Kinetic Modelling and Simulation of Carbon Dioxide Absorption into Aqueous Ammonia Solution

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the referenced and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SYAZANA FITRI BINTI ROZIAEDY

ABSTRACT

Nowadays, the amount of greenhouse gases in the atmosphere is nearly on the verge of alarming and one of the main components which is of highest the abundance is carbon dioxide (CO_2). Therefore, it is imperative that its emission be reduced. Through absorption, alkanolamines have been widely focused on as the solvent to absorb CO_2. However, it is found that using normal alkanolamines has its disadvantages, hence aqueous ammonia solution was found to be a possible replacement. It works effectively and also economically for the absorption of CO_2. This paper studies the kinetic modelling of CO_2 absorption into aqueous ammonia solution in order to better understand the chemical and physical kinetics and hydrodynamic properties of the absorption of CO2 in aqueous ammonia solution. This was done by simulating the developed model using Matlab. Using the work done by Rinker et al., the reaction rate kinetics were modelled and then simulated in order to calculate the apparent rate coefficient, k_{app}, which is then compared to that of Diethanolamine (DEA) since DEA is one of the more common amine solution used to absorb CO_2 due to its quicker reaction. The results indicate that ammonia is greater as compared to DEA in terms of the k_{app} where a lower temperature is required in order to obtain the same k_{app} with that of DEA and the kinetics of the reaction is encouraging for ammonia until temperatures approaching 310 K.

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CHAPTER1: INTRODUCTION

1.1 Background Study

Global energy consumption is currently rising due to increasing population and technology advancement. Fossil fuel supplies about 88% of that world energy demand. However, due to combustion of carbon based fossil fuels, many pollutants are being emitted to the environment and this is causing major environmental issues to rise. It causes a major global problem as most of the pollutants released from burning of fossil fuels consist of greenhouse gases (GHG) which are gases that trap heat in the atmosphere.

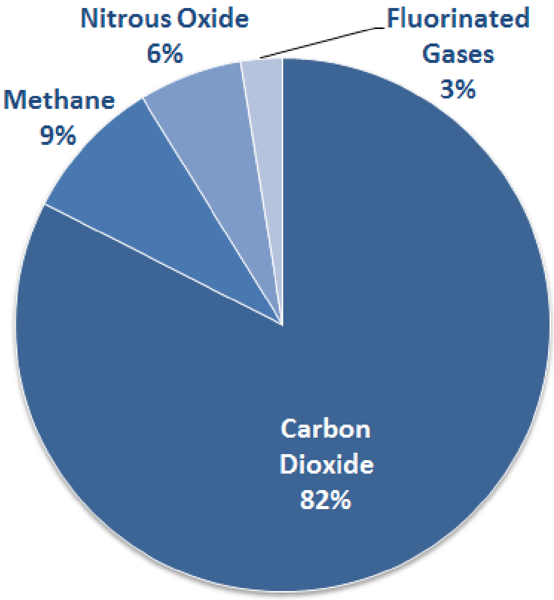


Figure 1: US CO_2 emissions by source[1]

According to the figure above, GHGs consist of many types of gases, methane, nitrous oxide, fluorinated gases and the one gas that dominates it all carbon dioxide. It can be seen that, in 2012, carbon dioxide takes up over 82% of all GHGs emitted from human activities [1].

With the high amount GHGs emitted, the Intergovernmental Panel on Climate Change (IPCC) predicted that an increase in the emission of GHGs will increase our global temperature that will ultimately lead to disastrous environmental impacts in its ‘Fourth Assessment Report released in the year 2007. It is even predicted that in the next century, our global average temperature is expected to increase by 2.5 to 10.0 ºC. Though the number seems small, even a slight increase in temperature can result in various effects such as decreasing snowpack in the western mountains of North America, increased risk of flash floods in Europe and a decrease in freshwater availability in Asia due to increased flooding in coastal areas [2].

Hence, that is why there are many researches that are being done in the removal of CO_2 from a mixture of gases. Currently, some of the various methods or technologies that are being used or researched on are chemical absorption, physical absorption, membrane separation, biological fixation and cryogenic methods [3]. In addition to that, out of all the methods mentioned, chemical absorption is said to be the most effective and commercially established way of removing CO_2 [4].

Carbon dioxide is an acid gas, and hence in the case of absorption from a gas stream, the most commonly used absorbents are various types of amines due to their alkali nature that may neutralize the CO_2. Common absorbents in the CO_2 capture process are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and amino-methylpropane (AMP) [5].

In choosing the best solvent for the absorption process, numerous factors must be taken into consideration, such as the operating temperature and pressure, regeneration energy consumption, CO_2 recovery, degradation of the solvent that is caused by irreversible reactions and also corrosion to the equipment, the amine solution strength, CO_2 loading and lastly lean amine loading [6].

Even though CO_2 absorption into alkanolamines are quite common and a commercially established method, there are still drawbacks in selecting that solvent for the absorption process, such as degrading easily, low loading capacity, slow absorption kinetics, high corrosion rate and also high energy requirement in case of regeneration [5]. It was also mentioned that aqueous ammonia, which differs from organic amines, has been considered as a potential candidate for a solvent for absorption of CO_2 economically and effectively due to its high loading capacity for CO_2, low cost, low corrosion and also less degradation when regenerating [5]. Therefore, due to this recent discovery of aqueous ammonia as a solvent for the absorption of CO_2, this paper focuses on the study and also modelling of the kinetics of CO_2 into aqueous ammonia solution in order to contribute to current available researches.

1.2 Problem Statement

Further study on the kinetics and mass transfer of CO_2 absorption into aqueous ammonia solution is crucial in developing further understanding and designing appropriate absorption equipment to achieve the desired for gas purification. Aqueous ammonia has recently been discovered to have a potential as a better solvent for CO_2 capture as compared to organic amines, alkanolamines, which have been used commonly then and also now [5]. Therefore, due to its recent potential, many studies have been and are being conducted in order to increase the understanding of using aqueous ammonia solution for CO_2 capture.

In order to evaluate the absorption properties of aqueous ammonia solution and the parameters, the reaction kinetics need to be investigated. On the other hand, absorption of gas to a liquid can actually occur due to molecular diffusion. However, natural molecular diffusion is a very slow process [6]. With the aid of chemical reactions, the mass transfer, rate of absorption and the absorption capacity in gas-liquid absorbing systems can be enhanced and increased. Investigation of both properties can help to better understand the processes and develop efficient absorption processes. In the present research work, attempts was made to develop absorption kinetics models. The models are then simulated using Matlab. The models are then validated using available literature data.

1.3 Objectives

The objectives of the present research work are:

- To develop absorption kinetics models for carbon dioxide absorption into aqueous ammonia solution.
- Conducting simulation using Matlab software.
- Evaluate and validate the model with literature data.
- Compare and contrast the model significance with earlier developed models.

1.4 The Scope of Study

To achieve the aforementioned objectives, the scopes of the present research work are:

- Study the kinetics of carbon dioxide absorption into aqueous ammonia solution.
- Develop absorption kinetics models and mass transfer model.
- Evaluate the developed model using software simulation.
- Validate the model with literature data and evaluate the significance of the models.

1.5 Relevancy and Feasibility of the Project

CO_2 removal is becoming one of the most developed and most researched fields of study in the industry today. This is due to the fact that the effect of CO_2 has on the environment is considerably becoming huge, therefore methods to decrease the amount of CO_2 in the atmosphere is under increasing research area and development. With regard to the current realization of ammonia's potential, it is imperative that the study on the absorption is done. With the aid of past and current literature, the outcome of this project has a substantial input in designing efficient absorption processes for capturing CO_2.

CHAPTER 2: LITERATURE REVIEW

2.1 CO2, Acid Gas and Greenhouse Gas (GHG)

In natural gas, acid gas is one of its major impurities, with hydrogen sulphide (H_2S) and carbon dioxide (CO_2) as the primary contaminants and constituents to it. There are also other types of gases, such as carbon monoxide (CO), nitrogen oxide (NO_x) and also sulphur oxide (SO_x).

Carbon dioxide which is deemed as acid gas forms an acidic solution when in contact with water and even though it is said to be an acid gas, it is less toxic. Besides that, CO_2 is also the primary GHG that is emitted as a result of human activities according to the EPA. Even though CO_2 is actually naturally present in the atmosphere, however, due to certain human activities such as combustion of fossil fuels, more CO_2 is being released uncontrollably into the atmosphere and thus resulting in global warming.

Hence, that is why, with an increase in awareness regarding global warming, many technologies and researches are being done to capture CO_2 in order to reduce the amount that is released to the environment. In purification of gases, there are several general categories [6]:

- Absorption into a liquid – when a soluble component is transferred from a gas phase into a liquid phase.
- Adsorption – a selective concentration of a component or more of a gas (the adsorbate) at the surface of a porous solid (the adsorbent).
- Membrane separation – a new technology in gas purification where the gases are separated by polymeric membranes.
- Chemical conversion into another compound – involves non-catalytic and catalytic reactions.

