MODELLING OF CO_2 SOLUBILITY IN *N*-METHYLDIETHANOLAMINE AQUEOUS SOLUTIONS USING MODIFIED KENT-EISENBERG MODEL

by

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12017

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

(Ir Dr Abdul Halim Shah Maulud)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 2012

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 references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD HAFIZ AZMI BIN MOHAMAD

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ABSTRACT

In this project, the main objective is to develop the Modified Kent-Eisenberg model by using computer software. This model has the important advantage of computational simplicity and thus, is selected in this study. Besides that, the objective is also to test the Modified Kent-Eisenberg model on experimental data of Xu et al. (1998) to see the model performance under extended operating pressure and temperature.

From the results and discussion, the Modified Kent-Eisenberg model is considered able to give a good prediction of CO_2 solubility data in aqueous MDEA solution at 313 – 373 K, at higher CO_2 partial pressure ranged between 0.1 kPa – 1000 kPa.

In comparison with the thermodynamics model of Xu et al. (1998), the performance of Modified Kent-Eisenberg at higher pressure is considered better than Xu et al. (1998) as its average error of 15.22% is lower than Xu et al (1998), which yield 17.91% average error.

Besides that, it is interesting to note that Modified Kent-Eisenberg model gives higher percentage of error as the temperature increase from 328 K to 353 K. It is recommended that the model is reassessed in order to improve the accuracy of the prediction under higher temperature. Besides that, the regression for the parameters of g_i and k_i shall include the effect of temperature into the analysis of factor F_i.

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CHAPTER 1

Project Background

1.1 Background Study

Raw natural gas from oil wells contains significant amounts of sulphur and carbon dioxide. Gases containing H_2S or CO_2 are commonly referred to as *acid gases* in the hydrocarbon processing industries. Processes within oil refineries or chemical processing plants that remove these acid gases are generally mentioned as *sweetening processes* because they result in products, which no longer have the sour, foul odours of the acid gases.

The sweetening process of natural gas stream is a very important process before the natural gas can be further used for manufacturing. A typical amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the downflowing amine solution absorbs H_2S and CO_2 from the upflowing sour gas to produce a sweetened gas stream as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2. This project from now on shall focus on the removal of CO_2 from the gas stream.

Aqueous alkanolamine solutions have been widely used for the capture and removal of CO_2 from acid gas streams, typically from natural gas refineries. Aqueous methyldiethanolamine (MDEA) solutions are the most widely used alkanolamine absorbents. MDEA is a relatively cheap chemical, has higher loading capacity (mole of CO_2/mole of amine), less regeneration energy, and high resistance to thermal and chemical degradation.

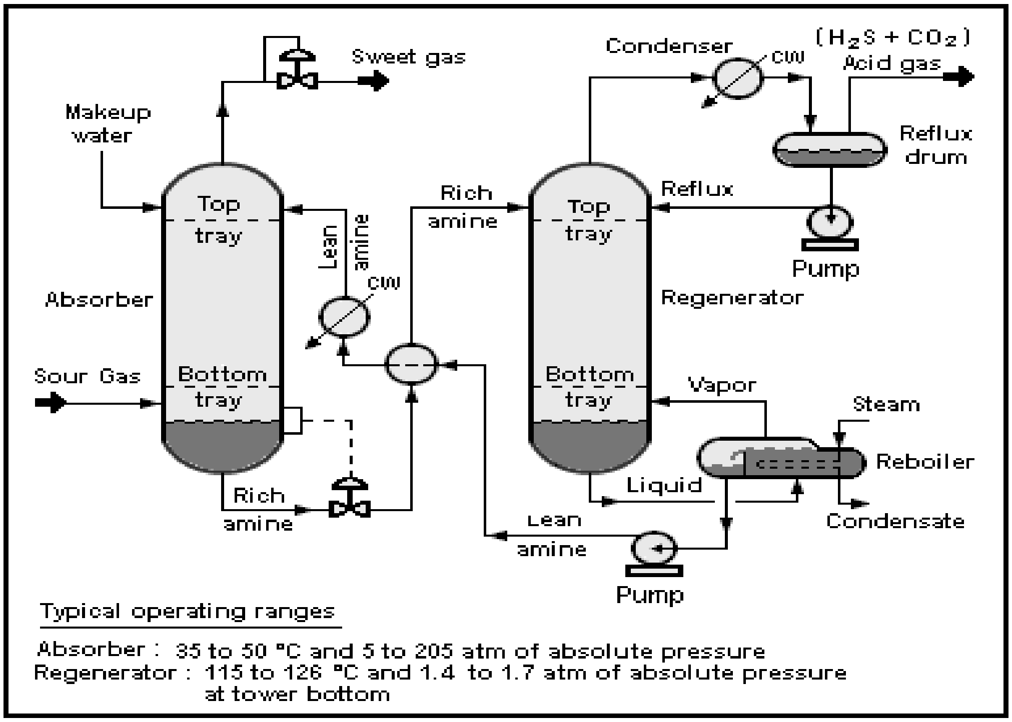


Figure 1.1: Process flow diagram of a typical amine treating process

Vapor–liquid equilibrium data (VLE) is probably the most important item of data for the design of treating plants. Numerous VLE studies have been conducted and reported to develop mathematical models to predict VLE relationships for different amine solutions. Most of these studies are concerned with the most commonly used amines like monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA).

