Reaction Kinetics and Dissociation constants ($pK_a$) of Tertiary Alkanolamines for Carbon Capture

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By

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Akintunde Jolade Aboaba, candidate for the degree of Master of Applied Science in Industrial Systems Engineering, has presented a thesis titled, *Reaction Kinetics and Dissociation constants (pKₐ) of Tertiary Alkanolamines for Carbon Capture,* in an oral examination held on August 4, 2017. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

This research work studies the absorption kinetics of CO$_2$ into aqueous solutions of four amines; {1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol, N, n, n’, n’’, n’’-pentamethyl-diethylenetriamine, N, n, n’, n’-tetrakis (2-hydroxyethyl) ethylenediamine, and N, n, n’, n’-tetrakis (2-hydroxypropyl) ethylenediamine}. The experimental results were reported in the form of second-order reaction rate constants ($k_2$).

The kinetics data were measured using the Stopped-flow technique within an amine concentration range of 200 to 1000 mol/m$^3$ and a temperature range of 298 to 318K. The equipment can determine the solution-based kinetics on a millisecond time scale by measuring the reaction rate of the reactants. The different tertiary alkanolamine solvents studied in this research work have no kinetics data published in the literature, and the solvents were selected the solvents for research studies because of their unique characteristics and properties.

The experimental procedure was validated using kinetic experiments using a Methydiethanolamine (MDEA) solution prepared at concentrations ranging from 200 to 1000 mol/m$^3$. Experimental pseudo-first order reaction rate constants were found to increase steadily with an increase in amine concentration and temperature.

In terms of pseudo first-order constant, the reaction rates of CO$_2$ absorption in 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol, N, n, n’’, n’’-pentamethyldiethylenetriamine and N, n, n’, n’-tetrakis (2-hydroxyethyl) ethylenediamine and N, n, n’, n’-tetrakis (2-hydroxypropyl) ethylenediamine were found to be faster than that of Methydiethanolamine at low concentrations and temperature. The values of pseudo-first order reaction rate constant increased steadily at higher concentrations and temperature. An aqueous solution of 1-[Bis [3-(dimethylamino) propyl] amino]-
2-propanol has the best overall reaction rate at the experimental conditions when compared with the other amines studied.

The values of the pseudo first-order rate constants \(k_0\) were interpreted using the base-catalyzed hydration mechanism. All experimental values of the pseudo first-order rate constants \(k_0\) obtained from the stopped-flow apparatus were compared with calculated values determined using the power-law equation. All calculated values of \(k_0\) were found to be in good agreement with the experimental values with an acceptable AAD of 4.3%.

In addition, the dissociation constants (pKa) of 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol, N, n, n”, n”-pentamethyldiethylenetriamine, N, n, n’, n’-tetrakis (2-hydroxypropyl) ethylenediamine and N, n, n’, n’-tetrakis (2-hydroxyethyl) ethylenediamine were determined using the potentiometric titration method at (298, 303, 313 and 323) K.

The pKa values obtained for each solvent reflect the basicity of that solution and are considered a critical parameter in the selection of alkanolamine solutions for CO\(_2\) removal. The pKa values were predicted using the Perrin-Dempsey-Serjeant empirical (PDS) method. The actual PDS method is somewhat better than the updated PDS with both approaches producing average absolute errors of 0.04 and 0.14, respectively.
Acknowledgements

I seize this opportunity to give thanks to Almighty God for giving me the grace, favor and endurance to complete this task successfully.

My heartfelt gratitude goes to my loving parents for their kind support and encouragement throughout my entire life. Likewise, I am overwhelmed with appreciation for the constant care and support of my affectionate wife during the challenging times of my graduate studies.

I would also like to express my profound gratitude to my supervisor, Dr. Amr Henni, for his adequate guidance and support during my graduate program, through his unique thought-provoking, supportive, and poised supervision approach. I firmly believe that I have been equipped with the right knowledge and training to apply the research values he has given me to find a solution to problems I encounter in my chosen career and profession.

I also appreciate the inputs of the examiners who provided positive feedback on my work. It is a challenging task to review a thesis, and I am grateful for their kind remarks.

Finally, I acknowledge the financial support of the Faculty of Graduate Studies and Research at the University of Regina for granting me the Graduate Studies Scholarship.
Dedication

I will like to dedicate this Thesis/Dissertation to:

My Parents and lovely wife for their endless prayers,
encouragement and moral support
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List of Symbols, Abbreviation and Nomenclature

A  Arrhenius constant (m$^3$ · mol$^{-1}$ · s$^{-1}$)
B  Base (amine, water, methanol, ethanol or hydroxyl ion)
$E_{act}$ Activation energy (kJ · mol$^{-1}$)
C$ \text{1}$ Constant in an equation
ECO$_2$, $\infty$ Infinite enhancement factor for CO$_2$
k$_{ps.f.o}$ Pseudo first order reaction rate constant (s$^{-1}$)
k$_L$ Liquid phase mass transfer coefficient (m·s$^{-1}$)
k$_{eq}$ Chemical equilibrium constant
k$_o$ Observed pseudo-first-order reaction rate constant (s$^{-1}$)
k$_{-1}$ Backward first-order reaction rate constant (s$^{-1}$)
k$_2$ Forward second-order reaction rate constant for the formation of the zwitterion (m$^3$ · mol$^{-1}$ · s$^{-1}$)
k$_{base}$ Rate constant for the deprotonation of the zwitterion by a base (amine, water, or hydroxyl ion) (m$^3$ · mol$^{-1}$ · s$^{-1}$)
k$_B$ Equal to $k_2k_{Base}/k^{-1}$ (m$^6$ · mol$^{-2}$ · s$^{-1}$)
k$_a$ Equal to $k_2k_{amine}/k^{-1}$ (m$^6$ · mol$^{-2}$ · s$^{-1}$)
k$_w$ Equal to $k_2k_{water}/k^{-1}$ (m$^6$ · mol$^{-2}$ · s$^{-1}$)
k$_m$ Equal to $k_2k_{methanol}/k^{-1}$ (m$^6$ · mol$^{-2}$ · s$^{-1}$)
k$_e$ Equal to $k_2k_{ethanol}/k^{-1}$ (m$^6$ · mol$^{-2}$ · s$^{-1}$)
M  Molarity (mol·L$^{-1}$)
MRD  Mean relative deviation
pK$\text{a}$ Acid dissociation constant
\( rCO_2 \)  Rate of reaction with respect to \( CO_2 \) (mol \( \cdot \) m\(^{-3}\) \( \cdot \) s\(^{-1}\))

R  Universal gas constant (0.008315 kJ \( \cdot \) mol\(^{-1}\) \( \cdot \) K\(^{-1}\)).

\( T \)  Temperature (K)

\( t \)  Time (second)

\( Y \)  A measure of the signal obtained (V)

\( Y_{\text{inf}} \)  Constant value of the signal (V) at equilibrium

[ ]  Concentration (mol \( \cdot \) m\(^{-3}\))

**Solvents**

1-AP  1-Amino-2-Propanol

3-AP  3-Amino-1-Propanol

AEEA  2-((2-Aminoethyl) amino) ethanol

Am  Alkanolamine

AMP  2-Amino-2-methyl-1-propanol

AMPD  2-Amino-2-methyl-1, 3-propandiol

BDMAPA2P  1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol

CO\(_2\)  Carbon dioxide

COS  Carbonyl sulphide

CS\(_2\)  Carbon disulphide

DEA  Diethanolamine

DEMEA  Diethylmonoethanolamine

1DMA2P  1-Dimethylamino-2-propanol

3DMA1P  3-Dimethylamino-1-propanol
<table>
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<td>1-(2-Hydroxyethyl) piperidine</td>
</tr>
<tr>
<td>DGA</td>
<td>Diglycolamine</td>
</tr>
<tr>
<td>DIPA</td>
<td>Di-2-propanolamine</td>
</tr>
<tr>
<td>2-DMAEMAE</td>
<td>2-[(2-dimethylamino)ethyl]-methylamino)ethanol</td>
</tr>
<tr>
<td>DMMEA</td>
<td>Dimethylmonoethanolamine</td>
</tr>
<tr>
<td>EAE</td>
<td>Ethylethanolamine</td>
</tr>
<tr>
<td>EDA</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>MDEA</td>
<td>N-Methyldiethanolamine</td>
</tr>
<tr>
<td>MEA</td>
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</tr>
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CHAPTER ONE: Introduction

1.1 Background

Electricity is generated at coal-fired power plants by burning coal to produce superheated steam at high pressure, which drives a series of electric generators. When coal burns, flue gas is released which contains carbon dioxide (CO\textsubscript{2}), a primary greenhouse gas that enters the atmosphere causing global climate change. The presence of massive amounts of CO\textsubscript{2} emission in the atmosphere has become a great concern to everyone because it is one of the most serious environmental problems.

To counteract global warming by the greenhouse effect, the need to develop a CO\textsubscript{2} capturing system that absorbs CO\textsubscript{2} from flue gases with minimal energy penalty has received much attention at present. The most widely recognized technique for capturing CO\textsubscript{2} is through chemical absorption with an amine-based absorbent. The absorption of carbon dioxide (CO\textsubscript{2}) with chemical solvents (alkanolamines) is believed to be a promising technology for CO\textsubscript{2} capture due to its maturity, cost-effectiveness and ability to handle massive amounts of an exhaust stream. A fundamental requirement for utilizing this technology is through the use of an effective solvent, that possesses fast reaction kinetics, high mass-transfer performance, excellent absorption capacity, minimal energy requirement for regeneration, low degradation rates and reduced corrosivity.

The reaction kinetics data are one of the most important parameters when selecting a chemical solvent for CO\textsubscript{2} absorption. When the reaction kinetics of promising solvents are measured, it provides the needed information required for designing and simulation of the absorption/regeneration columns effectively. To measure the reaction kinetics data for promising
solvents, an experiment on CO₂ absorption needs to be performed using laboratory-scale gas–liquid contactors such as the stirred cell reactor, wetted wall column, laminar jet absorber, wetted sphere absorber, a string of disc contactors or a stopped-flow apparatus. The absorption rate information obtained from the CO₂ absorption equipment can be explained using graphical methods. Simplified kinetic models that involve reaction mechanisms (i.e., zwitterion, termolecular or base-catalyzed hydration mechanisms) and a complete numerically solved reaction kinetics models which take into consideration the relationship between chemical equilibrium, mass-transfer and chemical kinetics of all potential reactions are available.

Carbon dioxide (CO₂) capture at power plants is an active effort to lower atmospheric emissions of power plants and to achieve world emissions targets. Post-combustion Carbon capture (PCC) is a short-to-medium-term solution, particularly modified for power plant retrofitting. Among post-combustion processes, chemical absorption with an amine-based absorbent is the most developed and industrially accepted process for carbon capture.

However, the successful application of this process to a power plant requires a steam draw-off from the power plant steam cycle, which causes a power plant efficiency loss of 10%-12% without advanced integration, including CO₂ compression. To lower this energy loss, a lot of academic and industrial studies are focused on the formulation and characterization of new promising solvents for the improvement of integrated flow schemes. On the other hand, these approaches should enhance the system because the optimal flow scheme depends on the solvent because of its unique physiochemical properties such as the kinetics of absorption, cyclic capacity, the heat of regeneration, and temperature of thermal degradation.
A simplified process flow diagram of the CO$_2$ capture process through chemical absorption is presented in Figure 1.1 below. This carbon capture process is made up of three sections:

The Absorber is where CO$_2$ in flue gas from the power plant is removed by chemical absorption using an aqueous solution of alkanolamine, The solvent undergoes regeneration in the stripper through heat provided by the reboiler, and an Economizer is where the functional heat between the CO$_2$ lean hot stream and the CO$_2$-rich cold stream is exchanged.

![Figure 1.1. Process flow diagram of a typical CO$_2$ Capture process by chemical absorption (Bernardo et al., 2016)](image-url)
Process simulation is an ideal way for evaluating the energy performance of some methods using different solvents before conducting tests on pilot plants and building operations on an industrial scale.

The ability of amines to react directly and reversibly with $\text{CO}_2$ makes them attractive for use in the post-combustion $\text{CO}_2$ capture process. The corresponding reaction kinetic, equilibrium and thermodynamic contributions of amines are the important chemical criteria that need to be taken into consideration when evaluating novel solvents for post-combustion carbon capture.

According to Couchaux et al. (2014), the physical size of the absorption and desorption columns, pumping equipment, as well as related capital and operating costs all contribute to the chemical performance of the solvent. Every information obtained from the reaction mechanism and kinetics of the reaction between $\text{CO}_2$ and the reactive constituent in the solvent is used in the design of the gas-liquid contactor and to enhance the complete absorption selectivity of other acid gases such as $\text{H}_2\text{S}$ from an exhaust gas stream containing $\text{CO}_2$ and other acid gases. For this reason, an in-depth knowledge of reaction mechanisms for the developed solvents in a $\text{CO}_2$ capture process and their corresponding reaction rate constants are mandatory.

For many years, the reaction kinetics between $\text{CO}_2$ and some aqueous amines have been published in literature considerably. A comprehensive review of data for reaction kinetics and the corresponding reaction mechanisms such as Zwitterion, Termolecular, and Base Catalysis Mechanisms have been published by (Couchaux et al., 2014).
Chia et al. (2003) suggested that carbon dioxide and other acid gases can also be removed from a flue gas stream by an aqueous solution of amino salts because of a relationship in their functional group with amines and established high selectivity of CO$_2$ and other acid gases in gas streams.

Versteeg et al. (2007) proposed that aqueous alkaline salts of amino acids can serve as an alternative solvent due to its numerous advantage of having an excellent stability for oxidative degradation as well as the ability to precipitate when absorbing CO$_2$. Due to precipitation, the partial equilibrium pressure of carbon dioxide (CO$_2$) remains nearly constant for every addition of the absorbing solvent. Throughout the absorption process, the procedure has an effect of higher solvent loadings, reduced energy consumption for the solvent regeneration, and a drop in the gas-liquid contactor size (Couchaux et al., 2014).

For a long time, different measurement techniques have been used to determine the reaction kinetics of CO$_2$ with aqueous alkanolamine solvents. The stirred-cell reactor, wetted wall and stopped-flow technique are the most prominent experimental methods utilized in the study of reaction kinetics of CO$_2$ with aqueous amine solutions. The reaction order is believed to approach infinity at low solvent concentrations. At higher solvent concentrations, the reaction order is found to have a value between 1 and 1.7.

There are three major conditioning processes, which prepare the CO$_2$ for capture in various ways: Post-combustion capture, Pre-combustion capture, and Oxyfuel.
**Post-combustion.** The process deals with the removal of CO\(_2\) from flue gas after the combustion of fuel. Air functions as the main oxidant of this process; hence the flue gas becomes mostly diluted with nitrogen.

**Pre-combustion.** The process involves a conversion of hydrocarbon fuel (i.e., gasified coal) into carbon monoxide (CO) and hydrogen (H\(_2\)). This transformation produces a synthesis gas. The shift conversion technique is employed to convert Carbon monoxide (CO) to carbon dioxide (CO\(_2\)). Lastly, the CO\(_2\) is then separated from H\(_2\).

**Oxyfuel CO\(_2\) Combustion.** This process uses pure oxygen as an oxidant instead of air, which in turn produces a flue gas mainly made up of highly-concentrated CO\(_2\) and steam.

*Post-combustion* capture has some benefits even though existing combustion technologies can be used without significant changes to them. The procedure simplifies the effort to implement the post-combustion capture technique as a retrofit option for existing power plants when compared to the two other approaches. Consequently, post-combustion capture is most likely the leading technology that will be used to reduce the amount of CO\(_2\) present in the environment.

The amount of energy required to remove CO\(_2\) from process gas stream requires a tremendous amount of energy and as such substantially determines the cost of the carbon capture process. Davison (2007) suggested that his activity accounts for 75-80% of the total cost of the carbon capture process.
Figure 1.2: Simplified schematic showing the various types of CO₂ capture process (Bernardo et al. 2016).

Even though carbon dioxide (CO₂) capture and separation is a traditional technology, and only utilized at small-scale, this means that at present, it is only commercially available to use in large power stations in two plants in Saskatchewan (Canada) and Texas (USA). The most difficult problem to overcome in Carbon Capture Utilization and Storage (CCUS) is looking for an effective method that satisfies environmental and economic conditions. Based on the findings of Leunga et al. (2014), some of the currently studied techniques by researchers for CO₂ capture from the three conditioning processes mentioned above are as follows: Absorption, Adsorption, Membranes, and Cryogenics.
The diagram presented in Figure 1.3 shows the different separation technologies available for post-combustion capture. The selection of an ideal separation technique to use in the capture of CO$_2$ from process gas streams depend on the properties of the dry flue gas stream, which is a function of the power plant technology.

Prospective coal-fired power plants would likely be designed to capture CO$_2$ before it is burnt into the atmosphere (using coal gasification systems), or the plant could utilize pure oxygen combustion in place of air to achieve a concentrated CO$_2$ stream for treatment.

**Figure 1.3**: Process technologies for PCC process (adapted from Rao and Rubin, 2002)
1.2 Summary of Amine-based CO₂ Capture Systems

The need to separate CO₂ from dry flue gas streams commenced in the 1970s, not because of the anxiety of the greenhouse effect, but as a cost-effective means of obtaining CO₂, primarily for Enhanced Oil Recovery (EOR) operations. According to the findings of Herzog (2000), some commercial CO₂ capture plants were constructed in the United States in the late 1970s and early 1980s. The major industrial application of CO₂ obtained by chemical absorption process is for enhanced oil recovery.

The earliest commercial CO₂ sequestration facility commenced operations in Norway in September 1996. The facility was setup in response to a Norwegian carbon tax which was implemented. From that time when the plant was fully operational, Statoil has been storing CO₂ captured in a sandstone aquifer 1000m beneath the North Sea, away from the Sleipner West gas field (Bennaceur et al., 2004). The international research community is closely monitoring the activity at this facility.

CO₂ capture at these plants is achieved through a process of chemical absorption using an amine-based solvent such as Monoethanolamine (MEA). MEA is an organic compound which belongs to a family of compounds known as alkanolamines. Amines were discovered over 60 years ago as a general, non-selective solvent for removing acidic gas impurities (e.g., H₂S, CO₂) from natural gas streams (Lee and Keener, 2009). The process has been modified to eliminate CO₂ from dry flue gas streams. Fluor Daniel Inc., Dow Chemical Co., Kerr-McGee Chemical Corp., and ABB Lummus Crest Inc. were some of the pioneer developers of MEA-based technology for CO₂.
capture. Characteristically, around 75-90% of the CO$_2$ in a dry flue gas stream is captured using this technology, leading to a nearly pure (>99%) CO$_2$ product stream.

1.3 Details on Amine-based CO$_2$ Capture Systems

Zhao et al. (2007) revealed that the primary amines used in commercial CO$_2$ absorption processes are Monoethanolamine (MEA), Diethanolamine (DEA), $N$-methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanol (AMP) as reported by Zhao et al. (2007). Research has shown that primary and secondary amines, like MEA and DEA, undergo a rapid reaction with CO$_2$ to form carbamates.

However, it is important to know that there is an enormous amount of heat associated with CO$_2$ absorption when producing carbamates. Hence, the cost for regenerating MEA and DEA is high (Yu et al., 2012). One of the shortcomings of MEA and DEA during an absorption process is a reduced CO$_2$ absorption capacity at 0.5 mol. of CO$_2$ per mol.1 of amine. Therefore, tertiary amines like MDEA, will not react with CO$_2$ directly. It functions as a base which supports the hydrolysis of CO$_2$ to form bicarbonate and protonated amine.