2.2 Absorption

Absorption is a transfer of a component in a gas phase into a liquid phase (solvent) where it is soluble in [7]. The reverse process of this is where a component (solute) of a liquid phase is stripped by a gas phase (solvent) is known as desorption or stripping.

The interaction between the absorbed gas phases with the liquid phase where the gas dissolves in, is an important factor in the absorption process. There are two types of absorption based on the processes that are happening [8]. They are:

- Physical absorption – where the gas phase component is dissolved in the solvent and keeps its chemical integrity. The equilibrium concentration of this type of absorption very highly depends on the partial pressure of the absorbate in the gas phase.
- Chemical absorption – where the gas that is dissolved reacts with a component of the liquid phase. The equilibrium concentration of this type of absorption highly depends on the partial pressure of the absorbate in the gas phase and the nature of the reaction of the absorbate with the absorbent.

In absorption, the most important thing to be considered is the solvent that is used. The characteristics of a good solvent are [9]:

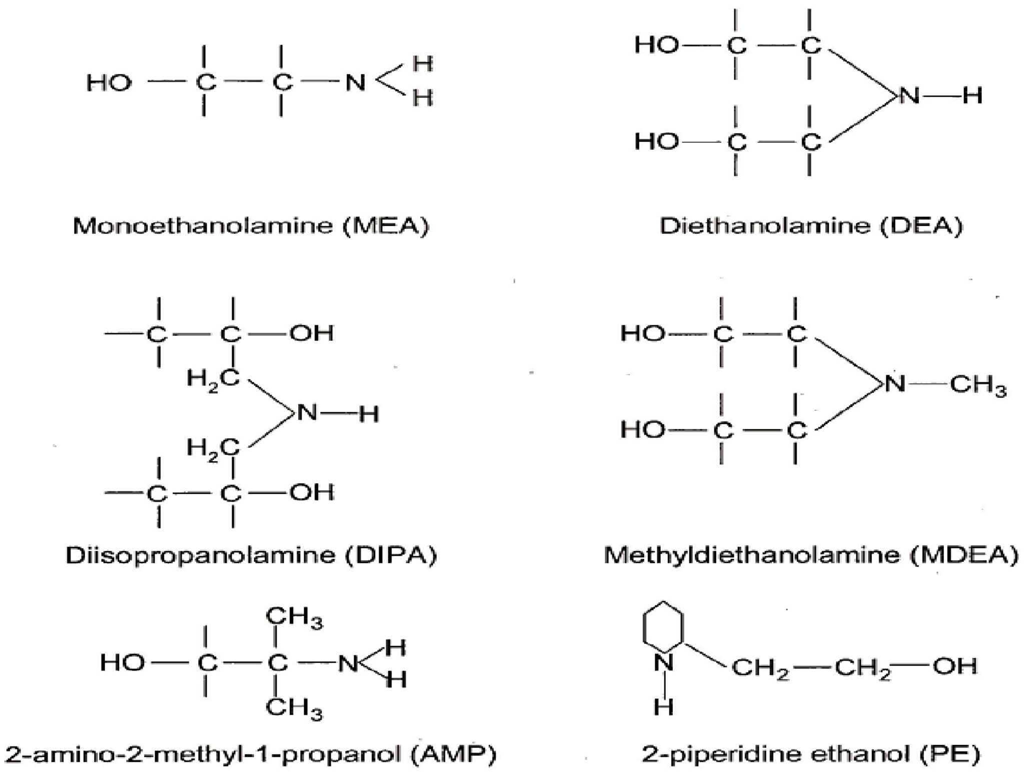
- High gas solubility
- Low volatility
- Low viscosity
- Low corrosivity
- Inexpensive
- Readily available
- Non toxic
- Non flammable
- Chemically stable

Some types of good solvents are generally amino acid salts, alkaline salts and alkanolamines, especially in the case of acid gas removal.

2.2 Alkanolamines

Alkanolamine solutions have been commonly used in the removal of acid gas from gas mixtures. Alkanolamine is a term that is used for a chemical compound that has an amino (NH2, -NHR, -NR2) group and at least one hydroxy (-OH) group. The amino group gives alkalinity in water that will allow for the absorption of the acid gas and the hydroxyl group is to reduce the vapour pressure and increase water solubility [10].

The number of hydrogen atoms in a compound that is attached to the nitrogen in the amine group actually determines the type of alkanolamine and hence its ability in absorbing acid gases. Figure 2.1 clearly describes the different types of alkanolamines that are commonly used. Primary amines have two hydrogen atoms connected to the nitrogen atom and secondary and tertiary amines are alkanolamines with one or no hydrogen atom that is attached to the nitrogen atom respectively. Primary amines have higher reactivity with acid gases compared to secondary and tertiary amines and secondary amines have higher reactivity than tertiary amines towards acid gases.



Monoethanolamine (MEA)

Diethanolamine (DEA)

Diisopropanolamine (DIPA)

Methyldiethanolamine (MDEA)

2-amino-2-methyl-1-propanol (AMP)

2-piperidine ethanol (PE)

Figure 2: Figure of the molecular structures of common alkanolamines

2.3 Absorption into Alkanolamines

As mentioned above, one of the most effective ways to remove CO_2 from a gas stream is by absorption using an alkanolamine as the solvent. Alkanolamine solutions are an industrially important class of compounds that is used in the oil and gas industry, such as natural gas, and petroleum chemical plants for the removal of CO_2 and H_2S from gas streams.

According to Kierkowska-Pawlak and Chacuk (2010), one of the most popular amines that have been of commercial interest is monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). The methyldiethanolamine has only been of popular interest quite recently and is actually still in the progressing stage of making the absorption process better (Kierkowska-Pawlak & Chacuk, 2010). When using MDEA, it has some considerable advantages when compared to using the primary or secondary amine. It has a higher capacity, smaller enthalpy of reaction when reacted with acid gases and a low vapour pressure as well (Kierkowska-Pawlak & Chacuk, 2010). However, there is one drawback of this MDEA when used alone. The CO_2 actually has a slow reaction rate with MDEA. Therefore, small amounts of faster reacting amines needs to be added in order to carry on the process using MDEA.

According to Derks and Versteeg (2009), using normal alkanolamines has several drawbacks. They are easy degradation, high corrosion rate and also a high heat of regeneration is required. Hence that is why research is still going on in order to find a better solvent to be used in the post combustion capture technology of CO_2.

The table below shows the comparison of past researches that are done when using various alkanolamines for the absorption of carbon dioxide.

Table 1: Comparison Table for Alkanolamines

Reference	Solvent	T (K)	Concentration	Experimental Technique	Results
[11]	DEA	293-343	Wide range	In a laminar-liquid jet absorber, mass-transfer model based on penetration theory	Data consistent with zwitterion mechanism
[6]	2(methyl)-aminoethanol (MAE)	303,310,320	1, 2 and 4 molar	Exp - Using stirred tank reactor with a flat gas-liquid interface Simulation - Using ANSYS Fluent to simulate the flow pattern	• Exposure time of the fluid element is determined using simulation • Used CFD tools, usage of sliding mesh and LES simulations, a high computational power is needed and a high resolution mesh is needed too. • Grid size and quality has no effect on the results

[12]	MDEA	293.15-333.15	10-20wt%	Using a stirred cell with a flat gas-liquid interface. Measurements based on batch isothermal absorption of the gas under pseudo first oreder regime	• Simplified kinetic model applied Second order rate constants of CO2 determined • New k2 were found to be in good agreement with literature values • Activation energy determined

2.4 Amine System for CO_2 Removal

Amine gas treating is a common method that is used in reducing acid gas impurities. The best approach in removing the acid gases, H_2S and CO_2, from natural gas has been said to be the alkanolamine process. As mentioned above, secondary amine, diethanolamine (DEA) and the tertiary amine, N-methyldiethanolamine (MDEA) are among the alkanolamines that are most commonly used. Compared to tertiary amines, secondary amines are often used to absorb CO2 because of the faster reaction. The best performance can be achieved by using blends of DEA and MDEA [13].

Rinker et al. has summarized the result of past literatures done on the kinetics between CO_2 and aqueous DEA. All but one reported the kinetics to be in fractional orders between 1 and 2 with respect to the DEA concentration [11]. However, the experiments were done under transient batch conditions and there is very limited kinetic data for temperatures other than 298 K. The rate of absorption of CO2 into the DEA solutions was measured in a laminar liquid jet absorber under continuous, steady-state conditions, over the temperature range of 293 – 343 K and wide range of DEA concentrations.