The first practical and widely used model was proposed by Kent and Eisenberg (1976). This model has the important advantage of computational simplicity and been incorporated into several computer models used for treating plant design. This model assumes that all activity coefficients and fugacity coefficients to be unity (i.e. ideal solutions and ideal gases) and forces a fit between experimental and predicted values by treating two of the equilibrium constants (K_1 and K_2) as variables. Extrapolation applicability outside the validity range is very limited. Process engineers commonly use this model because its complexity and required computational effort are relatively low.

A more generally applicable model was proposed by Deshmukh and Mather (1981). It uses the same chemical reactions in solution but estimates values for activity and fugacity coefficients, which are used in the calculation of liquid phase equilibrium constants and in the application of Henry's law to the VLE. However, in spite of the complexity of the calculations, the results of these rigorous models were not better than those of the Kent–Eisenberg model (Posey et al, 1996).

M. Z. Haji-Sulaiman et al. (1998) used Modified Kent-Eisenberg model to predict the data on CO_2 loading in aqueous solution of DEA and MDEA of various temperature and low CO_2 pressure (0.09 - 100 kPa) obtained from a stirred reactor. Modification of the original model by Kent and Eisenberg was prepared to include the free gas concentration in the solution and the amine concentration. The Modified Kent-Eisenberg model is able to give relatively good predictions on the total CO_2 loading in the solution.

Xu et al. (1998) proposed a thermodynamic model of an ionic solution based on solubility data of CO_2 and vapour pressure of water in 3.04 – 4.28 $kmol/m^3$ aqueous MDEA solutions at 313 – 373 K and 0.876 to 1013 kPa of CO_2 partial pressure.

Whereas, by using Modified Kent-Eisenberg model, no modelling prediction was developed yet on the solubility of CO_2 in MDEA solution at higher operating pressure around 100 - 1000 kPa. The purpose of this paper is to apply Modified Kent-Eisenberg model for CO_2 solubility prediction at higher pressure and compare the performance of the established model with other available data such as Xu et al. (1998) based on error analysis.

1.2 Problem Statement

As per mentioned earlier, the prediction of CO_2 solubility in aqueous MDEA solution, with respect to Modified Kent-Eisenberg model at higher operating pressure which ranged between 100 – 1000 kPa is not developed yet. The motivation of the studied system is to test the performance of Modified Kent-Eisenberg model corresponding to the high-pressure range and compare it with Xu et al. (1998) based on error analysis.

1.3 Objectives

1. To model the solubility of CO_2 over aqueous methyldiethanolamine (MDEA) solution by using Modified Kent-Eisenberg model.

2. To examine the model prediction performance of CO_2 loading under extended operating pressure and temperature by comparing to experimental data of Xu et al. (1998) based on error analysis.

1.4 Scope of study

This research paper mainly emphases on the solubility of CO_2 in MDEA solution. It will partly cover on Modified Kent-Eisenberg model to study on the absorption of CO_2 by the solution. Back to the objective of this paper, the error analysis and deviation are then will be compared with experimental data of Xu et al. (1998).

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide

The global climate change is one of the most important and challenging environmental issues facing the world community. CO_2 is found to be a major contributor to this environmental disaster as it is largely produced by many important industries such as fossil-fuel-fired power plants, steel production, chemical and petrochemical manufacturing, cement production, and natural gas purification. This has motivated intensive researches and studies on CO_2 capture and sequestration by the major industries.

CO_2 is a chemical molecule consisting of one carbon atom covalently bonded to two oxygen atoms. At atmospheric pressure and temperature, CO_2 is a colourless, odourless gas that exists naturally as a trace gas in the Earth's atmosphere. It is a fundamental component of the Earth's carbon cycle, with a considerable number of sources, both natural and man-made. Moreover, there are a significant number of natural carbon sinks including oceans, forests and other biota.

At higher concentrations, CO_2 has a sharp and acidic odour. At standard temperature and pressure, the density of carbon dioxide is around 1.98 kg/m^3, about 1.5 times that of air. At 1 atmosphere, the gas deposits directly to a solid at temperatures below −78.5 °C and the solid sublimes directly to a gas above −78.5 °C. In its solid state, carbon dioxide is commonly called dry ice. Figure 2.2 shows the phase diagram of carbon dioxide.