The reaction rate of CO$_2$ at room temperature in an aqueous solution of MEA is 1.3 – 4.0 times faster than the direct reactions of CO$_2$ in MDEA. Consequently, the heat associated with bicarbonate formation is much lower than that related to carbamate formation; hence, the solvent regeneration cost of MDEA is much lower than that of MEA and DEA.
MDEA has a greater advantage over MEA and DEA on CO$_2$ absorption capacity, even though it has a limitation of 1 mole of CO$_2$ per mole of amine. Primary sterically hindered amine, such as AMP, also react quickly with CO$_2$. With similar characteristics to MEA and DEA, AMP reacts directly with CO$_2$ to produce carbamate. Nevertheless, the carbamate produced from the reaction between CO$_2$ and AMP reaction is very unstable because of the huge branches of AMP. The unstable carbamate undergoes hydrolysis rapidly to form a bicarbonate and a free AMP.

Kim et al. (2013) suggest that the CO$_2$ absorption capacity of AMP is limited to 1 mole of CO$_2$ per mole of amine, which is greater than that of MEA and DEA. Recent studies on solvents containing polyamines, such as Piperazine (PZ), 2-([2-Aminoethyl] amino) ethanol (AEEA) and Diethylenetriamine (DETA) have received much attention due to the excellent absorption capacity and swift reaction kinetics of the solvents (Yu et al., 2012).

1.4 Scope of this research work

This research work is dedicated to the development and characterization of new and promising absorbents for CO$_2$ capture. The work involves selecting new absorbents, running screening tests, and determining the chemical reaction kinetics of the selected absorbent using the stopped-flow technique. For young researchers in this area, this thesis will provide information on the technology of carbon capture by chemical absorption, as well as provide a summary of literature information consulted. For experienced researchers, this thesis will give a review of recent progress on this topic and offer an overview of future research opportunities based on current achievements.
According to SaskPower 2015-16 Annual report, the 1,509MW of coal-fired power generation capacity in Saskatchewan Canada provides 34% of all electricity and accounts for 22% of all carbon emissions coming from electric power utilities. There are predictions for a sudden rise in the use of renewable resources to meet growing electricity demand in the province while making efforts to reduce carbon footprints in the environment.

Therefore, any new policies to considerably lessen the amount of CO$_2$ emissions during the next two or three decades must take into consideration not only the technology alternatives for new power plants but also the retrofitting of existing coal plants which will continue to operate for many more years to come. Such near-term efforts to lower the amount of CO$_2$ emissions in the atmosphere has received considerable attention in recent times. Hence, this research examines the feasibility of post-combustion carbon capture at existing power plants as well as new facilities.

Information gathered from the relevant literature show that past studies have reported that amine-based CO$_2$ absorption systems are the most appropriate for combustion-based power plants for some reasons:

i. These systems are ideal for treating dilute CO$_2$ streams, such as coal combustion flue gases, which contain only about 10%-12% CO$_2$ by volume.

ii. Amine-based CO$_2$ capture systems are a proven technology that is commercially available and in use today.

iii. Amine-based systems are comparable to other end-of-pipe environmental control systems used at power plants. These units can be operated at normal temperature and pressure.
CHAPTER TWO: Literature Review

2.1 Overview

The removal of carbon dioxide from the atmosphere has a significant importance globally due to its growing harmful effects on the environment and ecosystem (Benson and Cole, 2008). With the current obligations of developed countries around the world to lower some CO$_2$ emissions in the environment, research efforts are being made to discover new ways to remove and process CO$_2$ from flue gas streams. The process of removing acid gases like CO$_2$ and H$_2$S from process flue gas streams, it is referred to as Gas sweetening or Acid Gas Removal.

The concentrations of H$_2$S and CO$_2$ in process gas streams differ from several parts per million to 50% by volume. The procedure and requirements for a CO$_2$ capture process often vary widely on the technology employed and on the amount of CO$_2$ present in the flue gas. Most of the efforts on reducing carbon dioxide emissions in the atmosphere are focused on large point sources, with fossil fuel-fired power plants being a major target. Green et al., (2005) showed that the amount of CO$_2$ in most power plant flue gas varies from 4% to 9% by volume, depending on the type of fossil fuel burnt and on the system operating conditions. Most of the new power generation technologies have better control of the amount of CO$_2$ released into the environment which leads to a lower economic penalty. These modern features are yet to be retrofitted on many of the existing power plants today.

This chapter of my research work provides a review and a summary of all previous work and studies related to CO$_2$ capture by tertiary and cyclic amines in general with emphasis placed on determining the reaction kinetics of some promising solvent for CO$_2$ absorption. Useful
information found in the relevant literature on chemical reaction kinetics, the reaction mechanism of alkanolamines as well as equilibrium solubility at various operating conditions were reported.

2.2 Acid Gas Absorption Processes

When aqueous amine solvents are used to absorb acid gases from process flue gas streams, it is considered a mass transfer process which is enhanced by chemical reaction. After absorption occurs in the aqueous amine solution, the acid gas reacts either directly or indirectly with the alkanolamines, through an acid-base buffer mechanism to produce non-volatile ionic species. Ali et al. (2007) described in their public work that the mass transfer of acidic gases from the bulk gaseous phase to the bulk liquid phase where chemical reactions take place is explained below:

- Dispersion of some acidic gas constituents from the bulk gas phase to the gas-liquid interface followed by absorption into the liquid.
- Dispersion of the reactants from the gas-liquid interface to the bulk liquid phase.
- The reaction between the dissolved gas and the liquid reactant in the liquid phase takes place at the same time with all mass transfer.
- Dispersion of the reaction products into the bulk liquid phase due to concentration gradients formed during the chemical reactions.

Figure 2.1 shows how the process of mass transfer with a chemical reaction which can take place during the absorption of acid gas using an aqueous alkanolamine solution.
Figure 2.1: Equilibrium process of CO$_2$ gas absorption into aqueous amine solution (adapted from Solbraa, 2002)

Research and development on Carbon capture have developed some methods that can be used to absorb CO$_2$ and other acid gases from process gas streams. Physical and Chemical absorption can be used to separate CO$_2$ from process gas streams or flue gas. The type of process employed depends on the partial pressure of CO$_2$ in the gas stream, the composition of the gas stream and some other factors.

In figure 2.2 below, the schematic presents some of the most widely used technologies for CO$_2$ capture with the application of a particular process to a given situation (Shaw and Hughes, 2001).
**Figure 2.2:** Process selection chart for the CO₂ removal procedures, (adapted from Shaw and Hughes, 2001).

Alkanolamine solvents have different chemical rates of reaction with various types of acid gases. Similarly, different amines have different equilibrium solubility values in different acid gases; while possessing different stability and corrosion properties. During the absorption/stripping of acid gases with aqueous alkanolamine solvents, there are two types of equilibrium conditions taking place: *Chemical equilibrium* and *Phase equilibrium*. For this reason, it is important to determine the concentrations of the numerous dissolved molecular and ionic elements which are in equilibrium with each other.
2.3 **Amine Solvents for Carbon dioxide (CO\textsubscript{2}) capture**

The chemical structure of most commonly used alkanolamines are presented in Table 2.1. Each alkanolamine has an hydroxyl group (-OH) and one amino functional group attached to a member of the alkane family. The hydroxyl group (-OH) lowers the vapor pressure while increasing the solubility of the amine in water, whereas the amino group enhances the pH of the solution which allows the amine solvent to react efficiently with acidic gases like CO\textsubscript{2} and H\textsubscript{2}S to form a particular type of carbamate (Kohl and Nielsen, 1997)

Alkanolamines are chemical compounds which happen to be derivatives of ammonia. They can be classified as *Primary, Secondary or Tertiary* depending on the number of non-hydrogen substituent groups bonded to the nitrogen atom.

1. **Primary Alkanolamines**: This is the first group of alkanolamines that has one of the hydrogen atoms in the ammonia molecule substituted by an ethanol group. The best-known example of primary alkanolamine is monoethanolamine, MEA (HOCH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{3}).

2. **Secondary Alkanolamines**: This group of alkanolamines has two of the hydrogen atoms in the ammonia molecule substituted by ethanol groups, such as diethanolamine, DEA, ((HOCH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}NH) or Methylaminoethanol, MAE, (HOCH\textsubscript{2}CH\textsubscript{2}NH).

**Tertiary Alkanolamines**: This group of alkanolamines has three of the hydrogen atoms in the ammonia molecule substituted either an alkyl or alkanol groups. The most popular amines in this category are Triethanolamine, TEA, (HOCH\textsubscript{2}CH\textsubscript{2})\textsubscript{3}N and N-Methyldiethanolamine, MDEA (HOCH\textsubscript{2}CH\textsubscript{2})\textsubscript{2}NCH\textsubscript{3}.
Table 2.1: Molar mass and Chemical Structures of some commercially well-known amines

(Source: (Chemical book - Chemical Search engine, 2016))

<table>
<thead>
<tr>
<th>Name of Amine</th>
<th>Molar mass [g.mol(^{-1})]</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>61.08</td>
<td><img src="image1" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Diethanolamine (DEA)</td>
<td>105.14</td>
<td><img src="image2" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Triethanolamine (TEA)</td>
<td>149.19</td>
<td><img src="image3" alt="Chemical structure" /></td>
</tr>
<tr>
<td>N-methyldiethanolamine (MDEA)</td>
<td>119.16</td>
<td><img src="image4" alt="Chemical structure" /></td>
</tr>
<tr>
<td>2-Amino-2-methylpropanol (AMP)</td>
<td>89.14</td>
<td><img src="image5" alt="Chemical structure" /></td>
</tr>
<tr>
<td>2-Methylaminoethanol (MAE)</td>
<td>75.11</td>
<td><img src="image6" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>
According to Veawab et al. (1999), the important factors to consider when studying the properties of an amine solvent include its rate of absorption and regeneration characteristics, acid gas loading, corrosion profile and solvent stability. Solutions that require the lower energy of regeneration need high contact surface area. Furthermore, solutions that possess greater loading capacity are perhaps the most difficult to regenerate.

Other research efforts in the use of amine solutions for the absorption of CO$_2$ from flue gas streams require the use of amine blends (mixing a tertiary amine with a primary or secondary amine) or through the addition of activated amine using an accelerator (activator) such as piperazine (PZ). Several research studies also give attention to sterically hindered amines which exhibit enhanced acid gas absorption.

2.3.1 Common Industry Amines for Carbon Capture

An aqueous solution of monoethanolamine (MEA) is by far the most widely used alkanolamine absorbents due to its reduced cost, low molecular weight, high absorbing capacity and excellent thermal stability (Tourneux, 2007). MEA is a reasonably strong base with a high rate of reaction rate for absorbing more than 96% of CO$_2$ from natural gas and combustion gas streams. Some research studies were conducted on the solubility and kinetics of CO$_2$ in aqueous MEA, (Bishnoi., 2000; Lee and Keener, 2009; Xiao, 2015; Versteeg et al., 2007; Solbraa, 2002).

On the other hand, Veawab et al. (1999) mentioned in their work that aqueous MEA solutions are known to have high regeneration energy and cause high corrosion. Due to the formation of a stable carbamate, the stoichiometry of the reaction restricts the amount of CO$_2$ absorbed to a maximum of 0.5 mole CO$_2$ for every mole of amine. Another disadvantage of using MEA for the absorption CO$_2$ from flue gas is the degradation of the amine over time. The by-
products of MEA degradation are believed to lower the efficiency of CO\textsubscript{2} capture are also associated with the corrosion of machinery according to (Dupert et al., 1993).

\textit{N}-Methyldiethanolamine (MDEA) being a tertiary amine is believed to have a high loading capacity of up to 1.0 mole of CO\textsubscript{2} for every mole of amine and possesses less regeneration energy and greater resistance to thermal and chemical degradation. It is important to know that these amines have a lower rate of reaction rate (Bishop and Rochelle, 2012).

2.3.2 Kinetics of Amines Activated using Piperazine

By adding an activator such as piperazine (PZ) to an aqueous solution of any alkanolamine, it has found a useful application for the removal of carbon dioxide by chemical absorption.

Derks \textit{et al.} (2006) were able to prove in their work that when a blend of piperazine (PZ) is mixed with an aqueous amine solution, it produces a combined effect of a relatively high reaction rate of CO\textsubscript{2} with piperazine (PZ). The effect is due to a low heat of reaction between CO\textsubscript{2} and the tertiary alkanolamine. The outcome of this reaction process is an increased rate of absorption in the absorber column and a lower heat of regeneration in the stripper column.


Bishnoi and Rochelle (2002) studied the absorption rate of CO\textsubscript{2} in aqueous solutions of piperazine (PZ) in a wetted wall contactor. The study involved measuring the rate of absorption at
temperature ranges of 298 to 333 K in solutions of 0.6 and 0.2 M concentrations of aqueous piperazine (PZ). The rate order, constants, activation energy and solubility, was determined.

A model of the equilibrium information created and matched with those of Monoethanolamine (MEA), Diethanolamine (DEA) and diglycolamine (DGA). The research work was able to show that the reactivity of PZ is as a result of the combined effect of a cyclic and diamine structure.

Dugas (2009) studied the effect of blending MEA with PZ at a temperature of 40°C and pressures ranges of 0.1 to 100 kPa. The study proved that 7 M concentration of MEA mixed with a 2M concentration of PZ has a CO₂ absorption capacity greater than 45% when compared to CO₂ absorption capacity of 7 M concentrations of MEA. Furthermore, a unique blend of 7 M concentration of MEA/2 M concentration of PZ showed faster absorption rate and greater stability when compared to 7 M concentration of MEA.

Ali et al. (2007) investigated the solubility of CO₂ in aqueous amine solution activated using piperazine PZ. The experiment was conducted using a broad range of piperazine (PZ) concentration from 0.01 M to 0.1 M to enable DEA and MDEA retaining the total amine concentration at 2.0 M and a temperature range of 40 to 80°C and CO₂ and partial pressure of 0.05 to 95.7 kPa. He discovered that the solubility of CO₂ in activated PZ/MDEA blends and activated PZ/DEA blends are greater than in mixtures of DEA/MDEA. However, CO₂ has a lower solubility in an aqueous solution mixture of MDEA/PZ when compared to a combination of MEA/MDEA.
Numerous information on the solubility of CO$_2$ in aqueous PZ solutions has been reported in published literature of Freeman et al. (2010) along with information on blends of aqueous PZ-MDEA solutions (Derks et al., 2010). These findings show that the ability of PZ to improve the solubility of CO$_2$ in an aqueous solution of alkanolamines.

2.3.3 Kinetics of Sterically Hindered Amines

A sterically hindered amine is primary amines in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to a secondary or tertiary carbon atom. The practice of using sterically hindered amines was recommended by Sartori and Savage (1983) who studied 2-amino, 2-methyl, 1-propanol (AMP) as a promising solvent for CO$_2$ capture.

Wong and Bioletti (2002) demonstrated how the hindered amine theory is dependent on the reaction rates of the acid gases with various amine molecules. The scientists explained that during the removal of CO$_2$, the loading capacity of the solvent could be enhanced considerably by slowing down the formation of a carbamate and by providing steric hindrance to the reacting CO$_2$.

Steric hindrance takes place when a substitute functional group is attached to the nitrogen atom in the amine molecule. The outcome is a slow overall reaction rate which produces an unstable carbamate. Hence, by creating an unstable amine carbamate, the loading capacity of the amine solvent can be hypothetically doubled.

The fundamental theory behind CO$_2$ absorption with sterically hindered amines is through the control of its molecular structure. Amines can undergo synthesis to produce either a stable
carbamate ion, an unstable carbamate ion or zero carbamate ion. It is important to know that with the appropriate molecular configuration, an unstable carbamate ion could form in the presence of CO₂ which can further undergo hydrolysis to form bicarbonates. The effect is a theoretical loading ratio of one mole of CO₂ for every mole of amine. Zhao et al. (2012) proposed that improved selectivity is achieved with sterically hindered amines than with commonly used tertiary or secondary alkanolamines. A number of these amines have many advantages over MDEA when it comes to selectivity, acid gas loading, kinetics and product gas purity.

Bonenfant et al. (2003) presented some sterically hindered amines as promising solvents for CO₂ gas scrubbing, and its performance compared to that of MEA. Scientists have been able to prove that methyl groups can assume a position adjacent to the amine which will have a benefit of enhancing the absorption capacities of the solvent.

Hindered amines can be categorized as either moderately hindered or severely hindered amines. The moderately hindered amines have found substantial use in non-selective bulk removal of H₂S and CO₂ whereas the severely hindered amines are used for the selective removal of H₂S. The amines above have a high capacity which is around 1.0 mole of CO₂ for every mole of amine used (Bishnoi and Rochelle, 2002).

Mandal et al. (2001) in their work compared amount of CO₂ absorbed per unit amount of AMP; a primary sterically hindered amine with that of MDEA, a tertiary amine and suggested the use of aqueous solutions of a mixture of two amines in different compositions. They discovered that CO₂ loading in AMP is estimated to be 1 mole of CO₂/mole of AMP, especially at low
absorption temperature. Numerous researchers reported that when mixing the same concentration of AMP and MDEA, there is a significant improvement in CO₂ loading over the entire range of CO₂ partial pressures.

Vinoba et al. (2013) examined aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), a sterically hindered amine, as a possible CO₂ absorbent and matched its properties with monoethanolamine (MEA) solution. CO₂ is reported to have a greater solubility in 10 mass % aqueous solution of AHPD than when it is dissolved in 10 mass % aqueous solution of MEA above 4 kPa at 298.15 K, but below 4 kPa, the solubility behavior seemed to be the reverse. AHPD has more hydroxyl functional groups than non-hindered MEA, and therefore, the chemical changes in its C-13 NMR spectra significantly influenced by the pH values of the solution. When compared to MEA, its C-13 NMR spectra appears to be insensitive to pH values of the solution.

Yu et al. (2012) studied novel absorbents for CO₂ capture at 40°C. He was able to establish that a 30 mass % of aqueous 2-(2-aminoethyl-amino) ethanol, (AEEA) solution could be a good and promising absorbent for CO₂ capture from atmospheric flue gases because it offers high absorption rate combined with high absorption capacity.

The combined efforts of Mitsubishi Heavy Industries, Ltd. and Kansai Power Co. led to the creation of a proprietary blend of hindered amines used for acid gas removal from process flue gas streams. The anticipated hindered amine mixture is assumed to have a higher CO₂ absorption capacity of 67% and a lower heat of regeneration around 20% when compared to that of MEA. Research studies conducted by MacDowell et al. (2010) show that MEA is less corrosive and
possess greater resistance to degradation by oxidation, such that make-up requirements are one-fifth of those of MEA.

A lot of research work has gone into developing novel solvents that will be superior to amines. The features expected of different solvents which allow it to significantly surpass the performance of existing amines are lower cost, lower volatility, and better thermal stability, less degradation, low corrosive nature, and low energy requirement for regeneration and adaptability to an existing system. Amines possess excellent CO₂ solubility and selectivity. Environmental and economic effects are given close attention when choosing the requirement for the best suited CO₂ capture mechanism. A lot of research is in place to improve the performance of existing and mature technologies CO₂ capture. Research on novel materials and technologies could result in breakthroughs required to minimise the environmental and energy penalties of capture.

Sada et al. (1986) studied the reaction between CO₂ and monoethanolamine (MEA) at 303K in both aqueous and non-aqueous solvents and discovered a steady change in the reaction order from 1 to 1.90. Sada et al. (1986) also examined the behavior of DEA in water, ethanol, methanol and 2-propanol solution and established that the reaction order changes from 1.42 to 2.

Versteeg et al. (1996) reported a reaction order of 2 for the reaction between MEA and ethanol in ethylene glycol. The authors of the reviewed publications were unable to interpret reaction orders differently to the conventional method of using whole numbers because of its accuracy.
Versteeg and Van Swaaij (1996) performed investigations on the reaction kinetics between CO$_2$ and DEA in aqueous solutions of ethanol and butanol, and they discovered that the reaction order was between the first and second order in ethanol whereas for butanol it was reported as second order. 

Crooks and Donnellan (1989) also reported in their work that the reaction order between DEA and CO$_2$ in anhydrous ethanol was of the second-order.