The kinetic rate coefficients were estimated from the experimental absorption data using rigorous mass-transfer model that they developed based on penetration theory. For this, all the chemical reactions are considered to be reversible. Formation of zwitterion is represented in the following reaction [11]:

$$CO_2 + RR'NH \xleftrightarrow{k_1 k_1 K_1} RR'NH^+COO^- \qquad (1)$$

Neglecting the other bases and taking DEA as the only base that deprotonates the zwitterions, the deprotonation reaction is as below:

$$RR'NH^+COO^- + RR'NH \xleftrightarrow{k_2 k_2 K_2} RR'NH_2^+ + RR'NHCOO^- \qquad (2)$$

The sum of equations (1) and (2) gives:

$$CO_2 + 2RR'NH \xleftrightarrow{K_3 K_4} RR'NH_2^+ + RR'NHCOO^- \qquad (3)$$

Where $K_3 K_4 = \frac{k_3 k_4}{k_{-3} k_{-4}}$

Analysis of their experimental data gives the apparent second-order rate coefficient as below:

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(k_4 k_{-3})[RR'NH]} \tag{4}$$

The Arrhenius equation that fits the rate coefficient estimates of their work are:

$$k_3 = 1.24 \times 10^6 \exp(-\frac{1701}{T}) \tag{5}$$

$$\frac{k_3 k_4}{k_{-3}} = 3.18 \times 10^7 \exp(-\frac{3040}{T}) \tag{6}$$

The result was found to be consistent with the zwitterion mechanism. The authors in the end concluded that, for complicated kinetics such as that of CO_2 with aqueous DEA, employing such a model is the only reliable method for obtaining accurate estimates of the kinetic rate coefficients [11].

Aboudheir et al. (2003) had tabulated a summary of the available kinetic data of the reaction between CO_2 and aqueous MEA in past literature [14]. The authors grouped the reaction-rate constants based on decades they were obtained. Observed that the k value vary at certain same temperature. For example, at temperature equal to 298 K, the k value varies from 3880 to 8400dm3/mol.s. Thus, in the authors project work, a numerically solved absorption-rate/kinetic model were used to interpret the kinetics data of the reaction between carbon dioxide and high CO_2-loaded, concentrated aqueous solution of MEA obtained in a laminar-jet absorber [14].

In the literatures, the reaction between CO_2 and MEA solution have been describe by two mechanisms which are the zwitterions mechanism that has been discussed earlier and the termolecular mechanism. Aboudheir et al. discussed on the reactions mechanisms occurred when CO_2 absorbs into and reacts with aqueous MEA. The reactions are as below [14]:

Ionization of water:

$$2H_2O \overset{K_1}{\leftrightarrow} OH^- + H_3O^+ \tag{1}$$

Dissociation of dissolved CO2 through carbonic acid:

$$CO_2 + 2H_2O \xleftrightarrow{k_2 k_2 K_2} HCO_3^- + H_3O^+ \tag{2}$$

Dissociation of bicarbonate:

$$HCO_3^- + H_2O \overset{K_3}{\leftrightarrow} CO_3^{2-} + H_3O^+ \tag{3}$$

Zwitterion formation from MEA and CO_2 reaction:

$$CO_2 + RNH_2 \xleftrightarrow{k_4 k_4 K_4} RNH_2^+ COO^- \tag{4}$$

Carbamate formation by deprotonation of the zwitterion:

$$RNH_2^+ COO^- + RNH_2 \xleftrightarrow{k_5 k_5 K_5} RNH_3^+ + RNHCOO^- \tag{5}$$

$$RNH_2^+ COO^- + H_2O \xleftrightarrow{k_6 k_6 K_6} H_3O^+ + RNHCOO^- \tag{6}$$

$$RNH_2^+ COO^- + OH^- \xleftrightarrow{k_7 k_7 K_7} H_2O + RNHCOO^- \tag{7}$$

Carbamate reversion to bicarbonate (hydrolysis reaction):

$$RNHCOO^- + H_2O \xleftrightarrow{k_8 k_8 K_8} RNH_2 + HCO_3^- \tag{8}$$

Dissociation of protonated MEA:

$$RNH_3^+ + H_2O \xleftrightarrow{k_9 k_9 K_9} RNH_2 + H_3O^+ \tag{9}$$

Bicarbonate formation:

$$CO_2 + HO^- \xleftrightarrow{k_{10} k_{10} K_{10}} HCO_3^- \tag{10}$$

All species represented are in aqueous solution. Additional reactions become essential due to the significant concentrations of bicarbonates and carbonates in the aqueous solutions. These two species as well contributes to the zwitterions intermediate formation. The additional reactions are [14]:

$$RNH_2^+ COO^- + HCO_3^- \xleftrightarrow{k_{11} k_{11} K_{11}} H_2CO_3 + RNHCOO^- \tag{11}$$

$$RNH_2^+ COO^- + CO_3^{2-} \xleftrightarrow{k_{12} k_{12} K_{12}} HCO_3^- + RNHCOO^- \tag{12}$$

Therefore, the general rate of reaction of CO_2 with MEA via the zwitterions mechanism [14] is described as below:

$$r_{CO_2\_MEA} = \frac{[CO_2][RNH_2] - k_{-4}/k_4 [RNHCOO^-](\Sigma k_{-b}[BH^+]/\Sigma k_b [B]}{\frac{1}{k_4} + (\frac{k_{-4}}{k_4 \Sigma k_b [B]})} \tag{13}$$

B designates any base species in the solution that can deprotonates the zwitterions intermediate into carbamate. The termolecular mechanism assumes that the reaction between CO_2 and MEA is of a single-step. The initial product was claimed not to be zwitterions but a loosely bound encounter complex with a mechanism. Bond-formation and charge-separation occur only in the second step. The forward reaction rate is as below:

$$r_{CO_2\_MEA} = -k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O][RNH_2][CO_2] \tag{14}$$

Aboudheir et al. studied on the reaction between CO_2 and high CO_2 loaded, concentrated aqueous solutions of monoethanolamine (MEA) over the temperature range from 293 to 333 K. The MEA concentration ranged from 3 to 9M, and CO_2 loading from ~0.1 to 0.49 mol/mol. They obtained the experimental kinetic data in a laminar jet absorber at various contact-times between gas and liquid. Interpretation of the data was done with the aid of a numerically solved absorption rate/kinetic model.

With this kinetics model, they obtained results which are found to be in accord with the experimental behaviour obtained in laminar jet absorber. In their work, they utilized both mechanisms; zwitterions and termolecular to evaluate the kinetic data to find the explanation of previous literatures' data. From the previous forward reaction equation, the apparent reaction rate expression of the termolecular mechanism was presented by:

$$k_{app} = k_{RNH_2}[RNH_2]^2 + k_{H_2O}[H_2O][RNH_2] \tag{15}$$

Values of $kRNH2$ and $kH2O$ were obtained by fitting the experimental k_{app} constants obtained from the absorption-rate/kinetics model [14]. From the data a linear regression analysis then was done and kinetics expressions as below are obtained:

$$k_{RNH_2} = 4.61 \times 10^9 \exp(\frac{-4412}{T}) \tag{16}$$

$$k_{H_2O} = 4.55 \times 10^6 \exp(\frac{-3287}{T}) \tag{17}$$

Based on both the precious equations, the reversible reaction rate for CO2 absorption into MEA solutions can then be presented by:

$$r_{CO_2\_MEA} = -k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O] \times ([RNH_2][CO_2] + \frac{1}{k_{RNH_2}}[RNHCOO^-][H_3O^+])$$

The analysis results by using zwitterions mechanism are found to be the same as those obtained by using termolecular mechanism. Fitting the *kapp* constant, only two parameters were found to fit the experimental data which are $kRNH2$ and kH_2O which means that only [RNH2] and $[H_2O]$ are the bases that completed the deprotonation of the zwitterion. The analysis proves that the new developed kinetic model parameter can accurately predict published kinetics data at low concentrations and low loadings according to termolecular reaction mechanism. Together with the aid of numerically solved absorption model, the new model has been used to accurately predict for the first time CO_2 absorption into high CO_2 loaded and highly concentrated aqueous MEA solutions.

2.4 Absorption into Aqueous Ammonia Solution

With the mentioned drawbacks of normal alkanolamines, the search of a new and better solvent is currently on the high, and one particular solvent that is now being focused on is the aqueous ammonia solution. Aqueous ammonia is considered as the better solvent due to its high loading capacity of CO_2, low corrosion rate, less degradation and also low cost [5]. Aqueous ammonia besides being a relatively more effective solvent, it is also economically a better solvent for the removal of CO_2. Furthermore, it can also remove other acid gas pollutants besides CO_2 with an acceptable CO_2 removal efficiency.

2.5 Kinetic Study of Absorption using Aqueous Ammonia Solution

In the reaction kinetics of aqueous ammonia solution, the important liquid phase elementary chemical reactions involved are as follows [15]:

Table 2: Elementary chemical reactions in the CO_2–NH_3–H_2O system

Equation	Process	No.
$CO_2 + NH_3 \longleftrightarrow NH_2COO^{--} + H^+$	Formation of ammonia carbamate	(1)
$CO_2 + OH^- \longleftrightarrow HCO_3^-$	Formation of bicarbonate by combination of CO_2 with hydroxyl ions	(2)
$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+$	Formation of carbonate	(3)
$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$	Hydrolysis of ammonia	(4)
$H_2O \longleftrightarrow OH^- + H^+$	Dissociation of water	(5)

Based on the table above, the equations for the reaction rates are as follows:

Table 3: Rates of elementary reactions for Eqs. (1)-(5)

No.	Kinetics	
(1)	$R_{(1)} = 1.66 \cdot 10^{11} \exp(\frac{-61000}{R^G T}) C_{CO_2} C_{NH_3}$	
(2)	$R_{(2)} = 4.32 \cdot 10^{10} \exp\left(\frac{-55420}{R^G T}\right) C_{CO_2} C_{OH^-}$	
(3)-(5)	Instantaneous reactions	

The zwitterion mechanism was introduced in describing the reaction that happens between CO_2 and amines [5]. According to this mechanism, the amine and CO_2 first forms zwitterions and then the zwitterions are deprotonated by a base.

