behind this removal has been technical and/or economic. It has received special emphasis in order to increase the heating value of natural gas, reduce corrosion in pipelines and equipment during transportation, storage, and distribution, and to meet environmental requirements. Many separation techniques, such as membranes, physical adsorption, and cryogenics, can be used to capture CO_2 from process gases. However, the currently preferred technology for acid gas removal is chemical absorption using amine-based solvents. This method has been commercially used to capture the gas because it is highly effective at various CO_2 concentrations and is relatively low in cost. The removal of acid gases from natural gas has been an essential and important unit operation for many decades. Traditionally, the motivation behind this removal has been technical and/or economic. It has received special emphasis in order to increase the heating value of natural gas, reduce corrosion in pipelines and equipment during transportation, storage, and distribution, and to meet environmental requirements.

Chapter II : General Literature Review of Reaction Kinetics of Acid Gas Absorption Into Reactive Amine Solutions

Introduction :

Reaction kinetics is one of the key parameters in amine-based acid gas capture processes, as it determines the rate at which acid gases react with amines and is essential for the simulation and design of the absorption column (Kohl and Riesenfeld, 1997). One of the most common methods for removing acid gases from natural gas and industrial gas streams is the regenerative absorption of these gases into aqueous solutions of alkanolamines. Primary and secondary alkanolamines react rapidly with carbon dioxide (CO_2) to form carbamates. However, this reaction releases a significant amount of heat, which increases the energy required for solvent regeneration. In addition, the CO_2 loading capacity of these amines is limited to 0.5 mol of CO_2 per mol of amine. In contrast, tertiary alkanolamines lack a hydrogen atom bonded to the nitrogen atom, preventing the formation of carbamates and resulting in lower direct reactivity with CO_2. Instead, they promote the hydrolysis of CO_2 to form bicarbonates. A reaction that produces less heat and thus lowers regeneration costs. Furthermore, tertiary amines offer a higher CO_2 loading capacity, up to 1 mol of CO_2 per mol of amine. The CO_2 absorption rate of tertiary amines can be enhanced by adding small amounts of primary or secondary amines (Chakravarty, 1985). Absorption activators such as piperazine (PZ) may also be used to boost performance (Appl et al., 1982).

To obtain accurate reaction kinetics data, CO_2 absorption experiments must be conducted using laboratory-scale gas–liquid contactors, such as stirred cell reactors, wetted wall columns, laminar jet absorbers, wetted sphere absorbers, string-of-disc contactors, or stopped-flow apparatuses.

II.1) Stirred cell reactor:

In the stirred cell reactor (figure II. 1A), the gas and liquid phases are stirred separately using separated adjustable impellers. The gas–liquid interface needs to be smooth, and a consistent interface is achieved by controlling the agitation speed from impellers. A pressure transducer is located in the gas-phase side for measuring the total pressure in the reactor. In addition, temperature sensors are located in both the gas and liquid sides of the reactor, and baffles are installed in the liquid side in order to avoid formation of vortices. The gas absorption rate is

determined by measuring the change in total pressure in the reactor (Astarita et al., 1983; Pani et al., 1997). The advantage of the stirred cell reactor is that only gas-phase measurement is required.

However, its disadvantage is the difficulty of maintaining the smooth and consistent gas–liquid interface.

II.2) Wetted wall column:

The wetted wall column diagram is presented in Figure II.1B. The liquid is continuously pumped to the bottom of the wetted wall column then overflows from the interior of the tube and forms a thin liquid film over the outer surface of the tube. This thin liquid film contacts the inlet gas counter currently. The gas absorption rate can be calculated from the gas-phase material balance by measuring the concentration and volumetric flow rate of inlet gas and outlet gas (Saha et al. ,1995; Ko and Li,2000). The disadvantages of this equipment are the possibility of creating ripples in the liquid film and inactive film at the bottom of the column (Astarita et al., 1983).

II.3) Laminar jet absorber:

In this technique, the liquid solvent is first degassed by spraying it into a vacuum. After degassing, the liquid passes through a water jacket with controlled temperature to reach the desired operating conditions. The prepared liquid is then directed through a jet nozzle to produce a smooth, rod-like jet in the absorption chamber. A soap-film meter is used to measure the gas absorption rate, while a 2D microscope is employed to measure the jet height (hj) and diameter (dj). The discharged liquid is collected afterward, and the liquid flow rate (L) is determined (Rinker et al., 1996; Aboudheir et al., 2003). One of the main advantages of the laminar jet absorber is that the gas–liquid interface can be directly observed and measured using the microscope. Additionally, this technique is well-suited for studying highly reactive solvents due to the short contact time between gas and liquid.

However, the method has some limitations. Turbulence may develop on the liquid surface, gravity can reduce the stability of the liquid jet, and the receiver may create stagnant zones or ripples at the base of the jet. These issues can be minimized with proper design of the jet nozzle and receiver (Astarita et al., 1983; Aboudheir et al., 2004). Another drawback is that the jet length is not easily adjustable, which limits the range of gas–liquid interfacial area that can be studied.

II.4) Wetted sphere absorber:

The wetted sphere absorber (Figure II.1D) is similar to the laminar jet absorber. This technique introduces liquid solvent into the absorption chamber by overflowing the sphere instead of generating a liquid jet as in the laminar jet absorber (Seo and Hong, 2000). The absorption surface area can be calculated from the surface of the sphere. In addition, the operating procedure for the wetted sphere absorber is the same as the laminar jet absorber. The advantage of this technique is that the laminar liquid surface over the sphere can be generated and controlled easier than that of laminar jet absorber, since the liquid is flown over the sphere. However, the disadvantages of this equipment are that the absorption surface area cannot be varied, and the possibility of creating ripples in the liquid film and inactive film at the bottom of the sphere (Astarita et al., 1983).

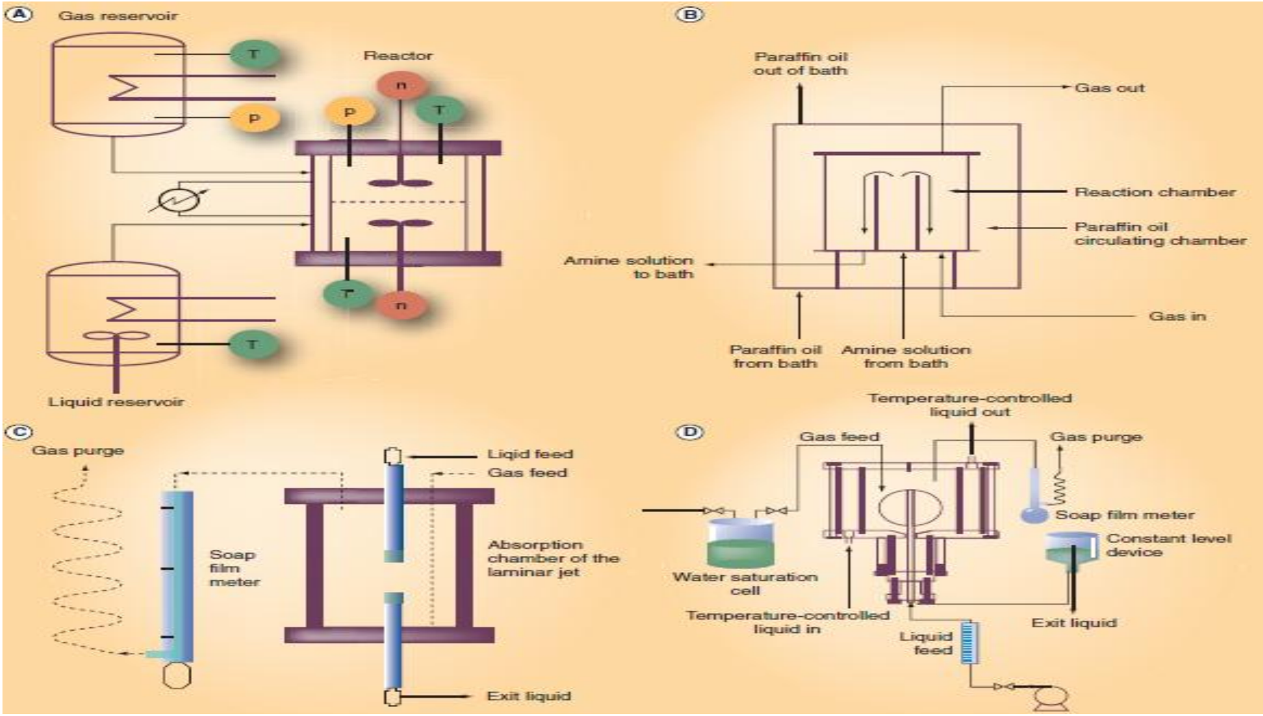

Figure II. 1: Experimental equipment for measuring the CO2 absorption rate. (A) Stirred cell reactor; (B) wetted wall column; (C) laminar jet absorber; and (D) wetted sphere absorber.

II.5) String of disc contactor:

A number of circular discs are held together by a vertical wire in the absorption column. The reactive liquid flows downward from the top of the contactor. CO_2 is introduced counter-currently from the bottom of the contactor. The active surface area can be calculated based on the diameter and number of the discs. In addition, the absorption surface area of this contactor can be varied by introducing or removing the disc elements in the column. A disadvantage of this contactor is that absorption rate at specific concentrations of liquids and/or gas cannot be achieved. This is because the concentration of CO_2 and the composition of reactive liquid are changed accordingly along the height of the string column (Danckwerts, 1979; Vaidya and Kenig, 2007). Therefore, the overall absorption rate, which can be calculated by the difference of mass flux at inlet and outlet of the column, is applied (Ma'mun, 2007).

II.6) Stopped-flow apparatus:

The stopped-flow technique is a homogeneous direct method for measuring the gas absorption into liquid solvent. Saturated gas and liquid solutions are mixed in the stopped-flow apparatus as presented in (Figure II.2). The conductivity cell monitors ion formation as a function of time, since the ion formation initiates a voltage change. Thereafter, the microcomputer automatically generates the observed pseudo first-order constant based on the output voltage values (Li et al., 2007). However, the disadvantage of this technique is that a conductivity measurement can only be done at low amine concentration. Lastly, for novel solvents screening, the stopped-flow apparatus is suggested. This is because a very small quantity of solvent is required and the experimental procedure is simple (Vaidya and Kenig, 2007; Li et al., 2007).

The stopped-flow technique is one of the most widely used rapid mixing methods for studying CO_2-amine reactions, which are the focus of our kinetic investigation. Unlike mass-transfer-based techniques, the stopped-flow method allows for accurate determination of kinetic rate constants in the range of approximately 0.01 to 1000 s^{-1}. One of its key advantages is that it eliminates gas–liquid mass transfer limitations, ensuring that the measured signal directly reflects the intrinsic chemical reaction occurring in the liquid phase. This makes the method highly reliable and reproducible for kinetic studies

Figure II. 2: Experimental equipment for measuring the CO2 absorption rate: stopped-flow apparatus

.II.7) Reaction mechanisms:

Alkanolamines are among the most commonly used absorbents for removing acid gases from process gas streams. Primary and secondary alkanolamines react quickly with CO_2 to form carbamates. In contrast, tertiary alkanolamines lack a hydrogen atom attached to the nitrogen, which prevents the formation of carbamates and results in lower reactivity with CO_2. Instead, tertiary amines promote the hydrolysis of CO_2, leading to the formation of bicarbonates. The reaction of CO_2 with primary, secondary, and sterically hindered amines is typically explained by the zwitterion mechanism, while the reaction with tertiary amines follows a base-catalyzed hydration pathway.

II.7.1) Zwitterion Mechanism:

The zwitterion mechanism was originally proposed by Caplaw (Caplaw,1968) and later reintroduced by Danckwerts (Danckwerts,1979) as a two-step reaction between CO_2 and primary or secondary amine (denoted as R_1R_2NH) through formation of a zwitterion intermediate

($R_1R_2NH^+COO^-$), and then a deprotonation of zwitterion intermediate by a base (denoted as B) to carbamate.

$$CO_2 + R_1R_2NH \xleftrightarrow{K_2^z, K_{-1}^z} R_1R_2NH^+COO^- \qquad \text{(II.1)}$$

$$R_1R_2NH^+COO^- + B \xleftrightarrow{K_b, K_{-b}} AMCOO^- + B\,H^+ \qquad \text{(II.2)}$$

Where, K_2^z, K_{-1}^Z are the second-order forward rate constant and first-order reverse rate constant for Equation 1, respectively, And a superscript Z represents the zwitterion mechanism. In Equation II.2, base (B) can be R_1R_2NH, OH^- or H_2O (Blauwhoff et al, 1983): By applying the pseudo-steady state approximation for the concentration of $R_1R_2NCOO^-$, the rate of CO_2 absorption based on the zwitterion mechanism can be derived as (Blauwhoff et al, 1983):

$$r_{CO2} = \frac{K_2^z[CO_2][R_1R_2NH]}{1+\frac{K_{-1}^Z}{\sum_b[B]}} = \frac{K_2^z[CO_2][R_1R_2NH]}{1+\frac{K_{-1}^Z}{K_{R_1R_1NH}[R_1R_2NH]+K_{OH^-}[OH^-]+K_{H_2O}[H_2O]}} \qquad \text{(II.3)}$$

In this case if $\frac{K_{-1}^Z}{\sum_b[B]}$ <<1, the equation (II.3) can be simplified to be the second-order rate reaction as (Blauwhoff et al, 1983):

$$r_{CO2} = K_2^z[CO_2][R_1R_2NH] \qquad \text{(II.4)}$$

If $\frac{K_{-1}^Z}{\sum_b[B]}$ >>1, the equation (II.3) can be simplified to be the second-order rate reaction as (Blauwhoff et al, 1983):

$$r_{CO2} = \frac{\sum_b[B]}{K_{-1}^Z} K_2^z[CO_2][R_1R_2NH] \qquad \text{(II.5)}$$

(Versteeg and van Swaaij, 1988), and (Laddha and Danckwerts, 1981) suggested that OH^- and H_2O are the minor contributors to a deprotonation of zwitterion (Equation II.2) due to a low concentration of OH^- and a low basicity of H_2O, compared with R_1R_2NH. Therefore, Equation (II.5) can be simplified as:

$$r_{CO2} = \frac{K_{R_1R_1NH}K_2^Z}{K_{-1}^Z}[CO2][R_1R_2NH]^2 \qquad \text{(II.6)}$$

If R_1R_2NH is the main contribution of Equation (II.2), as suggested by Versteeg and van Swaaij

(Versteeg and van Swaaij, 1988) and Laddha and Danckwerts (Laddha and Danckwerts, 1981) ,the overall reaction between CO2 and primary or secondary amine can be represented as:

$$CO_2 + R_1R_2NH \leftrightarrow R_1R_2NCOO + R_1R_2NH_2^+ \qquad (II.7)$$

Thus, it is implied from Equation (II.4) that the theoretical equilibrium loading capacity of primary and secondary amine is limited to 0.5 mol CO_2 per mol of amine . However, this statement is only applicable if the carbamate species is quite stable (e.g., carbamate species from MEA and DEA) (Saha et al, 1995)

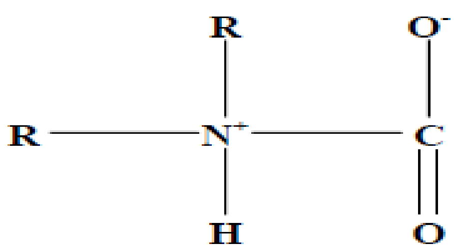

Figure II. 3: Zwitterion structure

II.7.2) Termolecular mechanism:

The termolecular mechanism was originally proposed by Crooks and Donnellan, (1989) and states that the reaction is a single step where the initial product is not a zwitterion, but a loosely bound encounter complex with a mechanism of the type as shown in Figure II.4. Most of these complexes are intermediates, which break up to give reagent molecules, again, while a few react with a second molecule of either R_1R_2NH, OH-, or H_2O to give ionic products. Bond formation and charge separation occur only in the second step (Aboudheir et al., 2003 ; Da Silva and Svendsen, 2004 ; Crooks and Donnellan, 1989).