According to Versteeg and Van Swaaij (1996) when the results for reaction kinetics of CO$_2$ in aqueous and non-aqueous solutions of amines are compared, it can be inferred that the reaction order varied between 1 and 2 which can only be interpreted accurately by the zwitterion mechanism. Da Silva and Svendsen (2004) studied the reaction mechanism for producing carbamates when CO$_2$ reacts with aqueous solutions of an alkanolamine. The initial study recommended a single step, third reaction order which is most suitable for explaining the reaction mechanism because it stands in good agreement with the experimental data.

However, the findings of Versteeg et al. (1996) concludes that the termolecular mechanism has its limitations because its lack of ability to describe the occurrence of broken order kinetics. The discovery was reported in the work of (Sada et al., 1986; Versteeg and Van Swaaij, 1996; Crooks and Donnellan, 1989) for systems of non-aqueous amines (Versteeg et al.,1996).

Also, the experimental data presented by Bonenfant et al. (2003) for blends of secondary amines can be adequately described by the zwitterion mechanism, unlike the termolecular mechanism which has a limitation for interpreting the reaction mechanism accurately.
2.3.4 Kinetics of aqueous solutions of Tertiary Alkanolamines

There are numerous advantages associated with the use of tertiary amines for CO$_2$ capture when compared to the use of primary and secondary alkanolamine. An essential property of tertiary amines which makes it very desirable for removing H$_2$S from gas streams is because the reaction of tertiary amines with H$_2$S involves a proton transfer mechanism which is extremely fast, but the reaction of tertiary amines with CO$_2$ happens at a slow rate (Versteeg and Swaaij 1988).

The efficiency of the stripping process requiring the use of tertiary amines can be improved by adjusting the pressure of the system, which in turn requires minimal stripping energy when compared to other conventional amines. The reaction kinetics data of tertiary amines measured using the stopped flow technique is often very accurate due to the ability of the instrument to measure pseudo first-order reaction rate ($k_0$) up to milliseconds. When tertiary amines undergo a chemical reaction with carbon dioxide, the product of the reaction is an alkyl ammonium hydrogen carbonate rather than the alkyl ammonium carbamate produced when a similar reaction takes place with a primary or secondary amine (Crooks and Donnellan 1990). The author was able to establish these findings by studying the reaction kinetics of CO$_2$ in aqueous solutions of N-Methyldiethanolamine (MDEA) and triethanolamine (TEA) within a temperature range of 288 K to 308 K.

N-methyl diethanolamine, MDEA was not used in commercial applications for capturing acidic gases until the 1970’s. From a price point, MDEA as a tertiary amine is believed to be more expensive than the solutions of MEA or DEA. Nevertheless, research findings proved that MDEA has some desirable properties which make it in an excellent choice for CO$_2$ capture purposes. Some
of these properties include low vapor pressure, low corrosivity and high resistance to thermal and chemical degradation. The research work of Versteeg and others (1996) show that the overall reaction order for MDEA is approximately one which is in good agreement with the base catalysis of CO$_2$ hydration according to (Donaldson and Nguyen, 1980).

Crooks and Donnellan (1990) made an effort to study the reaction of CO$_2$ with triethylamine and quinuclidine, which was unsuccessful due to high pH values of the solution which produces high pKa values of 10.75 and 10.95, respectively. The value of [OH-] was so great that $k_2[OH-]$ dominated $k_0$.

Some researchers (Versteeg and van Swaaij, 1988; Littel et al., 1990) made use of different techniques to explain the Bronsted relation between the rate constant and the primary strength pKa of an amine. This relationship provides additional information on the base catalysis of CO$_2$ hydration.

Experimental studies on the acid dissociation constant of tertiary help us to understand the absorption kinetics behavior when it reacts with acidic gases. Research activities conducted by Versteeg and Van Swaaij (1988) proved that the amount of CO$_2$ absorbed during a CO$_2$-tertiary amine study was the same amount as that when physically dissolved in the solution. A disparity in this findings can be associated with the presence of primary and secondary amine impurities.

Nevertheless, Henni and Mather (1995) discovered that the amount of CO$_2$ absorbed into MDEA was greater in a polar solvent solution when compared to the amount of the pure solvent, after the pressure of the system was adjusted to a maximum value of 4000 kPa. Consequently, experimental
studies on tertiary amines and non-aqueous solvents are yet to show that no reaction takes place when mixed. Additional information is required for data on anhydrous solutions of tertiary amines (Barzagli et al., 2013)

2.4 Chemical Solvent Management

2.4.1 Selecting a Chemical Solvent for CO\textsubscript{2} absorption

A critical phase of the amine-based CO\textsubscript{2} capture technology is the chemical solvent selection process. Popularly used amine solvents used include MEA, MDEA, DEA and AMP are likely to degrade under process operating conditions and release hazardous compounds. Solvent selection cannot be taken for granted because of two main reasons; Economics and Environment.

Research work on this topic has proven that the choice of chemical solvent used for the carbon capture process accounts for at least 10% of the total operating costs; especially when monoethanolamine (MEA) is used as a standard solvent (Rubin and Rao, 2001).

Intense research efforts are in place to develop an amine solution (single or blend) that will remain stable under process operating conditions and will possess greater CO\textsubscript{2} capture capacity with favorable thermodynamic properties (MacDowell et al., 2010; Kumar et al., 2014; Hasib-ur-Rahman and Larachi, 2012).

Some amine solvents investigated have been tested to date to have good CO\textsubscript{2} absorption capacity and satisfactory reaction kinetics under standard operating conditions of the absorber.
Nevertheless, there are plans in place to examine several promising amine solvents to find the best amine-based absorbent for CO₂ capture. Information found in literature shows that two amine solutions have demonstrated superior CO₂ capture capacity with feasible physical characteristics and thermal stability, like PZ and MOR under standard process operating conditions (Khatri et al., 2006; MacDowell et al., 2010).

On the other hand, there is a need for further research work on these solvents as a substitute for MEA. Products of degradation produced from PZ and MOR are yet to be measured and recognized entirely. Research studies explain that substantial amounts of nitrosamine and nitramine are formed through the degradation of PZ and MOR (Chandan et al., 2013; Fine et al., 2014).

It is important to remember that PZ and MOR have limited solubility in water due to the presence of an aromatic ring in their chemical structure. It is predicted that the reduced solubility of PZ and MOR can be enhanced by mixing them with other amines (Bishnoi and Rochelle, 2002; Zhang et al., 2003; Derks et al., 2010).

Nonetheless, a comprehensive study is yet to be performed on both systems to determine their efficiency for CO₂ absorption.

2.5 Post Carbon Combustion (PCC) emissions and its environmental concerns

When efforts are made to reduce the number of carbon dioxide emissions present in the environment, it comes at the expense of some other environmental pollutants (D'Alessandro et al., 2010).
During the capture of CO₂ with amine-based solvents, some of the wastes in the form of volatile organic compounds (VOCs), solid and liquid pollutants are released. (Thitakamol et al., 2007; Thibaut et al., 2013; Mazari et al., 2015). The used amine along with some degradation products and heavy-metal corrosion inhibitors emitted from the reclaimer can cause toxicity (Thitakamol et al., 2007).

Some of the volatile degradation products released from the reclaimer include 2-butanamine, ammonia, and ethylamine are lethal and can cause severe health conditions like skin burns and irritation once they are vaporized with treated flue gas (Thitakamol et al., 2007). Regardless of the adverse effects of gaseous emissions and traces of high, liquid pollutants from CO₂ capture plants, researchers are making efforts to lower its environmental impacts (Thitakamol et al., 2007).

On the other hand, the primary concern is the volatile emissions from CO₂ capture plants, which are primarily either amines or their degradation products. Some solvent losses can be estimated at 0.01-0.8 kg/ton of CO₂ captured (Freeman and Rochelle, 2012).

Ammonia is one of the volatile degradation products believed to be of the highest concentration out of the emissions from PCC while using MEA (Azzi et al., 2014).

In Norway, Alphen (2011) reported that the plans and policies put in place to structure a full-scale CO₂ capture system at the 420 MW gas power plant at Kårstø might release amine emissions estimated to be around 40-160 tonnes yearly. Although, the precise amount of emissions may vary
depending on some factors which include: the size of the power plant, flue gas composition and operating conditions of the plant. Some of the emissions may further deteriorate into harmful products through photo-oxidation and rain. Amine emissions are not only detrimental to the humans but could also cause havoc to the ecosystem (Mazari et al., 2015).

The most disturbing degradation products of amines are the nitrosamines and nitramines. Fugitive emissions are pollutants that find their way into the environment, without traveling through the discharge point of the treated flue gases. The escape may happen because of leakages created by some factors, operations or as a result of wear and tear on equipment members (Thitakamol et al., 2007).

There are emissions that are not easily controlled and may occur at any section of the plant. Some of the emissions may include; treated and untreated flue gas, solvents, corrosion inhibitors, degradation products, and chemical additives (Thitakamol et al., 2007). Unintentional release of pollutants is generally in a larger quantity than fugitive release which may be caused by the process equipment malfunctions.
CHAPTER THREE: Reaction Fundamentals of Alkanolamines

3.1 Reaction Mechanism of Primary and Secondary Amines

The overall equilibrium reaction between Carbon dioxide (CO$_2$) and primary or secondary amines can be explained as follows:

\[ CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH \] .......................................................... (3.1)

\[ R_1R_2NCOOH + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \] ...................... (3.2)

The first phase of the reaction process being bimolecular has a second-order reaction rate and is rate defining, whereas the second phase is meant to take place instantaneously. Nevertheless, this pattern is a simplified way of explaining the reaction mechanism which occurs when Carbon dioxide (CO$_2$) reacts chemically with primary or secondary amines (Sartori and Savage, 1983).

3.1.1 Zwitterion Mechanism

The Zwitterion mechanism was initially proposed by Caplow (1968) and re-established by (Danckwerts, 1979). It comprises of a two-step mechanism which describes the reaction between CO$_2$ and an amine, going through a phase of producing an intermediate called a zwitterion (reaction in equation 3.3) and the deprotonation of the zwitterion by a base B (reaction in equation 3.4).

\[ CO_2 + R_1R_2NH \xrightarrow{k_1} R_1R_2NH^+COO^- \] .................................................. (3.3)

\[ R_1R_2NH^+COO^- + B \xrightarrow{k_2} R_1R_2NCOO^- + BH^+ \] .......................... (3.4)

$R_1$ and $R_2$ in the equation above denotes a substituted group attached to the amine group; $B$ is used to represent a base molecule which could be a hydroxyl ion, water or an amine functionality.
In this research work, three different tertiary amines will be studied, and their chemical reaction kinetics will be determined using the *Stopped-Flow apparatus*. Pure ethanol will be employed as the solvent where needed.

Through the application of the pseudo-steady-state condition for the zwitterion concentration, the overall forward reaction rate can be expressed as follows:

\[
-r_{CO_2-R_1R_2NH}^{z} = \frac{k_2[CO_2][R_1R_2NH]}{1 + \frac{k_{-1}}{\sum k_b[B]}}
\]

(3.5)

In the equation below, \(\sum K_b[B]\) characterizes deprotonation of the zwitterions by any base like \(CO_3^{2-}, HCO_3^-, H_2O, OH^-\) or \(R_1R_2NH\), as well as by a mixture of more than one base.

The following equation can is used when the formation of zwitterions is the rate determining step.

\[
\frac{K_{-1}}{\sum K_b[B]} \geq 1
\]

Equation 3.5 from the previous page can be broken down to:

\[
-r_{CO_2-R_1R_2NH}^{z} = k_2[CO_2][R_1R_2NH]
\]

(3.6)

Equation 2.6 above illustrates a first-order rate dependency concerning the concentration of amine solvents and the concentration of \(CO_2\) from the flue gas stream.

Conversely, if the deprotonation of the zwitterion is the rate determining step i.e.

\[
\frac{K_{-1}}{\sum K_b[B]} \geq 1
\]

Then equation 2.5 can be expressed as follows:

\[
-r_{CO_2-R_1R_2NH}^{z} = \frac{k_2\sum k_b[B]}{k_{-1}}[CO_2][R_1R_2NH]
\]

(3.7)
In this research work, the amine is the only reacting base B, which suggests a broken order dependency from one to two concerning the concentration of the amine used. For this case the forward reaction can be summarized as:

\[
-\frac{d[R_i R_j N\text{H}]}{dt} = \frac{[CO_2][R_i R_j N\text{H}]}{1 + \frac{1}{k_2 + k_{R_i R_j N\text{H}}[R_i R_j N\text{H}]}}
\]  

(3.8)

3.1.2 Single-step Termolecular mechanism

The Termolecular mechanism was first discovered and initially recommended by Crooks and Donnellan (1989) who proposed that the bonding of amine to CO\(_2\), as well as proton transfer between their molecules, take place instantaneously and that the original product is lightly bound together and may likely produce some complexes. Most of these complexes break down to generate reagent molecules again while a few react with a second amine molecule to give an ionic product.

Da Silva and Svendsen (2004) have studied this mechanism in their research work through the use of ab-initio calculations and a solvation model and proposed that most likely mechanisms were comparable to one suggested by (Crooks and Donnellan, 1989). To some extent, a zwitterion-like intermediate is estimated to have a very short lifespan. They concluded from their study that in most circumstances, the single step mechanism is the most suitable technique for describing the nature of reaction taking place between amine and CO\(_2\). An important observation from that work is that the termolecular mechanism may likely explain broken order kinetics too. It has been
disputed before by Versteeg et al. (1996) that the termolecular mechanism is not capable of explaining the interaction.

\[
\begin{align*}
\text{By looking at the reaction taking place in equation 3.9, if amine and water are dominant bases the forward reaction rate for termolecular mechanism can be written as:}
\end{align*}
\]

\[
\begin{align*}
-\dot{r}_{\text{CO}_2-R_iR_2NH}^T &= \left\{ k^T_{R_iR_2NH} [R_iR_2NH] + k^T_{\text{H}_2\text{O}} [\text{H}_2\text{O}] \right\} [\text{CO}_2] [R_iR_2NH] \\
\end{align*}
\]

According to the zwitterion mechanism, equation (3.6) and equation (3.8) will demonstrate a lot of similarities when the deprotonation of zwitterion is the rate determining step. In this research work, the amine is the base in the chemical reaction, and the forward rate reaction from equation 3.10 can be written as:

\[
\begin{align*}
-\dot{r}_{\text{CO}_2-R_iR_2NH}^T &= \left\{ k^T_{R_iR_2NH} [R_iR_2NH] \right\} [\text{CO}_2] [R_iR_2NH] \\
\end{align*}
\]

### 3.2 Reaction mechanism of Tertiary Alkanolamines

Donaldson and Nguyen (1980) carried out numerous studies to determine the conditions in which tertiary alkanolamines will not react directly with CO\textsubscript{2}. Tertiary amines have a base-catalytic influence on CO\textsubscript{2} hydration. Versteeg and Van Swaaij (1996) were able to confirm this information through their work which involved the absorption of CO\textsubscript{2} into a water free solution of MDEA and ethanol. They determined that CO\textsubscript{2} was absorbed physically by the amine and that the reaction agrees with the proposed reaction mechanism.
\[ R_1 R_2 R_3 N + H_2O + CO_2 \xrightarrow{k'} R_1 R_2 R_3 NH^+ + HCO_3^- \] ............................. (3.12)

At greater pH values of (pH =13), a direct reaction between CO\(_2\) and tertiary amines have been reported by Little et al. (1999). On the other hand, at lower pH values (of pH < 11), the rate of the reaction can be neglected (Vaidya and Kenig, 2007).

Versteeg and Swaaij (1996) explained that the rate of absorption of CO\(_2\) into a solution of the MDEA-ethanol solution involves *physical absorption*, whose properties are a lot similar to the absorption of N\(_2\)O in the same solution.

The overall reaction rates of CO\(_2\) reacting with aqueous amine solutions is explained below:

\[ k_{ov} = \{k_{H2O}[H_2O] + k_{OH^-}[OH^-] + k'[R_1R_2R_3N]\}[CO_2] \] .......................... (3.13)

\[ k_{ov} \text{ is given by:} \]

\[ r_{ov} = \{k_{H2O}[H_2O] + k_{OH^-}[OH^-] + k'[R_1R_2R_3N]\} \] .......................... (3.14)

and \( k_{app} \) is:

\[ k_{app} = k'[R_1R_2R_3N] \] .......................... (3.15)

### 3.3 Determination of Kinetic rate constant

When determining the absorption rate of CO\(_2\) into aqueous amine solution, the overall reaction rate is expressed as follows:

\[ r'_{ov} = r_{CO_2-R_2R_3NH} + r_{CO_2-OH^-} \] .......................... (3.16)

The apparent kinetic rate constant \( k_{app} \) is defined as follows:

\[ k_{app} = k_{ov} - k'_{OH^-}[OH^-] \] .......................... (3.17)
In this case, where no water is present, it can be modified to:

\[ k_{app} = k_{ov} \]

A graphical method can be used to plot the relationship between \( k_{app}/[R_1R_2NH] \) and the \([R_1R_2NH]\) values for termolecular mechanism according to equation (3.11), value of slope is \( K^TR_1R_2NH \) itself. If equation (3.5) for zwitterion mechanism is valid, that means the plot between \( [R_1R_2NH]/k_{app} \) and \( 1/[R_1R_2NH] \) should produce a straight line with slope \( \frac{K_2K_b}{k_{-1}} \) and intercept \( k_2 \).

This method was used by (Crooks and Donnellan, 1989) (Versteeg and Van Swaaij, 1996).
CHAPTER FOUR: Reaction Kinetics and Dissociation Constants (pKa) of Tertiary Alkanolamines for Post-Combustion Carbon Dioxide (CO₂) Capture

Section 4A: Determination of reaction kinetics for promising amines

The experimental procedure used to determine the reaction kinetics of CO₂-Amine systems are in two categories at the laboratory scale: Measuring gas-liquid mass transfer rates and measuring the reaction rate of chemical solvents after rapid mixing. The two experimental procedures have advantages and shortcomings on data comparison and establishing a structure-activity relationship.

4.1 Mass-Transfer Procedures

There are numerous brands of gas-liquid reactors which are devoted to measuring the reaction kinetics of CO₂ absorption in alkanolamine solutions (Laurent et al., 1980). All the equipment have a limitation as to the amount of contact time or liquid mass-transfer coefficient, which for this reason permits measurement at defined concentrations for appropriate amine formulations.

Many researchers have discovered that the reaction rate of amines with CO₂ depend solely on some orders of magnitude. However, none of the equipment mentioned can satisfactorily provide a precise measurement of kinetic parameters in the large experimental region covered by the huge selection of amines. A good example is the determination of the kinetics of absorption for a 30 wt% monoethanolamine solution using a wetted-wall column. Puxty et al. (2009), and a study involving measurement of the kinetics of absorption for a 50 wt% (MDEA) that is analyzed using a stirred vessel (Versteeg and Van Swaaij, 1988).
These experimental procedures involve the use of a mass-transfer model to interpret all experimental data. This mass-transfer model considers various parameters like thermodynamic equilibrium, the hydrodynamics of gas and liquid phase, physical solubility, diffusion of reactants and products in the liquid phase to fit measured mass transfer rate. During these circumstances, predictions for the kinetic constants significantly depend on numerous hypotheses of the mass-transfer model which is capable of providing excellent dispersions on the data presented, (Danckwerts, 1979; Laurent and Charpentier, 1980; Charpentier, 1981).

Concerning diethanolamine, which is often used in gas treatment, Rinker et al. (1996) demonstrated that dispersion between second order reaction kinetic constants determined by numerous authors is higher than 50%.