Then there was another mechanism that was proposed, known as the termolecular mechanism. According to this mechanism, the reaction does not form a zwitterion, but a loosely bound encounter complex, where most of these complexes will then break up to form reagent molecules again. These reagent molecules do not react with any other second molecule of amine or water molecule to give ionic products. The charge separation and bond separation will occur later on. After several considerations, the termolecular mechanism was further developed and a single-step third-order reaction mechanism is needed in the formation of carbamate from CO_2 and alkanolamines in the solution. The broken-order and higher-order kinetics can be further explained into detail through this mechanism. In light of Liu et. al's paper, The termolecular mechanism was used to describe the reaction of aqueous ammonia and CO_2,and the correlation of $k_{2,}$ k_{NH3}^T and k_{H20}^T with temperature were fitted by the experimental data.

Many studies have been and are being conducted in order to better understand the kinetics and mass transfer theory of the process. Most of the studies that are being done vary in temperature and also the concentration of ammonia used. The current experimental ranges for the temperature and concentration of ammonia are still not wide enough [5]. Therefore, that is why this paper will be studying the current researches of the absorption of CO_2 into aqueous ammonia and hopefully more insight and data will be contributed to the study of the kinetics and mass transfer modelling of the process.

Table 4: Comparison Table for Ammonia

Reference	Solvent	T (K)	Concentration	Experimental Technique	Results
[16]	Ammonia	293 and 313	5,10,15,20 (wt%)	Tests conducted in semi-batch reactor Wetted wall column to study the absorption rate	• Best concentration found to be 5%-10% • Concentration of NH3 > 15% cause NH3 to volatize • Ammonia has high flux in WWC
[17]	Ammonia	278-298	0.1-7kmol/m3	In a stirred cell reactor where pseudo first order mass transfer regime was obeyed	• Reaction using ammonia is in the same order of magnitude as MEA and DEA, and faster than MDEA
[18]	Ammonia	298.3-321.9	0.9-5.4kmol/m3	Using string discs contactor Both zwitterion model and termolecular mechanism was applied	• Difficulties in determining the kinetics of CO2 absorption in ammonia solution • Reaction rate increase strongly with concentration but less strongly with temperature

[19]	Ammonia	279-304	1-10 wt%	Experiment by WWC Simulated using ASPEN Plus with UNIQUAC	• Exp - Rate of absorption of CO2 with 10wt% NH3 at 304K is in the same range as with 30wt% MEA at 314K • At low tempeerature, rate of absoprtion is lower than MEA. • Simulation - heat requirement was reduced compared with MEA but high CO2 loading is required (which could cause problem with the rate of absporption)
[5]	Ammonia	283,293,303, 313	1,2.5,5 - 7.5wt%	WWC	• The gas-side mass transfer coefficient, Kg, was fitted based on data using 30wt% MEA • Second order reaction rate constant of ammonia is lower than MEA and other active amines

[15]	Ammonia			2D modelling-based analysis of CO_2 reactive absorption in a falling film reactor	• NH_3 slippage can be limited by alleviated operating temperatures, optimised pH, increased pressure and large CO_2 absorption fluxes which force negative enhancement of NH_3 mass transfer

2.6 Simulation using Appropriate Software

In a paper by Abharchaei (2010), he studied the kinetic study of carbon dioxide absorption into solutions of 2(methyl)-aminoethanol. The simulation methods taken by him would be one of the same approaches that would need to be taken for this paper [6].

There are two main steps involved, which is the geometry and also the meshing. The software used is CFD tools called ANSYS and the FLUENT program. The first step in simulating this process is by building the geometry of the tank in the workbench design modeller as shown by the figure below.

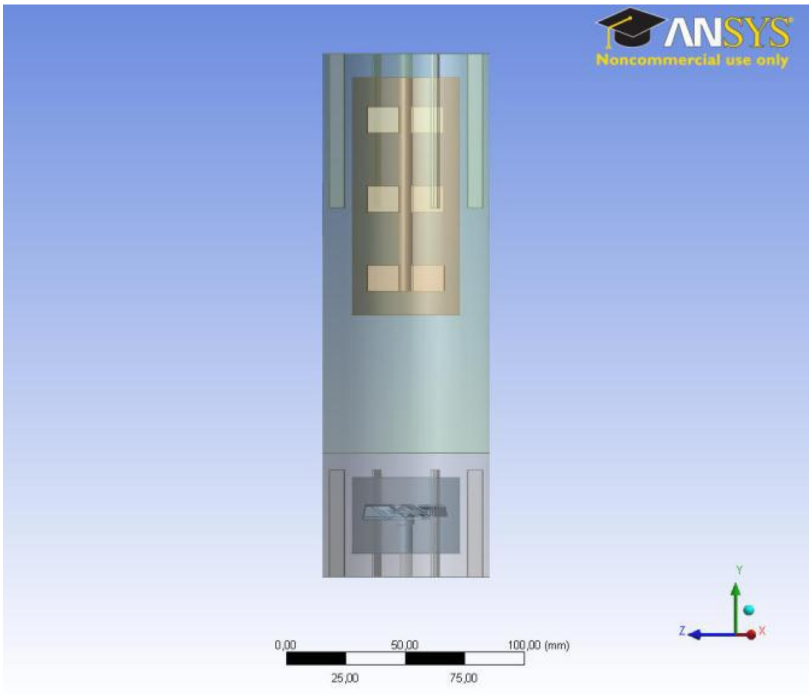


Figure 3: geometry of the stirred tank reactor

Then, the second step would be the meshing part, which gives a tetrahedral unstructured mesh for the tank which would allow the simulation process to be carried out as shown in the figure below.

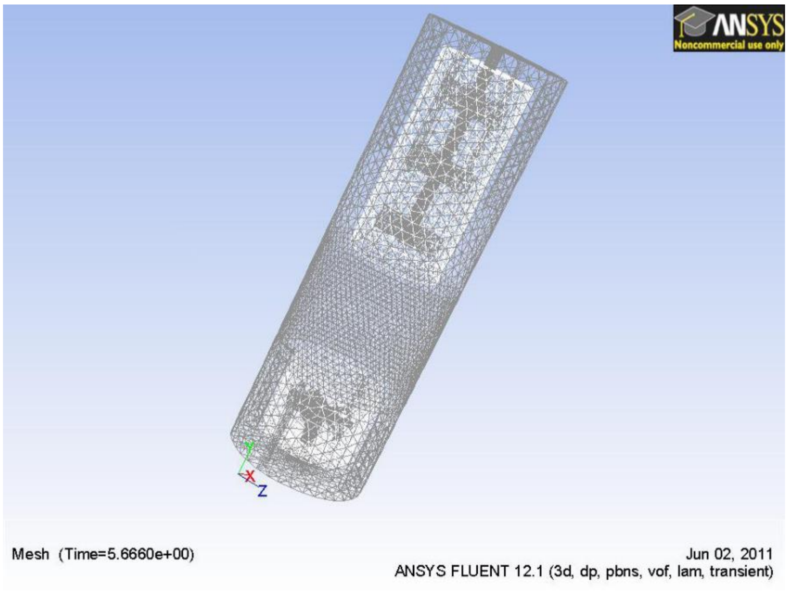


Figure 4: The tank with the tetrahedral mesh

After the meshing has been done, the simulation can then be carried out. From the practical track data, for carbon dioxide absorptions into 2(methyl)-aminoethanol, the particles very close to the walls and especially the baffles descend slowly and the particles spend a long time on the surface before they reach the middle where the impeller is affecting the flow strongly and then the descending speed increases. Besides that, from the simulation that was carried out using the CFD tools, when using the sliding mesh with the LES simulations, a high computational power is needed and also a high resolution mesh is needed to get a better result. The grid size and quality has a high effect on the results which is due to using the sliding mesh and also the nature of turbulence in the stirred tank system.

The paper mentioned above was done on 2(methyl)-aminoethanol. However, for the present paper, we would be studying on the effect when ammonia is used.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

The methodology of the present research work was mostly done by research, literature review, literature data collection and modelling of the absorption kinetics. An experimental and a modelling approach may be done. However, in the present work, the modelling and simulation approaches are used to study the kinetics and mass transfer properties of CO_2 absorption in aqueous ammonia solution.