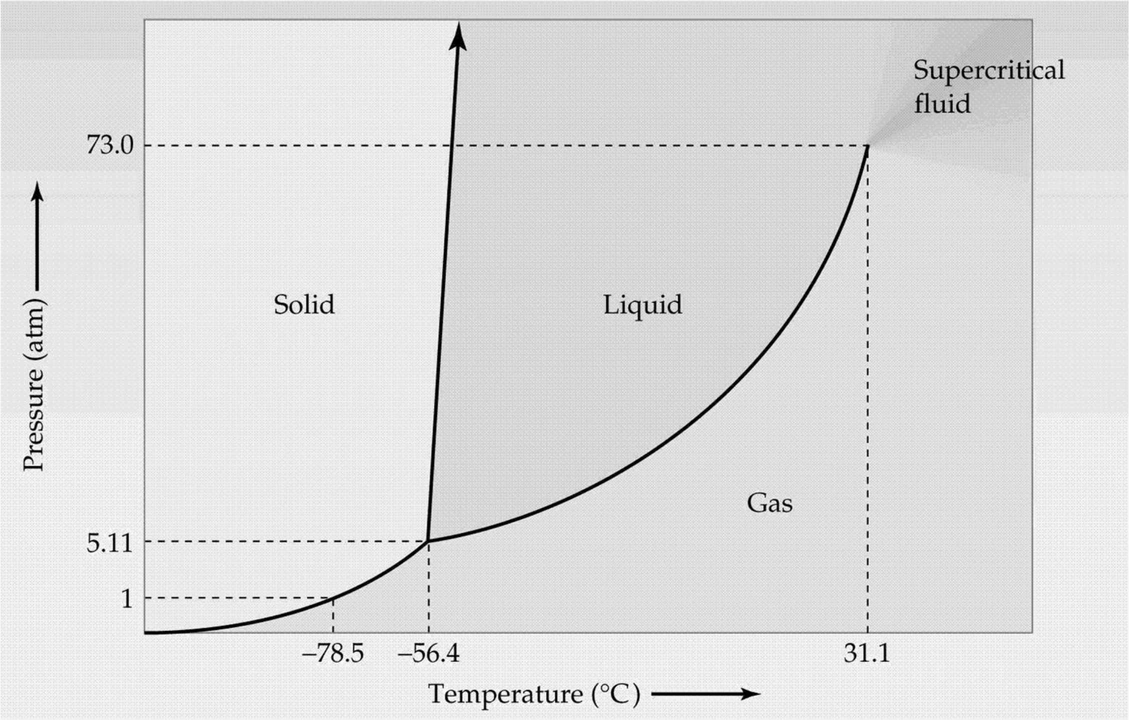


Figure 2.1: Phase diagram of carbon dioxide

The reasons for the CO_2 removal are based on several technical and economical concerns. Carbon dioxide present in natural gas will reduce the heating value of the gas and as an acid component it has the potential to cause corrosion in pipes and process equipment and also to cause catalyst poisoning in ammonia synthesis (G. Astarita et al., 1983). Natural gas pipelines usually permit from one to two percentage of CO_2 and sometimes as high as 5% (P. A. Buckingham, 1964).

In the past decades, CO_2 removal from flue gas streams started as a potentially economic source of CO_2, mainly for enhanced oil recovery (EOR) operations. Moreover, CO_2 was also produced for other industrial applications such as carbonation of brine, welding as an inert gas, food and beverage carbonation, dry ice, urea production, and soda ash industry (A. B. Rao and E. S. Rubin, 2002). However, environmental concerns, such as the global climate change, are now focused as one of the most challenging environmental issues, and have motivated intensive research on CO_2 capture and sequestration.

Carbon dioxide as one of the greenhouse gases (GHG) is currently responsible for over 60% of the enhanced greenhouse effect, methane (CH_4) contributes 20%, and the remaining 20% is caused by nitrous oxide (N_2O), a number of industrial gases, and ozone. Scientific evidence now strongly suggests that increased levels of GHG may lead to higher temperature, and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise by about 1.4–5.8^{o}C by the year 2100 (M. William, 2002).

A wide range of technologies currently exists for separation and capture of CO_2 from gas streams include adsorption on solid substrates, chemical absorption, gas permeation, and physical absorption (A. L. Kohl, 1997). Adsorption is economical for purification, typically reducing the CO_2 content from 3% down to 0.5 %. However, an adsorption process for a CO_2-rich natural gas streams would require a very frequent regeneration of the solid bed.

Chemical absorption has been used successfully for low-pressure gas streams containing between 3% and 25% of CO_2, but the large solvent regeneration costs associated with the process hamper its application to higher CO_2 contents. The degree of absorption is limited by the fixed stoichiometry of the chemical reaction. Therefore, the use of this process for CO_2-rich gas streams will lead to high solvent circulation flow rates and high-energy requirements. Meanwhile, gas permeation techniques are compact and flexible, and can be adapted easily to changes in CO_2 content. However, reliability is a concern because natural gas contaminants can lead to deterioration in the performance of the membrane.

Physical absorption is the most common technology for CO_2 removal today. The main advantage of such a process is that (unlike chemical absorption) physical solvents have no absorption limitation. The amount of CO_2 absorbed by the solvent is determined by the vapour-liquid equilibrium of the mixture, which is governed by the pressure and temperature. At high CO_2 partial pressure, the CO_2 loading capacity of the solvent is higher for a physical solvent than for a chemical solvent. Physical absorption processes are thus particularly appropriate for the treatment of CO_2-rich gas streams.

2.2 Alkanolamines and Methyldiethanolamine (MDEA)

Many solvents have been used for the absorption of CO_2 including, formulations of tributyl phosphate, polycarbonate, methylcyanoacetate, and n-formyl morpholine (S. A. Newman, 1985). There are two major drawbacks with such solvents: they are not easily disposable (for offshore operations) and could be involved in side reactions with other natural gas constituents.

Aqueous solutions of alkanolamines are the most commonly used chemical absorbents for the removal of CO_2 from natural, refinery, and synthesis gas streams. The technique has been proven to be reliable and has wide application in many chemical industries such as ammonia production, coal gasification and natural gas processing.