4.2 Rapid Mixing Procedures

In most research laboratories, the most commonly used rapid mixing techniques for CO$_2$-amine studies is the stopped-flow technique. By comparing the stopped-flow technique to other mass-transfer technologies, the stopped-flow procedure allows the research scientist to accurately determine reaction kinetic constants typically between the ranges of 0.01 and 1 000 s$^{-1}$, with the upper limit comparable to the inverse of the mixing time which is close to 1 ms. However, the stopped flow technique has a limitation of not be suitable to determine the reaction kinetics of fast-reacting alkanolamines used in industrial environments.

It is important to know that when the stopped-flow technique is used to determine reaction kinetics, the procedure is free from gas-liquid mass transfer limitations. The signal obtained from the
stopped-flow apparatus depends on the reaction mechanism as well as the optical properties of reactants at the liquid phase which makes the values of an experiment to be reproducible.

The research work of Rayer et al. (2011) confirms that the general uncertainty of data obtained from a stopped-flow experiment is estimated at around 5%. Moreover, this method is ideal for drawing a quantitatively structured activity relationship between natural reaction kinetic values of reaction for various amines with CO₂ during a comparison study experiment.

4.2.1 How to treat data obtained from the Stopped-flow Apparatus

There are two different ways that kinetic parameters can be obtained from Stopped-flow data during an experimental study: Numerical model and Analytical model.

Both methods will be discussed below and with careful considerations on the advantages and disadvantages of both approaches. The main reason for using this method is because it allows any researcher to make an informed decision on the most suitable method when valuable information needs to be obtained.

4.2.1.1 Numerical Model

The Numerical model in any stopped-flow experimental study takes into consideration all chemical species involved in the reaction and the thermodynamic equilibria in which they are involved. All parameters of a kinetics experiment have often been optimized to lower deviations between the model and experimental data. According to the work of (Wang et al., 2011; McCann, 2008), this model has found significant use when spectrophotometric detection is used to monitor a
reaction or when the working conditions, such as the CO\textsubscript{2} loading is not well-suited for an analytical solution of the model.

Even though this technique is somewhat exhaustive, the outcome of a reaction kinetic experiment are constants which are closely dependant on the mechanistic theories or thermodynamic model for non-ideal solutions.

### 4.2.1.2 Analytical Model

The Analytical model is a very traditional method used during stopped-flow studies of amine-CO\textsubscript{2} reaction. This technique takes into consideration a single, irreversible reaction of CO\textsubscript{2} with an amine to a significant excess, following first-order reaction conditions. Frequently, researchers experiment using a total concentration of amine at least ten times more than the concentration of carbon dioxide. Under these circumstances, the difference in concentration of the chemical species depends on the pseudo first-order kinetic constant \( k_0 \) according to a mono-exponential deviation.

In regards to conductivity stopped flow measurements, the difference in concentrations of ionic species can be checked by using the change in conductance of the resulting solution. The inverse of the electric resistance \( R \) (Ω) gives the value of Conductance \( G \) (S) for the ionic species. \( A \) (S) is the amplitude of the signal, \( k_0 \) is the pseudo first order kinetic constant, \( t \) (s) is the time, and \( C \) (S) is the value of the conductance at the end of the observed reaction. According to Ali \textit{et al.} (2005), deviations in the value of conductance is interrelated to the formation of amine salts as well as values of the pseudo first order kinetic constant \( k_0 \).
Some apparatus have been used to determine the reaction kinetics of solvents. Some of the standard equipment that you will find at most research labs include: The Laminar Jet Absorber, Wetted-Wall Column, Stirred-Cell Absorber, or Stopped Flow technique.

The Laminar Jet Absorber, Wetted-Wall Column, Stirred-Cell Absorber are considered indirect procedures for determining reaction kinetics, and the rate at which carbon dioxide gets absorbed into the alkanolamine solution can be measured where both the diffusivity and the solubility of carbon dioxide is required. These two parameters are challenging to acquire directly.

4.3 Chemical Reaction Kinetics of Tertiary Amines

The research work of Donaldson and Nguyen (1980) suggested that the base-catalyzed hydration mechanism can be used to interpret the reaction between CO$_2$ and tertiary amines because the amine does not react directly with CO$_2$, but works as a base which catalyzes the hydration of CO$_2$. Since MDEA is considered a tertiary amine and because three of the hydrogen atoms attached to the nitrogen atom has been replaced by a substituent such as an alkyl or aryl group, the absorption mechanism of MDEA, then follows the base-catalyzed hydration mechanism and is expressed as:

$$
\text{MDEA} + \text{CO}_2 + \text{H}_2\text{O} \xrightarrow{k_2} \text{MDEAH}^+ + \text{HCO}_3^- \quad \text{................................................. (4.1)}
$$

The following reaction is said to occur in an aqueous solution of CO$_2$

$$
\text{CO}_2 + \text{OH}^- \xrightarrow{k_{OH}} \text{HCO}_3^- \quad \text{....................................................... (4.2)}
$$

$$
\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{k_{H2O}} \text{H}_2\text{CO}_3 \quad \text{.............................................................. (4.3)}
$$

By looking at the reactions represented by equation (4.1) - (4.3), the overall reaction rate of CO$_2$ absorption ($r_{\text{CO}_2}$: kmol/m$^3$ s) can be expressed as:

$$
r_{\text{CO}_2} = k_0 \cdot [\text{CO}_2] = \{k_2 [\text{MDEA}] + k_{\text{OH}}[\text{OH}^-] + k_{\text{H2O}} [\text{H}_2\text{O}]\} [\text{CO}_2] \quad \text{............... (4.4)}
$$
Where

\[ k_0 \] = Observed pseudo-first-order reaction rate constant (s\(^{-1}\)),
\[ k_2 \] = Second-order reaction rate constant of reaction 1 (m\(^3\)/kmols)
\[ k_{OH^-} \] = Reaction rate constant of reaction 2 (m\(^3\)/kmols)
\[ k_{H2O} \] = Reaction rate constant of reaction 3 (m\(^3\)/kmols)

As a result of the slow reaction rate involving a mass transfer in step 1 and step 2, step 3 can be neglected. Consequently, the reaction rate expression based on the reaction happening in step 1 and step 2 can be explained using the equation below:

\[ r_{CO_2} = k_0.[CO_2] = \{k_2.[MDEA] + k_{OH^-}[OH^-]\} [CO_2] \] ................. (4.5)

In a prepared aqueous amine solution, the influence of OH\(^-\) to overall reaction could be neglected. The key element in the reaction above is the tertiary amine, which in this case is MDEA. The overall reaction rate expression of CO\(_2\) absorption into aqueous of MDEA based on the base-catalyzed hydration mechanism is described below:

\[ r_{CO_2} = k_0.[CO_2] = k_2.[MDEA].[CO_2] \] ................. (4.6)

Therefore,

\[ k_0 = k_2.[MDEA] \] ................. (4.7)

**Experimental Section**

**Chemicals**

All the reagent grade chemicals used for this research work was purchased from Sigma-Aldrich. The exceptions are methanol and acetone used to clean the equipment which was supplied by
Commercial Alcohols Inc. The purity level of the solvents, chemical structure, and values for the relevant physical properties of the chemicals used in this work is revealed in Table 4.1.

All the chemicals purchased from Sigma-Aldrich were utilized in the supplied state without further purification. Deionized water at the laboratory was used in the appropriate amount to achieve the desired concentration of samples where needed. The purity level of the Carbon dioxide gas purchased from Praxair is 99.99 vol. %.

Table 4.1: List of Chemical solvents used in this research study

<table>
<thead>
<tr>
<th>Name of Amine</th>
<th>Molecular weight [g/mol]</th>
<th>Molecular formula</th>
<th>Boiling pt. [°C]</th>
<th>Purity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Methyldiethanolamine</td>
<td>119.16</td>
<td>CH₃N(CH₂CH₂OH)₂</td>
<td>246-248</td>
<td>99</td>
</tr>
<tr>
<td>(CAS Number: 105-59-9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-[Bis [3-(dimethylamino)propyl] amino]-2-propanol</td>
<td>245.40</td>
<td>[(CH₃)₂N(CH₂)₂NCH₂CH(OH)CH₃]</td>
<td>290</td>
<td>98</td>
</tr>
<tr>
<td>(CAS Number: 67151-63-7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N, N, N', N'', N'''-Pentamethyldiethylenetriamine</td>
<td>173.30</td>
<td>[(CH₃)₂NCH₂CH₂NC₃H₃]</td>
<td>198</td>
<td>99</td>
</tr>
<tr>
<td>(CAS Number: 3030-47-5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N, N', N'-Tetrakis (2-hydroxyethyl) ethylenediamine</td>
<td>236.31</td>
<td>(HOCH₂CH₂NCH₂ÈH₂N(CH₂CH₂OH)₂</td>
<td>280</td>
<td>98</td>
</tr>
</tbody>
</table>
4.3.1 Measurement of reaction kinetics data using the stopped-flow apparatus

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 four different tertiary 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 4.1. 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°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 is the movement of the drive plate located at the bottom of the internal syringes that contain the CO₂ solution and amine solution.

For each experimental procedure, a fresh solution of CO₂ 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 CO₂ can be prepared by bubbling the gas through double-distilled water whereas a non-aqueous solution is prepared by bubbling the gas through a non-aqueous solution of methanol or ethanol.

The fresh CO₂ solution used during the experiment was prepared by bubbling research grade CO₂ for at least 30 minutes through the double-distilled water until the water was completely saturated with CO₂. The bubbling procedure took place by allowing CO₂ 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.

The gas chromatograph (GC-6890 from Agilent) was used to measure the amount of CO$_2$ bubbled into the solution when saturation was reached at room temperature.

**Figure 4.1:** A schematic diagram of the *Stopped-flow* apparatus
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 KinetAssyst 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 CO₂ 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. Mandel et al. (1978) developed a circuit which measures the conductivity change and produces an output voltage directly proportional to the solution conductivity as reported in many kinds of literature. 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. A representative graph of voltage plotted against time is shown in Figure 4.2. The variations in conductivity with respect to time profile is described according to an exponential equation similar to a first-order kinetic equation.

\[
Y = -A e^{\frac{k_0 t}{Y_\infty}} + Y_\infty \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.8)
\]

According to the equation above,

- \( A \) = Amplitude of the signal
- \( k_0 \) = Pseudo-first order reaction constant
- \( t \) = time (second)
- \( Y \) = Signal measured by the Conductivity Control Unit (V)
- \( Y_\infty \) = Constant value of the signal (V) at equilibrium

Information in the equation above is defined according to the work of (Ali et al. 2000).
It is important to know that gas absorption does not take place during a stopped flow procedure such that the findings tally with the intrinsic homogeneous reaction rate of solutions (Aboudheir et al., 2003). The reversibility of a reaction does not affect the data from this direct procedure or eliminate any possible errors associated with the experiment due to the depletion of the amine in a gas-liquid interface. 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 4.2: A graphical plot of the stopped-flow experiment at a set temperature.](image)

**RESULTS AND DISCUSSION**

4.3.1.1 Absorption kinetics of CO$_2$ in MDEA

To accurately determine the absorption kinetics of CO$_2$ in tertiary amines, the stopped-flow apparatus was first used to measure the reaction kinetics of CO$_2$ with an aqueous solution of
MDEA, to ensure the accuracy of data from the equipment. This reaction has been widely studied by numerous research scientists, with data available in reputable literature publications using the stopped flow technique.

The overall reaction rate constant for this experiment can be determined by using the formula in equation 4.7 above. All values of the pseudo-first order reaction rate constants \(k_0\) obtained from the experimental procedure along with the calculated values of the second order reaction rate constants \(k_2\) for MDEA within a temperature range of 298-313 K is presented in Table 4.2. 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 4.3. According to the graphical plot shown in figure 4.3, all values on the y-axis and x-axis represent the pseudo-first order reaction rate constant \(k_0\) and amine concentration respectively. The plot produces a straight line at each temperature, and the value of the slope of this graph gives the value of the rate constant of \(k_{MDEA}\), at that temperature.

When looking at the plot in Figure 4.3, it can be observed that the values of the slope increase progressively as the temperature of the experiment increases, which is evident because of the rate constant increases steadily with increasing temperature. The Arrhenius plot for this reaction is obtained by plotting the Ln values of the second-order rate constant of \((Lnk_2)\) for MDEA at different temperatures against the inverse of the experimental temperature \((1/T)\) in kelvin as shown in Fig. 4.4. It can be concluded that the values of \(k_2\) for MDEA fits well into the following Arrhenius equation below:

\[
k_2 = 2.91 \times 10^{-1} \exp (7357.1/T)
\]  

\……………………………………………………(4.9)
Table 4.2: The reaction rate constants of \((\text{CO}_2 + \text{H}_2\text{O} + \text{MDEA})\) at different temperatures.

<table>
<thead>
<tr>
<th>[Amine] mol/m³</th>
<th>Temperature [K]</th>
<th>[Water] mol/m³</th>
<th>Pseudo first-order rate constant [k/s]</th>
<th>Second Order rate constant [k\text{mol}^2\text{m}^{-4}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>199.9958</td>
<td>298</td>
<td>54182</td>
<td>3.071 ± 0.2</td>
<td>0.0154</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td></td>
<td>4.355 ± 0.2</td>
<td>0.0151</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>6.179 ± 0.3</td>
<td>0.0150</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>10.734 ± 0.4</td>
<td>0.0149</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>13.288 ± 0.5</td>
<td>0.0148</td>
</tr>
<tr>
<td>399.9891</td>
<td>298</td>
<td>52849</td>
<td>6.360 ± 0.2</td>
<td>0.0218</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td></td>
<td>8.499 ± 0.2</td>
<td>0.0216</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>13.068 ± 0.3</td>
<td>0.0213</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>20.835 ± 0.4</td>
<td>0.0212</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>28.601 ± 0.5</td>
<td>0.0207</td>
</tr>
<tr>
<td>599.9904</td>
<td>298</td>
<td>51526</td>
<td>8.851 ± 0.2</td>
<td>0.0341</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td></td>
<td>12.960 ± 0.2</td>
<td>0.0340</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>20.375 ± 0.3</td>
<td>0.0336</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>31.398 ± 0.4</td>
<td>0.0527</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>42.421 ± 0.5</td>
<td>0.0309</td>
</tr>
<tr>
<td>799.9919</td>
<td>298</td>
<td>49204</td>
<td>11.881 ± 0.2</td>
<td>0.0537</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td></td>
<td>16.961 ± 0.3</td>
<td>0.0523</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>27.245 ± 0.4</td>
<td>0.0521</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>41.714 ± 0.4</td>
<td>0.0521</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>51.658 ± 0.5</td>
<td>0.0521</td>
</tr>
<tr>
<td>999.9799</td>
<td>298</td>
<td>50108</td>
<td>14.813 ± 0.2</td>
<td>0.0715</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td></td>
<td>20.739 ± 0.3</td>
<td>0.0707</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td></td>
<td>33.599 ± 0.4</td>
<td>0.0664</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>52.069 ± 0.4</td>
<td>0.0646</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td></td>
<td>64.447 ± 0.5</td>
<td>0.0645</td>
</tr>
</tbody>
</table>
**Figure 4.3:** A plot of the pseudo-first order rate constant, $k_0$ values against MDEA concentrations of the reaction between CO$_2$ + MDEA at different temperatures.
Figure 4.4: The Arrhenius plot for CO$_2$-MDEA second-order reaction rate constant against (1/T)

By carefully looking at the experimental results and comparing it with that published by (Versteeg and Van Swaaj, 1988; Sodiq et al., 2014), the data obtained has an absolute deviation of 3.89% from the data published by (Sodiq et al., 2014). The data obtained in this work has an absolute deviation of 8.6% from the data published by Versteeg and Van Swaaj (1988). This enormous difference in data is due to using a different measurement instrument; the stirred vessel was employed by Versteeg and Van Swaaj (1988) to measure the reaction rate of CO$_2$ in MDEA as opposed to the stopped-flow apparatus used by (Sodiq et al., 2014).
Hence, it can be concluded that the experimental data obtained from the stopped flow apparatus was in good agreement with that obtained by (Sodiq et al., 2014). The value for activation energy calculated from this experimental work is determined to be 49.26 kJ/mol, which is in close agreement with the calculated value of 49.15 kJ/mol in published literature. Also, the pre-exponential factor, $\ln k_0$, obtained in this work is comparable to the value presented Sodiq et al. (2014) with less than 1% deviation. The results of the experiment conducted in this research work using MDEA, validate that the procedures used are very accurate and can, therefore, be used as a reliable method for producing accurate reaction kinetics data for promising tertiary alkanolamine solvents.

4.3.1.2 Absorption kinetics of CO$_2$ in BDMAPA2P

To understand the reaction kinetics of CO$_2$ and 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol, BDMAPA2P as a promising solvent for chemical absorption, an experiment was performed using the stopped-flow apparatus. Samples of 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol were prepared with a concentration range of 200–1000 mol/m$^3$, and the experimental temperature set within a range of 298–313K.

Pseudo first-order conditions were maintained throughout the experiment, and the values of the pseudo first-order reaction rate constant ($k_0$) obtained from the stopped flow apparatus are presented in Table 4.3. The trend in values is dependent on temperature and the concentration of 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol. A graphical plot of the pseudo-first order values against the concentration of BDMAPA2P (kmol/m$^3$) is presented in Figure 4.5.
It was observed that the reaction kinetics of CO\textsubscript{2} in 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol with respect to the pseudo first order reaction rate constant (\(k_0\)), appreciated in values for every increase in amine concentration within a given temperature.

The pseudo first-order rate constants \(k_0\) obtained experimentally from the stopped flow apparatus were interrelated using the empirical power law relationship in Figure 4.5 to determine the reaction order for the CO\textsubscript{2}-amine reaction. Experimental results revealed that the reaction orders were 0.89, 0.92, 0.86, 0.82 and 0.82, with respect to [BDMAPA2P] for 298, 303 308, 313 and 318 K, respectively.

All experimental values for the reaction order can be approximated as 1.0 and with an average reaction order of 0.86. Therefore, the experimental values of \(k_0\) at different concentrations and temperatures of BDMAPA2P (from Table 4.3) can be interpreted using the base-catalyzed hydration mechanism. The values presented in Table 4.4 shows all the results for the fitted values of second-order reaction rate constant \(k_2\), which is closely dependent on temperature. It is an established theory that the second-order reaction rate constant \(k_2\) can be explained using the Arrhenius expression below:

\[
\begin{align*}
\frac{k_2}{A} &= 4.625 \times 10^{-1} \exp \left(\frac{-5497.3}{T}\right) \\
\text{.......................................................... (4.10)}
\end{align*}
\]

[The value of \(R^2\) for this plot = 0.99]

Definitions:

\(A\) = Arrhenius constant (m\textsuperscript{3}/mols),
\(E_a\) = The activation energy (kJ/mol)
\(R\) = The universal gas constant (0.008315 kJ/mol K), respectively.
**Table 4.3:** Experimental kinetics data (in terms of $k_0$) of BDMAPA2P obtained from stopped-flow apparatus (BDMAPA2P concentration ranging from 0.20 kmol/m$^3$ to 1.00 kmol/m$^3$ temperature ranged from 298 to 318 K).