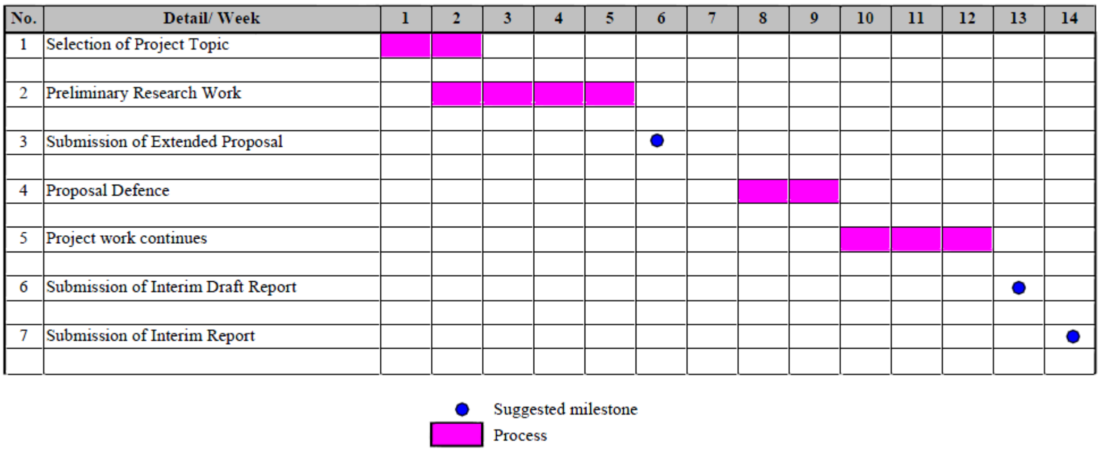
3.2 Flow of the Project and Project Activities

The flow of the project and the project activities will be:

- Preliminary study on past and current researches that is related to the project.
- Detection of the limitation or the key parameter of the project.
- Conducting absorption kinetics modelling as well as simulate the model to see its parametric effect during absorption processes.
- Collection of literate data and running the simulation of the process and compare it with current research results.
- Model analysis and discussion.
- Conclusion.

3.3 Gantt Chart and Key Milestone

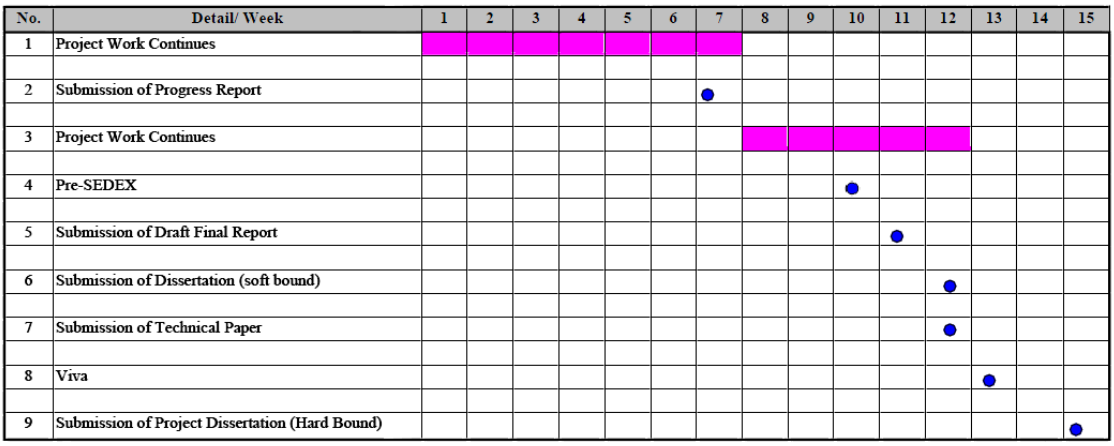
Timelines for FYP 1



No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	▨	▨												
2	Preliminary Research Work		▨	▨	▨	▨									
3	Submission of Extended Proposal						●								
4	Proposal Defence								▨	▨					
5	Project work continues										▨	▨	▨		
6	Submission of Interim Draft Report													●	
7	Submission of Interim Report														●

● Suggested milestone
▨ Process

Timelines for FYP 2



No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	▨	▨	▨	▨	▨	▨	▨								
2	Submission of Progress Report							●								
3	Project Work Continues								▨	▨	▨	▨	▨			
4	Pre-SEDEX										●					
5	Submission of Draft Final Report											●				
6	Submission of Dissertation (soft bound)												●			
7	Submission of Technical Paper												●			
8	Viva													●		
9	Submission of Project Dissertation (Hard Bound)															●

Figure 5: Timeline and key milestones for the project

As mentioned above, the key milestones would be:

- Conducting absorption kinetics modelling as well as simulate the model to see its parametric effect during absorption processes.
- Collection of literate data and running the simulation of the process and compare it with current research results.
- Model analysis and discussion.
- Conclusion.

CHAPTER 4: RESULTS AND DISCUSSION

The reaction kinetics equation between CO_2 and the aqueous ammonia solution was developed based on literatures and other references too. The reaction mechanism proposed by Rinker et. al (1996) is adapted to represent the CO_2 absorption reaction with the aqueous ammonia solution.

4.1 Adaptation of Kinetics Modelling Approach Proposed by Rinker et. al [11]

In moving forward with the kinetics modelling, the same mechanism scheme is followed from Rinker et. al's paper except that it is assumed that the aqueous ammonia solution acts as the DEA solvent with 10% increment in apparent rate coefficient, $k_{app,}$ for the reaction between CO_2 and the aqueous ammonia.

Overall reaction of aqueous ammonia absorption with carbon dioxide:

$$CO_2 + H_2O \overset{K_1 k_1}{\longleftrightarrow} H_2CO_3 \tag{1}$$

$$CO_2 + OH^- \overset{K_2 k_2}{\longleftrightarrow} HCO_3^- \tag{2}$$

$$CO_2 + NH_3 \overset{K_3 k_3 k_3}{\longleftrightarrow} {NH_3}^+COO^- \tag{3}$$

$${NH_3}^+COO^- + NH_3 \overset{K_4 k_4 k_4}{\longleftrightarrow} NH_4^+ + NCOO^- \tag{4}$$

$${NH_3}^+COO^- + H_2O \overset{K_5 k_5 k_5}{\longleftrightarrow} 2H_3O^+ + NCOO^- \tag{5}$$

$${NH_3}^+COO^- + OH^- \overset{K_6 k_6 k_6}{\longleftrightarrow} H_2O + NCOO^- \tag{6}$$

$${NH_3}^+COO^- + \ HCO_3^- \overset{K_7 k_7 k_7}{\longleftrightarrow} H_2CO_3 + NCOO^- \tag{7}$$

$${NH_3}^+COO^- + \ CO_3^{2-} \overset{K_8 k_8 k_8}{\longleftrightarrow} HCO_3^- + NCOO^- \tag{8}$$

$${NH_3}^+COO^- + H_2O \overset{K_9 k_9}{\longleftrightarrow} NH_3 + HCO_3^- \tag{9}$$

$${NH_3}^+COO^- + OH^- \overset{K_{10}}{\leftrightarrow} NH_3 + H_2O \tag{10}$$

$$HCO_3^- + OH^- \overset{K_{11}}{\leftrightarrow} CO_3^{2-} + H_2O \tag{11}$$

$$HCO_3^- + H_3O^+ \overset{K_{12}}{\leftrightarrow} H_2CO_3 + H_2O \tag{12}$$

$$2H_2O \overset{K_{13}}{\leftrightarrow} OH^- + H_3O^+ \tag{13}$$

Reaction (3) represents the formation of zwitterion while reactions (4) – (8) are the zwittterion deprotonation reactions. K_i, k_i and k_{-i} are the equilibrium constants, the forward rate coefficient and the reverse rate coefficient for reaction (i), respectively. Reaction (1) – (9) are considered to be reversible with finite reaction rates whereas reactions (10) – (13) are considered to be reversible and instantaneous with respect to mass transfer and at equilibrium, since they involve only proton transfer. For convenience, the chemical species are renamed as follows:

$$u_1 = [CO_2]$$

$$u_2 = [NH_3]$$

$$u_3 = [NH_4^+]$$

$$u_4 = [HCO_3{}^+]$$

$$u_5 = [OH^-]$$

$$u_6 = [CO_3^{2-}]$$

$$u_7 = [H_3O^+]$$

$$u_8 = [NCOO^-]$$

$$u_9 = [H_2CO_3]$$

$$u_{10} = [H_2O]$$

In 1996, Rinker et al. [11] used Higbie's penetration model to describe the absorption of CO_2 into aqueous ammonia solutions of primary and secondary alkanolamine in a laminar-liquid jet absorber. We assume that the ammonia will act similarly when it comes in contact with CO_2. All reactions were treated as reversible reactions. Reactions (1) – (9) have finite reaction rates which are given by the following reaction rate expressions. R_i is the reaction rate expression for reaction (i):

$$R_1 = -k_1 u_1 + \frac{k_1}{K_1} u_9 \tag{14}$$

$$R_2 = -k_2 u_1 u_5 + \frac{k_2}{K_2} u_4 \tag{15}$$

Assuming pseudo-steady state with respect to the concentration of zwitterions intermediates ($NH_3^+COO^-$), the equation below is derived:

$$R_{3,\ldots,8} = \frac{-k_3[u_1u_2-\left(\frac{A}{B}\right)u_8]}{1+\frac{1}{B}} \tag{16}$$

Where,

$$A = \left(\frac{k_4}{k_{-3}}\right)\frac{u_3}{K_3K_4} + \left(\frac{k_5}{k_{-3}}\right)\frac{u_7}{K_3K_5} + \left(\frac{k_6}{k_{-3}}\right)\frac{u_{10}}{K_3K_6} + \left(\frac{k_7}{k_{-3}}\right)\frac{u_9}{K_3K_7} + \left(\frac{k_8}{k_{-3}}\right)\frac{u_4}{K_3K_8} \tag{17}$$

And

$$B = \left(\frac{k_4}{k_{-3}}\right)u_2 + \left(\frac{k_5}{k_{-3}}\right)u_{10} + \left(\frac{k_6}{k_{-3}}\right)u_5 + \left(\frac{k_7}{k_{-3}}\right)u_4 + \left(\frac{k_8}{k_{-3}}\right)u_6 \tag{18}$$

$$R_9 = -k_9u_8 + \frac{k_9}{K_9}u_2u_4 \tag{19}$$

The aqueous ammonia to be used will be in the form of an unloaded solution. Therefore, the works by Rinker et al. are followed with some reasonable modification.