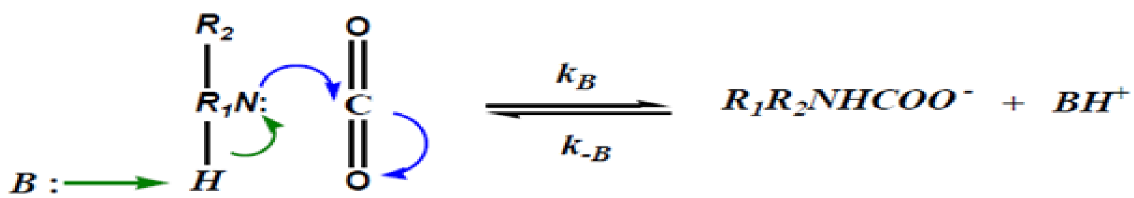

Figure II. 4: *Schematic drawing of single-step termolecular reaction mechanism (Crooks and Donnellan, 1989)*

II.7.2) Base-catalyzed hydration mechanism:

The base-catalyzed hydration mechanism of carbon dioxide (CO_2) in the presence of a tertiary amine (denoted as R_3N) was first proposed by Donaldson and Nguyen in 1980. They suggested that the tertiary amine does not react directly with CO_2, but rather acts as a base that catalyzes the hydration of CO_2, as illustrated in Equation (II.11).

$$R_3N + CO_2 + H_2O \overset{K_{R3N}}{\longleftrightarrow} R_3NH^+ + HCO_3^- \quad \text{(II.11)}$$

The rate expression for the base-catalyzed hydration mechanism for tertiary amine can be written as (Caplaw, 1968):

$$r_{CO2} = K_{\mathrm{R_3N}}[CO_2][R_3N] \quad \text{(II.12)}$$

In the case of the base-catalyzed hydration mechanism, the rate of CO_2 absorption is a second-order reaction rate. (K_2: m^3/ kmol.s), because K_2 directly represents the reaction kinetics (speed of the reaction) and is required for process simulation and design of the absorption column (Kohl, 1997; Danckwert, 1979, Astarita et al., 1983, Aboudheir et al., 2003).

After measuring the CO_2 absorption rate using experimental gas–liquid contactors (such as a stirred cell reactor, wetted wall column, laminar jet absorber, wetted sphere absorber, string of disc contactor, or stopped-flow apparatus), it is necessary to interpret the kinetic data in order to determine the second-order reaction rate constant. For CO_2 absorption into amine solutions, several approaches have been employed, including graphical methods, simplified models based on the reaction mechanism, and a comprehensive model solved numerically.

II.8) Graphical method:

The graphical method was used during the 1980s until the mid-1990s for determining the order of reaction, and the reaction rate constant of MEA, DEA, TEA and AMP (Saha et al.,1995; Blauwhoff et al.,1983; Versteeg and van Swaaij,1988; Donaldson and Nguyen,1980; Alvarez et al.,1980).Assuming that the reaction between CO_2 and amine is an m^{th} order reaction with respect to concentration of dissolved CO_2 at the interface and an n^{th} order reaction with respect to amine concentration, the reaction rate expression for a single amine system can be written as (Saha et al.,1995):

$$r_{CO2} = K_{\mathrm{mn}}\, {C^*_{CO_2}}^m {C^*_{Am}}^n \tag{II.13}$$

Where, K_{mn} is the reaction rate constant (m^3/kmol.s) and $C^*_{CO_2}$ is the molar concentration of CO_2 at the interface (kmol/m^3), which can be calculated by the Henry's law relationship, as presented in Equation II.14; C^*_{Am} is the molar concentration of amine (kmol/m^3) and He is Henry's law constant (kPa m^3/kmol):

$$C^*_{CO_2} = \frac{P_{CO2}}{He} \tag{II.14}$$

II.9) Simplified model based on reaction mechanism:

In this approach, the reaction rate/kinetics data obtained from the gas–liquid contactor are interpreted based on the proposed mechanism between CO_2 and amine (i.e., zwitterion and base-catalyzed hydration mechanisms). In addition, the single and blended amines solutions are also treated differently. First, the overall rate of CO_2 absorption (r_{ov}) is defined as (Ramachandran et al, 2006)**:**

$$r_{ov} = K_{\mathrm{ov}}[CO_2] \tag{II.15}$$

(K_{ov}) can be calculated via the experimental measurement of CO_2 absorption rate.

1) Primary & secondary amines:

For the primary and secondary amines (e.g., MEA and DEA), the overall reaction rate for CO_2 absorption based on the zwitterion mechanism can be written as (Blauwhoff et al,1983; Versteeg and van Swaaij,1988):

$$r_{CO2} = \quad K_{\mathrm{ov}}[CO_2] \quad = \frac{K_2^Z[CO_2][R_1R_2NH]}{1+\frac{K_{-1}^Z}{K_{\mathrm{R_1R_1NH}}[R_1R_2NH]+K_{OH^-}[OH^-]+K_{\mathrm{H_2O}}[H_2\mathrm{O}]}} + K_{OH^-}{}^*[OH^-][CO_2] \tag{II.16}$$

The apparent rate constant (k_{app}) is defined as (Blauwhoff et al, 1983; Versteeg and van Swaaij, 1988):

$$K_{\mathrm{app}} = K_{\mathrm{ov}} - K_{OH^-}{}^*[OH^-] \tag{II.17}$$

Therefore, k_{app} for aqueous primary or secondary amine solution can be written as (Blauwhoff et al., 1983; Versteeg and van Swaaij, 1988):

$$K_{\mathrm{app}} = \frac{K^{Z}_{2,\mathrm{R_1R_1NH}}[CO_2][R_1R_2NH]}{1+\frac{K^{Z}_{-1}}{K_{\mathrm{R_1R_1NH}}[R_1R_2NH]+K_{OH^-}[OH^-]+K_{\mathrm{H_2}O}[H_2\mathrm{O}]}} \quad \text{(II.18)}$$

Where, $K^{Z}_{2,\mathrm{R_1R_1NH}}$ is a second-order reaction rate constant of primary or secondary amine based on the zwitterion mechanism for reaction (1). $K_{\mathrm{R_1R_1NH}}$, K_{OH^-} and $K_{\mathrm{H_2}O}$ are reaction-rate constants for deprotonation of the zwitterion intermediate (reaction 2) by R_1R_2NH, OH^- and H_2O, respectively.

The concentration of OH^- can be estimated using a relation proposed by Astarita et al (Astarita et al., 1983), as :

$$[OH^-] = \frac{K_w}{K_a}\left(\frac{1-\alpha}{\alpha}\right) \quad for\ \alpha \geqslant 10^{-3} = \sqrt{\frac{K_w}{K_a}[Amine]} \quad for\ \alpha \geqslant 10^{-3} \quad \text{(II.19)}$$

Where K_w is equilibrium dissociation constant of water (K_w= $[H^+][OH^-]$), K_a, is equilibrium deprotonation constant of amine:

$$K_a = \frac{[R_1R_2NH][H^+]}{[R_1R_2NH_2^+]} \quad \text{(II.20)}$$

And α is CO_2 loading (mol CO_2 /mol amine). In addition, OH^- can also be estimated with the vapor–liquid equilibrium model (Aboudheir et al, 2003; Ramachandran et al, 2006). The experimental values of k_{app} at specific temperatures are now correlated with the zwitterion mechanism of Equation (II.18) in order to obtain individual rate constants of $K^{Z}_{2,\mathrm{R_1R_1NH}}$, K_{OH^-} and $K_{\mathrm{H_2}O}$.

2) Tertiary amine:

Tertiary amine (e.g., TEA and MDEA) does not react with CO_2 directly, but it acts as a base that catalyzes the hydration of CO_2 (base-catalyzed hydration mechanism). The apparent rate constant for tertiary amine based on the base-catalyzed hydration mechanism can be expressed as (Yu et al., 1985):

$$K_{app} = K_{\mathrm{R3N}}[R_3N] \quad \text{(II.21)}$$

3) Primary sterically hindered amine:

One of the best-known hindered amines is AMP, which is the hindered amine of MEA. The reaction kinetics of AMP has been studied widely. Chakraborty et al., were among the first to study the reaction mechanism and kinetics of CO_2 absorption in AMP solution (Chakraborty et al., 1985). By using ^{13}C NMR, they observed that no carbamate peak can be detected. Therefore, they suggested the hydration of CO_2 as shown in equation II.22, as an alternative mechanism instead of carbamate formation (denoted $R'R''NH$ as AMP):

$$R'R''NH + CO_2 + H_2O \leftrightarrow R'R''NH_2^+ + HCO_3^- \quad \text{(II.22)}$$

In addition, Yi and Shen assumed that carbamate species cannot be formed in the case of AMP (Yih and Shen, 1988). Therefore, they suggested an alternative mechanism as shown in

$$R'R''NCOO^-H^+ + H_2O \leftrightarrow R'R''NH_2^+ + HCO_3^- \quad \text{(II.23)}$$

However, these mechanisms do not represent the fast absorption rate of AMP very well. Later, Alper (1990), and Bosch et al., (1990), successfully applied the zwitterion mechanism to AMP. Since an unstable carbamate species is formed in the case of AMP, the unstable carbamate is then hydrolyzed to form bicarbonate, as shown in Equation (II.24):

$$R'R''NCOO^- + H_2O \leftrightarrow R'R''NH + HCO_3^- \quad \text{(II.24)}$$

In addition, Alper (1990) and Bosch et al. ,(1990)., also found that the reaction order with respect to CO_2 concentration and AMP concentration is 1 (the overall reaction order is 2).

Based on the zwitterion mechanism, k_{app} can be written as (Bosch et al., 1990):

$$K_{\mathrm{app}} = \frac{K_{2,\mathrm{AMP}}^{z}[CO_2][AMP]}{1+\frac{K_{-1}^{z}}{K_{\mathrm{AMP}}[R_1R_2NH]+K_{OH^-}[OH^-]+K_{\mathrm{H}_2O}[H_2O]}} \quad \text{(II.25)}$$

4) Solvents containing polyamines:

PZ (which is a secondary cyclical amine with two secondary amine groups) has been studied the most due to its high reactivity and absorption capacity (Dang and Rochelle, 2003). Since PZ is a secondary amine, the zwitterion mechanism has been generally applied. In addition, PZ has two nitrogen atoms, and carbamate species can be formed from both of them. The reactions between CO_2 and PZ can be written as:

$$PZ + CO_2 \overset{K_b}{\leftrightarrow} PZH^+COO^- \tag{II.26}$$

$$PZH^+COO^- + B \xleftrightarrow{K_{2,PZ}} \mathrm{PZ}COO^- + BH^+ \tag{II.27}$$

By applying a pseudo-steady state approximation for the zwitterion, the rate expression of PZ is found to be the same as that of primary and secondary amines

$$r_{CO2} = \frac{K^Z_{2,PZ}[CO_2][PZ]}{1+\frac{K^Z_{-1}}{\sum_b[B]}} \tag{II.28}$$

It has been reported by several researchers that: $\frac{K^Z_{-1}}{\sum_b[B]}$ <<1, in the case of PZ (Bishnoi and Rochelle, 2002; Ko and Li, 2000, Derks et al., 2006). This is because of the high basic strength of PZ (pKa value of PZ is 9.731).

5) Blended amine system:

Chakravarty et al. (1985) were the first to propose blending primary or secondary amines with tertiary amines to leverage the advantages of each type, where the strengths of one amine compensate for the weaknesses of another. The effectiveness of such blended amine systems has been widely demonstrated in the literature, with examples including MEA–MDEA, MEA–AMP, MEA–PZ, MDEA–PZ, and AMP–PZ (Edali et al., 2010; Ko and Li, 2000; Ramachandran, 2006; Caplaw, 1968; Xiao et al., 2000; Bruder et al., 2011). The simplified kinetic model for blended amines follows the same approach used for single amines, where the overall reaction rate accounts for the contribution of each individual amine in the blend.

Conclusion:

Reaction kinetics is one of the most critical parameters in amine –based acid gas capture processes, as it determines how quickly the acid gas reacts with the amine. It is also a key parameter in the simulation and design of the absorption column. To obtain kinetic data, CO_2 absorption experiments must be carried out using laboratory-scale gas liquid contactors, such as a stirred cell reactor, wetted wall column, laminar jet absorber, watted sphere absorber, sring of disc contactor, or a stopped-flow apparatus.

The stopped-flow technique is the most widely used rapid-mixing method for studying CO_2 amine reactions and is the technique used in our kinetic study. This method is free from gas-liquid mass transfer limitations, and the signal obtained directly reflects the intrinsic liquid-phase reaction, making the results highly reproducible.

For the absorption of CO_2 into our amine solutions, a simplified model based on the reaction mechanism approach has been applied. The kinetic data obtained from the gas-liquid contactor are interpreted according to the proposed mechanisms of CO_2 amine interaction, such as the zwitterion machanism and the base-catalyzed hydration machanism.

Chapter III : Kinetics of Absorption of Carbon Dioxide in Aqueous MDEA, Blended (MDEA+PZ), (MDEA+Sulfolane)

Introduction:

The presence of carbon dioxide in natural gas increases its volume, reduces its heating value, and may enhance corrosion in pipelines and processing plants. Reaction kinetics data are crucial when selecting a chemical solvent for CO_2 absorption. Measuring the reaction kinetics of promising solvents provides the necessary information for the design and simulation of absorption/regeneration columns.

The reason for using such blends lies in the relatively high rate of CO_2 reaction with the activator, combined with the advantages of tertiary amines in terms of regeneration and stoichiometric loading capacity. This leads to higher absorption rates in the absorber column while maintaining low regeneration heat in the stripper section.

The primary objective of this investigation is to present the kinetic properties for the absorption of CO_2 in aqueous solutions of MDEA, MDEA mixed with PZ, and MDEA mixed with Sulfolane using the classical stopped-flow technique.

III.1) Experimental Section:

III.1.1) Chemicals:

Reagent-grade PZ with a mass purity of 99%, MDEA (99%), and Sulfolane (99%) were sourced from Sigma-Aldrich Co., Canada. All chemicals were used as received, without further purification. Deionized water available in the laboratory was used in appropriate amounts to achieve the desired sample concentrations where necessary. The purity of the Carbon dioxide (CO_2) gas, is 99.99 vol. %. For each experiment, an aqueous solution of CO_2 was prepared by bubbling research-grade CO_2 into water for up to two hours. The solution was then further diluted with water to ensure an amine concentration significantly higher than that of CO_2, maintaining a concentration of amines at least ten times lower than CO_2 in order to achieve pseudo-first-order reaction conditions.