Alkanolamine is broadly classified into primary, secondary and tertiary depending on the number of alkyl group(s) attached to the nitrogen atom in the structure of the molecule. Both primary and secondary amines generally exhibit low CO_2 loadings (mol of CO_2 captured/mol of amine) but with a high rate of absorption. In contrast, tertiary amines showed the opposite behaviour.

Recently, a new class of amine known as sterically hindered amine has been introduced which shows a high absorption rate and high maximum gas loading. However, the choice of a particular amine will depend not only on the absorption rate and maximum loading that can be achieved, but also on other factors such as regeneration energy, corrosion tendency and the cost of the solvent.

The absorption of CO_2 in aqueous solution of alkanoalamine couples physical absorption with chemical reaction, which fix the CO_2 in the solution as carbonates, bicarbonates and carbamates depending on the type of amine being used.

Similar reaction steps are involved for all types of amine including the protonation of amine as well as the ionization of different species in the solution. However, an additional step, which is the formation of carbamate ion, has been proposed for a system involving primary and secondary amines. It is the formation of this carbamate ion, which limits the maximum CO_2 loading of 0.5 for these classes of amine.

Aqueous monoethanolamine (MEA) and aqueous methyldiethanolamine (MDEA) solutions are the most widely used alkanolamine absorbents. The former is preferred for its low molecular weight, high reactivity, low cost and reasonable thermal stability. Meanwhile, the latter is known for its higher loading capacity (mole of CO_2/mole of amine), less regeneration energy, and high resistance to thermal and chemical degradation.

Methyldiethanolamine (MDEA) is a clear, colorless or pale yellow liquid with an ammonia odour. It is miscible with water, alcohol and benzene. MDEA is also known as *N*-Methyl diethanolamine and has the formula of $CH_3N(C_2H_4OH)_2$. MDEA is a tertiary amine and is widely used as a *sweetening agent* in chemical, oil refinery, syngas production and natural gas.

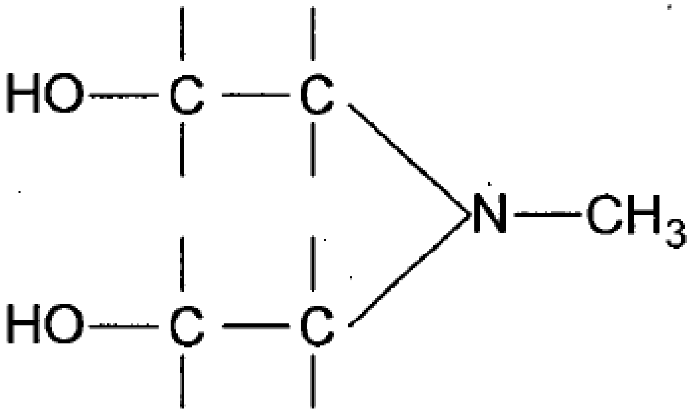


Figure 2.2: Molecular structure of Methyldiethanolamine (MDEA)

2.3 Modified Kent-Eisenberg Model

Vapor–liquid equilibrium data (VLE) is the most important item of data for the design of treating plants. Numerous VLE studies have been conducted and reported to develop mathematical models to predict VLE relationships for different amine solutions.

The first practical and widely used model was proposed by R. L. Kent and B. Eisenberg (1976). This model has the important advantage of computational simplicity and been incorporated into several computer models used for treating plant design.

This model assumes that all activity coefficients and fugacity coefficients to be unity (i.e. ideal solutions and ideal gases) and forces a fit between experimental and predicted values by treating two of the equilibrium constants (K_1 and K_2) as variables. Extrapolation applicability outside the validity range is very limited. Process engineers commonly use this model because its complexity and required computational effort are relatively low.

In understanding the Modified Kent-Eisenberg model, it is important to have overview knowledge on the mechanism of the process. An equilibrium solution of CO_2 in aqueous solution of alkanolamine is governed by the following set of equations:

$$RR'NH_2^+ \overset{K_1}{\Leftrightarrow} RR'NH + H^+ \tag{1}$$

$$RR'NCOO^- + H_2O \overset{K_2}{\Leftrightarrow} RR'NH + HCO_3^- \tag{2}$$

$$CO_2 + H_2O \overset{K_3}{\Leftrightarrow} HCO_3^- + H^+ \tag{3}$$

$$HCO_3^- \overset{K_4}{\Leftrightarrow} CO_3^= + H^+ \tag{4}$$

$$H_2O \overset{K_5}{\Leftrightarrow} OH^- + H^+ \tag{5}$$

Equation (1) represents the protonation of amine, equation (2) corresponds to the hydrolysis of carbamate and is only considered in systems consisting of primary and secondary amines. Equations (3), (4) and (5) are the ionization reactions for the different species in the solutions.