<table>
<thead>
<tr>
<th>BDMAPA2P Concentration [AM] mol/L</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order rate $[k_0]$ (s$^{-1}$)</td>
<td>25.675 $\pm$ 0.2</td>
<td>31.811 $\pm$ 0.3</td>
<td>56.288 $\pm$ 0.3</td>
<td>71.644 $\pm$ 0.4</td>
<td>80.256 $\pm$ 0.4</td>
</tr>
<tr>
<td>Pseudo-first order rate $[k_0]$ (s$^{-1}$)</td>
<td>37.622 $\pm$ 0.2</td>
<td>59.171 $\pm$ 0.2</td>
<td>75.638 $\pm$ 0.3</td>
<td>92.532 $\pm$ 0.4</td>
<td>139.226 $\pm$ 0.5</td>
</tr>
<tr>
<td>Pseudo-first order rate $[k_0]$ (s$^{-1}$)</td>
<td>61.891 $\pm$ 0.3</td>
<td>87.507 $\pm$ 0.2</td>
<td>124.379 $\pm$ 0.4</td>
<td>159.468 $\pm$ 0.4</td>
<td>177.357 $\pm$ 0.5</td>
</tr>
<tr>
<td>Pseudo-first order rate $[k_0]$ (s$^{-1}$)</td>
<td>86.217 $\pm$ 0.2</td>
<td>106.295 $\pm$ 0.3</td>
<td>159.601 $\pm$ 0.3</td>
<td>196.715 $\pm$ 0.5</td>
<td>259.814 $\pm$ 0.5</td>
</tr>
<tr>
<td>Pseudo-first order rate $[k_0]$ (s$^{-1}$)</td>
<td>101.725 $\pm$ 0.3</td>
<td>145.815 $\pm$ 0.2</td>
<td>225.224 $\pm$ 0.3</td>
<td>264.303 $\pm$ 0.4</td>
<td>297.115 $\pm$ 0.4</td>
</tr>
</tbody>
</table>

**Table 4.4:** The calculated values of the second-order reaction rate constant $k_2$ for BDMAPA2P which is closely dependent on temperature.

<table>
<thead>
<tr>
<th>BDMAPA2P</th>
<th>Temperature [K]</th>
<th>Second Order reaction rate $(k_2)$ average [m$^3$.mol$^{-1}$.s$^{-1}$]</th>
<th>$1/T$ [K$^{-1}$]</th>
<th>Ln $K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.069</td>
<td>0.003355705</td>
<td>-2.6679</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>0.090</td>
<td>0.00330033</td>
<td>-2.4057</td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>0.115</td>
<td>0.003246753</td>
<td>-2.1663</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.155</td>
<td>0.003194888</td>
<td>-1.8618</td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.192</td>
<td>0.003144654</td>
<td>-1.6482</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.5: Effect of BDMAPA2P concentration and temperature on the pseudo first-order reaction rate constant ($k_0$) over a concentration range of 200-1000mol/m$^3$ and a temperature range of 298-318K
Figure 4.6: Parity plot for the experimental and predicted pseudo first-order rate constants for an aqueous solution of BDMAPA2P.

Figure 4.6 above represents a parity scheme for the predicted values of the pseudo first-order reaction rate constant against the experimental values for BDMAPA2P. The figure demonstrates the projected increase in the pseudo first-order rate for every increase in amine concentration and temperature.
The four tertiary amines studied in this research work are compared in figure 4.7 above, using the pseudo-first order reaction rate constant \((k_0)\) obtained from the stopped-flow apparatus. At 298K, the values of the pseudo-first order reaction rate constant \((k_0)\) increase steadily with increasing concentration of amine. The accelerated rate of kinetics is due to the basicity of the solvent. Detailed information on pKa calculation is explained in Section B of this manuscript.

As a promising solvent, \(1-[Bis\ [3-(dimethylamino)\ propyl\]\ amino]-2-propanol\) is the best performing solvent among the four tertiary alkanolamine solvents compared in figure 4.7.
BDMAPA2P has the highest pKa value and second-order rate constant. \((k_2 = \text{0.107 m}^3\text{.mol}^{-1}\text{.s}^{-1} \text{ at 298K})\) and a pKa \((1)\) value = 8.38 at 298K].

A performance comparison between BDMAPA2P and other conventional tertiary amines

BDMAPA2P, 1-{Bis [3-(dimethylamino) propyl] amino}-2-propanol is believed to be a promising tertiary triamine, and it would be realistic to compare the absorption performance of BDMAPA2P with other conventional amines (i.e., MDEA, 2DMAEMAE, DMMEA, 3DMA1P, 1DMA2P, and TEA).

By comparing the absorption kinetics of BDMAPA2P with that of other tertiary amines, it will provide valuable information about utilizing BDMAPA as a promising alternative absorbent for Carbon dioxide capture. As presented in Figure 4.7, the second-order reaction rate constant of BDMAPA2P when compared with those of MDEA, 3DMA1P, 1DMA2P, 2DMAEMAE, DMMEA, and TEA over a temperature range of 298–313K. It was observed that the reaction rates of the seven tertiary amines compared have the following trend:

\[
3\text{DMA1P/3-dimethyl-amino-1-propanol} > 1\text{DMA2P/1-dimethylamino-2-propanol} > 2\text{DMAEMAE/2-}\{2-(\text{Dimethylamino})\text{ethyl\]methylamino\}ethanol} > \text{BDMAPA2P/1-\{Bis[3-(dimethylamino)propyl]amino\}-2-propanol} > \text{DMMEA/Dimethylmonoethanolamine} > \text{MDEA/N-Methyldiethanolamine} > \text{TEA/Triethanolamine}.
\]

Research findings have proven that the absorption kinetics of CO\(_2\) with tertiary amines can be related to its pKa value. The higher the pKa value of a solvent, the faster the reaction kinetics of the solution with CO\(_2\) during an absorption process.
Consequently, the reaction kinetics and properties of a promising alkanolamine can be understood from dissociation of its ions by calculating its pKa which will be discussed in detail at the pKa section of this report.

Figure 4.8: Arrhenius plot for CO$_2$-BDMAPA2P second order rate constant against (1/T)

Many research scientists believe that the higher the value of the second-order reaction rate constant ($k_2$), the higher the reaction kinetics of the solvent. The data shown in Table 4.5 indicates that BDMAPA2P can react with CO$_2$ faster than DMMEA, MDEA, and TEA), whereas the absorption kinetics of BDMAPA2P (in terms of $k_2$) with CO$_2$ was found to be slower than that of 3DMA1P, 1DMA2P, and 2DMAEDMAE.
Also, the activation energy (kJ/mol) for BDMAPA2P was calculated together with those of 3DMA1P, 1DMA2P, 2DMAEDMAE, DMMEA, MDEA and TEA in Table 4.5. It was observed from Table 4.5 that the values of the activation energy for BDMAPA2P is higher than those of 2DMAEDMAE, MDEA, and TEA but lower than 3DMA1P, 1DMA2P and DMMEA.

**Table 4.5:** Second Order Reaction Rate Constant ($k_2$) at 298K and Activation Energy of 3DMA1P, 1DMA2P, BDMAPA2P, MDEA, DMMEA, 2DMAEDMAE

<table>
<thead>
<tr>
<th>Tertiary Amines</th>
<th>$k_2$ (m$^3$/kmol.s)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DMA1P</td>
<td>233</td>
<td>74.32</td>
</tr>
<tr>
<td>1DMA2P</td>
<td>160</td>
<td>62.2</td>
</tr>
<tr>
<td>2DMAEDMAE</td>
<td>131</td>
<td>43.05</td>
</tr>
<tr>
<td>BDMAPA2P</td>
<td>107</td>
<td>45.70</td>
</tr>
<tr>
<td>DMMEA</td>
<td>27.20</td>
<td>53.63</td>
</tr>
<tr>
<td>MDEA</td>
<td>12</td>
<td>41.93</td>
</tr>
<tr>
<td>TEA</td>
<td>2.70</td>
<td>35.79</td>
</tr>
</tbody>
</table>

The reaction kinetics of 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol is compared with six other tertiary alkanolamines from literature, to fully understand its performance as a different solvent for CO$_2$ capture. An observation is that there is a linear relationship between the second-order rate constants ($k_2$) and activation energy. BDMAPA2P ranks 4$^{th}$ place in value for the second-order reaction rate constant with the amines compared. A similar relationship was established between the pKa value of the solvents compared which will be discussed later in this report. The solvent studied is a triamine, with a possibility of a better performance regarding
kinetics, but this ability diminishes due to the effect of a steric hindrance; which is due to the presence of methyl groups in a position that decreases chemical reactivity.

4.3.1.3 Absorption kinetics of CO$_2$ in THPEDA

To fully understand the reaction kinetics of CO$_2$ and $N$, $N$, $N'$, $N'$-Tetrakis (2-Hydroxypropyl) ethylenediamine, THPEDA as a promising solvent for chemical absorption, an experiment was performed using the stopped-flow apparatus. Different samples of $N$, $N$, $N'$, $N'$-Tetrakis (2-Hydroxypropyl) ethylenediamine were prepared with a concentration range of 200–1000 mol/m$^3$, and the experimental temperature set within a range of 298–313K.

Pseudo first-order conditions were maintained throughout the experiment, and the values of the pseudo first-order reaction rate constant ($k_0$) obtained from the stopped flow apparatus which is a function of temperature and concentration of $N$, $N$, $N'$, $N'$-Tetrakis (2-Hydroxypropyl) ethylenediamine achieved in this work is presented in Table 4.6. A graphical plot of the pseudo-first order values against the concentration of PMDETA (kmol/m$^3$) is provided in Figure 4.9.

It was observed that the reaction kinetics of CO$_2$ in $N$, $N$, $N'$, $N'$-Tetrakis (2-Hydroxypropyl) ethylenediamine with respect to the pseudo first-order reaction rate constant ($k_0$), appreciated in values for every increase in amine concentration within a given temperature.

The pseudo first-order rate constants $k_0$ obtained experimentally from the stopped flow apparatus were interrelated using the empirical power law relationship to determine the reaction order for the CO$_2$-Amine reaction. Experimental results revealed that the reaction orders were 0.99, 0.93, 0.87, 0.86 and 0.83, with respect to [THPEDA] for 298, 303 308, 313 and 318K, respectively.
All experimental values for the reaction order can be approximated as 1.0 and with an average reaction order of 0.90. Therefore, the experimental values of \( k_0 \) at different concentrations and temperatures of THPEDA (from Table 4.6) can be interpreted using the base-catalyzed hydration mechanism. The values presented in Table 4.7 shows all the results for the fitted values of second-order reaction rate constant \( k_2 \), which is closely dependent on temperature. It is an established theory that the values of the second-order reaction rate constant \( k_2 \) can be represented using the Arrhenius expression below.

\[
k_2 = 2.39 \times 10^{-1} \exp \left( \frac{-4896.1}{T} \right)
\]  

(4.11)

[The value of R\(^2\) for this plot = 0.99]

<table>
<thead>
<tr>
<th>THPEDA</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration [AM] mol/m(^3)</td>
<td>Pseudo first order ([k_0]) (s(^{-1}))</td>
<td>Pseudo first order ([k_0]) (s(^{-1}))</td>
<td>Pseudo first order ([k_0]) (s(^{-1}))</td>
<td>Pseudo first order ([k_0]) (s(^{-1}))</td>
<td>Pseudo first order ([k_0]) (s(^{-1}))</td>
</tr>
<tr>
<td>199.8652</td>
<td>14.025 (\pm) 0.2</td>
<td>20.437 (\pm) 0.3</td>
<td>27.059 (\pm) 0.3</td>
<td>38.101 (\pm) 0.4</td>
<td>49.264 (\pm) 0.4</td>
</tr>
<tr>
<td>399.7918</td>
<td>26.452 (\pm) 0.3</td>
<td>33.296 (\pm) 0.3</td>
<td>45.242 (\pm) 0.4</td>
<td>56.717 (\pm) 0.4</td>
<td>68.933 (\pm) 0.5</td>
</tr>
<tr>
<td>599.9239</td>
<td>43.428 (\pm) 0.1</td>
<td>51.321 (\pm) 0.2</td>
<td>62.413 (\pm) 0.3</td>
<td>85.566 (\pm) 0.3</td>
<td>108.999 (\pm) 0.3</td>
</tr>
<tr>
<td>799.9147</td>
<td>59.583 (\pm) 0.2</td>
<td>74.259 (\pm) 0.2</td>
<td>90.436 (\pm) 0.3</td>
<td>124.213 (\pm) 0.4</td>
<td>140.489 (\pm) 0.3</td>
</tr>
<tr>
<td>999.8753</td>
<td>65.038 (\pm) 0.4</td>
<td>86.574 (\pm) 0.3</td>
<td>107.510 (\pm) 0.4</td>
<td>145.647 (\pm) 0.4</td>
<td>186.183 (\pm) 0.5</td>
</tr>
</tbody>
</table>

**Table 4.6**: Experimental kinetics data (in terms of \( k_0 \)) of THPEDA obtained from stopped-flow apparatus (THPEDA concentration ranging from 0.20 kmol/m\(^3\) to 1.00 kmol/m\(^3\) temperature ranged from 298 to 318 K).
Table 4.7: The calculated values of the second-order reaction rate constant $k_2$ for THPEDA which is closely dependent on temperature.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Second Order reaction rate (k$_2$) average [m$^3$.mol$^{-1}$.s$^{-1}$]</th>
<th>1/T [K$^{-1}$]</th>
<th>Ln K$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.069</td>
<td>0.003355705</td>
<td>-2.6679</td>
</tr>
<tr>
<td>303</td>
<td>0.090</td>
<td>0.00330033</td>
<td>-2.4057</td>
</tr>
<tr>
<td>308</td>
<td>0.115</td>
<td>0.003246753</td>
<td>-2.1663</td>
</tr>
<tr>
<td>313</td>
<td>0.155</td>
<td>0.003194888</td>
<td>-1.8618</td>
</tr>
<tr>
<td>318</td>
<td>0.192</td>
<td>0.003144654</td>
<td>-1.6482</td>
</tr>
</tbody>
</table>

Figure 4.9: Effect of THPEDA concentration and temperature on the pseudo first-order reaction rate constant ($k_0$) over a concentration range of 200-1000mol/m$^3$ and a temperature range of 298-318K
Figure 4.10: Parity plot for the experimental and predicted pseudo first-order rate constants for an aqueous solution of THPEDA.

Figure 4.10 above represents a parity scheme for the predicted values of the pseudo first-order reaction rate constant against the experimental values for THPEDA. The figure demonstrates the projected increase in pseudo first-order rate with respect to an increase in amine concentration and temperature.
The four tertiary amines studied in this research work are compared in figure 4.11 above, using the pseudo-first order reaction rate constant \((k_0)\) obtained from the stopped-flow apparatus.

At 298K, the values of the pseudo-first order reaction rate constant \((k_0)\) increase steadily with increasing concentration of amine. The accelerated rate of kinetics is due to the basicity of the solvent. Detailed information on the pKa calculation is explained in Section B of this manuscript.

As a promising solvent, \(N, N, N', N'-\text{Tetrakis (2-Hydroxypropyl) ethylenediamine}\) ranks third place in terms of performance when compared with the other four tertiary alkanolamine solutions presented in figure 4.7. THPEDA has the third highest pKa value and second-order rate constant \([k_2 =0.069 \text{ m}^3.\text{mol}^{-1}.\text{s}^{-1} \text{ at } 298K]\) and a pKa \((1)\) value = 7.69 at 298K.
A performance comparison between THPEDA and other conventional tertiary amines

As $N, N, N', N'-\text{Tetrakis (2-Hydroxypropyl) ethylenediamine}$ is believed to be a promising tertiary amine; it would be realistic to compare the absorption performance of THPEDA with other conventional amines (i.e., MDEA, 2DMAEDMAE, DMMEA, 3DMA1P, 1DMA2P and TEA). By comparing the absorption kinetics of THPEDA with that of other tertiary amines, it will provide valuable information about utilizing THPEDA as a promising alternative absorbent for Carbon dioxide capture. As presented in Figure 4.10, the second-order reaction rate constant of THPEDA is compared with those of MDEA, 3DMA1P, 1DMA2P, 2DMAEDMAE, DMMEA and TEA over a temperature range of 298–313K. It was observed that the reaction rates of the seven tertiary amines compared have the following trend.

$$3\text{DMA1P/3-dimethyl-amino-1-propanol} > 1\text{DMA2P/1-dimethylamino-2-propanol} > 2\text{DMAEMAE/2-\{[2-(Dimethylamino)ethyl]methylamino\}ethanol} > \text{THPEDA/ N, N, N', N'-Tetrakis (2-Hydroxypropyl) ethylenediamine} > \text{DMMEA/Dimethylmonoethanolamine} > \text{MDEA/N-Methyldiethanolamine} > \text{TEA/Triethanolamine}.$$  

It has been established from research findings that the absorption kinetics of CO$_2$ with tertiary amines can be associated with its pKa value. The higher the pKa value of a solvent, the faster the reaction kinetics of the solution with CO$_2$ during an absorption process.

Consequently, the reaction kinetics and properties of a promising alkanolamine can be better understood from dissociation of its ions by calculating its pKa which will be discussed in detail at the pKa section of this report.
Many research scientists believe that the higher the value of the second-order reaction rate constant \(k_2\), the higher the reaction kinetics of the solvent. The data shown in Table 4.8 indicates that THPEDA can react with CO\(_2\) faster than DMMEA, MDEA, and TEA, but the absorption kinetics of THPEDA (regarding \(k_2\)) with CO\(_2\) was found to be slower than that of 3DMA1P, 1DMA2P and 2DMAEDMAE.

Also, the activation energy (kJ/mol) for THPEDA was calculated together with those of 3DMA1P, 1DMA2P, 2DMAEDMAE, DMMEA, MDEA and TEA in Table 4.8. It is observed from Table
4.8 that the value of the activation energy for THPEDA is higher than that for TEA but lower than that of 3DMA1P, 1DMA2P, MDEA, DMMEA and 2DMAEDMAE.

**Table 4.8:** Second Order Reaction Rate Constant \((k_2)\) at 298K and Activation Energy of 3DMA1P, 1DMA2P, 2DMAEDMAE, THPEDA, DMMEA, MDEA, TEA

<table>
<thead>
<tr>
<th>Tertiary Amines</th>
<th>(k_2) (m³/kmol.s)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DMA1P</td>
<td>233</td>
<td>74.32</td>
</tr>
<tr>
<td>1DMA2P</td>
<td>160</td>
<td>62.2</td>
</tr>
<tr>
<td>2DMAEDMAE</td>
<td>131</td>
<td>43.05</td>
</tr>
<tr>
<td><strong>THPEDA</strong></td>
<td><strong>69.4</strong></td>
<td><strong>40.71</strong></td>
</tr>
<tr>
<td>DMMEA</td>
<td>27</td>
<td>53.63</td>
</tr>
<tr>
<td>MDEA</td>
<td>12</td>
<td>41.93</td>
</tr>
<tr>
<td>TEA</td>
<td>2.7</td>
<td>35.79</td>
</tr>
</tbody>
</table>

The reaction kinetics of \(N, N, N', N'-\text{Tetrakis (2-Hydroxypropyl) ethylenediamine}\) is compared with six other tertiary alkanolamines from literature, to fully understand its performance as a different solvent for CO\(_2\) capture. It was observed that the value of the second-order rate constants \((k_2)\) of THPEDA ranks 4\(^{th}\) place in comparison with other amines. The pKa value of \(N, N, N', N'-\text{Tetrakis (2-Hydroxypropyl) ethylenediamine}\) is a good reflection of the kinetics behavior of the solvent when used for CO\(_2\) capture. The position of the methyl group attached to a branch in its chemical structure produces a steric hindrance which also affects the reactivity of the solvent.

**4.3.1.4 Absorption kinetics of CO\(_2\) in THEEDA**

To fully understand the reaction kinetics of CO\(_2\) and \(N, N, N', N'-\text{Tetrakis (2-hydroxyethyl) ethylenediamine}\), THEEDA as a promising solvent for chemical absorption, an experiment was
performed using the stopped-flow apparatus. Samples of \(N, N, N', N'-\text{Tetrakis (2-hydroxyethyl) ethylenediamine}\) was prepared with a concentration range of 200–1000 \(\text{mol/m}^3\), and the experimental temperature set within a range of 298–313K.

Pseudo first-order conditions were maintained throughout the experiment, and the values of the pseudo first-order reaction rate constant \((k_0)\) obtained from the stopped flow apparatus which is a function of temperature and concentration of \(N, N, N', N'-\text{Tetrakis (2-hydroxyethyl) ethylenediamine}\) achieved in this work is presented in Table 4.9. A graphical plot of the pseudo-first order values against the concentration of THEEDA \((\text{kmol/m}^3)\) is provided in Figure 4.13.