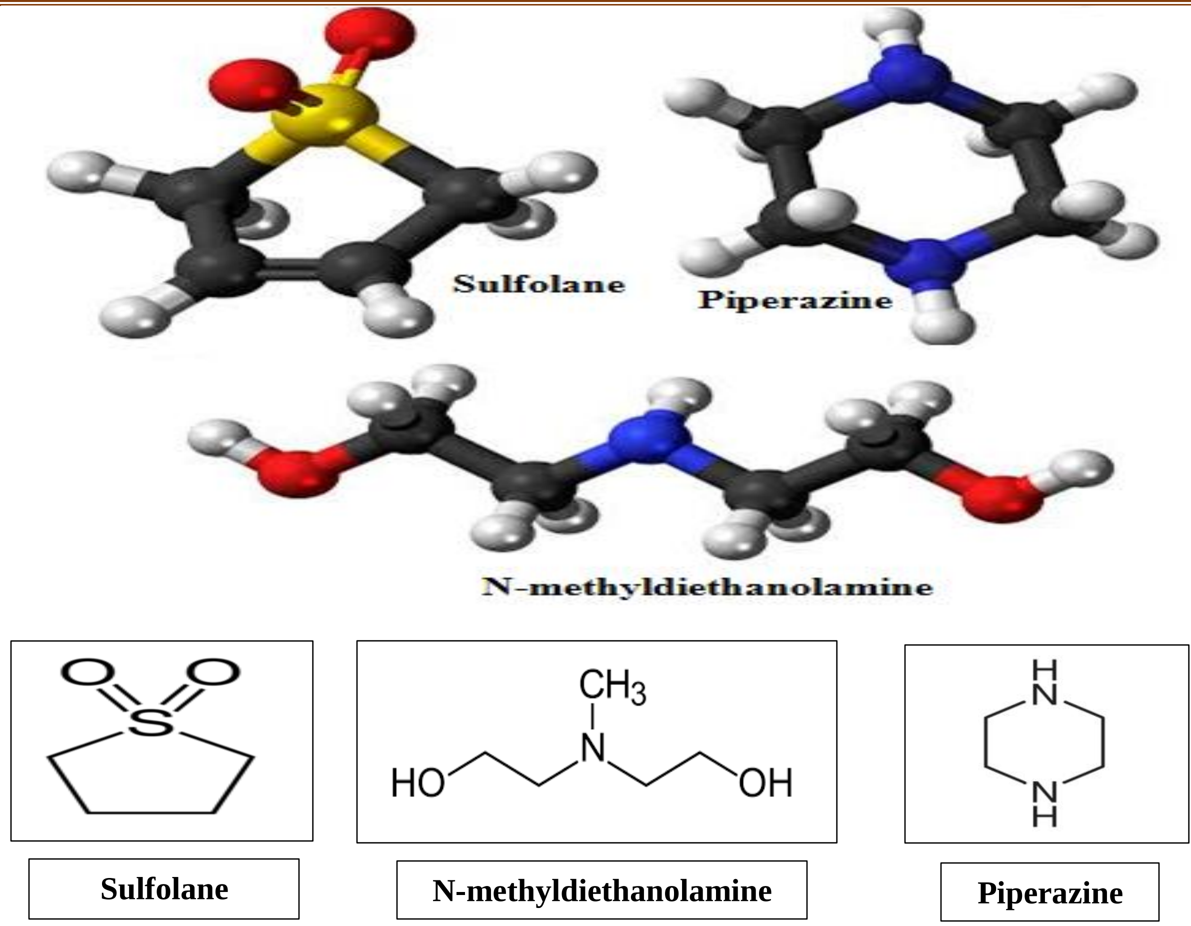

Figure III.1: Chemical structure of the selected amines in this study

III.1.2) Experimental Setup:

This research work involves the use of the Stopped flow technique to directly measure the pseudo first-order reaction kinetics, K_0, for aqueous solutions of different alkanolamines at various concentrations over a range of temperatures.

The equipment configuration for the stopped-flow technique consists of a standard SF-51 stopped flow unit from Hi-Tech Scientific Ltd., UK. The setup is an assembly of four equipment components; a sample-handling unit, a conductivity-detection cell, an A/D converter and a microprocessor. The external case of the sample-handling unit is made up of stainless steel which provides rigidity and support for the sample flow circuit as well as an enclosure for all the internal components. A schematic drawing of the experimental stopped-flow equipment for the sample handling unit is presented in Figure III.2.

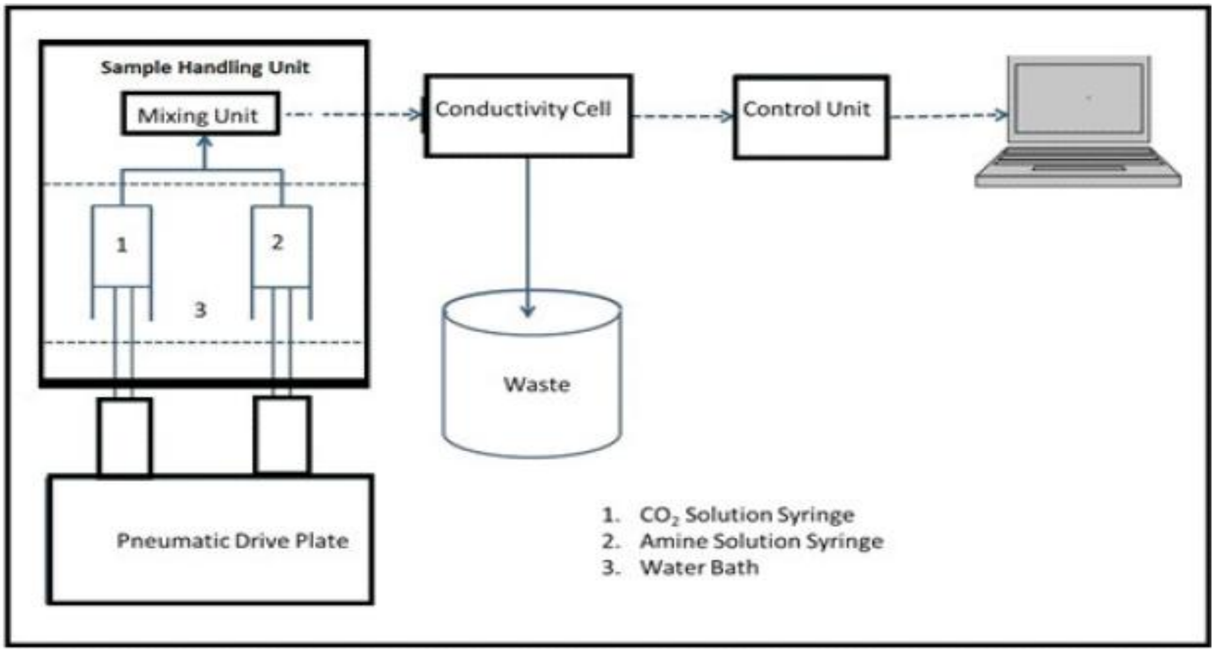

Figure III.2: Schematic diagram of stopped-flow equipment showing the major units

The complete flow circuit, except the stop/waste syringe, is sealed off securely in a thermostat and the temperature at which the reaction takes place is kept steady by an external water bath. The temperature of the water bath can be set to desired value within ± 0.1 K. The digital display on the front panel of the sample handling unit shows the temperature at which the reaction is taking place. The temperature on the digital display can be changed by adjusting the temperature reading on the control module for the HAAKE DC 30 attached to the water bath which can provide temperature increments of 0.1^{o}C. The control valves on the sample handling unit are driven by compressed air supplied by an air cylinder located in the laboratory.

The front panel of the unit has an air pressure indicator which shows the current air pressure is provided to drive the valves and mechanism. Other areas powered by the pneumatic air supply are the movement of the drive plate located at the bottom of the internal syringes that contain the CO_2 solution and amine solution. For each experimental procedure, a fresh solution of CO_2 was prepared and loaded into a 5ml plastic syringe along with a new solution of alkanolamines of known concentration, loaded into a second plastic syringe. An aqueous solution of CO_2 can be prepared by bubbling the gas through double-distilled water. The fresh CO_2 solution used during the experiment was prepared by bubbling research grade CO_2 for at least 02 hours through the double-distilled water until the water was completely saturated with CO_2. The bubbling procedure took place by allowing CO_2 gas supplied in a gas cylinder, to travel through a gas line completely immersed in the measured amount of water. A plastic film was used to cover the conical flask during the bubbling procedure to keep the pressure of the system constant. This saturation point was verified by measuring the pH of the solution during the bubbling process and waiting for the pH value to remain constant when the saturation point was reached. A small amount of double-distilled water was used to dilute the prepared CO_2 solution to achieve a solution whose concentration is at least ten times lower than the amine solution to fulfill pseudo first-order reaction conditions.

To run an experiment, the solvent samples were loaded into the Sample Handle Unit using plastic syringes before turning on the equipment. The valve on the air cylinder is open to allow compressed air to flow to power the pneumatic valves. By clicking the “Single shot” button within the KinetAsyst software for an experimental run, the plates drive the Stop/Waste valve based on program instructions from the software, supporting the stop syringe and allowing the valve to automatically advance to the waste position as it empties the stop syringe. After this time, the valve would proceed back to the drive position, and the pneumatic drive plate forces the fresh solution to move down the observation cell, replacing the old solution used during the previous run. The stopped-flow conductivity detection system is designed to measure the intrinsic rate of rapid homogeneous reaction directly. The sample flow circuits are fully equipped with a temperature probe inside the observation cell to measure the temperature of the system so that the temperature of the reaction remains constant until it reaches the desired set-point. The range for the temperature control is around -0.1 K, (Yan *et al.*, 2000). It is of vital importance to state that the amine and the CO_2 solutions are drawn into sealed drive

syringes, and an equal amount of the solution is injected into the observation cell of the apparatus. The rate of formation of ions is monitored closely in relation to time by the conductivity cell. The computer connected to the stopped-flow equipment automatically indicates the observed pseudo first-order constant based on the output voltage values. All other sections of the equipment coordinate the operation of the stepper motor, powering on/off all internal components and the sample handling unit, as well as driving the feature that automatically empties all waste fluid during the Drive/Waste/Flush cycle in addition to the air drive control circuitry. “KinetAsyst" software is a program that runs on the computer connected to the stopped-flow equipment via a data cable and is used to operate the pneumatically controlled drive plate which pushes the precise amount of prepared solution into the conductivity detection cell through a mixing loop. The change in conductivity is measured about time by a circuit as described by Knipe *et al.,* (1974), which produces an output voltage relative to the solution conductivity. The observed experimental data of each experimental run for the amine/CO_2 reaction was generated based on the output conductivity values. For all amine concentrations, every experiment run in the same temperature was repeated at least 10 times to ensure accurate results. The conductivity change of each experimental run with respect to time is fitted based on the relation G(t) , Knipe *et al.,* (1974) which was shown as

$$G(t) = -A\,exp(-K_0 t) + C \qquad \text{(III.1)}$$

Where K_0 is the pseudo-first-order reaction rate constant, G(t) is the value of conductivity obtained from the conductivity meter, A is the amplitude of the signal, C is the constant conductance value at the end of observed reaction and t is the time (s). This method was deemed to not involve a gas-phase absorption, so the experiment results were able to be directly correlated with reaction rate of an intrinsic homogeneous reaction between amine and CO_2 in liquid phase.

A significant advantage to using the stopped-flow technique is that each experimental run only requires a small amount of reactants (approximately 0.1 ml each) and the equipment is easy to operate.

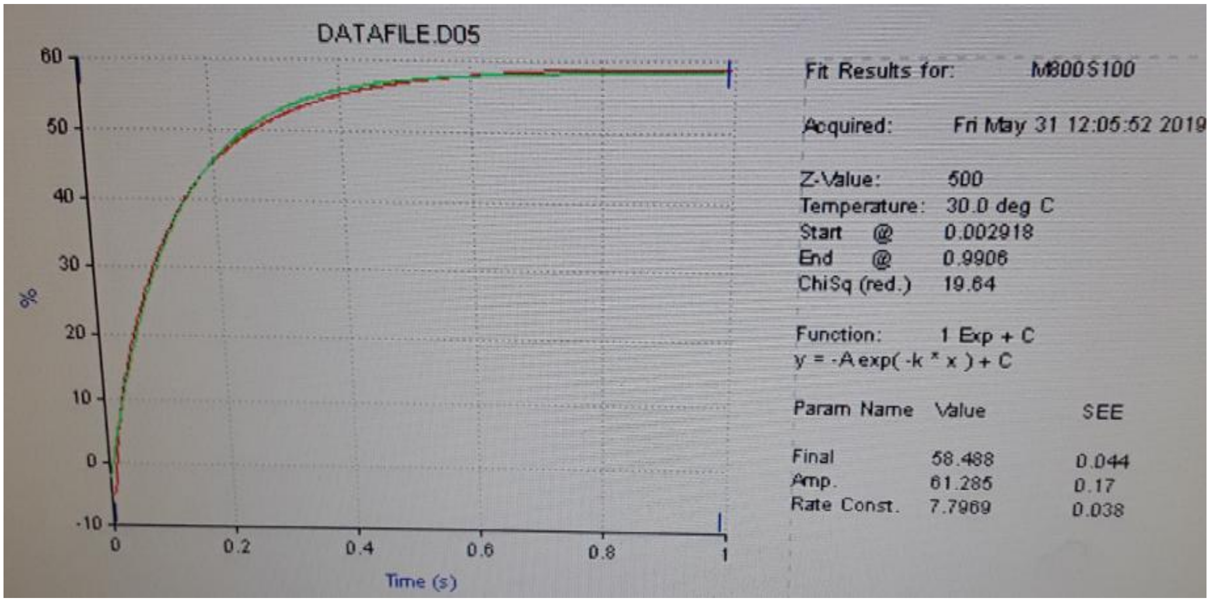

Figure III.3: A graphical plot of the stopped-flow experiment at a set temperature

III.1.3) Experimental validation:

To accurately determine the absorption kinetics of CO_2 in selected amines, the stopped-flow apparatus was first used to measure the reaction kinetics of CO_2 with an aqueous solution of MEA, ensuring the accuracy of the data obtained from the equipment. This reaction has been extensively studied by numerous researchers, with data available in reputable literature publications using the stopped-flow technique. To validate the stopped-flow technique, several runs were conducted to measure the kinetics of CO_2 with MEA across a concentration range of (5 to 34) mol/m³ and a temperature range of (298.15 to 313.15) K. The results were then compared with corresponding published data, as shown in Figure III-4. The reproducibility of the measurements was better than 3%, with an absolute average deviation (AAD) of 15 sets of values from the mean. The values obtained in this study compare favorably with those published by Sodiq et al. (2014), showing an AAD of less than 5% for all concentrations and temperatures. These results confirm that the methodology employed in this research is highly accurate and can, therefore, be considered a reliable method for generating precise reactionkinetics data for the selected solvents in this study.