In addition to the above equations, the following set of conditions must also be satisfied:

Amine balance:

$$[RR'NH]_t = [RR'NH]_e + [RR'NH^+{}_2]_e + [RN'NCOO^-]_e \qquad (6)$$

CO_2 balance:

$$\alpha[RR'NH]_t = [HCO^-{}_3]_e + [RR'NCOO^-]_e + [CO^={}_3] + P_{CO_2}/H_{CO_2} \qquad (7)$$

Charge balance:

$$[RR'NH^+{}_2]_e = [HCO^-{}_3]_e + [RR'NCOO^-]_e + 2[CO^={}_3]_e \qquad (8)$$

where α is the gas loading. The concentration of carbon dioxide in the liquid phase can be estimated from Henry's law, i.e.

$$P_{CO_2} = H_{CO_2}[CO_2] \qquad (9)$$

Following W. Hu and A. Chakma (1990), the apparent equilibrium constants, K'_i, for reactions (1) and (2) as defined in terms of the concentration of the corresponding species, are taken to be dependent on the partial pressure of CO_2 and the amine concentration in the solution. Since the equilibrium constant at infinite dilution, K_i, is only a function of temperature, a factor F_i is introduced which takes into account the effects of CO_2 partial pressure and the amine concentration. Thus,

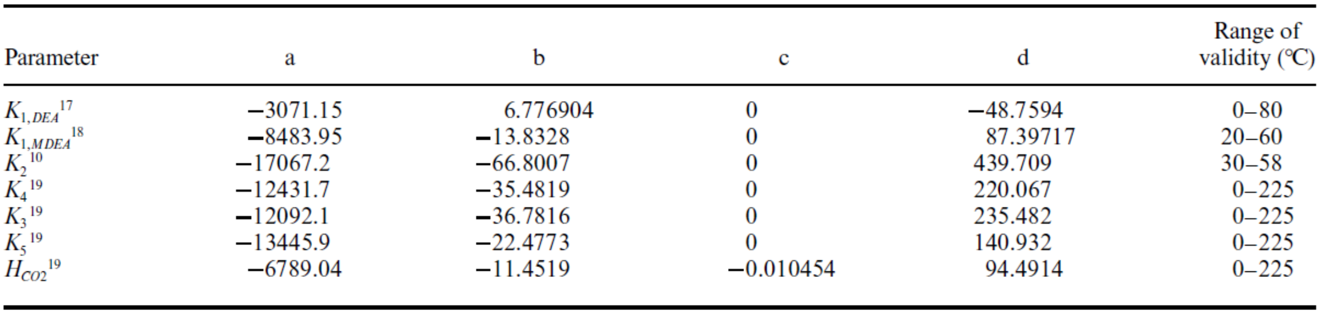
$$K'_i = K_i F_i \qquad (10)$$

The dependency of the equilibrium constant, K_i, as well as the Henry's constant, H, with temperature is expressed as

$$K_i(\text{or } H) = e^{((ai/T) + b_i \ln T + c_i T + d_i)} \qquad (11)$$

where a_i – d_i are constants. Values of these constants for all of the reactions (1) – (5) and that for the Henry's constant are taken from the literature, as given in Table 2.1.

Table 2.1: Values of the constants used in equation (11)



Parameter	a	b	c	d	Range of validity (°C)
$K_{1,DEA}$[17]	−3071.15	6.776904	0	−48.7594	0–80
$K_{1,MDEA}$[18]	−8483.95	−13.8328	0	87.39717	20–60
K_2[10]	−17067.2	−66.8007	0	439.709	30–58
K_4[19]	−12431.7	−35.4819	0	220.067	0–225
K_3[19]	−12092.1	−36.7816	0	235.482	0–225
K_5[19]	−13445.9	−22.4773	0	140.932	0–225
H_{CO2}[19]	−6789.04	−11.4519	−0.010454	94.4914	0–225

In this work, F_i is defined in a general form as:

$$F_i = e^{\left(\frac{f_i}{P_{CO_2}} + g_i \ln P_{CO_2} + h_i P_{CO_2} + \frac{j_i}{[RR'NH]} + k_i \ln[RR'NH] + m_i[RR'NH]\right)} \qquad (12)$$

Similarly, $f_i - m_i$ are constants which are to be regressed. For reactions (3) – (5) only the equilibrium constants at infinite dilution, K_i, were used.

For MDEA solutions, no stable carbamates are formed. Thus, reaction (2) does not exist in the system and $RR'NCOO^-$ was omitted in the charge and mass balance equations. Thus for this system, equation (1) – (9) can be reduced to a single polynomial equation in terms of the concentrations of hydrogen ions, $[H^+]$, and the equilibrium constants as follows:

$$A'[H^+]^4 + B'[H^+]^3 + C'[H^+]^2 + D'[H^+] + E' = 0 \qquad (13)$$

where

$A' = 1$

$B' = [RR'NH] + K'_{1,MDEA}$

$C' = K_3 (P_{CO2}/H_{CO2}) + K_5$

$D' = -(2K_3K_4 (P_{CO2}/H_{CO2}) + K'_{1,MDEA} K_5 + K_{1,MDEA} K_3 (P_{CO2}/H_{CO2}))$

$E' = -2K'_{1,MDEA} K_3 K_4 (P_{CO2}/H_{CO2})$

Consequently, the total CO_2 loading, α, can be expressed as:

$$\alpha = \frac{\frac{P_{CO2}}{H_{CO2}}\left([H^+]^2+K_3[H^+]+K_3K_4\right)}{[H^+]^2[RR'NH]+K_5[H^+]-[H^+]^3+K_3[H^+]\left(\frac{P_{CO2}}{H_{CO2}}\right)+2K_3K_4\left(\frac{P_{CO2}}{H_{CO2}}\right)} \quad (14)$$