The carbamate to bicarbonate reversion reaction is found to be very slow in Rinker's work [11], thus we assume the contribution of reaction (9) to the rate of absorption is negligible. The gas-liquid contact times found in the experiment was very short, the concentration of bicarbonate and carbonate in aqueous solution are very small and contribution to deprotonation of the zwitterions is negligible. Thus, reaction (7) and (8) are eliminated.

Concentration of hydroxide is very small and changes significantly as CO_2 is absorbed, reaction (6) is neglected. This is due to the difficulties to quantify the contribution of hydroxide to the deprotonation of the of the zwitterion [11]. In Rinker's work, they also found that the effect of water as the deprotonating base was so small. Thus we neglected water as a deprotonating base in the interpretation of our data and we eliminate reaction [11].

Hence, we have neglected reactions (5) – (9) in this work. Therefore, the equation (16) – (18) can be reduced to the following rate expression for the consumption of CO_2 according to the zwitterion mechanism, with the ammonia as the only base that deprotonates the zwitterions:

$$R_{3,4} = \frac{-k_3}{1+\frac{1}{(\frac{k_4}{k_{-3}})u_2}}(u_1u_2 - \frac{1}{\frac{K_4}{K_3}}\frac{u_3u_8}{u_2}) \tag{20}$$

K_4/K_3 is the equilibrium constant of the overall reaction between CO_2 and the solvent which is the sum of the reaction (3) and (4):

$$CO_2 + NH_3 \overset{K_3K_4}{\longleftrightarrow} {NH_3}^{+}COO^{-} + NCOO^{-} \tag{21}$$

And $\frac{K_4}{K_3} = \frac{k_3k_4}{k_{-3}k_{-4}}$,

From the analysis of their experimental data Rinker et al. has come out with an apparent second-order rate coefficient which is defined as equation below:

$$k_{app} = \frac{-k_3}{1+\frac{1}{(\frac{k_4}{k_{-3}})u_2}} \tag{22}$$

Equation (22) is then arranged to:

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(\frac{k_4}{k_{-3}})u_2} \tag{23}$$

Hence, this is the equation that is used to generate k_3 and $k_3(k_4/k_{-3})$ after the adaptation of Rinker's approach and equation of the prediction of k_{app}.

4.2 The generated apparent rate coefficient, k_{app}

The range of k_{app} obtained by Rinker et al. in their experiment at 298K is between 300 – 1800 m^3/kmol.s for DEA concentration between 0.1 – 3.0 kmol/m^3 [11]. We assume the performance of the aqueous ammonia will be 10% higher for the same solution concentration. This assumption was made due to the finding of Rivera-Tinoco and Bouallou where it was found that aqueous ammonia is more superior than MEA in capacity in absorbing CO_2 through the finding of the k_{app} [20]. Therefore, we assume the performance of the aqueous ammonia will be 10% higher than that of DEA here since DEA is the better solvent as compared to MEA. Hence, the estimated k_{app} value would be:

Table 5: Assumption of k_{app} for this project work at 298K

$[NH_3]$ kmol/m^3	0.1	1.0	2.0	3.0
k_{app} m^3/kmol.s	330	990	1430	1980

4.3 Estimation of k_3 and $k_3(k_4/k_{-3})$

Equation (23) will be used to estimate the value of k_3 and $k_3(k_4/k_{-3})$. The steps that were involved are:

Step 1: Plot generated k_{app} for aqueous ammonia at 298K

Step 2: Replot the reciprocal of k_{app} at 298K with respect to the reciprocal of solvent concentration to fit equation (23)

Step 3: Estimate the reciprocal value of k_3 and $k_3(k_4/k_{-3})$ at 298K from the generated graph

Step 4: Calculate for k_3 and $k_3(k_4/k_{-3})$at 298K

Step 5: Estimating k_3 and $k_3(k_4/k_{-3})$ at other temperatures following the same trend as in Rinker's work

Step 6: Fit k_3 and $k_3(k_4/k_{-3})$ into the Arrhenius equation

4.4 Adaptation of Rinker et al. [11] proposed model to generate Arrhenius Equation

4.4.1 Step 1: Increase the k_{app} reported by Rinker et al. [11] by 10%

As mentioned earlier, the same mechanism scheme is followed from Rinker et. al's paper except that it is assumed that the aqueous ammonia solution acts as the DEA solvent with 10% increment in apparent rate coefficient, $k_{app,}$ for the reaction between CO_2 and the aqueous ammonia. Therefore, when the equation is simulated using MATLAB, the figure below is obtained:

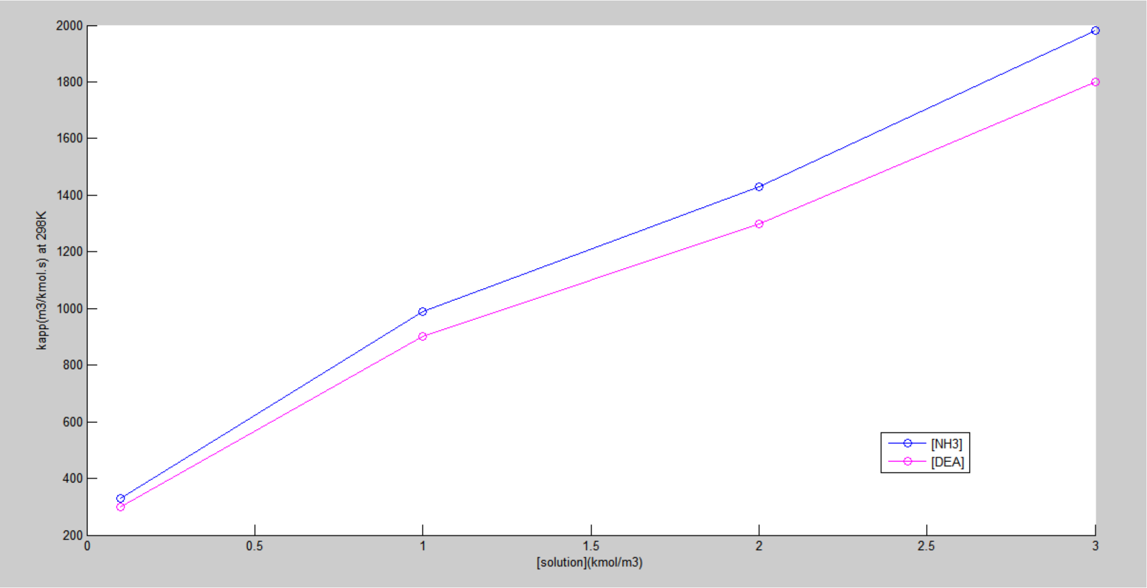


Figure 6: Assumed k_{app} for aqueous ammonia at 298K according to Rinker et al.

Figure 6 shows the comparison of the aqueous ammonia apparent second-order rate coefficient, k_{app}, where the value is assumed to be 10% higher than that of DEA in Rinker et. al's work [11].

4.4.2 Step 2: Fitting the reciprocal of the generated k_{app} with respect to the reciprocal of increasing solution concentration into equation (23)

The value of slope and intercept is to be obtained from the graph and then used to calculate k_3 and $k_3(k_4/k_{-3})$.