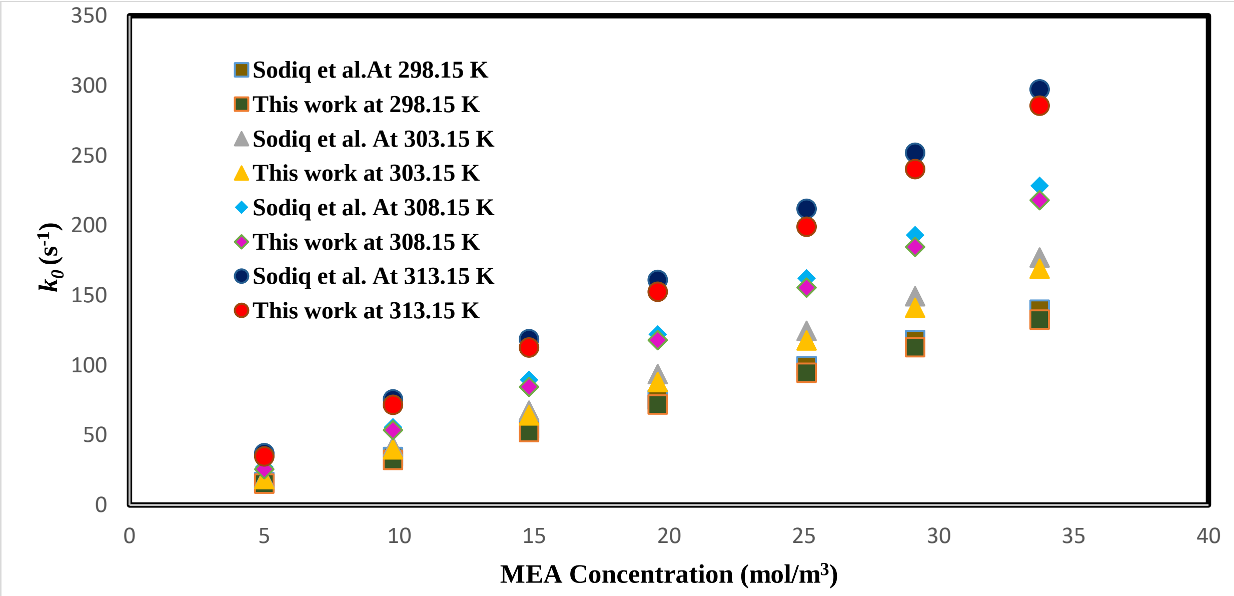

Figure III.4: Comparison of k0 values for CO2 reaction with aqueous MEA with those published by Sodiq et al., (2014) at different temperatures and concentrations

III.2) Kinetics of CO_2 absorption into aqueous amine solutions:

The kinetics of CO_2 absorption into aqueous amine solutions have been the subject of extensive research involving both single and blended amines such as MEA, DEA, MDEA, AMP, and their combinations (Versteeg and Van Swaaij, 1988b; Saha and Bandyopadhyay, 1995; Mandal et al., 2001; Zhang et al., 2001; Sun et al., 2005; Edali et al., 2009). Saha and Bandyopadhyay (1995) investigated CO_2 absorption in aqueous AMP using a wetted wall column over a range of temperatures (294–318 K) and concentrations (0.5–2 M), applying the zwitterion mechanism and determining rate constants and reaction orders graphically. Ramachandran et al. (2006) studied CO_2 absorption in CO_2-loaded MEA-MDEA blends using a laminar jet absorber, fitting experimental data to both the zwitterion and termolecular mechanisms.

Further investigations by Rinker et al. (1995, 2000) used a wetted sphere absorber to explore the kinetics in unloaded MDEA and DEA-MDEA solutions over a temperature range of 293–342 K and 10–30 wt% MDEA. Their models incorporated chemical equilibrium, mass transfer, and reaction kinetics. This comprehensive modeling approach was later extended to blends such as MEA-MDEA and MDEA-PZ (Edali et al., 2007; 2009).

The reaction of CO_2 with alkanolamines is significantly influenced by amine structure. Primary and secondary amines form carbamate ions via a zwitterion intermediate, as described by Caplow (1968) and Danckwerts (1979), whereas tertiary amines, incapable of carbamate formation, facilitate CO_2 hydrolysis to bicarbonate ions, as proposed by Donaldson and Nguyen (1980).

III.3) Reaction mechanisms:

III.3.1) Reaction kinetics of CO_2 in aqueous MDEA:

MDEA is currently the most widely used tertiary amine for acid gas removal, surpassing earlier amines such as TEA , which was the first amine employed in gas sweetening applications (Bottoms, 1930). When appropriate additives are incorporated, MDEA offers several advantages over other amines for bulk CO_2 removal (Bullin et al., 1990, 1992). In aqueous solutions, the primary reaction between MDEA and CO_2 results in the formation of bicarbonate. Unlike primary and secondary amines, MDEA does not form carbamates due to the lack of a hydrogen atom attached to the nitrogen atom, which leads to a slower absorption rate. To enhance the reaction rate, activating agents, such as other amines with faster reaction rates, can be added to the MDEA solution. MDEA also reacts rapidly with H_2S, following the same fast reaction mechanism seen in primary and secondary amines. This makes MDEA highly effective in selectively absorbing H_2S in the presence of CO_2.

MDEA can be used in concentrations as high as 50 wt% in combination with significant CO_2 loadings. Additionally, MDEA exhibits minimal amine loss due to its low vapor pressure and slow degradation rate. Compared to other amines like MEA and DEA, MDEA solutions are less corrosive (Bullin et al., 1990). The most widely accepted mechanism for the CO_2 reaction in MDEA solutions is that MDEA acts as a base catalyst for CO_2 hydration. It functions as a homogeneous catalyst in the CO_2 hydrolysis reaction. Versteeg and Van Swaaij (1988b) also supported the notion that the base catalysis of CO_2 hydration governs the reaction between CO_2 and tertiary amines. The kinetic reaction can be represented by the following equation, as proposed Donaldson and Nguyen (1980):

$$MDEA + H_2O + CO_2 \overset{K_2}{\Rightarrow} MDEA^+ + HCO_3^- \quad (III.2)$$

The following reactions also occur:

$$CO_2 + OH^- \overset{K_{OH^-}}{\Longleftrightarrow} HCO_3^- \quad (III.3)$$

$$CO_2 + H_2O \overset{K_{H_2O}}{\Longleftrightarrow} H_2CO_3 \quad (III.4)$$

$$r_{CO2} = K_0[CO_2] = [CO_2](K_2[MDEA] + K_{H_2O}[H_2O] + K_{OH^-}[OH^-]) \quad (III.5)$$

In aqueous solutions, the contribution of un-catalyzed equation (III.4) to the overall reaction is usually negligible, as the reaction rate is slow with respect to mass transfer compared to equations (III.2) and (III.3) according to Littel et al., (1990):

$$Am + H_2O \overset{K_p}{\Leftrightarrow} AmH^+ + OH^- \quad (III.6)$$

Where K_p is amine protonation rate constant .

According to Littel et al., (1990), reactions (III.2) and (III.3) are parallel pseudo first order reactions, and they reduced the expression for the reaction rate constant from Equation (III.5) to:

$$r_{CO_2} = K_0[CO_2] = [CO_2](K_2[MDEA] + K_{OH^-}[OH^-]) \quad (III.7)$$

This mechanism leads to the increase of the reactivity towards the carbon dioxide and the weakness of the O-H bond in the water because of the formation of a hydrogen bond between the tertiary amine and water. By considering the contribution of OH^- ions to be negligible, this expression reduces to the following rate expression:

$$r_{CO_2} = K_0[CO_2] = [CO_2](K_2[MDEA]) \quad (III.8)$$

The equation (III.2) becomes:

$$K_0 = K_2[MDEA] \quad (III.9)$$

III.3.2) Reaction Kinetics of CO_2 in the Blended Aqueous MDEA-PZ System:

In the MDEA/PZ system, a combination of the Zwitterion and base-catalysis mechanisms, as proposed by Ali et al. (2010), is used to describe the reaction kinetics. The reaction rate expression is given by:

$$K_0 = K_{2,MDEA}[MDEA] + \frac{[PZ]}{\frac{1}{K_{2,PZ}} + \frac{1}{K_{PZ,PZ_Z}[PZ] + K_{MDEA,PZ_Z}[MDEA] + K_{w,PZ_Z}[w]}} \quad \text{(III.10)}$$

In this system, MDEA, being a tertiary amine, contributes to the deprotonation of the zwitterion.

III.3.3) Reaction kinetics of CO_2 in blended Aqueous MDEA-Sulfolane system:

The main reaction in the blended Aqueous MDEA-Sulfolane system involves CO_2 reacting with MDEA, while secondary reactions include CO_2 interacting with water and the hydroxyl ion (OH-), in addition to the physical absorption of CO_2 by Sulfolane and water. The mechanism governing these reactions is well-understood and described by Donaldson and Nguyen (1980) as a "base-catalyzed hydration" process, commonly used to explain the interaction between CO_2 and tertiary amines. According to Xu et al. (1991), Sulfolane, as a physical solvent, only facilitates the deprotonation of the zwitterion in aqueous solutions. The reaction rate is expressed as:

$$k_0 = k[\mathrm{MDEA}]^{\mathrm{n}} \quad \text{(III.11)}$$

In this study, the data were modeled by keeping the Sulfolane concentration constant to determine the reaction order with respect to MDEA. The resulting values for the reaction order (n) were consistently close to one across all tested Sulfolane concentrations, while the MDEA concentration varied for each temperature studied.

III.4) Results and discussion:

III.4.1) Absorption kinetics of CO_2 in aqueous MDEA:

The absorption of CO_2 in an aqueous MDEA solution with concentrations ranging from 200 to 800 mol/m^3 was studied at different temperatures (298.15, 303.15, 308.15, and 313.15 K) with a 5 K temperature interval. The observed pseudo-first-order rate constants (K_0) for MDEA in aqueous solution are shown in Figure III.5 as a function of MDEA concentration. The amine concentration was kept at least ten times the CO_2 concentration to maintain the pseudo-first-order reaction conditions. The pseudo-first-order rate constants (K_0) increase with the increase in aqueous MDEA concentration as well as temperature (Table III.1).

Table III. 1: Experimental kinetic data for (CO2-MDEA-Water) at different temperatures

[MDEA)] (mol/m^3)	T (K)			
	298.15	**303.15**	**308.15**	**313.15**
	k_0 (s^{-1})			
200	1.79	2.79	3.62	4.81
300	2.87	4.18	5.39	7.19
400	3.51	5.62	7.22	9.62
500	4.51	7.09	9.08	12.11
600	5.45	8.38	10.78	14.39
700	6.31	9.81	12.61	16.79
800	7.32	11.22	14.38	19.21

Table III.1 shows all the values of pseudo-first order reaction rate constants (K_0) obtained from the experimental procedure for MDEA within a temperature range of (298.15-313.15) K. The experimental values of the pseudo-first order reaction rate constant, K_0 was plotted against the concentration of *N*-Methyldiethanolamine, [MDEA] and shown in figure III.5

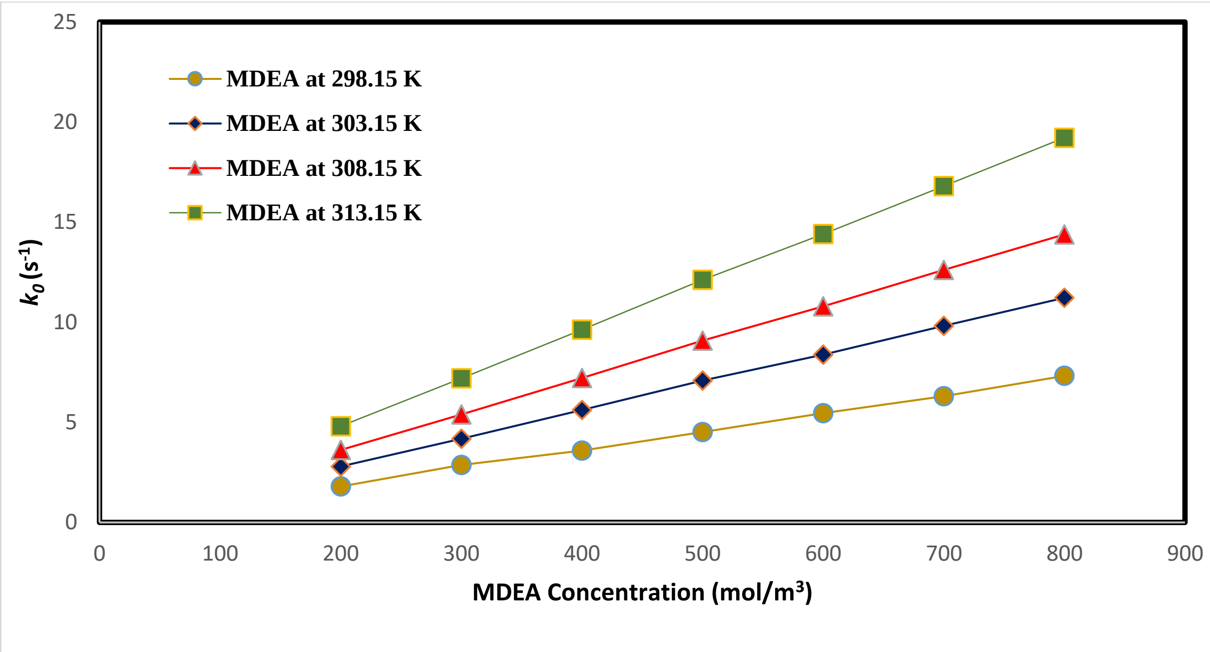

Figure III.5: Plot of pseudo-first-order reaction rate constants K0 versus MDEA concentrations at different temperatures

In Figure III.5, the graphical plot shows the relationship between the pseudo-first-order reaction rate constant (K_0) on the y-axis and the amine concentration on the x-axis. It is evident from the plot that as the temperature increases, the slope values progressively rise, indicating that the rate constant increases steadily with temperature. At all temperatures, the pseudo-first-order reaction rate constant (K_0) also increases as the amine concentration increases. This acceleration in reaction kinetics is attributed to the basicity of the solvent. The pseudo-first-order rate constants for aqueous MDEA across a temperature range of 298.15 to 313.15 K were modeled using power-law kinetics as a function of amine concentration, expressed by the equation:

$$K_0 = K_{Am}[Am]^n \qquad \text{(III.12)}$$

Here, K_{Am} represents the power-law constant (in m^{3n}/mol^n s), [Am] is the amine concentration, and n is the reaction order. By fitting the empirical power-law kinetics to the experimentally observed pseudo-first-order rate constants for CO_2 in Figure 3, the reaction orders with respect to [MDEA] were determined as 0.992, 1.002, 0.997, and 0.999 at temperatures of 298.15, 303.15, 308.15, and

313.15 K respectively. This empirical curve fitting indicates that the reaction order with respect to [MDEA] is approximately 1. The Arrhenius plot for this reaction was derived by plotting the natural logarithm of the second-order rate constant (Ln K_2) at different temperatures against the inverse of the experimental temperature (1/T in Kelvin), as shown in Figure III.6 .

The Arrhenius equation for the reaction is given by:

$$K_2 = Aexp\left({}^{-E_a}/_{RT}\right) \tag{III.13}$$

Where A is the Arrhenius constant (m^3/mol·s), (E_a) is the activation energy (kJ/mol), and R is the universal gas constant (0.008315 kJ/mol·K).

Figure III.6 displays the corresponding Arrhenius plot, from which the activation energy (Ea) for the reaction of aqueous CO_2 with aqueous MDEA was determined to be 49.15 kJ/mol. The derived Arrhenius equation for the CO_2-MDEA system is:

$$K_2\,(m^3/mol.\ s) = 3.917\times10^6\ Exp\,(-5912/T)\ ,\ [R^2 = 0{,}9878] \tag{III.14}$$

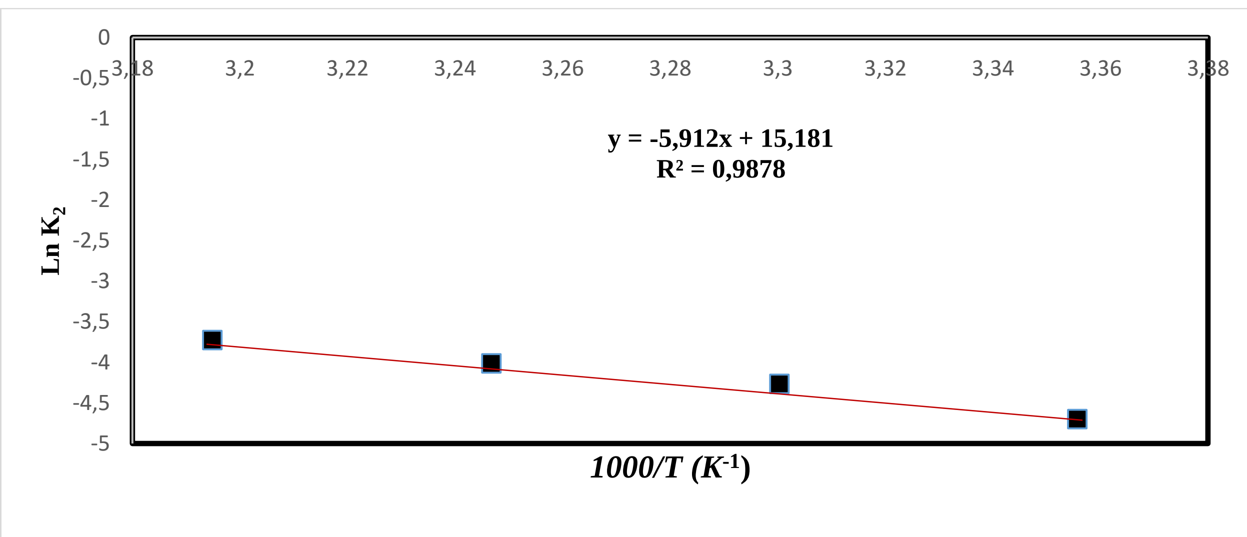

Figure III.6: Arrhenius plots of aqueous (CO2-MDEA) rate constants using base catalysis mechanism

Table III.2 presents the estimates of the second-order rate constants (K_2) obtained in this study, along with selected literature values determined using various research methods. As shown in

Table III.2, the second-order rate constants (K_2) (in $m^3/mol \cdot s$) exhibited an increasing trend with respect to both concentration and temperature. These values were then compared with those reported in the literature.