M. Z. Haji-Sulaiman et al. (1998) used Modified Kent-Eisenberg model to predict the data on CO_2 loading in aqueous solution of DEA and MDEA of various temperature and low CO_2 pressure (0.09 - 100 kPa) obtained from a stirred reactor. The data was fitted simultaneously, using the Modified Kent-Eisenberg model as discussed above, to generate the different parameters $f_i - m_i$ of equation (12). It was found that for the protonation of amine, only g_i and k_i are important. However, for the formation of carbamate, the contribution from g_i and j_i is significant. Based on these analyses, F_i is finally expressed as:

Protonation of amine

$$F_i = g_i \ln P_{CO_2} + k_i \ln[\mathrm{RR'\,NH}] \quad (15)$$

Formation of carbamate

$$F_i = g_i \ln P_{CO_2} + \frac{j_i}{[\mathrm{RR'NH}]} \quad (16)$$

Values of these parameters, g_i, j_i and k_i, that best fit the observed data are given by M. Z. Haji-Sulaiman et. al as Table 2.2.

Table 2.2: Generated parameters for equations (15) and (16)

Parameter	g_i	j_i	k_i
$F_{1,DEA}$	−0.4559	0	0.2584
$F_{2,DEA}$	−0.002386	2.88	0
$F_{1,MDEA}$	−0.03628	0	0.6262

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

Throughout this project, there were five main phases of activities. Figure 3.1 shall clearly explain on the methodology of the project.

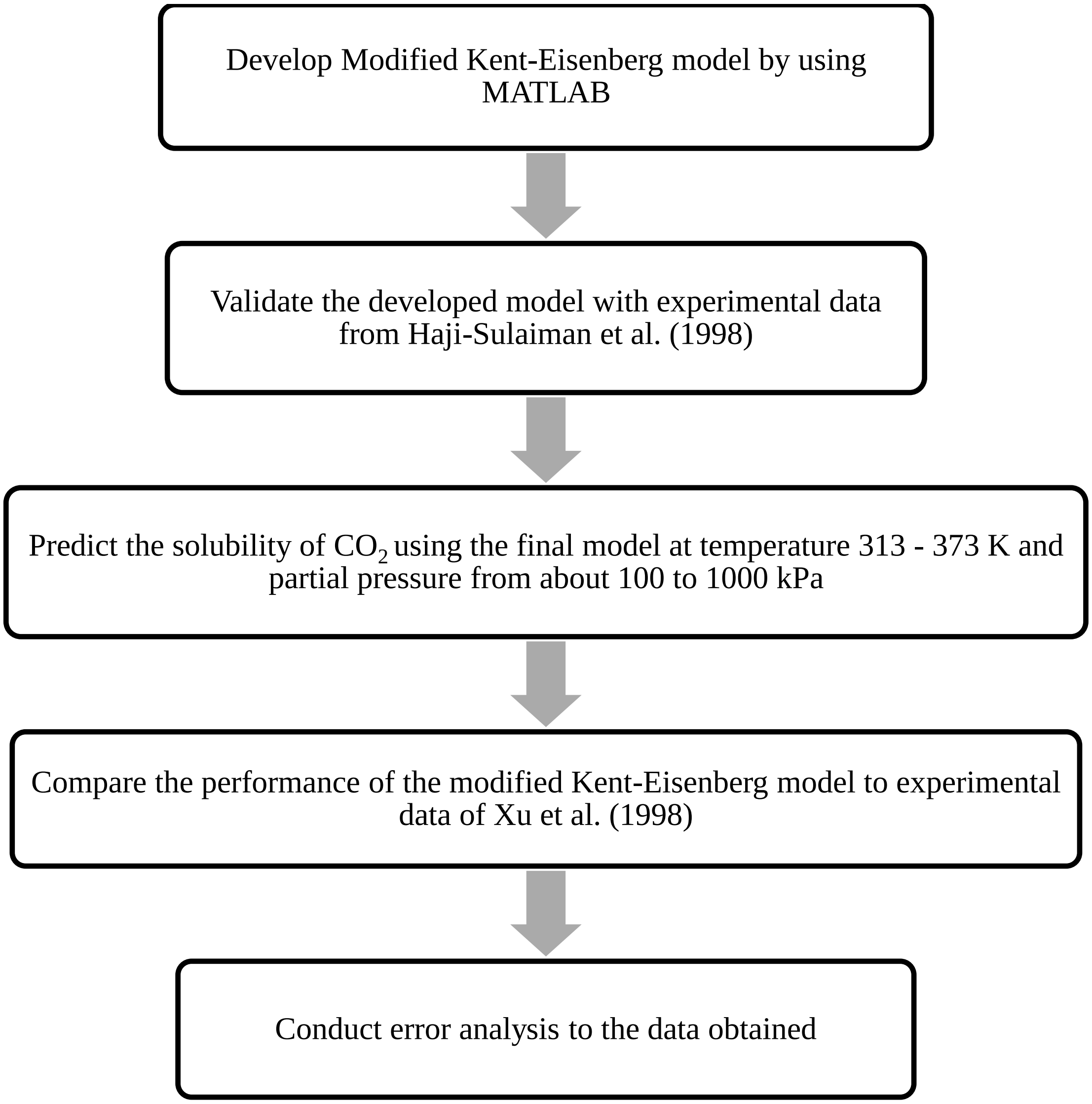


Figure 3.1: Project Flowchart

The very first phase was to develop the Modified Kent-Eisenberg model by using computer software such as MATLAB and Microsoft Excel. During this phase, tutoring sessions with supervisor and peers were scheduled to enhance the capability and skills of using MATLAB. The activities were aimed in giving better understanding and increase progress in developing the model. At the end of this phase, a working MATLAB model was established and ready for the second phase. The sample of the model coding are as in APPENDIX I.