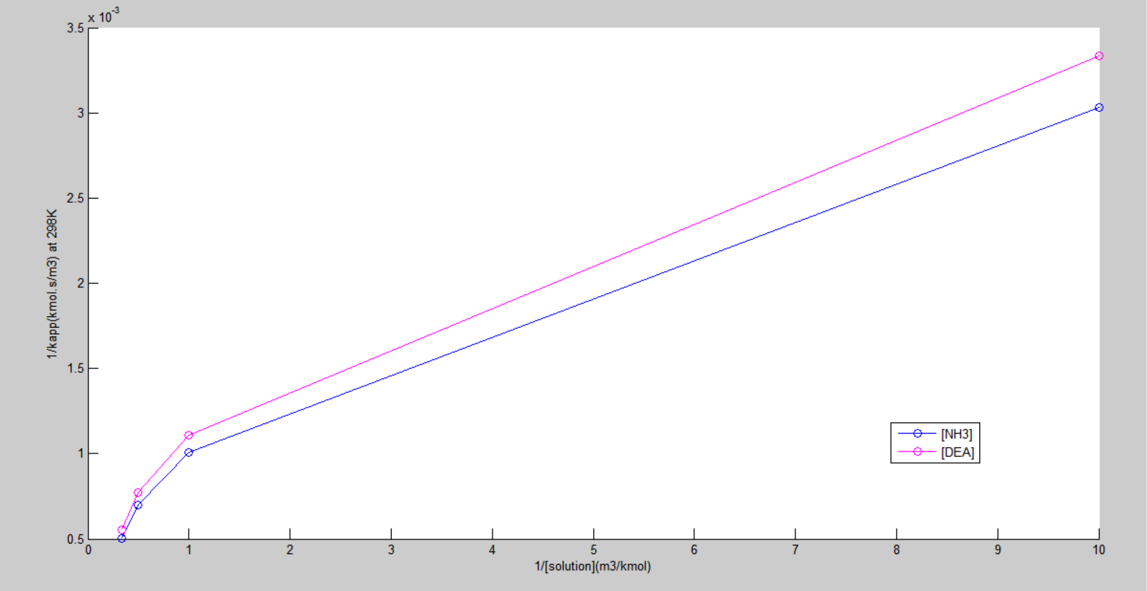


Figure 7: Fitting k_{app} into equation (23)

$$k_{app} = \frac{1}{k_3} + \frac{1}{k_3(\frac{k_4}{k_{-3}})u_2} \leftrightarrow y = c + mx$$

Where,

$$\frac{1}{k_3} = c \text{ and } \frac{1}{k_3(\frac{k_4}{k_{-3}})} = m$$

Estimating the value of k3at 298K:

From Table 2 in Rinker et al.’s work, the k_3 at 298K is 4089 m3/kmol.s, which means:

$$\frac{1}{k_3} = c = 2.446 \times 10^{-4} kmol.s/m^3$$

The above value is the $\frac{1}{k_{app}}$ value at a very high concentration of DEA. The aqueous ammonia should react better than DEA since it has a higher capacity for CO_2 loading and since we assumed that it will behave 10% better than DEA, the $\frac{1}{k_{app}}$ value at very high concentration of aqueous ammonia will be 1/1.1 times more than DEA at the same temperature.

Therefore, the estimated value is:

$$\frac{1}{k_{app}} = \frac{1}{k_3} = c = 2.224 \times 10^{-4} kmol.c/m^3$$

$$k_3 = 4497.14 \frac{m^3}{kmol.s}$$

Estimating the value of $k_3(k_4/k_{-3})$ at 298 K:

From Figure 7:

$$\frac{1}{k_3(\frac{k_4}{k_{-3}})} = 2.244 \times 10^{-4} kmol^2.s/m^6$$

$$k_3\left(\frac{k_4}{k_{-3}}\right) = 4456.33 \frac{m^6}{kmol^2.s}$$

4.4.3 Step 3: Estimating the k_3 and $k_3(k_4/k_{-3})$ value at other temperatures

Based on the approach proposed by Rinker et al. [11] who confirmed the works of Derks & Versteeg [17], a linear relationship between k_3 and $k_3(k_4/k_{-3})$ with respect to 1000/T was proposed.

Estimating k_3 value at other temperatures:

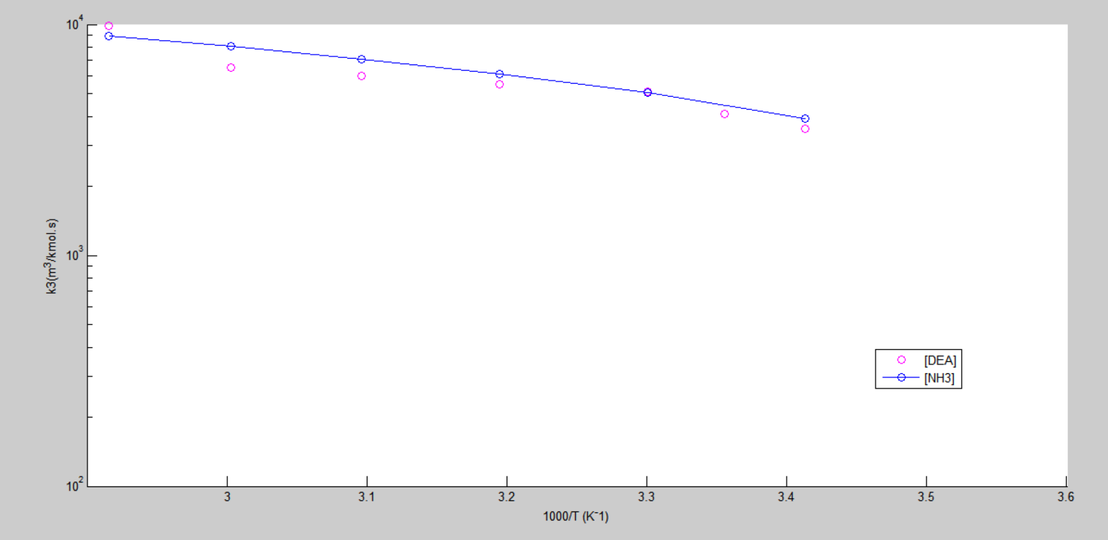


Figure 8: Comparison of the temperature dependence of k_3

In order to get the data for aqueous ammonia, the linear relationship given by the data from Rinker et al.'s work was used to generate the same trend,

$$y = -1.0e^4 x + 3.8e^4$$

Estimating the value of $k_3(k_4/k_{-3})$ value at other temperatures:

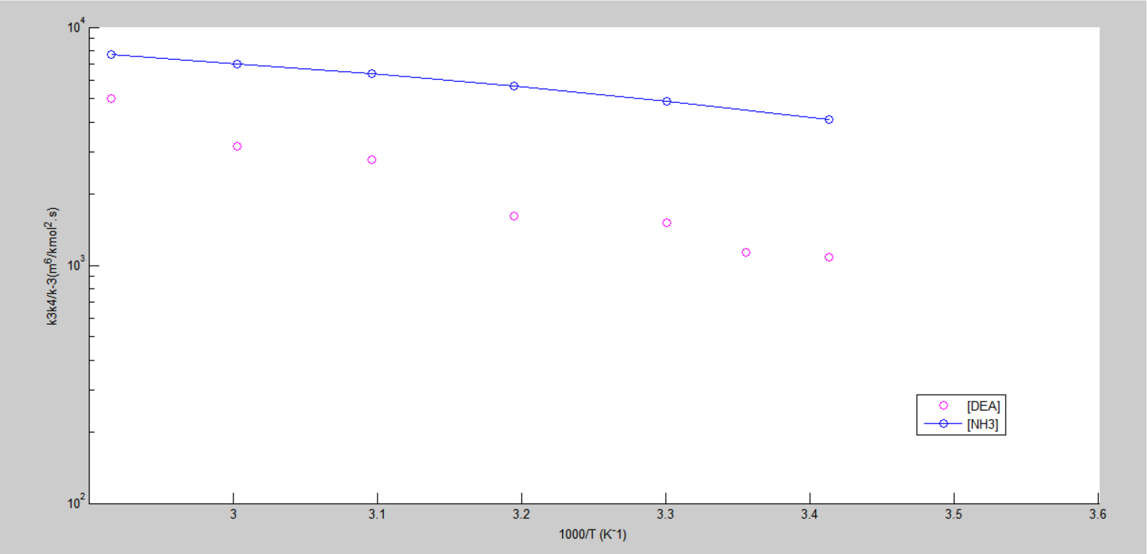


Figure 9: Comparison of the temperature dependence of $k_3(k_4/k_{-3})$

In order to get the data for aqueous ammonia, the linear relationship given by the data from Rinker et al.'s work was used to generate the same trend,

$$y = -7.2e^3x + 2.5e^4$$

4.4.4 Step 4: Fitting estimated k_3 and $k_3(k_4/k_{-3})$ value into the Arrhenius equation

To obtain the Arrhenius equation that fits both k_3 and $k_3(k_4/k_{-3})$ for the aqueous ammonia, data in the table below is plotted again and simulated in MATLAB.