Table III. 2: Second-order rate constants (K2) of MDEA with CO2 at different temperatures

T (K)	K_2 (m^3/mol. s)		
	MDEA[a]	MDEA[b]	MDEA[c]
298.15	0.012	0.009	0.007
303.15	0.016	0.014	0.01
308.15	0.022	0.018	0.015
313.15	0.028	0.024	0.021

[a]Versteeg and Swaaij(1996), [b]This work, [c]Kiezkowska-Pawlak et al,(2011)

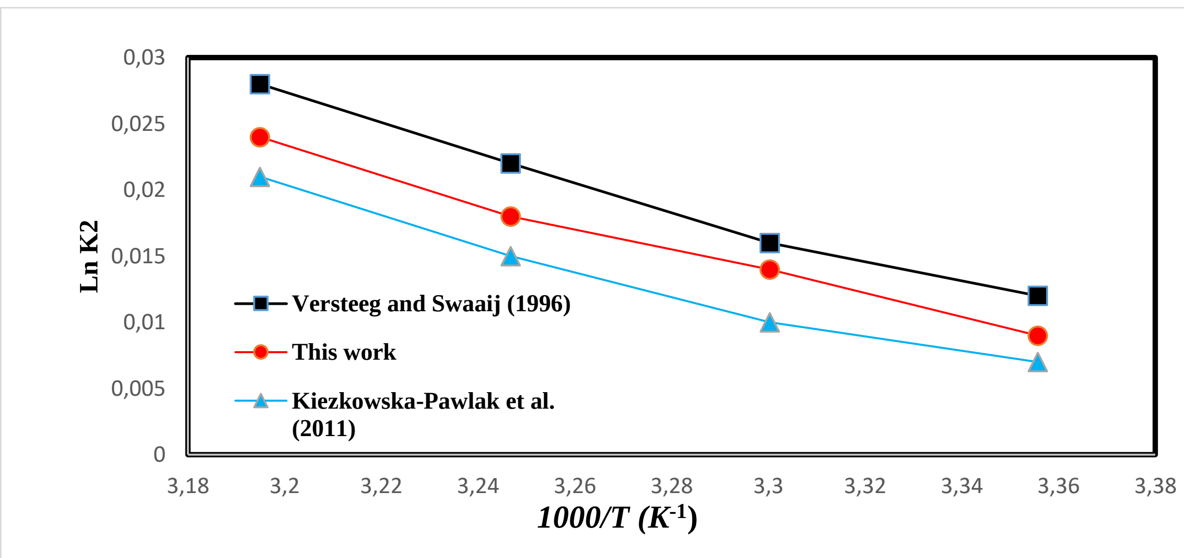

Figure III.7: Comparison of Arrhenius plots of aqueous (CO2-MDEA) rate constants of this work and the literature

The estimates of K_2 are presented in Figure III.7 for comparison with selected literature values obtained using different research methods. The values of K_2 determined in this study show good agreement with those reported by Versteeg and Swaaij (1996) across the entire temperature range. As shown in Figure III.7, the K_2 values from Kierzkowska-Pawlak et al. (2011).

The use of MDEA, a tertiary amine, offers several advantages over the use of MEA (a primary amine) or DEA (a secondary amine). First, MDEA selectively removes H_2S from gas streams, with a very fast reaction rate through a proton transfer mechanism. In contrast, the reaction of CO_2 with MDEA is relatively slow and finite. Since MDEA does not react directly with CO_2 during the absorption process, stripping can be achieved easily through simple pressure reduction. As a result, the energy required for stripping is significantly lower compared to conventional amines. Due to its low vapor pressure, MDEA can be used in high concentrations. Additionally, MDEA is highly resistant to both thermal and chemical degradation and is essentially non-corrosive. It has a low specific heat and heats of reaction with H_2S and CO_2 and is only sparingly miscible with hydrocarbons (Henni, 2002).

III.4.2) Absorption kinetics of CO_2 in aqueous blended (MDEA + PZ) system:

A kinetic study of the reaction between aqueous CO_2 and a solution of MDEA/PZ was conducted using the stopped-flow technique, across concentration ranges of 200 to 800 mol/m³ for MDEA and 10 to 40 mol/m³ for PZ, and within a temperature range of 298.15 to 313.15 K, with 5 K intervals. The results demonstrated that the reaction rate for PZ reactions is significantly higher than that for the MDEA-catalyzed hydration reaction. Therefore, the main reaction occurring in the blended (MDEA + PZ) solution is the formation of carbamates.

A model based on a hybrid reaction rate, incorporating a zwitterion mechanism for PZ and a simplified first-order reaction for MDEA, was used to correlate the overall reaction rate constant, K0. The kinetic data were well represented by Eq. (III.10). The observed pseudo-first-order rate constants k_0 (S^{-1}) for the reaction between aqueous MDEA + PZ and aqueous CO_2, obtained in this study, are shown in Figures III.8, 9, 10, and III.11. These figures also illustrate the expected trend of an increasing reaction rate as both concentration and temperature increase, as evidenced by the K_0 values.

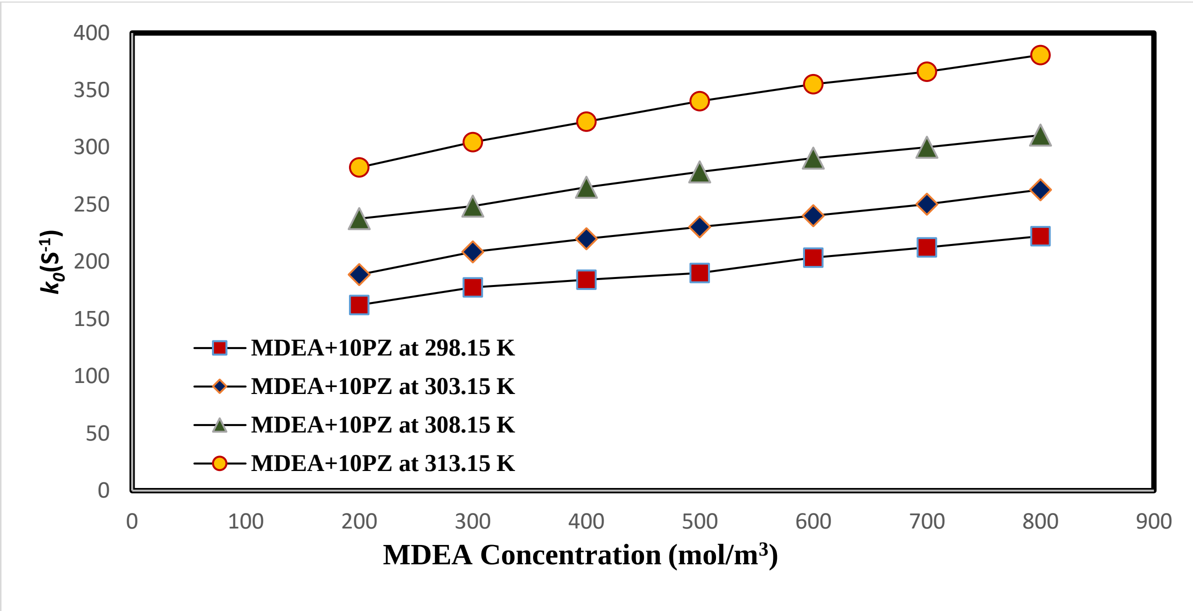

Figure III.8: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 10 mol/m3)] solutions at different concentrations and temperatures.

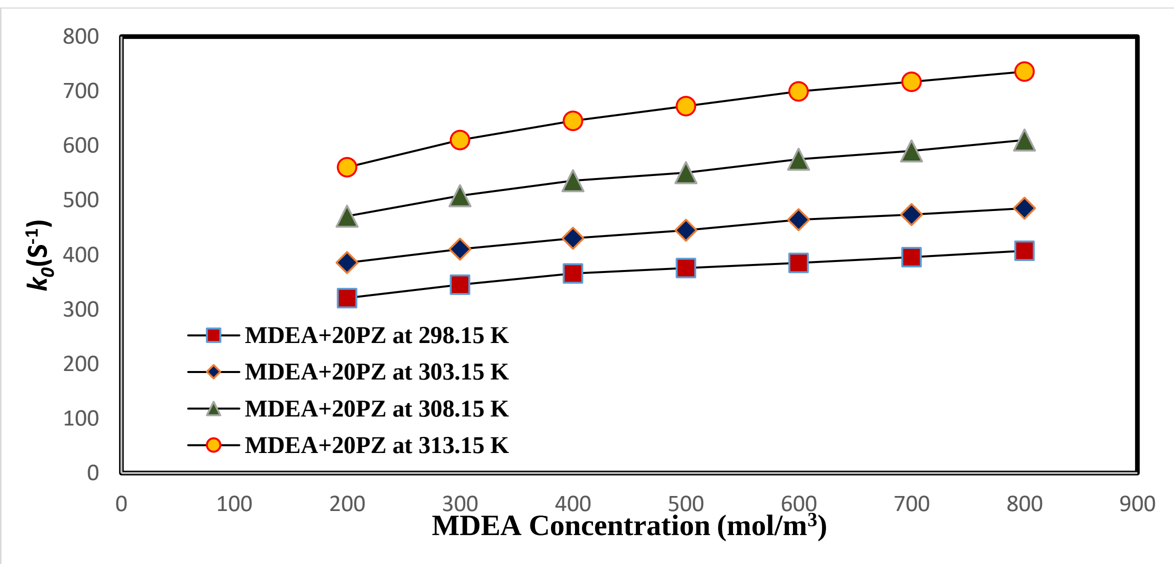

Figure III.9: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 10 mol/m3)] solutions at different concentrations and temperatures.

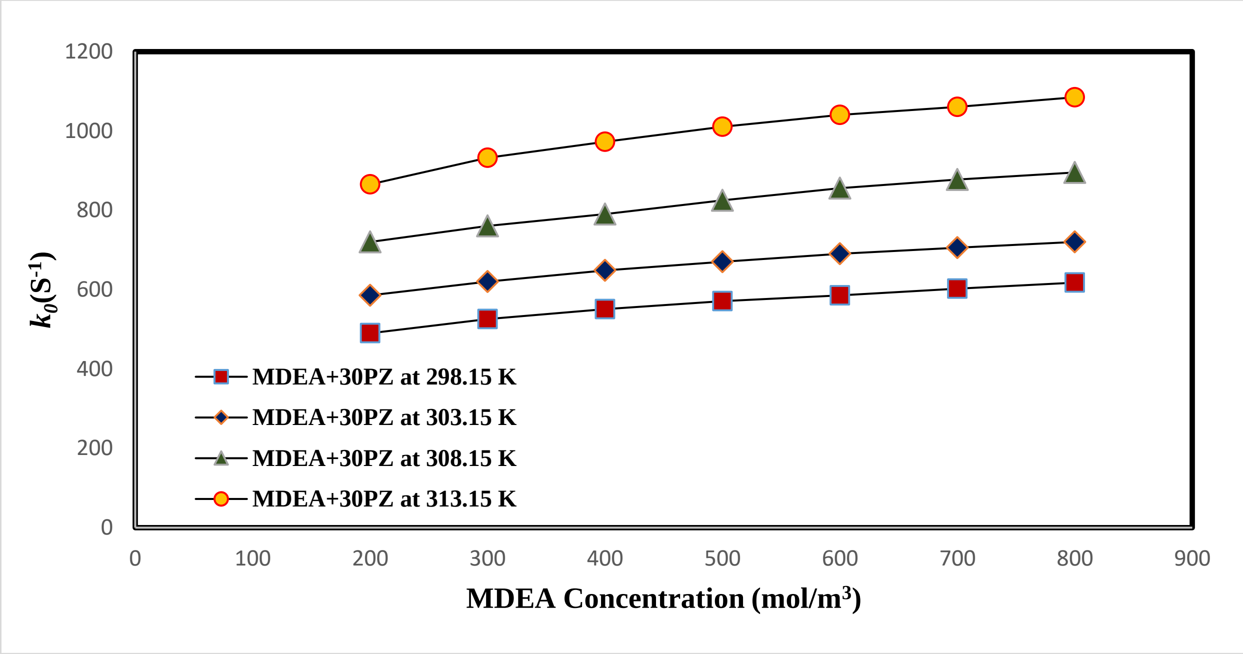

Figure III.10: K0 values of the reaction between aqueous CO2 and aqueous [MDEA+PZ at 30mol/m3)] solutions at different concentrations and temperatures.

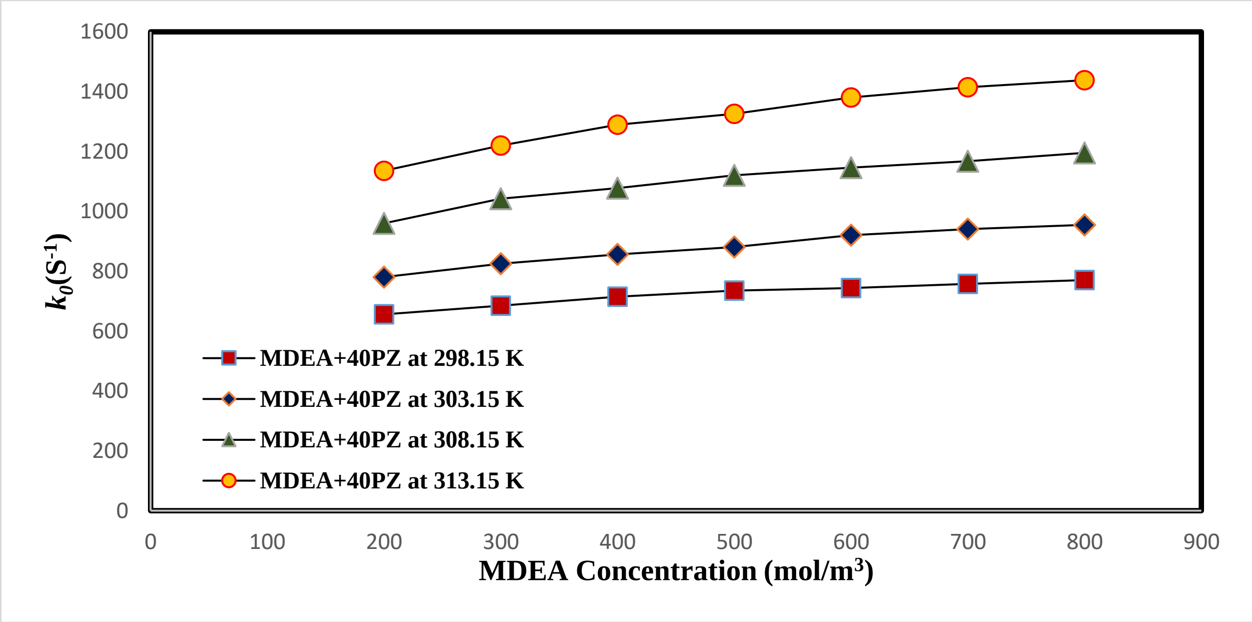

Figure III.11: K0 values of the reaction between aqueous CO2 and aqueous [MDEA/ PZ (40mol/m3)] at different concentrations and temperatures.