Second phase was to verify the developed MATLAB model with experimental data from Haji-Sulaiman et al. (1998) in order to ensure the set of coding of the developed model is right. The gas loading data from different MDEA concentration, temperatures and CO_2 partial pressure, with reference to Haji-Sulaiman et al. paper, were fitted into the developed model.

After that, comparison of the prediction data of the developed model with the experimental data was conducted by using error analysis. The error analysis was done using the following equation:

$$\text{Error Percentage (\%)} = \left|\frac{\alpha_{p_i} - \alpha_{exp_i}}{\alpha_{exp_i}}\right| \times 100\%$$

where,

α_{exp} = experimental CO_2 loading

α_p = predicted CO_2 loading

If the developed model yields less than 15% of error percentage, whereby the predicted data was close enough to the experimental data, the project can moves on to the next phase. If not, the MATLAB coding must undergo correction and then be verified and validated again.

Next phase was to predict the solubility of CO_2 using the final MATLAB model at temperature 313 – 373 K and partial pressure from about 100 to 1000 kPa, with reference to Xu et al. (1998). After the MATLAB coding has been validated and verified for its workability, the parameters and data were fitted into the model. The prediction data was then recorded for the next error analysis phase.

The fourth phase was to perform error analysis on the results obtained by using the experimental data of Xu et al. (1998) as reference. With the error analysis, the CO_2 partial pressures versus error graph were plotted for different concentration and temperature to observe the effect of different parameters to the performance of the model.

Final phase was to compare the performance between the modified Kent-Eisenberg model and the data of Xu et al. (1998). By using the calculated error percentage, the value will be compared with the error percentage of Xu et al. (1998) work. If the value is smaller than the newly developed model, it can be proposed as better than Xu et al. (1998) work and vice versa. Comparison with other papers of similar partial pressure range can be prepared, shall there is any, to demonstrate the performance of the developed model.

3.2 Gantt Chart

There are nine processes that has been decided in order to make sure the research work can be done within given period. Table 3.1 depicts the Gantt chart for the project development.

The first seven weeks of the semester has been allocated for the students to proceed with the research works. During this period of time, steps 2 and 3 have been done. Artificial neural network has been successfully modelled and verified using reference papers.

In week 8, preparation of progress report has been done where the research findings have to be reported to respective supervisor. Steps or methodology must be indicated clearly so that the supervisor understand what the student have done so far. Any problem also needs to be addressed so that the way out can be discussed before it is too late to do any modification on the research methodology. The report has to be submitted to the supervisor at the end of week 8.

After the submission of progress report, students may proceed with project work and need to finish the project within the allocated time frame which is until week 12. Project work continues where several methodologies needed to be modified and more information on the neural network has to be added.

On week 11, pre-SEDEX was held where students performed poster presentation on the research progress. Submission of draft report has been done to the supervisor and feedbacks received were to make addendum and correction prior to the submission of soft-bounded dissertation and technical report on week 13.

Final oral presentation will be held on week 14 where students have to present the whole project to the external examiner and submission of final project dissertation, which is hard-bounded report, must be done on week 15.

Table 3.1: Project Gantt Chart

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	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Milestone
■ Process

3.3 Software Required

Throughout this project, the main softwares needed to run this model are:

a) Microsoft Excel:
    i. This software shall help in tabulating data and performing error analysis and calculation.

b) MATLAB:
    i. This software shall help in developing the Modified Kent-Eisenberg model and perform more complex model calculations.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Validation of the Model

After MATLAB coding have been developed, the solubility data of CO_2 in aqueous MDEA solution of 2M and 4M concentration, at 303 – 323 K and CO_2 partial pressure of 0.09 – 100 kPa were generated by fitting the data into the model. Table 4.1 shows the data generated from the developed model.

$\boldsymbol{\alpha}_{\mathbf{expt}}$ were the CO_2 loading data published by Jou et al. (1982), $\boldsymbol{\alpha}_{\mathbf{calc1}}$ were CO_2 loading data predicted by Haji-Sulaiman et al. (1998) as in the paper, and $\boldsymbol{\alpha}_{\mathbf{calc2}}$ were CO_2 loading data generated by the developed Modified Kent-Eisenberg model, by using MATLAB.

As observed in $\boldsymbol{\alpha}_{\mathbf{calc2}}$ data, their values were not in the range of 0.0 to 1.0 mol CO_2/mol MDEA, which is the acceptable range of CO_2 loading data. In contrast, $\boldsymbol{\alpha}_{\mathbf{calc2}}$ data were in the range of 50 to 9000 mol CO_2/mol MDEA, which is not a logical range for solubility data. The average error of data was more than 100% and too large compared to the experimental data. The coding have been checked and corrected repeatedly, but still, there was no much change in the range of solubility data.

From the observation, it can be inferred that Modified Kent-Eisenberg model as in Haji-Sulaiman et al. (1998) paper might not directly accurate due to some typing, printing or human error by its authors. Therefore, the representation of the model, formula or symbol was not accurate as its authors intended to report it. These mistakes caused the prediction data of the model, which was directly referred from the paper, to be not in the acceptable range of CO_2 solubility data.