It was observed that the reaction kinetics of \(\text{CO}_2\) in \(N, N, N', N'-\text{Tetrakis (2-hydroxyethyl) ethylenediamine}\) with respect to the pseudo first-order reaction rate constant \((k_0)\), appreciated in values for every increase in amine concentration within a given temperature.

The pseudo first-order rate constants \(k_0\) obtained experimentally from the stopped flow apparatus were interrelated using the empirical power law relationship into determining the reaction order for the \(\text{CO}_2\)-Amine reaction. Experimental results revealed that the reaction orders were 1.20, 0.87, 0.88, 0.88 and 0.85, with respect to [THEEDA] for 298, 303, 308, 313 and 318 K respectively.

All experimental values with a reaction order can be approximated as 1.0 and with an average reaction order of 0.94. Therefore, the experimental values of \(k_0\) at different concentrations and temperatures of THEEDA (from Table 4.9) can be interpreted using the base-catalyzed hydration mechanism. The values presented in Table 4.10 shows all the results for the fitted values of second-order reaction rate constant \(k_2\), which is closely dependent on temperature.
It is an established theory that the values of the second-order reaction rate constant $k_2$ can be represented by the Arrhenius equation below.

$$k_2 = 2.14 \times 10^{-1} \exp \left( \frac{-6045.5}{T} \right) \quad \text{…………….. (4.12)}$$

[The value of $R^2$ for this plot = 0.99]

**Table 4.9:** Experimental kinetics data (in terms of $k_0$) of THEEDA obtained from stopped-flow apparatus (THEEDA concentration ranging from 0.20 kmol/m$^3$ to 1.00 kmol/m$^3$ temperature ranged from 298 to 318 K).

<table>
<thead>
<tr>
<th>THEEDA [AM] mol/m$^3$</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>Pseudo first order $[k_0]$ (s$^{-1}$)</td>
<td>Pseudo first order $[k_0]$ (s$^{-1}$)</td>
<td>Pseudo first order $[k_0]$ (s$^{-1}$)</td>
<td>Pseudo first order $[k_0]$ (s$^{-1}$)</td>
<td>Pseudo first order $[k_0]$ (s$^{-1}$)</td>
</tr>
<tr>
<td>199.8214</td>
<td>6.072 $\pm$ 0.2</td>
<td>15.342 $\pm$ 0.2</td>
<td>21.612 $\pm$ 0.3</td>
<td>27.583 $\pm$ 0.3</td>
<td>33.153 $\pm$ 0.4</td>
</tr>
<tr>
<td>399.9611</td>
<td>15.366 $\pm$ 0.3</td>
<td>22.402 $\pm$ 0.1</td>
<td>34.638 $\pm$ 0.2</td>
<td>45.874 $\pm$ 0.4</td>
<td>51.134 $\pm$ 0.4</td>
</tr>
<tr>
<td>599.9801</td>
<td>22.989 $\pm$ 0.3</td>
<td>34.903 $\pm$ 0.3</td>
<td>52.856 $\pm$ 0.4</td>
<td>63.810 $\pm$ 0.2</td>
<td>86.164 $\pm$ 0.2</td>
</tr>
<tr>
<td>799.8736</td>
<td>35.332 $\pm$ 0.2</td>
<td>45.757 $\pm$ 0.3</td>
<td>73.181 $\pm$ 0.3</td>
<td>97.606 $\pm$ 0.4</td>
<td>102.031 $\pm$ 0.5</td>
</tr>
<tr>
<td>999.8931</td>
<td>44.915 $\pm$ 0.3</td>
<td>63.446 $\pm$ 0.2</td>
<td>86.597 $\pm$ 0.4</td>
<td>109.608 $\pm$ 0.3</td>
<td>126.639 $\pm$ 0.3</td>
</tr>
</tbody>
</table>
Table 4.10: The calculated values of the second-order reaction rate constant $k_2$ for THEEDA which is closely dependent on temperature.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Second Order reaction rate $k_2$ average [m$^3$.mol$^{-1}$.s$^{-1}$]</th>
<th>1/T [K$^{-1}$]</th>
<th>Ln K$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.039</td>
<td>0.00336</td>
<td>-3.24419</td>
</tr>
<tr>
<td>303</td>
<td>0.062</td>
<td>0.00330</td>
<td>-2.77740</td>
</tr>
<tr>
<td>308</td>
<td>0.092</td>
<td>0.00325</td>
<td>-2.38380</td>
</tr>
<tr>
<td>313</td>
<td>0.118</td>
<td>0.00319</td>
<td>-2.13538</td>
</tr>
<tr>
<td>318</td>
<td>0.139</td>
<td>0.00314</td>
<td>-1.97616</td>
</tr>
</tbody>
</table>

Figure 4.13: Effect of THEEDA concentration and temperature on the pseudo first-order reaction rate constant ($k_0$) over a concentration range of 200-1000mol/m$^3$ and a temperature range of 298-318K.
Figure 4.14: Parity plot for the experimental and predicted pseudo first order rate constants for an aqueous solution of THEEDA.

Figure 4.14 above represents a parity scheme for the predicted values of the pseudo first-order reaction rate constant against the experimental values for THEEDA. The figure demonstrates the projected increase in pseudo first-order rate with respect to an increase in amine concentration and temperature
Figure 4.15: Comparison of the pseudo first-order rate constants for THEEDA and other research amines at 298K

The four tertiary amines studied in this research work are compared in figure 4.15 above, using the pseudo-first order reaction rate constant \( k_0 \) obtained from the stopped-flow apparatus.

At 298K, the values of the pseudo-first order reaction rate constant \( k_0 \) increase steadily with increasing concentration of amine. The accelerated rate of kinetics is due to the basicity of the solvent. Research studies have linked the high absorption performance of an alkanolamine solution to its high dissociation behavior of its ions. Detailed information on pKa calculation is explained in Section B of this manuscript.
A performance comparison between THEEDA and other conventional tertiary amines

As *N, N, N', N'-Tetrakis (2-hydroxyethyl) ethylenediamine* is believed to be a promising tertiary amine, and it would be realistic to compare the absorption performance of THEEDA with other conventional amines (i.e., MDEA, DMMEA, 3DMA1P, 1DMA2P, 2DMAEMAE and TEA).

By comparing the absorption kinetics of THEEDA with that of other tertiary amines, it will provide valuable information about utilizing THEEDA as a promising alternative absorbent for Carbon dioxide capture. As presented in Figure 4.13, the second-order reaction rate constant of THEEDA is compared with the values of MDEA, 3DMA1P, 1DMA2P, 2DMAEMAE, DMMEA and TEA over a temperature range of 298–313K. It was determined that reaction rates of the seven tertiary amines compared have the following trend:

\[
3DMA1P/3\text{-dimethyl-amino-1-propanol} > 1DMA2P/1\text{-dimethylamino-2-propanol} > 2DMAEMAE/2-\{[2-(\text{Dimethylamino})\text{ethyl}]\text{methylamino}\}\text{ethanol} \quad \text{THEEDA/} \quad N, N, N', N'-\text{Tetrakis (2-hydroxyethyl) ethylenediamine} > \text{DMMEA/Dimethylmonoethanolamine} > \text{MDEA/} \quad N\text{-Methyldietanolamine} > \text{TEA/Triethanolamine.}
\]

It has been established from research findings that the absorption kinetics of CO₂ with tertiary amines can be associated with the value of its pKa value. The higher the pKa value of a solvent, the faster the reaction kinetics of the solution with CO₂ during an absorption process.
Many research scientists believe that the higher the value of the second-order reaction rate constant ($k_2$), the higher the reaction kinetics of the solvent. The data shown in Table 4.11 reveals that THEEDA can react with CO$_2$ faster than DMMEA, MDEA, and TEA, but the absorption kinetics of THEEDA (in terms of $k_2$) with CO$_2$ was found to be slower than that of 3DMA1P, 1DMA2P and DEMEA.

Also, the activation energy (kJ/mol) for THEEDA was calculated together with those of 3DMA1P, 1DMA2P, 2DMAEMAE, DMMEA, MDEA and TEA in Table 4.11. It is observed from Table...
4.11 that the values of the activation energy for THEEDA is greater than those of 2DMAEMAE, MDEA and TEA but lower than 3DMA1P, 1DMA2P and DMMEA.

**Table 4.11**: Second Order Reaction Rate Constant ($k_2$) at 298K and Activation Energy of 3DMA1P, 1DMA2P, THEEDA, MDEA, DMMEA, 2DMAEMAE

<table>
<thead>
<tr>
<th>Tertiary Amines</th>
<th>$k_2$ (m³/kmol.s)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DMA1P</td>
<td>233</td>
<td>74.32</td>
</tr>
<tr>
<td>1DMA2P</td>
<td>160</td>
<td>62.20</td>
</tr>
<tr>
<td>2DMAEMAE</td>
<td>131</td>
<td>43.05</td>
</tr>
<tr>
<td>THEEDA</td>
<td>39.00</td>
<td>50.30</td>
</tr>
<tr>
<td>DMMEA</td>
<td>27.00</td>
<td>53.63</td>
</tr>
<tr>
<td>MDEA</td>
<td>12.00</td>
<td>41.93</td>
</tr>
<tr>
<td>TEA</td>
<td>2.70</td>
<td>35.79</td>
</tr>
</tbody>
</table>

The reaction kinetics of $N, N, N', N''$-Tetrakis (2-hydroxyethyl) ethylenediamine is compared with six other tertiary alkanolamines from literature, to fully understand the reaction kinetics performance as a different solvent for CO$_2$ capture. It was observed that there is linear relationship between the second-order rate constants ($k_2$) and its pKa value which will be discussed later in Section B. The Arrhenius equation was used to obtain a value for the activation energy (50.30 kJ/mol) which tells us that an enormous amount of energy is required for the molecules to collide and initiate a reaction.

**4.3.1.5 Absorption kinetics of CO$_2$ in PMDETA**

To fully understand the reaction kinetics of CO$_2$ and $N, N, N', N''$, $N'''$-Pentamethyldiethylenetriamine, PMDETA as a promising solvent for chemical absorption, an
experiment was performed using the stopped-flow apparatus. Samples of \( N, N', N'', N'''-\text{Pentamethyldiethylenetriamine} \) was prepared with a concentration range of 200–1000 mol/m\(^3\), and the experimental temperature set within a range of 298–313K.

Pseudo first-order conditions were maintained throughout the experiment, and the values of the pseudo first-order reaction rate constant \((k_0)\) obtained from the stopped flow apparatus which is a function of temperature and concentration of \( N, N', N'', N'''-\text{Pentamethyldiethylenetriamine} \) achieved in this work is presented in Table 4.12. A graphical plot of the pseudo-first order values against the concentration of PMDETA (kmol/m\(^3\)) is shown in Figure 4.17.

It is expected that the reaction kinetics of CO\(_2\) in \( N, N', N'', N'''-\text{Pentamethyldiethylenetriamine} \) with respect to the pseudo first-order reaction rate constant \((k_0)\), appreciated in values for every increase in amine concentration within a given temperature.

The pseudo first-order rate constants \(k_0\) obtained experimentally from the stopped flow apparatus were interrelated using the empirical power law relationship was used to determine the reaction order for the CO\(_2\)-Amine reaction. Experimental results revealed that the reaction orders were 0.94, 0.86, 0.92, 0.87 and 0.86, with respect to [PMDETA] for 298, 303 308, 313 and 318K, respectively.

All experimental values with a reaction order can be approximated as 1 and with an average reaction order of 0.89. Therefore, the experimental values of \(k_0\) at different concentrations and temperatures of PMDETA (from Table 4.12) can be interpreted using the base-catalyzed hydration
mechanism. The values presented in Table 4.13 shows all the result of the fitted values of second-order reaction rate constant $k_2$, which is closely dependent on temperature. It is an established theory that the values of the second-order reaction rate constant $k_2$ can represent using the Arrhenius expression below.

$$k_2 = 3.36 \times 10^{-1} \exp \left( \frac{-5286.3}{T} \right) \text{........................................... (4.13)}$$

[The value of $R^2$ for this plot = 0.97]

**Table 4.12:** Experimental kinetics data (in terms of $k_0$) of PMDETA obtained from stopped-flow apparatus (PMDETA concentration ranging from 0.20 kmol/m$^3$ to 1.00 kmol/m$^3$ temperature ranged from 298 to 318 K).

<table>
<thead>
<tr>
<th>PMDETA</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[AM] mol/m$^3$</td>
<td>Pseudo first order $[k_0]$</td>
<td>Pseudo first order $[k_0]$</td>
<td>Pseudo first order $[k_0]$</td>
<td>Pseudo first order $[k_0]$</td>
<td>Pseudo first order $[k_0]$</td>
</tr>
<tr>
<td>199.9142</td>
<td>20.382 $\pm$ 0.2</td>
<td>26.663 $\pm$ 0.1</td>
<td>35.124 $\pm$ 0.3</td>
<td>52.285 $\pm$ 0.3</td>
<td>67.945 $\pm$ 0.4</td>
</tr>
<tr>
<td>399.9921</td>
<td>31.119 $\pm$ 0.3</td>
<td>47.867 $\pm$ 0.2</td>
<td>60.616 $\pm$ 0.2</td>
<td>71.364 $\pm$ 0.4</td>
<td>96.713 $\pm$ 0.3</td>
</tr>
<tr>
<td>599.9908</td>
<td>56.191 $\pm$ 0.2</td>
<td>62.588 $\pm$ 0.3</td>
<td>86.984 $\pm$ 0.3</td>
<td>116.111 $\pm$ 0.2</td>
<td>145.787 $\pm$ 0.3</td>
</tr>
<tr>
<td>799.9984</td>
<td>71.741 $\pm$ 0.3</td>
<td>87.779 $\pm$ 0.3</td>
<td>112.818 $\pm$ 0.4</td>
<td>157.657 $\pm$ 0.4</td>
<td>215.596 $\pm$ 0.4</td>
</tr>
<tr>
<td>999.9936</td>
<td>87.676 $\pm$ 0.3</td>
<td>106.974 $\pm$ 0.3</td>
<td>148.573 $\pm$ 0.4</td>
<td>206.957 $\pm$ 0.4</td>
<td>263.370 $\pm$ 0.3</td>
</tr>
</tbody>
</table>
Table 4.13: The calculated values of the second-order reaction rate constant $k_2$ for PMDETA which is closely dependent on temperature.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Second Order reaction rate $(k_2)_{\text{average}}$ [m$^3$.mol$^{-1}$.s$^{-1}$]</th>
<th>$1/T$ [K$^{-1}$]</th>
<th>Ln $K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.0904</td>
<td>0.003355705</td>
<td>-2.403511012</td>
</tr>
<tr>
<td>303</td>
<td>0.1148</td>
<td>0.00330033</td>
<td>-2.164563795</td>
</tr>
<tr>
<td>308</td>
<td>0.1526</td>
<td>0.003246753</td>
<td>-1.87993516</td>
</tr>
<tr>
<td>313</td>
<td>0.2076</td>
<td>0.003194888</td>
<td>-1.572142128</td>
</tr>
<tr>
<td>318</td>
<td>0.2714</td>
<td>0.003144654</td>
<td>-1.304161532</td>
</tr>
</tbody>
</table>

Figure 4.17: Effect of PMDETA concentration and temperature on the pseudo first-order reaction rate constant $(k_0)$ over a concentration range of 200-1000mol/m$^3$ and a temperature range of 298-318K
Figure 4.18: Parity plot for the experimental and predicted pseudo first-order rate constants for an aqueous solution of PMDETA.

Figure 4.18 above represents a parity scheme for the predicted values of the pseudo first-order reaction rate constant against the experimental values for THEEDA. The figure demonstrates the projected increase in pseudo first-order rate with respect to an increase in amine concentration and temperature.
Figure 4.19: Comparison of the pseudo first-order rate constants for PMDETA and other research amines at 298K

The four tertiary amines studied in this research work are compared in the graph above, using the pseudo-first order reaction rate constant ($k_0$) obtained from the stopped-flow apparatus.

At a temperature of 298K, the values of the pseudo-first order reaction rate constant ($k_0$) increase steadily with increasing concentration of amine.
A performance comparison between PMDETA and other conventional tertiary amines

As N, N, N', N'', N'''-Pentamethyldiethylenetriamine is believed to be a promising tertiary amine; it would be realistic to compare the absorption performance of PMDETA with other conventional amines (i.e., MDEA, 2DMAEMA, DMMEA, 3DMA1P, 1DMA2P and TEA).

By comparing the absorption kinetics of PMDETA with that of other tertiary amines, it will provide valuable information about utilizing PMDETA as a promising alternative absorbent for Carbon dioxide capture. As presented in Figure 4, the second-order reaction rate constant of PMDETA is compared with those of MDEA, 3DMA1P, 1DMA2P, 2DMAEMAE, DMMEA and TEA over a temperature range of 298–313K. It can be concluded that reaction rates of the seven tertiary amines being compared have the following trend:

Many research scientists believe that the higher the value of the second-order reaction rate constant \((k_2)\), the higher the reaction kinetics of the solvent. The data shown in Table 4.14 reveals that PMDETA can react with CO\(_2\) faster than DMMEA, MDEA, and TEA, but the absorption kinetics of PMDETA (in terms of \(k_2\)) with CO\(_2\) was found to be slower than that of 3DMA1P, 1DMA2P and 2DMAEMAE.
Also, the activation energy (kJ/mol) for PMDETA was presented together with those of 3DMA1P, 1DMA2P, 2DMAEMAE, DMMEA, and MDEA in Table 4.14. It is observed from Table 4.14 that the values of the activation energy for PMDETA is lower than those of 3DMA1P, 1DMA2P and DEMEA but higher than 2DMAEMAE, MDEA and TEA.

Table 4.14: Second Order Reaction Rate Constant ($k_2$) at 298K and Activation Energy of 3DMA1P, 1DMA2P, PMDETA, MDEA, DMMEA, 2DMAEMAE

<table>
<thead>
<tr>
<th>Tertiary Amines</th>
<th>$k_2$ (m$^3$/kmol.s)</th>
<th>Activation Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DMA1P</td>
<td>233</td>
<td>74.32</td>
</tr>
<tr>
<td>1DMA2P</td>
<td>160</td>
<td>62.20</td>
</tr>
<tr>
<td>2DMAEMAE</td>
<td>131</td>
<td>43.05</td>
</tr>
<tr>
<td><strong>PMDETA</strong></td>
<td><strong>90.40</strong></td>
<td><strong>43.90</strong></td>
</tr>
<tr>
<td>DEMEA</td>
<td>79.80</td>
<td>51.87</td>
</tr>
<tr>
<td>MDEA</td>
<td>12.00</td>
<td>41.93</td>
</tr>
<tr>
<td>TEA</td>
<td>2.70</td>
<td>35.79</td>
</tr>
</tbody>
</table>

The reaction kinetics of $N, N, N', N''-Pentamethyldiethylenetriamine$ is compared with six other tertiary alkanolamines from literature, to fully understand the kinetics behavior of the different solvent for CO$_2$ capture. It was observed that there is a close relationship between the second-order rate constants ($k_2$) and its pKa value which will be discussed later in this report.

PMDETA is an alkanol-triamine which is expected to have a better performance in terms of kinetics, but this ability diminished due to the effect of a steric hindrance; which is due to the
presence of methyl groups in a position that decreases the chemical reactivity of the solvent. Another limiting factor could be the absence of an OH⁻ group attached to its chemical structure.

**Section 4B: Dissociation Constant (pKa) for Tertiary Alkanolamines**

Aqueous solutions of alkanolamine have received a lot of attention as promising solvents for CO₂ capture. The CO₂ emitted during the combustion of fossil fuels is absorbed chemically, and upon absorption, unique compounds known as carbamates, bicarbonates, and protonated amines are formed (in the case of primary and secondary amines). During an independent process operation, regeneration of amines takes place at elevated temperatures during the production of carbamates or protonated amines for reuse in a cyclic process. While the production of primary and secondary amine produce carbamates which enhance the reaction rate of CO₂ with alkanolamines, it presents a huge challenge to regenerate the amine after the carbamate formation.