Based on K_0 values, the concentration of PZ has strongly impacted the CO_2 absorption rate blended (MDEA + PZ) solutions. Higher concentrations of PZ in (MDEA + PZ) solution gave much higher K_0 values at all temperatures.

After replacing the values of the known rate constants $k_{2,PZ}$, $k_{PZ/PZZ}$, $k_{W/PZZ}$, and $k_{2,MDEA}$ reported in Table III.2 , the only unknown remaining is $k_{MDEA/PZZ}$. This value is obtained by regressing the kinetic data with Equation (III.10) using Excel's Solver program and the results are reported in Table III.3 .

Table III.3 displays the variation of k_2 (m^3/mol· s) valued for both MDEA and PZ as temperature increases. The constants are found to increase in the sequence of $k_{MDEA,PZZ} > k_{PZ,PZ} > k_{W/PZZ}$ at all temperatures. The table also shows that the MDEA molecule has more strength in deprotonating the PZ zwitterion than water. The extent of the reaction enhancement taking place depended on the specific amine, and the concentration of each amine constituent.

Table III. 3: Rate constants regressed using Equation III.10 for aqueous (MDEA+PZ) systems

T (K)	$k_{2,PZ}$ [a]	$k_{2,MDEA}$ [b]	$k_{PZ,PZZ}$ [b]	$k_{MDEA,PZZ}$	$k_{W,PZZ}$ [b]	R^2	AAD%
298.15	22.00	0.009	0.02136	0.1951	1.56 E-04	0.9911	1.77
303.15	26.06	0.014	0.02574	0.2355	1.84 E-04	0.9943	1.27
308.15	32.04	0.018	0.02852	0.2700	1.88 E-04	0.9997	2.16
313.15	40.04	0.024	0.03245	0.3135	1.96 E-04	0.9966	2.16

[a] Table 2; [b] Table 4

Figure III.12 presents a parity plot comparing the predicted pseudo first-order reaction rate constants with the experimental values for blended (MDEA + PZ) systems. The plot clearly demonstrates a strong overall agreement between the predicted and experimental values.

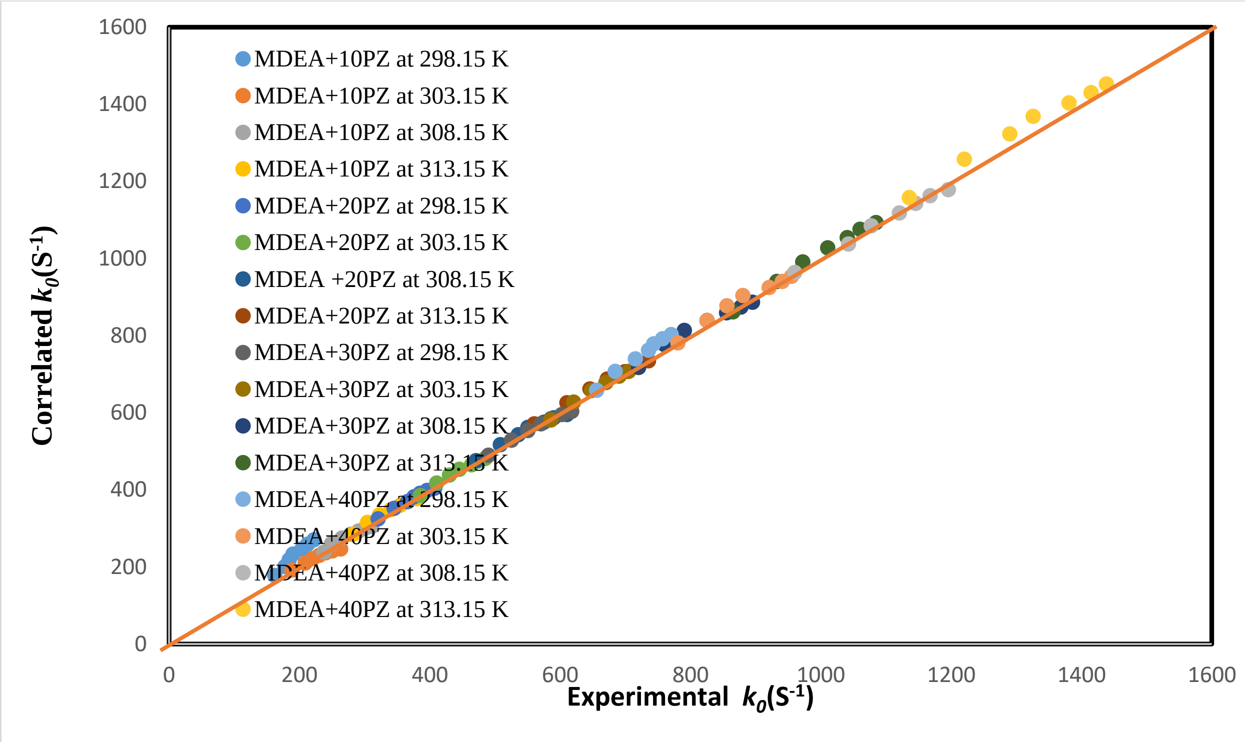

Figure III.12: Parity plot for the experimental and predicted pseudo first-order rate constants for aqueous solutions of (MDEA+PZ) at different temperatures using Zwitterion mechanism.

III.4.3) Reaction of aqueous CO2 with aqueous MDEA + Sulfolane:

To gain a comprehensive understanding of the reaction kinetics between CO_2 and (MDEA-Sul) as a promising solvent for chemical absorption, an experiment was performed using the stopped-flow apparatus. Different samples of (MDEA-Sul) were prepared with concentrations ranging from 200 to 1000 mol/m³ for MDEA and 10 to 200 mol/m³ for Sulfolane, with the experimental temperature set between 298.15 K and 313.15 K.

Graphical plots of the pseudo-first-order rate constants for selected values versus the concentration of (MDEA-Sul) (mol/m³) are shown in Figures III.13, 14, 15, 16, and III.17.

By comparing the absorption kinetics of (MDEA-Sul) with that of MDEA, this will provide valuable insights into the potential of (MDEA-Sul) as a promising alternative absorbent for carbon dioxide capture.

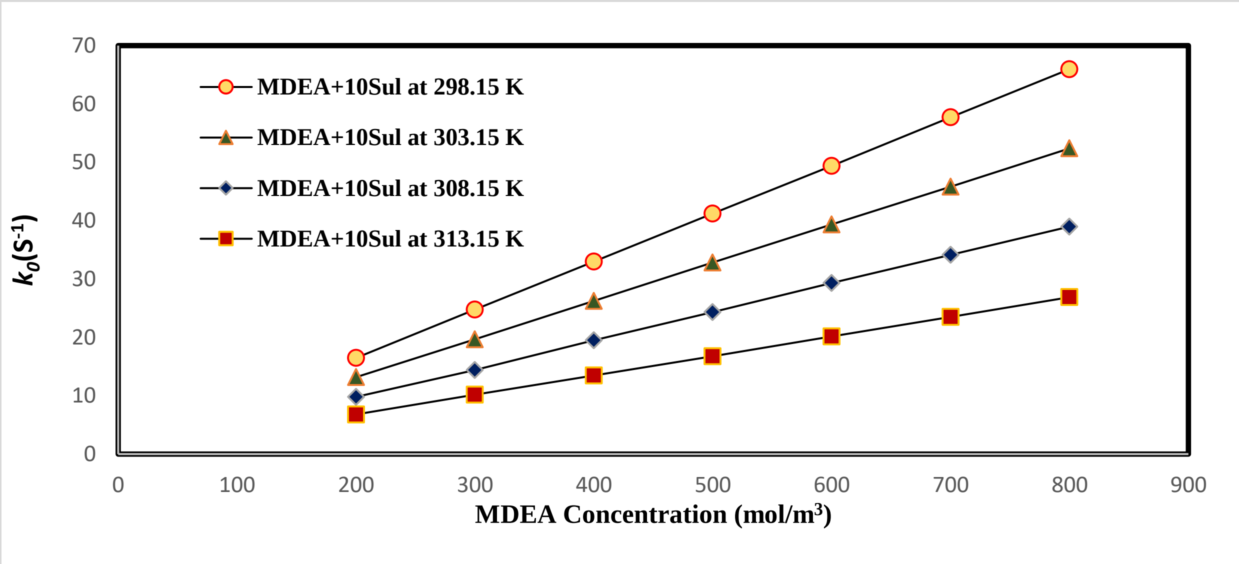

Figure III.13: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 10 mol/m3] solutions at different concentrations and temperatures.

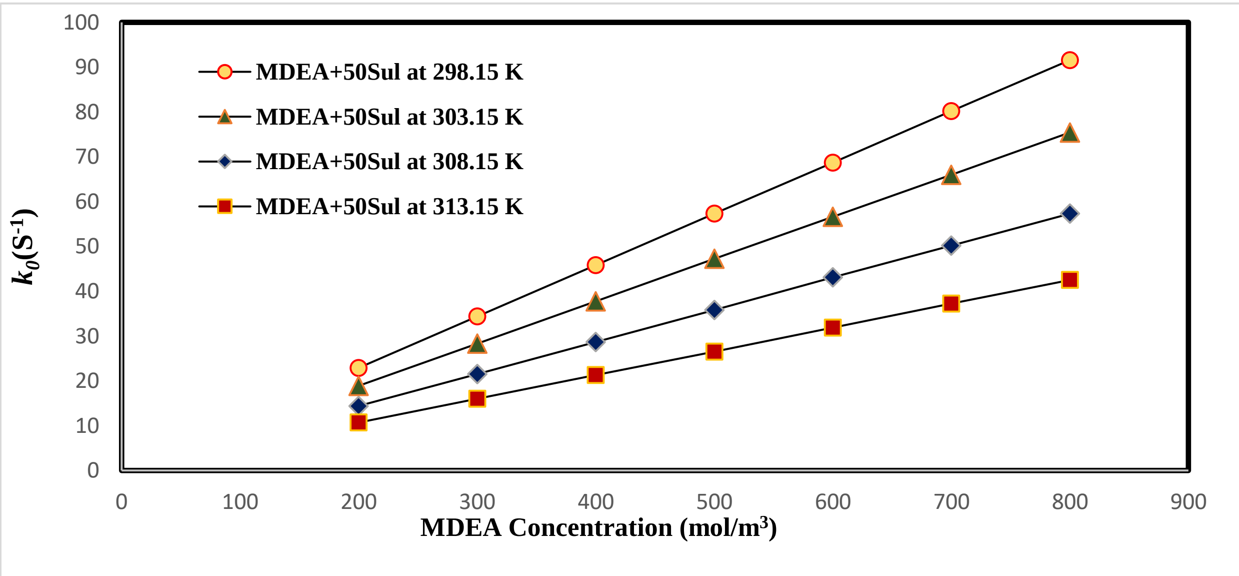

Figure III.14: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 50 mol/m3] solutions at different concentrations and temperatures.

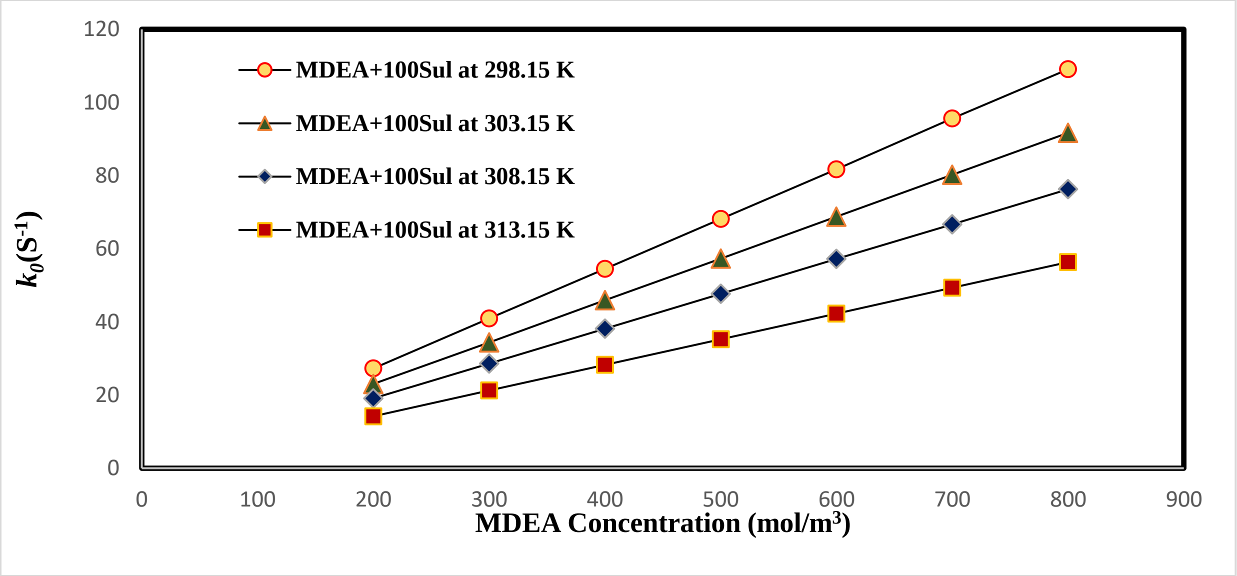

Figure III.15: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 100 mol/m3] solutions at different concentrations and temperatures.

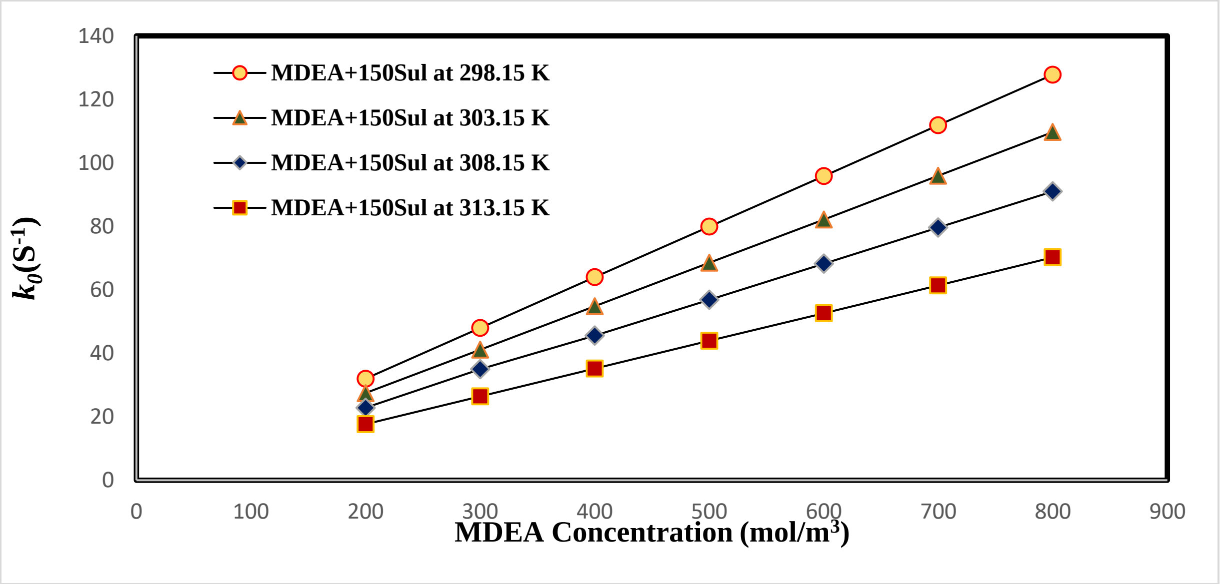

Figure III.16: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 150 mol/m3] solutions at different concentrations and temperatures.