Table 6: Aqueous ammonia data from MATLAB simulation

T (K)	k_3 (m^3/kmol.s)	$k_3(k_4/k_{-3})$ (m^6/$kmol^2$.s)
293	3923.4	4083.7
303	5049.7	4894.7
313	6104.2	5653.9
323	7093.3	6366.1
333	8023.0	7035.5
343	8898.5	7665.8

An Arrhenius equation is given by:

$$k = Ae^{-E/RT}$$

By taking logs on both sides of the equation:

$$\ln k = \ln A - \frac{E}{RT}$$

Then, a plot of $\ln k$ versus 1/T was obtained, and the linear fitting line was obtained:

For k_3:

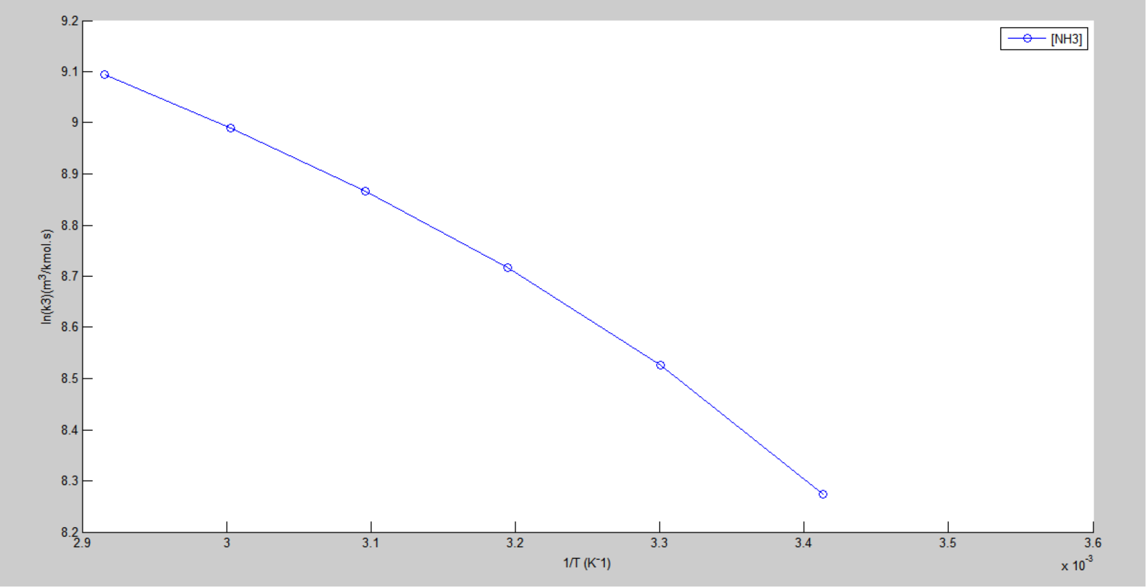


Figure 10: ln k versus 1/T for k_3

The linear fitting line gives the equation:

$$y = -1.6e^3 x + 14$$

The slope of the graph represents –E/R and the intercept represent ln A.

Hence, calculating for A:

$$\ln A = 14$$

$$A = 1.203 \times 10^6$$

Therefore,

$$k_3 = 1.203 \times 10^6 e^{\left(-\frac{1600}{T}\right)}$$

For $k_3(k_4/k_{-3})$:

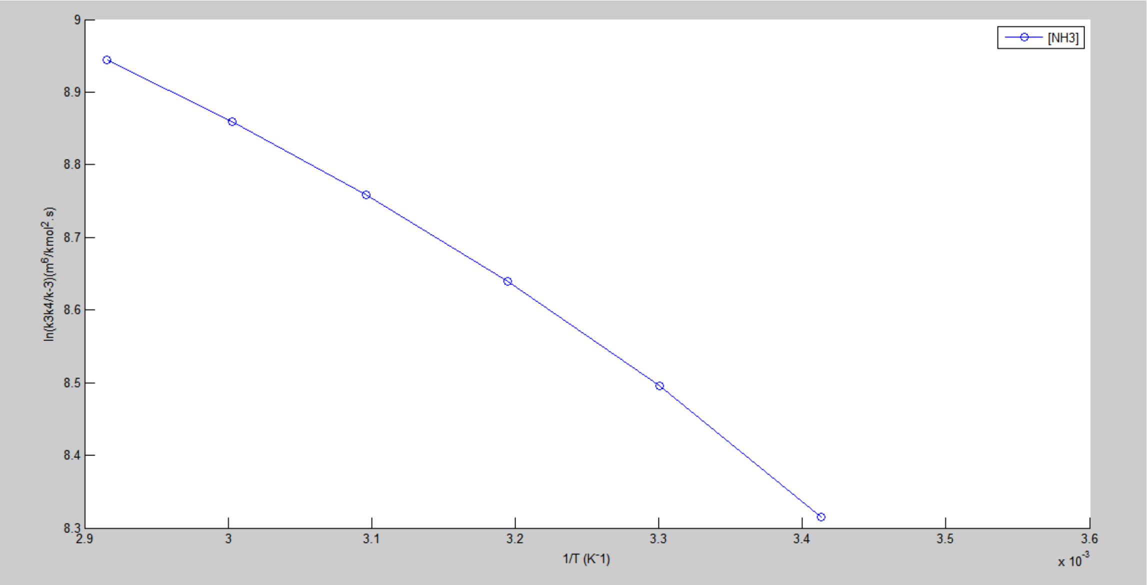


Figure 11: ln k versus 1/T for $k_3(k_4/k_{-3})$

The linear fitting line gives the equation:

$$y = -1.3e^3x + 13$$

The slope of the graph represents –E/R and the intercept represent ln A.

Hence, calculating for A:

$$\ln A = 13$$

$$A = 4.424 \times 10^5$$

Therefore,

$$k_3\left(\frac{k_4}{k_{-3}}\right) = 4.424 \times 10^5 e^{\left(-\frac{1300}{T}\right)}$$

4.5 Comparison of k_{app} with previous literature work

With the equation of for k_3 and $k_3(k_4/k_{-3})$, equation for k_{app} is used to calculate the generated k_{app} :

$$k_3 = 1.203 \times 10^6 e^{\left(-\frac{1600}{T}\right)}$$

$$k_3\left(\frac{k_4}{k_{-3}}\right) = 4.424 \times 10^5 e^{\left(-\frac{1300}{T}\right)}$$

$$\frac{1}{k_{app}} = \frac{1}{k_3} + \frac{1}{k_3(\frac{k_4}{k_{-3}})u_2}$$

Therefore:

$$k_{NH_3} = 164.5 \times e^{\left(-\frac{2900}{T}\right)}$$

For comparison, the correlations previously used by Rivera-Tinoco & Bouallou [21] is used, where:

$$k_{DEA} = 6.138 \times 10^6 \times e^{\left(-\frac{4187}{T}\right)}$$

For the comparison, the inverse apparent reaction rate constant, k_{app} was used to determine the better reaction.

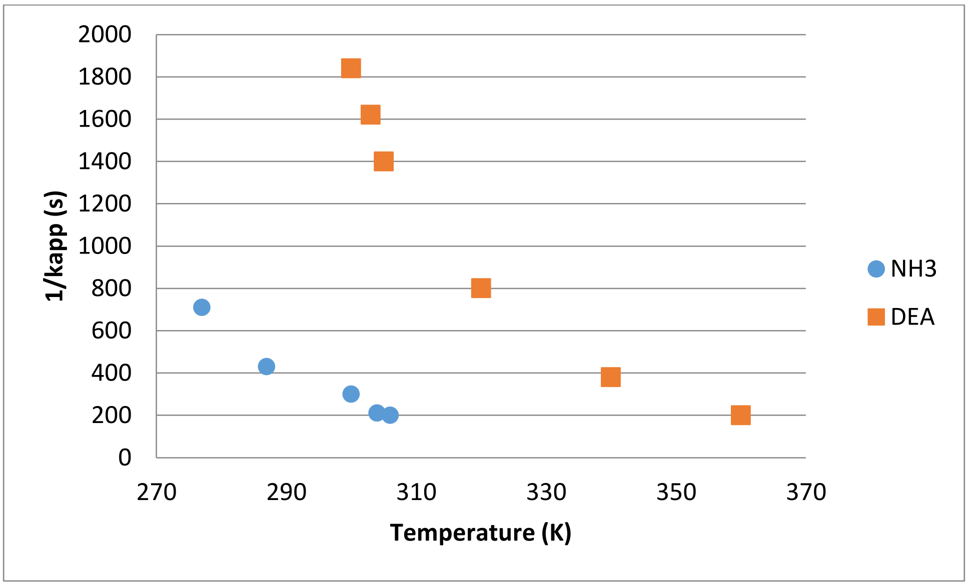


Figure 12: Comparison of Data

It can be seen that the values of the k_{app} of ammonia is higher than that of DEA and a lower temperature is needed to obtain the same k_{app} with that of DEA and the kinetics of the reaction is encouraging for ammonia until temperatures approaching 310 K.

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CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

In this work, the reaction kinetics of the reaction between CO_2 and aqueous ammonia were modelled and simulated using Matlab. The kinetics of the reaction can be described using the zwitterion mechanism. Using the work done by Rinker et al., the reaction rate kinetics were modelled and then simulated using Matlab in order to calculate the apparent rate coefficient, k_{app}, which is then compared to that of Diethanolamine (DEA) since DEA is one of the more common amine solution used to absorb CO_2 due to its quicker reaction. The results indicate that ammonia is greater as compared to DEA in terms of the k_{app} where a lower temperature is required in order to obtain the same k_{app} with that of DEA and the kinetics of the reaction is encouraging for ammonia until temperatures approaching 310 K.

Recommendations

Further study must still be done on the reaction kinetics between CO_2 and aqueous ammonia so that the best and optimized conditions for the reaction to take place may be known. The relationship between the concentration of ammonia with respect to temperature, pressure and time should be modelled individually and thoroughly. Besides that, the experimental procedure should also be taken besides the modelling and simulation approach so that the results can be justified with both methods.

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