It is important to know that tertiary amines chemically absorb CO₂ through bicarbonate formation at a reduced reaction rate, which in turn simplifies the process of amine regeneration. Consequently, significant studies on the protonation and deprotonation processes of amines in aqueous solution give a better understanding of the absorption and kinetic behavior of amines.

Furthermore, the conforming equilibrium constants are very useful in identifying promising amine solvents with unique properties for CO₂ capture during a research study. Many analytical scientists and process engineers have demonstrated interests in dissociation constants of amines because it gives them an opportunity to identify the type of separation techniques that can be used to isolate reacting species. The dissociation constants for conjugate acids of amines, alkanolamines, amino
acids, and cyclic amines were measured by numerous research scientists to help them understand the behavior of these solvents during a chemical reaction.

Sharma et al. (1965) studied the rate constants of various solutions used to capture CO$_2$ during fossil power generation and was able to conclude that there exists a relationship between the rate constant and basicity of the amine.

Information gathered from the literature shows that Versteeg et al. (1996) performed some research studies to investigate the relationship between the second-order rate constant for the formation of zwitterions and the dissociation constants of amines used to capture CO$_2$ from fossil power plants, and suggested a connection which takes the form of a Brönsted relationship. The published work of Versteeg and Van Swaaij (1988) was able to give a detailed explanation of the Brönsted relationship between the second order rate constant and the pKa of the amines.

The work of Khalili et al. (2009) and Hamborg et al. (2007) have proven that pKa is a key attribute of most electrolytes because it describes the biological and chemical activities of its ions. Aqueous solutions of tertiary alkanolamines such as N-Methyldiethanolamine have been widely used as chemical solvents on a commercial scale for post-combustion CO$_2$ capture purposes, and its application in this process has been studied extensively by numerous researchers.

The potentiometric titration technique established by Albert and Serjeant (1984) was employed in this research study. Potentiometric titration is a prevalent method for pK$_a$ determination. This experimental procedure is quick and easy to use when the pK$_a$ of a compound needs to be established, and it provides results with minimal errors and great accuracy.

In this research study, the potentiometric titration method was employed to determine the pK$_a$ values of tertiary amines whose values range from 7.80 to 8.50. The pK$_a$ values of the last four
tertiary amines presented in Table 4.11 are yet to be reported in the literature, and the experiment was conducted at different temperatures between (298.15 and 313.15) K.

4.1 Chemicals and Apparatus

The five tertiary amines used in this research study were purchased from Sigma-Aldrich Canada. Table 4.15 lists the molecular structure of the tertiary amine solvents employed in this research work along with their purities. The pH meter used to determine the pH values of the aqueous amine solutions is a model 270 pH/ion//Conductivity/Titration controller manufactured by Denver Instrument, was used to identify pH values of the aqueous amine solutions.

A way to reduce the number of errors during the experimental procedure, the electrode of the pH meter was first calibrated with buffer solutions at specific temperature values. The buffer solutions used for calibrating the electrode was supplied by VWR International and came with accuracy values as follows: pH 4.00 (± 0.01), pH 7.00 (± 0.01) and pH 10.00 (± 0.02). The pH values of the three buffer solutions measured at different temperatures are presented in Table 4.15.

Table 4.15: Molecular structures of the tertiary amines for pKₐ determination

<table>
<thead>
<tr>
<th>Purity</th>
<th>Solvent</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥99%</td>
<td>N-Methyldiethanolamine [MDEA]</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>≥98%</td>
<td>N, N', N'-Tetrakis (2-Hydroxypropyl) ethylenediamine [THPEDA]</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol [BDMAPA2P]

N, N, N', N''-Pentamethyldiethylenetriamine [PMDETA]

N, N, N', N'-Tetrakis (2-Hydroxyethyl) ethylenediamine [THEEDA]

<table>
<thead>
<tr>
<th>T/K</th>
<th>Buffer 1</th>
<th>Buffer 2</th>
<th>Buffer 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>4.00 ± 0.01</td>
<td>7.02 ± 0.01</td>
<td>10.06 ± 0.02</td>
</tr>
<tr>
<td>298</td>
<td>4.00 ± 0.01</td>
<td>7.00 ± 0.02</td>
<td>10.00 ± 0.01</td>
</tr>
<tr>
<td>303</td>
<td>4.01 ± 0.02</td>
<td>6.99 ± 0.01</td>
<td>9.94 ± 0.03</td>
</tr>
<tr>
<td>308</td>
<td>4.02 ± 0.03</td>
<td>6.99 ± 0.02</td>
<td>9.90 ± 0.02</td>
</tr>
<tr>
<td>313</td>
<td>4.02 ± 0.01</td>
<td>6.97 ± 0.02</td>
<td>9.85 ± 0.03</td>
</tr>
</tbody>
</table>

Table 4.16: Measured pH values of the buffer solution during calibration
To obtain accurate results from the pka experiment, 0.10 Molar aqueous solution of Hydrochloric acid purchased from VWR International was titrated with an aqueous solution of tertiary amines prepared at 0.01 Molar concentration. Nitrogen gas obtained from Praxair was supplied with a purity level of (≥ 99.99 %) and was used for blanketing the mixing solutions during the titration procedure. A jacket beaker connected to a water bath was used to keep the temperature constant throughout the experimental procedure. The aqueous solutions of tertiary amines of 0.01 Molar concentration were prepared in the laboratory using double distilled water from the laboratory. Before running the experiment, the required temperature for titration was set on the poly science programmable digital controller to regulate the temperature of water in the water bath which in turn establishes the temperature of the experiment. The pH meter was calibrated with three buffer solutions: buffer 4.01, buffer 7.00 and buffer 10.01 to ensure the accuracy of results read with the pH/ATC electrode.

A controlled stream of nitrogen gas was introduced into the mixture using a thin gas line to blanket the solution while the temperature of the solution was increased gradually to the required temperature. The necessary adjustments on the programmable controller of the water bath were made based on requirements for the experimental procedure. An aqueous solution of hydrochloric acid prepared at 0.1 Molar concentration was used to titrate the prepared sample of aqueous amine solution (50 mL). Equal portions of hydrochloric acid were added to the solution using a glass burette, each portion being 0.5 mL.

The pH value of the solution was recorded as soon as equilibrium was reached for every drop of titrant added to the solution using a glass burette. Information on the calculated pKa values from
the experimental pH data and calculation of the thermodynamic correction is available as supporting information.

### 4.1.1 Determination of pKa values

The experimental procedure described in this section was used to determine the pKa values of [MDEA] and all the tertiary amines utilized in this research study. \([MDEAH^+]\) is an acidic base which can ionize in an aqueous solution according to the following process:

\[
MDEAH^+ + H_2O \overset{K_a}{\leftrightarrow} MDEA + H_3O^+ \quad \text{…………………………………….. (4.14)}
\]

In the equation above, \([MDEAH^+]\) represents the protonated amine of \([MDEA]\), and \([MDEA]\) is the \(N\)-Methyldiethanolamine molecule. Considering the mole fraction of water as one, and expressing the concentration of hydronium ion, \([H_3O^+]\) as \([H^+]\), the pKa of the amine is determined using the expression below:

\[
pK_a = pH + \log \frac{[MDEAH^+]}{[MDEA]} \quad \text{………………………………………………. (4.15)}
\]

The ionic strength of the solution is assumed to be zero at infinite dilution to develop equation 4.15, with the equation valid for establishing the pKa of solutions whose pH value are within the range of 4.0 and 10.0 as described by (Albert and Serjeant, 1984).

The activity of the protonated amine ions was calculated using the following relation:

\[
\{BH^+\} = [BH^+] \cdot \gamma_{BH^+} \quad \text{………………………………………………. (4.16)}
\]
Activity coefficient of the ionized species ($\gamma_{BH^+}$) was calculated using the Debye-Huckel equation presented below:

$$-\log (\gamma_{BH^+}) = \frac{AZ_i^2 I^{1/2}}{1 + Bk_i l^{1/2}}$$

(4.17)

Using the following definitions:

$A$ and $B$ = Constants of the Debye-Huckel equation,

(These constants as a result of the dielectric constants and temperature of the solvent)

$Z_i$ = Charge or Valency of the ion,

$k_i$ = The mean distance of approach of the ions (ionic size parameter).

It is important to know that the A and B constants were taken from Manov et al. (1943) and the ionic size parameter ($k_i$) values were taken from (Kielland et al., 1937). $I$ is the ionic strength which is a function of the concentration of the solution according to the equation below.

$$I = 0.5 \sum_i C_i z_i^2$$

(4.18)

Where, $C_i$ is the molecular concentration of an ion and $Z$ is the valency

At the endpoint of a validation experiment involving MDEA, nine $pK_a$ values (addition of 5 mL of 0.100 M HCl to neutralize 5 ml of a portion of the total amine available) by using equation 4.15 and the average value in $pK_a$ for [MDEA], is presented in Table 4.17.

4.2 Results and Discussions

By looking at the data presented in Table 4.17, the $pK_a$ values were calculated from pH values of [MDEA] at 298.15 K. The first column of the table shows the amount of titrant (HCL) added to
the prepared sample of 50 ml solution of 0.010 M [MDEA] using a glass burette. The pH value of
the solution after each titrant was added is recorded in the second column, and obtained from the
pH meter. The values of \( \frac{[MDEAH^+]}{[MDEA]} \) ratio for the first 10 rows is presented in the third column, after
the addition of titrant (0.5 mL of 0.100 M HCL), only one-tenth of the tertiary alkanolamine
molecule [MDEA] would be protonated at this point. As equal amounts of the titrant is added using
the glass burette until a measure equal to 5 mL of 0.100 M HCl, all the [MDEA] molecules will
be protonated [MDEAH^+]. Consequently, [MDEAH^+] will be the only ionized species in the
solution. This phase is considered the first end point also known as pK_a (1).

Tertiary amines can either be monoamine, diamines or triamines and their respective pK_a values
are determined by using anyone of the equations presented below.

Monoamines: \[ pK_a(1) = pH + \log \frac{[AmH^+]}{[Am]} \] ......................................................... (4.19)

Diamines: \[ pK_a(2) = pH + \log \frac{[AmH^{2+}]}{[AmH^+]} \] ......................................................... (4.20)

Triamines: \[ pK_a(3) = pH + \log \frac{[AmH^{3+}]}{[AmH^{2+}]} \] ......................................................... (4.21)

Due to dissociation of water, a certain amount of hydroxyl ion (OH^-) is released. However, it is
important to know that the amount of hydroxyl ion (OH^-) formed is insignificant when compared
to the concentration of (H^+). The data for thermodynamic corrections are presented in the fifth
column, and this was taken into consideration in the calculations. When the first round of
experiment is complete, nine pK_a values can be calculated using Equation 4.19, and the average
pK$_a$ value after thermal corrections is the pK$_a$ of [MDEA] at the set temperature. A second validation experiment was conducted using THPEDA to ensure the accuracy of readings obtained from the pH meter. When the first round of analysis for THPEDA is complete, nine pK$_a$ values can be calculated using Equation 4.20, and the average pK$_a$ value after thermal corrections is the pK$_a$(1) of [THPEDA] at the set temperature. This experiment proceeds further to produce another set of nine pK$_a$ values determined using equation 4.21, The average of this second round of values will give us pK$_a$(2) of [THPEDA] at the set temperature. All values are shown in Table 4.18. The actual pK$_a$ value of [THPEDA] at the set temperature is calculated from the average of pK$_a$(1) and pK$_a$(2). The pK$_a$ values for all amines studied in this research work were determined similarly and are listed in Table 4.19 – 4.21.

The measured pK$_a$ values were used to calculate the dissociation constants in correlation with temperature using the following relationship:

\[
\ln K_a = - \ln(10^{pK_a}) = C_1 + \frac{C_2}{T/K} \quad \text{...............................................} (4.22)
\]

By applying the Van’t Hoff equation which relates the change in the equilibrium constant, $k_{eq}$, of a chemical reaction to changes in temperature, T, the standard enthalpy change ($\Delta H^\circ / \text{kJ} \cdot \text{mol}^{-1}$) and entropy change ($\Delta S^\circ / \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) for this process was calculated using equations 4.23 and 4.24 with the data presented in Table 4.22.

\[
\ln K_a = \frac{\Delta S^\circ}{R} + \frac{(-\Delta H^\circ)}{RT} \quad \text{...............................................} (4.23)
\]

\[
C_1 = \frac{\Delta S^\circ}{R} ; \quad C_2 = \frac{(-\Delta H^\circ)}{R} \quad \text{...............................................} (4.24)
\]
Table 4.17: Tabulated pK\textsubscript{a} values of [MDEA] at 298.15 K

<table>
<thead>
<tr>
<th>HCL ml</th>
<th>pH</th>
<th>[MDEAH\textsuperscript{+}] / [MDEA]</th>
<th>log [MDEAH\textsuperscript{+}] / [MDEA]</th>
<th>Thermodynamic correction</th>
<th>pK\textsubscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10.18</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>0.5</td>
<td>9.50</td>
<td>0.11</td>
<td>-0.95</td>
<td>0.02</td>
<td>8.53</td>
</tr>
<tr>
<td>1.0</td>
<td>9.17</td>
<td>0.25</td>
<td>-0.60</td>
<td>0.02</td>
<td>8.55</td>
</tr>
<tr>
<td>1.5</td>
<td>8.95</td>
<td>0.43</td>
<td>-0.37</td>
<td>0.03</td>
<td>8.55</td>
</tr>
<tr>
<td>2.0</td>
<td>8.75</td>
<td>0.67</td>
<td>-0.18</td>
<td>0.03</td>
<td>8.54</td>
</tr>
<tr>
<td>2.5</td>
<td>8.58</td>
<td>1.00</td>
<td>0.00</td>
<td>0.04</td>
<td>8.54</td>
</tr>
<tr>
<td>3.0</td>
<td>8.39</td>
<td>1.50</td>
<td>0.18</td>
<td>0.04</td>
<td>8.53</td>
</tr>
<tr>
<td>3.5</td>
<td>8.20</td>
<td>2.33</td>
<td>0.37</td>
<td>0.04</td>
<td>8.53</td>
</tr>
<tr>
<td>4.0</td>
<td>7.96</td>
<td>4.00</td>
<td>0.60</td>
<td>0.04</td>
<td>8.53</td>
</tr>
<tr>
<td>4.5</td>
<td>7.61</td>
<td>9.00</td>
<td>0.95</td>
<td>0.05</td>
<td>8.51</td>
</tr>
<tr>
<td>5.0</td>
<td>5.81</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td></td>
<td>pK\textsubscript{a}</td>
<td>8.53±0.02</td>
</tr>
</tbody>
</table>

A literature comparison for the values of the dissociation constant (LnK\textsubscript{a}) of [MDEA] was plotted against the inverse of the temperature (1/T) is shown in Figure 4.17. From the graph, there was a slight deviation in the (LnK\textsubscript{a}) values for MDEA when compared with those published by (Versteeg and Van Swaaij, 1988; Rayer \textit{et al.}, 2014; Tagiuri \textit{et al.}, 2015) by (3.57, 1.03 and 0.98) %,
respectively. In general, the deviations are as a result of using different instruments and techniques to calculate the protonation reaction. The research work of by Hamborg and Versteeg et al. (2007) shows that electromotive force measurement technique was used to determine the pKa data of MDEA whereas (Kim et al., 1987; Little et al., 1990) employed the potentiometric titration method to determine the dissociation constants.

**Table 4.18**: Tabulated pK_a Values of [THPEDA] at 298.15 K

<table>
<thead>
<tr>
<th>HCL ml</th>
<th>pH</th>
<th>[THPEDAH^+]</th>
<th>log[THPEDAH^+]</th>
<th>Thermodynamic correction</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10.15</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>0.5</td>
<td>8.91</td>
<td>0.11</td>
<td>-0.95</td>
<td>0.02</td>
<td>7.93</td>
</tr>
<tr>
<td>1.0</td>
<td>8.56</td>
<td>0.25</td>
<td>-0.60</td>
<td>0.02</td>
<td>7.93</td>
</tr>
<tr>
<td>1.5</td>
<td>8.23</td>
<td>0.43</td>
<td>-0.37</td>
<td>0.03</td>
<td>7.84</td>
</tr>
<tr>
<td>2.0</td>
<td>7.92</td>
<td>0.67</td>
<td>-0.18</td>
<td>0.03</td>
<td>7.71</td>
</tr>
<tr>
<td>2.5</td>
<td>7.64</td>
<td>1.00</td>
<td>0.00</td>
<td>0.04</td>
<td>7.60</td>
</tr>
<tr>
<td>3.0</td>
<td>7.45</td>
<td>1.50</td>
<td>0.18</td>
<td>0.04</td>
<td>7.59</td>
</tr>
<tr>
<td>3.5</td>
<td>7.24</td>
<td>2.33</td>
<td>0.37</td>
<td>0.04</td>
<td>7.56</td>
</tr>
<tr>
<td>4.0</td>
<td>6.99</td>
<td>4.00</td>
<td>0.60</td>
<td>0.04</td>
<td>7.55</td>
</tr>
<tr>
<td>4.5</td>
<td>6.58</td>
<td>9.00</td>
<td>0.95</td>
<td>0.05</td>
<td>7.48</td>
</tr>
<tr>
<td>5.0</td>
<td>5.95</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>
The value of $pK_a$ (2) for THPEDA = 4.29±0.02

After careful comparison of the experimental values used to calculate the $pK_a$ data for THPEDA, and information found in literature published by Ali et al. (2015), it was observed that there is a slight deviation in the values at each temperature respectively. All deviations are within the satisfactory limit of experimental deviations for both tertiary amines; [MDEA], and [THPEDA] used in the validation procedure to ensure the accuracy of apparatus.
**Table 4.19:** Measured First pKa values for the studied Tertiary Amines at different Temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>298.15 ±0.02</th>
<th>303.15 ±0.03</th>
<th>308.15 ±0.02</th>
<th>313.15 ±0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MDEA]</td>
<td>8.53 ±0.02</td>
<td>8.49 ±0.03</td>
<td>8.41 ±0.02</td>
<td>8.31 ±0.02</td>
</tr>
<tr>
<td>[THPEDA]</td>
<td>7.69 ±0.02</td>
<td>7.63 ±0.03</td>
<td>7.41 ±0.01</td>
<td>7.34 ±0.02</td>
</tr>
<tr>
<td>[BDMAPA2P]</td>
<td>8.38 ±0.03</td>
<td>8.24 ±0.01</td>
<td>7.98 ±0.02</td>
<td>7.75 ±0.02</td>
</tr>
<tr>
<td>[THEEDA]</td>
<td>7.65 ±0.02</td>
<td>7.60 ±0.02</td>
<td>7.38 ±0.04</td>
<td>7.29 ±0.02</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>7.94 ±0.01</td>
<td>7.81 ±0.03</td>
<td>7.72 ±0.04</td>
<td>7.69 ±0.03</td>
</tr>
</tbody>
</table>

*Standard uncertainties are u (pKa) = 0.03 and u (T) = 0.01 K.