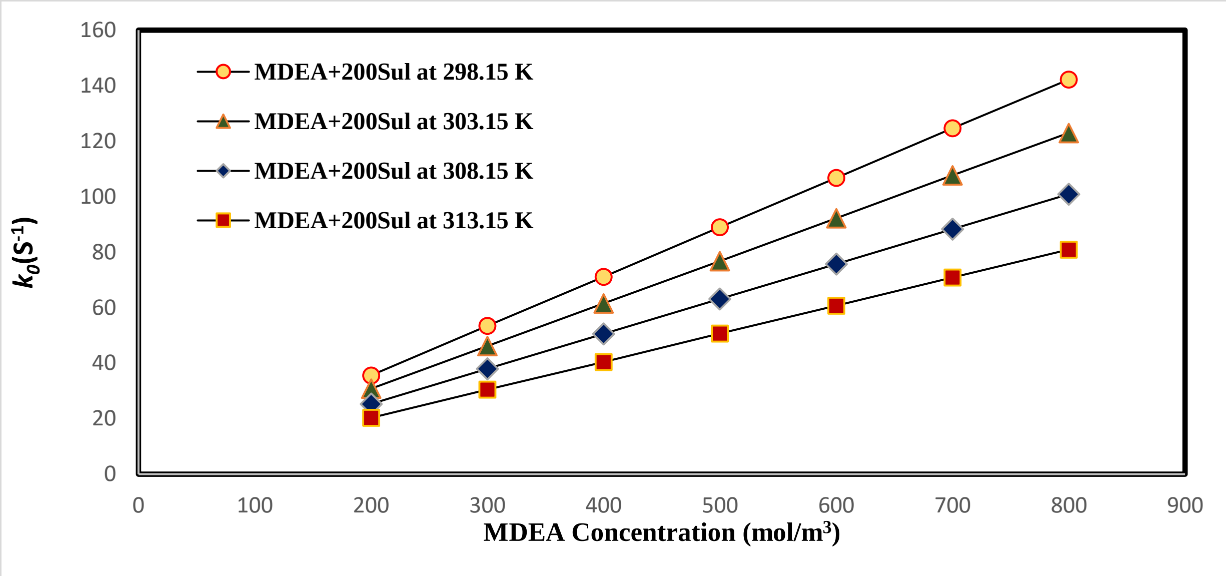

Figure III.17: Comparison of K0 values of the reaction between aqueous CO2 and aqueous MDEA, and aqueous blended [MDEA+ Sulfolane at 200 mol/m3] solutions at different concentrations and temperatures.

The absorption rates of carbon dioxide in the aqueous mixed solvent solution of (MDEA and Sulfolane) were significantly higher and faster compared to those of standalone MDEA at the same concentrations, across all temperatures (298.15–313.15 K). This provides direct evidence that the presence of Sulfolane, a polar solvent, enhances CO2 absorption in aqueous MDEA, partially justifying the commercial use of the Sulfinol-M process technology. According to the study by Xu et al. (1991) on the effect of Sulfolane on CO2 absorption in the mixed solvent, the apparent kinetic rate of Sulfolane with CO2 is negligible and can be disregarded. Only the contribution of Sulfolane to the deprotonation process needs to be considered. Adding Sulfolane to MDEA significantly improved the CO2 absorption rates, and a mechanism was used to correlate the kinetic rates. The reaction orders were found to be approximately 1 at all temperatures and Sulfolane concentrations. The data were modeled by keeping Sulfolane concentrations constant while varying the MDEA concentrations.

Table III. 4*:* Reaction orders of aqueous (MDEA + Sulfolane) systems at different temperatures and Sulfolane concentrations

[MDEA] (mol/m³)	**[Sul] (mol/m³)**	**Order [n]**			
		298.15K	**303.15K**	**308.15 K**	**313.15 K**
200-800	10	1.0001	0.9960	1.0016	0.9902
200-800	50	0.9997	0.9985	0.9974	0.9944
200-800	100	0.9997	0.9965	0.9987	0.9932
200-800	150	0.9991	0.9986	0.9904	0.9954
200-800	200	0.9995	0.9987	0.9971	0.9974

Table III.4 presents a comparison of different K_2 values (m³/mol·s) for the reaction between CO_2 in both aqueous MDEA and aqueous (MDEA + Sulfolane) mixtures, using the base catalyst mechanism. The addition of Sulfolane to the MDEA solution led to a significant increase in CO_2 absorption rates. The absorption kinetic rate constants for CO_2 in the aqueous (MDEA + Sulfolane) mixed solvent were considerably higher (ranging from 59% to 92%) than those in standalone aqueous MDEA across all temperatures, as shown in Table III.5 and Figure III.18. It is important to note that in both cases, the reaction order with respect to MDEA was close to 1. Additionally, unlike aqueous MDEA, the rate constants in the mixed solvent were higher at the lowest temperature and decreased with increasing temperature. The K_2 values in aqueous MDEA were very low, but the addition of Sulfolane significantly enhanced the reaction rate.

Table III. 5: Values of k2 (m3/mol·s) for the reaction between CO2 and aqueous MDEA and (MDEA+ Sulfolane) solutions based on base catalyst mechanism

T(K)	**k_2 (aq. MDEA+ Sulfolane) (m³/mol·s)**	**k_2 (aq. MDEA) (m³/mol·s)**	**Increase (%)**
298.15	0.127	0.009	92.9
303.15	0.113	0.014	87.6
308.15	0.091	0.018	80.2
313.15	0.069	0.024	65.4

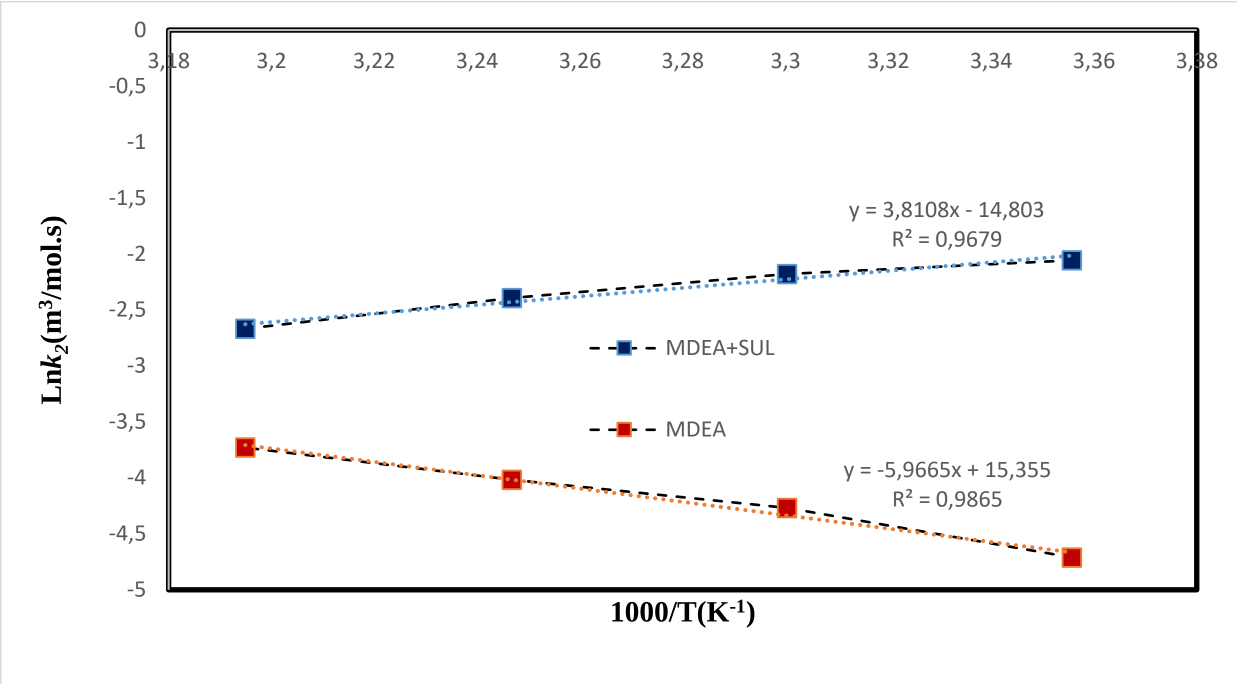

Figure III.18 : Variation of k2 as function of temperature for aqueous (CO2+MDEA) and aqueous (CO2+MDEA+Sulfolane) systems

The regression analysis of the k_2 values yields the following Arrhenius equation:

$k_{MDEA/Sul}$ (m^3/mol·s) = 3.7251 x 10^{-7} Exp (3810.8/T), R^2 =0.9679 (III.15)

The Average Absolute Deviation (AAD) between the experimental pseudo-first-order reaction rate constant (k_0) and those calculated using the kinetic model was 0.52%.

Conclusion:

Pseudo first-order rate constants (k_0) for the CO_2 reactions in aqueous MDEA solutions and its blends with PZ or Sulfolane were studied at temperatures 298.15, 303.15, 308.15, and 313.15 K using the stopped-flow technique. Results showed that MDEA reacts slowly with CO_2 due to its tertiary amine nature. However, the addition of PZ or Sulfolane significantly increased the reaction rate. The (MDEA+PZ) system showed enhanced absorption, which was successfully correlated using a hybrid model combining base-catalyst and zwitterion mechanisms.

The (MDEA+Sulfolane) mixture also exhibited higher absorption rates than MDEA alone.

General Conclusion

General Conclusion

The use of mixed solvents is an attractive alternative to either chemical or physical solvents alone. Mixed solvents, which combine a chemical and a physical solvent, benefit from both physical and chemical absorptions.

Pseudo first-order rate constants (k_0) for the CO_2 reactions in aqueous solutions of MDEA, (MDEA + PZ), (MDEA + Sulfolane) measured at temperatures of 298.15, 303.15, 308.15, and 313.15 K using the stopped-flow technique. MDEA, due to its tertiary amine characteristics, reacts relatively slowly with CO_2. The base catalyst mechanism successfully correlated the standalone MDEA data. The reaction kinetics of CO_2 in aqueous standalone MDEA increased with both temperature and concentration. The addition of small amounts of PZ to MDEA significantly enhanced the CO_2 absorption rates.

New data for the reaction kinetics of carbon dioxide in aqueous amine solutions with Sulfolane (MDEA+ Sulfolane) were reported. The absorption rates of carbon dioxide in aqueous mixed solvent solutions of (MDEA+ Sulfolane) and (MDEA + PZ), were higher than those for standalone MDEA at the same concentrations at all temperatures from (298.15 to 313.15) K. The reaction kinetics increased with the increase in temperature and concentration.

Enhancement by Sulfolane over aqueous solution varied from 59 % to 93 % if the kinetic data were regressed with the same base catalyst model used for tertiary amines. A hybrid model (base catalyst and Zwitterion) was capable of correlating very well all data for aqueous amine blends of (PZ+MDEA). The base catalysis mechanism was used to regress very well data for aqueous (MDEA + sulfolane) and a hybrid model based on the combination of the Zwitterion and base catalysis mechanisms were able to successfully correlate the experimental data for the mixed aqueous (MDEA + PZ) systems.

Referances

Referances

Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R., 2004.Novel design for the nozzle of laminar jet absorber. Ind. Eng. Chem. Res.43, 2568-2574.

Aboudheir, A., Tontiwachwuthikul, P., Chakma, A., Idem, R., 2003.Kinetics of the reactive absorption of carbon dioxide in high CO_2-loaded, concentrated aqueous monoethanolamine solutions. Chem. Eng. Sci. 58, 5195–5210.

Ali, S. H., Al-Rasheed, O., Merchant, S. Q., 2010.Opportunities for faster carbon dioxide removal: A kinetic study on the blending of methyl Monoethanolamine and morpholine with 2-amino-2-methyl-1-propanol. Sep. Purif. Technol.74,64-72.

Anufrikov, Y.A., Kuranov, G.L., Smirnova, N.A., 2007.Solubility of CO_2 and H_2S in alkanolamine containing aqueous solutions. Russian Journal of Applied Chemistry. 80, 515-527.

Alper E., 1990.Reaction mechanism and kinetics of aqueous solutions of 2-amino-2-methyl-1-propanol and carbon dioxide. Ind. Eng. Chem. Res.29, 1725 -1728.

Alvarez-Fuster, C., Midoux, N., Laurent, A., Charoentier, J.C., 1980. Chemical kinetics of carbon dioxide with amine in pseudo m–nth order conditions in aqueous and organic solutions. Chem. Eng. Sci.35, 1717-1723.

Appl, M., Wagner, U., Henrici, H.J., Kuessnet K., Volkamer, F., Ernst-Neust N., 1982.Removal of CO_2 and/or H_2S and/ or COS from gases containing these constituents. US Patent 4336233.

Astarita, G., Savage, D.W., Bisio, A., 1983.Gas Treating with Chemical Solvents. John Wiley, NY,USA .

Baker, R. W., 2004.Membrane Technology and Applications (2ndedition), John Wiley & Sons. ISBN 0-470-85445-6,West Sussex.

Barvek, O., Alper, E., 1999.Reaction Mechanism and Kinetics of Aqueous Solutions of Primary and Secondary Alkanolamines and Carbon Dioxide,'' Turk. J. Chem. 23, 293-300.

Bernardo, P., Drioli, E., Golemme, G., 2009.Membrane gas separation: a review/state of the art. Industrial & Engineering Chemistry Research.48, 4638-4663.

Bishnoi, S., Rochelle, G.T., 2002. Thermodynamics of Piperazine-Methyldiethanolamine-Water-Carbon dioxide, Ind. Eng.Chem.Res.41 , 604-612.

Bishnoi, S., Rochelle, G.T., 2002.Absorption of carbon dioxide in aqueous piperazine-methyldiethanolamine. AIChE. J. 48, 2788-2799.

Blauwhoff, P. M. M., Versteeg, G.F., van Swaaij, W.P.M., 1983.A study on the reaction between CO_2 and alkanolamines in aqueous solution. Chem. Eng. Sci.38, 1411-1429.

Bosch, H., Versteeg, G.F., van Swaaij, W.P.M., 1990. Kinetics of the reaction of CO_2 with the sterically hindered amine 2-amino-2-methylpropanol at 298 K. Chem. Eng. Sci.4, 1167-1173.

Bottoms, R.R., 1930.Process for separating acidic gases, U.S. Patent1783901.

Bruder, P., Grimstvedt, A., Mejdell, T., Svendsen, H.F., 2011. CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. Chem. Eng. Sci.66, 6193-6198.

Bullin, J.A., Polasek, J.C., Iglesias-Silva, G.A., 1992. Presented at the 71st GPA Annual Convention, Anaheim, CA.

Bullin, J.A., Polasek, J.C., Donnelly, S.T., 1990.Proceedings of the 69th GPA Annual Convention, Phoenix, AZ.135-139.

Burggraaf, A. J., 1996.Important characteristics of inorganic membranes.Membrane Science and Technology. 4, 21-34.

Caplow, M., 1968.Kinetics of carbamate formation and breakdown, J. Am. Chem. Soc.24, 6795-6803.