**Table 4.20:** Measured Second pKa values for the studied Tertiary Amines at Different Temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>298.15 ±0.02</th>
<th>303.15 ±0.03</th>
<th>308.15 ±0.02</th>
<th>313.15 ±0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>[THPEDA]</td>
<td>4.29 ±0.02</td>
<td>4.15 ±0.03</td>
<td>4.09 ±0.01</td>
<td>3.93 ±0.02</td>
</tr>
<tr>
<td>[BDMAPA2P]</td>
<td>6.15 ±0.03</td>
<td>5.96 ±0.01</td>
<td>5.73 ±0.02</td>
<td>5.64 ±0.02</td>
</tr>
<tr>
<td>[THEEDA]</td>
<td>4.24 ±0.02</td>
<td>4.13 ±0.02</td>
<td>4.05 ±0.04</td>
<td>3.88 ±0.02</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>5.81 ±0.01</td>
<td>5.60 ±0.03</td>
<td>5.23 ±0.04</td>
<td>5.20 ±0.03</td>
</tr>
</tbody>
</table>
Table 4.21: Measured Third pKₐ values for the studied Tertiary Amines at Different Temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>298.15</th>
<th>303.15</th>
<th>308.15</th>
<th>313.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BDMAPA2P]</td>
<td>3.67 ± 0.03</td>
<td>3.61 ± 0.01</td>
<td>3.51 ± 0.02</td>
<td>3.46 ± 0.02</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>2.65 ± 0.01</td>
<td>2.59 ± 0.03</td>
<td>2.53 ± 0.04</td>
<td>2.50 ± 0.03</td>
</tr>
</tbody>
</table>

Figure 4.21: Comparison of the dissociation constants for MDEA at different temperatures
Figure 4.22: Comparison plot of the dissociation constants for THPEDA at various temperatures

Table 4.22: Thermodynamic quantities for the first dissociation of amines in aqueous solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$pK_a$</th>
<th>$-\Delta_r G_m^\circ$</th>
<th>$\Delta_r H_m^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MDEA]</td>
<td>8.53 ± 0.02</td>
<td>48.79</td>
<td>26.38</td>
<td>-0.08</td>
</tr>
<tr>
<td>[THPEDA]</td>
<td>7.69 ± 0.02</td>
<td>44.01</td>
<td>45.38</td>
<td>0.01</td>
</tr>
<tr>
<td>[BDMAPA2P]</td>
<td>8.38 ± 0.03</td>
<td>48.02</td>
<td>76.74</td>
<td>0.10</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>7.94 ± 0.02</td>
<td>45.19</td>
<td>30.14</td>
<td>-0.05</td>
</tr>
<tr>
<td>[THEEDA]</td>
<td>7.65 ± 0.03</td>
<td>43.82</td>
<td>46.42</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Standard uncertainties are $u(pK_a) = 0.03$; $u(T) = 0.01$ K.; $u(\Delta_r G_m^\circ) = 0.05$; $u(\Delta_r H_m^\circ) = 0.05$; $(\Delta S^\circ) = 0.05$
Table 4.23: Thermodynamic quantities for the second dissociation of amines in aqueous solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>pKₐ</th>
<th>−Δ_rG_m⁰</th>
<th>Δ_rH_m⁰</th>
<th>ΔS⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>/kJ·mol⁻¹</td>
<td>/kJ·mol⁻¹·K⁻¹</td>
<td></td>
</tr>
<tr>
<td>[THPEDA]</td>
<td>4.29±0.02</td>
<td>24.47</td>
<td>40.72</td>
<td>0.05</td>
</tr>
<tr>
<td>[BDMAPA2P]</td>
<td>6.15±0.03</td>
<td>35.03</td>
<td>63.02</td>
<td>0.09</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>5.81±0.02</td>
<td>33.07</td>
<td>78.84</td>
<td>0.15</td>
</tr>
<tr>
<td>[THEEDA]</td>
<td>4.24±0.03</td>
<td>24.26</td>
<td>41.39</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Standard uncertainties are u (pKa) = 0.03; u (T) = 0.01 K.; u(Δ_rG_m⁰) = 0.05; u(Δ_rH_m⁰) = 0.05; (ΔS⁰) = 0.05

Table 4.24: Thermodynamic quantities for the third dissociation of amines in aqueous solution

<table>
<thead>
<tr>
<th>Solvent</th>
<th>pKₐ</th>
<th>−Δ_rG_m⁰</th>
<th>Δ_rH_m⁰</th>
<th>ΔS⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>/kJ·mol⁻¹</td>
<td>/kJ·mol⁻¹·K⁻¹</td>
<td></td>
</tr>
<tr>
<td>[BDMAPA2P]</td>
<td>3.67±0.03</td>
<td>20.97</td>
<td>26.10</td>
<td>0.02</td>
</tr>
<tr>
<td>[PMDETA]</td>
<td>2.65±0.02</td>
<td>15.10</td>
<td>18.26</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Standard uncertainties are u (pKa) = 0.03; u (T) = 0.01 K.; u(Δ_rG_m⁰) = 0.05; u(Δ_rH_m⁰) = 0.05; (ΔS⁰) = 0.05

EFFECT OF SUBSTITUENT GROUPS ON THE VALUES OF pKₐ FOR A SOLVENT

The slight changes in the pKa values of some novel solutions are due to the influence of substituent groups added are presented in Figure 4.23. The base weakening influence of adding a (-OH) group to a solution has proven to have significant effects on the pKa values and will considerably reduce upon the insertion of (-OH) groups to the chemical structure of the amines. For example, when the
pKa value of two tertiary amines are compared, the pKa value is seen to drop by 0.25 units due to the addition of two (-OH) groups from PMDETA to THPEDA which significantly agrees with the research findings of (Rayer et al., 2014).

It is important also to note that the effect of adding a (-CH$_3$) group is not as noticeable even though the base weakening effect of the (-CH$_3$) group can be seen greatest when the methyl group is directly attached to the Nitrogen atom as is the case with THPEDA and THEEDA.

Another factor that can affect the pKa value of a solvent is the type of tiny group attached to the chemical structure of the amine being studied. Researchers have reported numerous instances whereby the hydrogen atom in a secondary amine like MEA is being substituted with a benzyl group. The attachment of the atomic group on its structure causes a reduction in the pKa value of the solvent unit which could occur due to the limiting effects of the large benzyl group.
**Figure 4.23:** Effect of (-CH₃) and (-OH) groups on the experimental pKa values at 298.15 K.

**PREDICTION OF pKₐ VALUES USING GROUP ADDITIVITY METHOD**

Perrin-Dempsey-Serjeant empirical method (PDS) was used to predict pKa values of the different amines employed in this research study. The method utilizes a linear free energy relationship to predict the pKₐ value of a chemical solvent using a base value of its the parent amine and adding a fixed value of pKa which corresponds to the particular substituent group attached to the chemical structure of the amine. The parent amines have a unique base value which is an attribute of the
class of amine (primary, secondary or tertiary). When substituent groups are added to the chemical structure of an amine, it could either have an effect which is base weakening or strengthening.

Other parameters taken into consideration in this research work include the effect of OH, OR, NHR, and NR₂ attached to the β position, besides the influence of methyl groups attached to the nitrogen atom in the chemical structure. The pKa values obtained from experimental procedures are presented in Table 4.25 along with the PDS predictions and calculated error between them due to deviations. Through careful examination of the experimental values obtained from PDS predictions, and errors of 0.43 and 0.04 were discovered in the MDEA and PMDETA systems, respectively. According to Sumon et al., (2012), the updated PDS method is known to produce accurate predictions of pKa by many renowned researchers in this field. The method was used to predict the pKa value of solvents employed in this research study. Both methods were used to establish acceptable results with a satisfactory range of error. The actual PDS method is somewhat better than the updated PDS with both approaches producing average absolute errors of 0.04 and 0.14 respectively.
Table 4.25: Base weakening effect according to Group Additivity Method (PDS) at 298.15 K

<table>
<thead>
<tr>
<th>Amine</th>
<th>Type</th>
<th>Base value</th>
<th>N-CH₃</th>
<th>β-OH</th>
<th>β-NR₂</th>
<th>PDS</th>
<th>Exp.</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MDEA]</td>
<td>3°</td>
<td>10.50</td>
<td>-0.2</td>
<td>-2.2</td>
<td>0</td>
<td>8.10</td>
<td>8.53</td>
<td>0.43</td>
</tr>
<tr>
<td>[THPEDA]*</td>
<td>3°</td>
<td>10.50</td>
<td>0</td>
<td>-2.2</td>
<td>-0.9</td>
<td>7.70</td>
<td>7.69</td>
<td>-0.01</td>
</tr>
<tr>
<td>[THEEDA]*</td>
<td>3°</td>
<td>10.50</td>
<td>0</td>
<td>-2.2</td>
<td>-0.9</td>
<td>7.70</td>
<td>7.65</td>
<td>-0.05</td>
</tr>
<tr>
<td>[PMDETA]*</td>
<td>3°</td>
<td>10.50</td>
<td>-1.0</td>
<td>-1.1</td>
<td>-0.9</td>
<td>7.90</td>
<td>7.94</td>
<td>0.04</td>
</tr>
<tr>
<td>[BDMAPA2P]*</td>
<td>3°</td>
<td>10.50</td>
<td>-0.8</td>
<td>-1.1</td>
<td>-0.9</td>
<td>8.10</td>
<td>8.38</td>
<td>0.28</td>
</tr>
</tbody>
</table>

*Statistical factor (logN) was added to account for the number of sites available for proton addition (N)

Table 4.26: Base weakening effect according to updated Group Additivity Method (PDS) at 298.15 K

<table>
<thead>
<tr>
<th>Amine</th>
<th>Type</th>
<th>Base value</th>
<th>N-CH₃</th>
<th>β-OH</th>
<th>β-NR₂</th>
<th>PDS</th>
<th>Exp.</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MDEA]</td>
<td>3°</td>
<td>10.60</td>
<td>-0.2</td>
<td>-2.0</td>
<td>0</td>
<td>8.40</td>
<td>8.53</td>
<td>0.13</td>
</tr>
<tr>
<td>[THPEDA]*</td>
<td>3°</td>
<td>10.60</td>
<td>0</td>
<td>-2.0</td>
<td>-1.0</td>
<td>7.90</td>
<td>7.69</td>
<td>-0.21</td>
</tr>
<tr>
<td>[THEEDA]*</td>
<td>3°</td>
<td>10.60</td>
<td>0</td>
<td>-2.0</td>
<td>-1.0</td>
<td>7.90</td>
<td>7.65</td>
<td>-0.25</td>
</tr>
<tr>
<td>[PMDETA]*</td>
<td>3°</td>
<td>10.60</td>
<td>-1.0</td>
<td>-1.0</td>
<td>-1.0</td>
<td>8.0</td>
<td>7.94</td>
<td>-0.06</td>
</tr>
</tbody>
</table>
**EFFECT OF TEMPERATURE**

During CO₂ capture with chemical absorbents, a present challenge of researchers in this industry is the high-energy requirements for the regeneration process. The heat of absorption/regeneration is an essential prerequisite of promising amines that needs to be taken into consideration when evaluating the performance of different aqueous amine systems. The enthalpy of protonation characterizes a substantial portion of the total heat content studied particularly for tertiary amines because it constitutes a significant share of the overall heat of absorption. In Figure 4.24, the dissociation constants of the amine considered are presented in a plot of the graph at different temperatures for all tertiary amines explored in this research work. It is observed from this study that THPEDA as a tertiary amine has the greatest value of slope when compared to the other tertiary amines presented in the report.

When a tertiary amine produces a small slope value in the plot, it can be interpreted as a reduced change in standard enthalpy with temperature which implies that the amine has lower heat requirements for the regeneration process. A good understanding of the amines molecular structure presented in Table 4.11, the presence of OH group at various positions in the chemical structure produces lower pKa values.

For instance, by looking at the data presented in Table 4.27, for the amines studied in this work, [BDMAPA2P] and [PMDETA] had the highest pKa values, and [THPEDA] had the lowest.
In general, alkanolamines that possess high pKa values react more aggressively in an acid-base reaction which requires an active interaction with the absorbed molecules, thereby resulting in a greater heat requirement for its regeneration. This characteristic is due to the existence of a linear relationship between the values of its pKa and the second-order rate constant ($k_2$) as defined by (Hetzer et al., 1966). In Figure 4.20, a plot is prepared to demonstrate the relationship between the pKa values and the values of standard enthalpy change which shows the behavior of various amines based on their pKa values concerning enthalpy changes. It was discovered that all the four tertiary amines studied in this research work have pKa values within the ranges of (7.65 – 8.40) and enthalpy of (30.10kJ/mol – 76.75kJ/mol).

**Figure 4.24:** Standard enthalpy and pKa values of the research amines studied at 298.15K for applications in the CO$_2$ capture process. The area in the schematic with red dotted lines represents the favored region for efficient CO$_2$ capture applications.
The activation energies for the reaction in each case study $E_a$ was determined using an Arrhenius equation ($\ln k_2$ vs. $1/T$) for the temperature range of (298.15 to 323.15) K.

Reaction rate constants ($k_2$) were fitted to an Arrhenius expression:

$$ k_2 = A \exp \left(-\frac{E_a}{RT}\right) $$

With the following definitions:

$A = \text{The Arrhenius constant (m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1})$

$E_a = \text{The activation energy (kJ}\cdot\text{mol}^{-1})$

$R = \text{The universal gas constant (0.008315 kJ/mol}\cdot\text{K)}$.

The values for the second-order reaction rate constants and activation energies were determined by approximating the reaction order to have finite values for all tertiary amines, and the result is presented in Table 4.27.

The results obtained for all four promising tertiary alkanolamine – diamines: $N, N, N', N''\text{-Tetrakis (2-Hydroxypropyl) ethylenediamine}$, $N, N, N', N''\text{-Tetrakis (2-hydroxyethyl) ethylenediamine}$ and triamines: $1\text{-[Bis [3-(dimethylamino) propyl] amino]-2-propanol}$, $N, N, N', N''\text{-Pentamethyl diethylenetriamine}$, are compared with the published work of (Li et al., 2007; Kadiwala et al., 2008; Rayer et al., 2012; Sodiq et. al., 2014; Liu et al., 2015) and over a range of temperatures.
Figure 4.25: A plot of the pKa values for all studied amines against experimental temperature.
Table 4.27. Second order reaction rate constants, the order of reaction, and activation energy for CO\textsubscript{2} in aqueous solutions of 3DMA1P, 1DMA2P, TEA, MDEA, 2-DMAEMAE, BDMAPA2P, PMDETA, THPEDA and THEEDA.

<table>
<thead>
<tr>
<th>Name of Amine</th>
<th>Order (n)</th>
<th>$k_2$ (m\textsuperscript{3}.mol\textsuperscript{-1}s\textsuperscript{-1})</th>
<th>E\textsubscript{a}/kJ.mol\textsuperscript{-1}</th>
<th>pKa (T = 298.15K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3DMA1P</td>
<td>0.95 - 1.20</td>
<td>$5.71 \times 10^{11} \ exp (-9087/T)$</td>
<td>74.32</td>
<td>$9.54^{+}_{-0.03}$</td>
</tr>
<tr>
<td>1DMA2P</td>
<td>0.85 – 1.03</td>
<td>$1.91 \times 10^{9} \ exp (-7523/T)$</td>
<td>62.20</td>
<td>$9.50^{+}_{-0.02}$</td>
</tr>
<tr>
<td>TEA</td>
<td>0.97 - 1.03</td>
<td>$1.01 \times 10^{4} \ exp (-4415/T)$</td>
<td>35.79</td>
<td>$7.88^{+}_{-0.02}$</td>
</tr>
<tr>
<td>MDEA</td>
<td>0.94 – 1.06</td>
<td>$8.16 \times 10^{4} \ exp (-4610.8/T)$</td>
<td>41.93</td>
<td>$8.57^{+}_{-0.03}$</td>
</tr>
<tr>
<td>2-DMAEMAE</td>
<td>1.01 – 1.02</td>
<td>$11.92 \times 10^{6} \ exp (-5177.7/T)$</td>
<td>43.05</td>
<td>$9.18^{+}_{-0.03}$</td>
</tr>
<tr>
<td>BDMAPA2P</td>
<td>0.81 – 0.93</td>
<td>$11.36 \times 10^{6} \ exp (-5497.2/T)$</td>
<td>45.70</td>
<td>$8.38^{+}_{-0.03}$</td>
</tr>
<tr>
<td>PMDETA</td>
<td>0.85 – 0.96</td>
<td>$4.44 \times 10^{4} \ exp (-5286.2/T)$</td>
<td>40.70</td>
<td>$7.94^{+}_{-0.03}$</td>
</tr>
<tr>
<td>THPEDA</td>
<td>0.83 – 1.01</td>
<td>$9.41 \times 10^{6} \ exp (-4896.1/T)$</td>
<td>43.90</td>
<td>$7.91^{+}_{-0.02}$</td>
</tr>
<tr>
<td>THEEDA</td>
<td>0.85 – 1.20</td>
<td>$2.76 \times 10^{5} \ exp (-6045.5/T)$</td>
<td>50.30</td>
<td>$7.88^{+}_{-0.03}$</td>
</tr>
</tbody>
</table>
CHAPTER FIVE: Conclusions and Recommendation

In this research work, the absorption kinetics of CO$_2$ into aqueous solutions of four tertiary alkanolamines {1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol (BDMAPA2P); N, N, N’, N”-Pentamethyldiethylenetriamine (PMDETA); N, N, N’, N’-Tetrakis (2-Hydroxypropyl) ethylenediamine (THPEDA); N, N, N’, N’-Tetrakis (2-hydroxyethyl) ethylenediamine (THEEDA)} were determined experimentally using the stopped-flow apparatus. All samples of the amine used in this study were prepared with the concentration ranging between 0.20 and 1.00 kmol/m$^3$ and a temperature range of 298-318 K.

The base-catalyzed mechanism was used to interpret all experimental data to better understand the reaction between tertiary amines and Carbon dioxide during chemical absorption.

The reaction order for all the studied amines concerning the respective amine concentration: [BDMAPA2P], [PMDETA], [THEEDA], [THPEDA] were found to vary considerably with a temperature between 0.82 and 1.01 respectively with an average reaction order of about 0.86, 0.90, 0.94, 0.89 respectively. These values are approximated 1 for the range of temperatures studied for each tertiary amine.

The experimental results show that among the studied amines in this research work, BDMAPA2P was found to have the highest reaction kinetics with CO$_2$. It was also discovered that the reaction rate increases with both increasing BDMAPA2P concentration and increasing temperature.
When the absorption kinetics of all four tertiary amines are compared, the order of absorption kinetics at 298.15K follow these sequential order: 1-[Bis [3-(dimethylamino) propyl] amino]-2-propanol (BDMAPA) > N, N, N', N''-Pentamethyldiethylenetriamine (PMDETA) > N, N', N'-Tetrakis (2-Hydroxypropyl) ethylenediamine (THPEDA) > N, N, N', N'-Tetrakis (2-hydroxyethyl) ethylenediamine (THEEDA).

There is a progressive increase in the absorption kinetics of BDMAPA2P as the temperature rises gradually. Each of the amines was then compared to five other well-known tertiary amines from literature to assess their performance. It was discovered that the best performing tertiary amine in this research study, BDMAPA2P is slower than 3DMA-1-P, 1DMA2P, 2-DMAEMAE but faster than DMMEA, MDEA and TEA.

Additionally, the dissociation constants of four tertiary amines were measured at four temperatures (298.15, 303.15, 308.15 and 313.15) K. The experimental results prove that both the Arrhenius relationship and Brønsted relationship obtained in this work can be used to predict the second-order reaction rate constant. Thermodynamic quantities for the dissociation of amines in water were determined using the van’s Hoff equation. The experimental results were compared with data found in published literature. The effect of adding of (OH) and (CH₃) groups to the chemical structure of the amine was investigated. [PMDETA] was identified to have the second highest pKa and lowest enthalpy of absorption so can, therefore, be considered in this regard, a promising amine in CO₂ removal applications. The pKa prediction using PDS was found to give satisfactory results with values close to the experimental values.
REFERENCES


Mandal, B. P., Kundu, M. and Bandyopadhyay, S. S. (2005). Physical solubility and diffusivity of N₂O and CO₂ into aqueous solutions of (2-amino-2-methyl-1-propanol+...
monoethanolamine) and (N-Methyldiethanolamine+ monoethanolamine). *Journal of Chemical and Engineering Data* Volume 50 Issue 2, pp. 352-358.