Caro, J., Noack, M., Kölsch, P., Schäfer, R., 2000. Zeolite membranes-state of their development and perspective. Microporous and mesoporous materials.38,3-24.

Cavenati, S., Grande, C.A., Rodrigues, A.E., 2006. Removal of carbon dioxide from natural gas by vacuum pressure swing adsorption. Energy & Fuels.20,2648-2659.

Chakraborty, A.K., Astarita, G., Bischoff, K.B., 1986.CO_2 absorption in aqueous solutions of hindered amines. Chem. Eng. Sci.41,997-1003.

Chakravarty, T., Phukan, U. K., Weiland, R. H., 1985.Reaction of acid gases with mixtures of amines," Chem. Eng. Prog.81, 32-36.

Danckwerts, P.V., 1979.The reaction of CO_2 with ethanolamine. Chem. Eng. Sci.34, 443-446.

Dang, H.Y., Rochelle, G.T., 2003. CO_2 absorption rate and solubility in monoethanolamine / piperazine / water. Sep. Sci. Tech.38, 337-357.

Davison, J.; , Freund, P., Smith, A.,2001. Putting carbon back into the ground (1st edition), IEA Greenhouse Gas R&D Programme. ISBN 1 898373 28, Cheltenham.

Derks, P.W.J., Kleingeld, C., van Aken, C., Hogendoorn, J.A., Versteeg, G.F., 2006.Kinetics of absorption of carbon dioxide in aqueous piperazine solution. Chem. Eng. Sci. 61, 6837-6854.

Donaldson, T. L., Nguyen, Y. N., 1980. Carbon dioxide reaction kinetics and transport in aqueous amine membrane," Ind. Eng. Chem. Fundam.19, 260-266.

Dortmundt, D., Doshi, K., 1999. Recent Developments in CO_2 Removal Membrane Technology, In design consideration.16.08.11.

Ebenezer, S. A., Gudmunsson, J. S.,2005.Removal of Carbon Dioxide from Natural Gas for LPG Production. Semester project work, academia.edu.

Edali, M., Idem, R., Aboudheir, A., 2010.1D and 2D absorption-rate/kinetic modeling and simulation of carbon dioxide into aqueous solutions of MDEA and PZ in a laminar jet apparatus. Int. J. Greenh. Gas Control.4, 143-151.

Edali, M., Aboudheir, A., Idem, R., 2009.Kinetics of carbon dioxide into mixed aqueous solutions of MDEA and MEA using laminar jet apparatus and a numerically solved 2D absorption rate/kinetics model. International Journal of Greenhouse Gas Control.3, 550-560.

Edali, M., Aboudheir, A., Idem, R., 2007.Kinetics of carbon dioxide absorption into mixed aqueous solutions of MDEA and MEA using laminar jet apparatus and numerically solved absorption-rate/kinetic model. The COMSOL Conference, Boston.

Glasscock, D. A., 1990.Modeling and experimental study of carbon dioxide absorption into aqueous alkanolamines, PhD thesis. University of Texas at Austin, Texas.1-292.

Hashemifard, S. A., Ismail, A. F., Matsuura, T., 2010.Prediction of gas permeability in mixed matrix membranes using theoretical models. Journal of Membrane Science.347, 53-61.

Henni, A., 2002. Solubility of Gases in Physical Solvents and Absorption of CO_2 in a Mixed Solvent (Doctoral dissertation, PhD. Dissertation, University of Regina, Saskatchewan, Canada).

Hermann, W., Bosshar, P., Hung, E., Hunt, R., Simon, A.J., 2005.An Assessment of Carbon Capture Technology and Research Opportunities, In: Physical Adsorption.25.08.11.

Ismail, A. F., David, L. I. B.,2001.A review on the latest development of carbon membranes for gas separation. Journal of Membrane Science.193, 1-18.

Ko, J.J., Li, M.H., 2000.Kinetics of the absorption of carbon dioxide into solutions of N-methyldiethanilamine + water. Chem. Eng. Sci.55,4139-4147.

Kohl, A. L., Riesenfeld, F. C., 1997. Gas Purification, Gulf Publishing Co, Houston, 5th edition.

Kohl, A.L. , Nielsen, R.B.1997.Gas purification. Houston: Gulf Publishing Co, 5th edition.

Kerry, F. G., 2007.Industrial Gas Handbook: Gas Separation and Purification, CRC.ISBN 978-0-8493-9005-0,New York.

Kierzkowska-Pawlak, H., Siemieniec, M., Chacuk, A.,2011.Reaction kinetics of CO_2 in aqueous Methyldiethanolamine solutions using the stopped-flow technique. Chem. Process Eng. 33, 7-18.

Kovvali, A. S., Sirkar, K. K., 2002.Carbon dioxide separation with novel solvents as liquid membranes. Industrial & Engineering Chemistry Research.41, 2287-2295.

Laddha, S.S.; Danckwerts, P.V., 1981.Reaction of CO_2 with ethanolamine; kinetics from gas absorption. Chem. Eng. Sci.36, 229-230.

Li, J., Henni, A., Tontiwachwuthikul, P.,2007.Reaction kinetics of CO_2 in aqueous ethylenediamine, ethyl ethanolamine, and diethyl monoethanolamine solutions in the temperature range of 298-313 K using stopped-flow technique. Ind. Eng. Chem. Res.46,4426-4434.

Littel, R.J., Van Swaaij, W.P.M., Versteeg, G.F., 1990. Kinetics of carbon dioxide with tertiary amines in aqueous solution, AIChE J.11,1633–1640.

Ma'mun, S., Dindore, V.Y., Svendsen, H.F., 2007.Kinetics of the reaction of carbon dioxide with aqueous solutions of 2-2-aminoethyl-amino- ethanol. Ind. Eng. Chem. Res.46, 385-394.

Mandal, B.P., Guha, M., Biswa, A.K., Bandopadhyay, S.S., 2001.Removal of carbon dioxide by absorption in mixed amines modeling of absorption in aqueous /MEA and AMP/MEA solutions. Chem. Eng. Sci.51, 6217-6244.

Mersmann, A., Kind, M., Stichlmair, J., 2011.Thermal Separation Technology Principles, Methods, Process Design, Springer. ISBN 978-3-642-12524-9, New York.

Meyers, R. A., 2001.Chemical Engineering. Encyclopedia of Physical Science and Technology 3rd edition), Ramtech, Inc. California.

Pal, R., 2007.New models for thermal conductivity of particulate composites. Journal of Reinforced Plastics and Composites.26,643.

Pandey, P., Chauhan, R. S., 2001. Membranes for gas separation.Progress in Polymer Science. 26, 853-893.

Pani, F., Gaunand, A., Cadours, R., Bouallou, C., Richon, D., 1997.Kinetics of absorption of CO_2 in concentrated methyldiethanolamine solutions in the range 296 K to 343 K. J. Chem. Eng. Data .42, 353–359.

Porter, M. C., 1990.Handbook of Industrial Membrane Technology, Noyes Publications.ISBN 08155-1205-8, New Jersey.

Ramachandran, N., Aboudheir, A., Idem, R., Tontiwachwuthikul, P., 2006. Kinetics of the absorption of CO_2 into mixed aqueous loaded solutions of monoethanolamine and methyldiethanolamine. Ind. Eng. Chem. Res.45,2608–2616.

Rinker, E.B., Ashour S.S., Sandall, O.C.,1996.Kinetics and modeling of carbon dioxide absorption into aqueous solutions of diethanolamine. Ind. Eng. Chem. Res.35, 1107-1114.

Ritter, J. A., Ebner, A. D., 2007.Carbon Dioxide Separation Technology: R&D Needs For the Chemical and Petrochemical Industries, In: Recommendation for future R&D. 22.06.11.

Saha, A.K., Bandyopadhyay, S.S., Biswas, A.K., 1995.Kinetics of absorption of CO_2 into aqueous solutions of 2-amino-2-methyl-1-propanol.Chem. Eng. Sci. 50, 3587–3598.

Seo, D.J., Hong, W.H., 2000. Effect of piperazine on the kinetics of carbon dioxide with aqueous solutions of 2-amino-2-methyl-1-propanol. Ind. Eng. Chem. Res. 39, 2062–2067.

Shekhawat, D., Luebke, D. R., Pennline, H. W., 2003. A review of carbon dioxide selective membranes: A topical report (No. DOE/ NETL-2003/1200).

Sodiq, A., Rayer, A., Abu-Zahra, M.R.M., 2014. The Kinetic Effect of Adding Piperazine Activator to Aqueous Tertiary and Sterically-Hindered Amines Using Stopped-Flow Technique, Energy Procedia .63,1256 –1267.

Sridhar, S., Smitha, B., Aminabhavi, T.M., 2007.Separation of carbon dioxide from natural gas mixtures through polymeric membranes-a review. Separation & Purification Reviews.36, 113-174.

Stern, A., 1994. Polymers for gas separations: the next decade. Journal of Membrane Science . 94, 1-65.

Sun, W. C., Yong, C. B., Li, M. H., 2005. Kinetics of the absorption of carbon dioxide into mixed aqueous solutions of 2-amino-2-methyl-1-propanol and piperazine. Chem. Eng. Sci.60, 503–516.

Tobin, J., Shambaugh, P., 2006. The crucial link between natural gas production and its transportation to market in: stages in the production of pipeline-quality natural gas and NGLs. 13.07. 11.

Vaidya, P.D., Kenig, E.Y., 2007. Gas–liquid reaction kinetics: a review of determination methods. Chem. Eng. Comm. 194, 1543 –1565.

Versteeg, G. F., Van Swaaij,W. P. M.,1988a.On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions-I. Primary and secondary amines. Chem. Eng Sci.43, 573-587.

Vu, D. Q.,2001.Formation and Characterization of Asymmetric Carbon Molecular Sieve and Mixed Matrix Membranes for Natural Gas Purification, PhD thesis. University of Texas at Austin, Texas. 1-362.

Xiao, J., Li, C.W., Li, M.H., 2000. Kinetics of absorption of carbon dioxide in aqueous solutions of 2-amino-2-methyl-1- propanol + mono-ethanolamine. Chem. Eng. Sci.55, 161–175.

Xu, S., Wang, Y., Otto, F. D., Mather, A. E.,1991.Rate of Absorption of CO_2 in a Mixed Solvent, Ind. Eng. Chem. Res. 30, 1213-1217.

Yang, R.,1997.Gas Separation by Adsorption Processes, Imperial College Press. ISBN 9781860940477, Singapore.

Yang, R. T. , Wiley, J.,2003. Adsorbents: fundamentals and applications, John Wiley & Sons. 2003. ISBN 9780471297413, New Jersey.

Yih, S.M., Shen, K.P., 1988. Kinetics of carbon dioxide reaction with sterically hindered 2-amino-2-methyl-1-propanol aqueous solutions. Ind. Eng. Chem. Res.27, 2237–2241.

Yu, W.C., Astarita, G., Savage, D.W.,1985.Kinetics of carbon dioxide absorption in aqueous solutions of methyldiethanolamine. Chem. Eng. Sci. 40, 1585–1590.

Zhang, X., Zhang, C.F., Qin, S.J., Zheng, Z.S., 2001.A kinetics study on the absorption of carbon dioxide into a mixed aqueous solution of methyldiethanolamine and piperazine. Ind. Eng. Chem. Res. 40, 3785-3791.

Abstract:

The presence of carbon dioxide within the natural gas causes an increase in gas volume, reduces its heat value and may enhance corrosion within pipelines and processing plants. Amine-based absorption technique is a well-known and widely used method for removing CO_2.The use of mixed solvents is an attractive alternative to either chemical or physical solvents alone. Mixed solvents, which combine a chemical and a physical solvent, benefit from both physical and chemical absorptions. Using the stopped flow technique, kinetic rates of CO_2 in aqueous solutions of (MDEA), (MDEA + PZ), and (MDEA + sulfolane) were measured and reported in terms of pseudo-first-order rate constants (k_0). The second-order reaction rate constants (k_2) were regressed from the data when possible. Experiments were performed over new concentration ranges of (200–800), (200–800, 10–40), and (200–800, 10–200) mol/m^3 for the above-mentioned Three systems, respectively, and at temperatures varying from (298.15–313.15 K). The absorption rates of carbon dioxide in aqueous mixed solvent solutions of were higher than those for standalone MDEA at the same concentrations at all temperatures from (298.15 to 313.15) K. The kinetic rates were highest at 298.15 K and decreased at higher temperatures for aqueous (MDEA + Sulfolane) solutions but increased with temperature for aqueous (MDEA + PZ) systems.

The base catalysis mechanism was used to regress very well data for aqueous (MDEA + sulfolane) and a hybrid model based on the combination of the Zwitterion and base catalysis mechanisms were able to successfully correlate the experimental data for the mixed aqueous (MDEA + PZ) systems. The reaction kinetics increased with the increase in temperature and concentration.

Keywords: Mixed solvents, Piperazine, Stopped flow, Sulfolane.

الملخص:

يؤدي وجود غاز ثاني أكسيد الكربون في الغاز الطبيعي إلى زيادة في حجم الغاز، وتقليل قيمته الحرارية، كما قد يعزز من حدوث التآكل في خطوط الأنابيب ومحطات المعالجة. تُعد تقنية الامتصاص باستخدام الأمينات وسيلة معروفة ومستخدمة على نطاق واسع لإزالة ثاني أكسيد الكربون. ويُعد استخدام المذيبات المختلطة بديلاً جذاباً مقارنة باستخدام المذيبات الكيميائية أو الفيزيائية وحدها، حيث تجمع المذيبات المختلطة بين مذيب كيميائي وآخر فيزيائي، مما يمنحها مزايا الامتصاص الفيزيائي والكيميائي معًا.

وباستخدام تقنية التدفق المتوقف (Stopped Flow)، تم قياس معدلات تفاعل ثاني أكسيد الكربون في محاليل مائية من MDEA، و(MDEA + PZ)، و(MDEA + Sulfolane)، وتم الإبلاغ عنها من حيث ثوابت السرعة من الرتبة الأولى الزائفة (k_0). كما تم استنتاج ثوابت سرعة التفاعل من الرتبة الثانية (k_2) من البيانات عندما كان ذلك ممكنًا. وقد أجريت التجارب على نطاقات جديدة من التركيز بلغت (200–800)، و(200–800، 10–40)، و(200–800، 10–200) مول/م^3 للأنظمة الثلاثة المذكورة أعلاه، وعلى درجات حرارة تراوحت بين (298.15–313.15 كلفن).

كانت معدلات امتصاص ثاني أكسيد الكربون في المحاليل المائية للمذيبات المختلطة أعلى من تلك الخاصة بـMDEA وحده عند نفس التراكيز وفي جميع درجات الحرارة من (298.15 إلى 313.15 كلفن). وكانت معدلات التفاعل الحركي الأعلى عند درجة حرارة 298.15 كلفن، وانخفضت مع ارتفاع درجات الحرارة في حالة محاليل (MDEA + Sulfolane)، بينما زادت مع درجة الحرارة في أنظمة (MDEA + PZ) المائية.

وقد تم استخدام آلية التحفيز القاعدي (Base Catalysis) بنجاح كبير في تمثيل البيانات الخاصة بمحاليل (MDEA + Sulfolane) المائية، في حين تم استخدام نموذج هجين يجمع بين آلية التفاعل عبر أيون Zwitterion وآلية التحفيز القاعدي لتمثيل بيانات أنظمة (MDEA + PZ) المائية المختلطة بنجاح. وازدادت سرعة التفاعلات الحركية مع زيادة كل من درجة الحرارة والتركيز.

الكلمات المفتاحية: مذيبات مختلطة، بيبرازين، تدفق متوقف، سلفولان.