Table 4.1: Experimental and calculated CO_2 loading, based on Haji-Sulaiman et al (1998)

M	**T (K)**	**P_{CO2} (kPa)**	**α_{expt} (mol/mol)**	**α_{calc1} (mol/mol)**	**Error percentage (%)**	**α_{calc2} (mol/mol)**	**Error percentage (%)**	**α_{calc3} (mol/mol)**	**Error percentage (%)**
2M	303	1.064	0.114	0.112	1.75	497.58	436370.65	0.177	55.44
		3.130	0.244	0.234	4.10	1034.64	423932.44	0.288	18.20
		4.802	0.333	0.300	9.91	1380.33	414414.11	0.346	3.78
		10.535	0.483	0.452	6.42	2329.82	482264.65	0.469	2.96
		29.756	0.673	0.691	2.67	4557.46	677086.28	0.650	3.45
		48.370	0.793	0.799	0.76	6147.56	775128.54	0.729	8.02
		95.830	0.880	0.905	2.84	9106.17	1034692.54	0.822	6.57
	313	1.064	0.103	0.091	11.65	355.98	345510.11	0.136	32.14
		3.069	0.197	0.177	10.15	730.53	370729.85	0.224	13.76
		5.176	0.267	0.243	8.99	1038.77	388952.11	0.283	6.10
		10.029	0.374	0.353	5.61	1614.30	431530.71	0.375	0.13
		30.349	0.603	0.585	2.99	1648.16	273227.16	0.561	6.98
		47.520	0.688	0.698	1.45	4359.12	633493.14	0.641	6.87
		93.956	0.805	0.837	3.98	6465.09	803016.85	0.753	6.46
	323	0.997	0.079	0.065	17.72	256.01	323957.77	0.102	28.99
		2.938	0.148	0.133	10.14	533.40	360305.52	0.172	16.28
		4.761	0.194	0.180	7.22	738.73	380688.41	0.216	11.34
		9.725	0.298	0.275	7.72	1190.54	399411.60	0.298	0.03
		28.435	0.471	0.483	2.55	2392.11	507779.11	0.461	2.17
		44.136	0.590	0.585	0.85	3146.87	533267.77	0.538	8.80
		91.514	0.726	0.752	3.58	4827.70	664872.53	0.669	7.85
				Average	**5.86**	**Average**	**507649.14**	**Average**	**11.73**
4M	303	0.099	0.027	0.014	48.15	105.27	389792.38	0.032	19.68
		0.984	0.061	0.067	9.84	496.13	813232.44	0.098	61.24
		4.918	0.149	0.185	24.16	1454.58	976130.19	0.210	40.61
		9.853	0.284	0.276	2.82	2297.07	808726.87	0.285	0.27
		29.509	0.516	0.480	6.98	4626.89	896583.49	0.442	14.32
		49.100	0.633	0.601	5.06	6305.55	996037.14	0.528	16.57
		98.200	0.761	0.758	0.39	9333.67	1226401.13	0.649	14.70
	313	0.095	0.015	0.011	26.67	73.23	488126.28	0.024	57.68
		0.954	0.052	0.049	5.77	347.62	668407.02	0.073	40.69
		4.762	0.086	0.136	58.14	1018.89	1184657.97	0.159	84.56
		9.523	0.190	0.207	8.95	1607.98	846204.96	0.219	15.04
		28.521	0.384	0.391	1.82	3244.56	844838.39	0.351	8.59
		47.535	0.513	0.495	3.51	4421.44	861778.46	0.429	16.40
		95.234	0.654	0.653	0.15	6591.94	1007842.24	0.547	16.36
	323	0.090	0.010	0.007	30.00	53.06	530511.67	0.017	74.12
		0.901	0.037	0.035	5.41	251.45	679491.38	0.054	46.62
		4.514	0.084	0.103	22.62	739.66	880449.15	0.120	42.34

	9.028	0.151	0.159	5.30	1168.63	773824.61	0.166	10.18
	27.084	0.251	0.308	22.71	2368.28	943438.44	0.274	9.23
	45.139	0.363	0.400	10.19	3244.19	893614.91	0.341	6.16
	90.279	0.516	0.548	6.20	4849.35	939697.41	0.447	13.34
			Average	**14.52**	**Average**	**840466.03**	**Average**	**28.99**

Due to the problem, the derivation of the Modified Kent-Eisenberg model had to be conducted again based on Haji-Sulaiman et al. (1998) paper and others such as H. Pahlavanzadeh et al. (2011). The re-derivation is as shown in APPENDIX II.

After the model has been derived again, it was developed into the MATLAB coding and the parameters of Haji-Sulaiman et al. (1998) were refitted into the model. As in Table 4.1, $\boldsymbol{\alpha}_{\mathbf{calc3}}$ were the CO_2 loading data of the newly derived Modified Kent-Eisenberg model.

As observed in $\boldsymbol{\alpha}_{\mathbf{calc3}}$ data and Figure 4.1 and 4.2, the values are in the range of 0.0 to 1.0 mol CO_2/mol MDEA, which is the acceptable range of CO_2 loading data. Besides that, the average error of 20.36% showed the predicted CO_2 loading data was more accurate and improved than the previous model as in the paper.

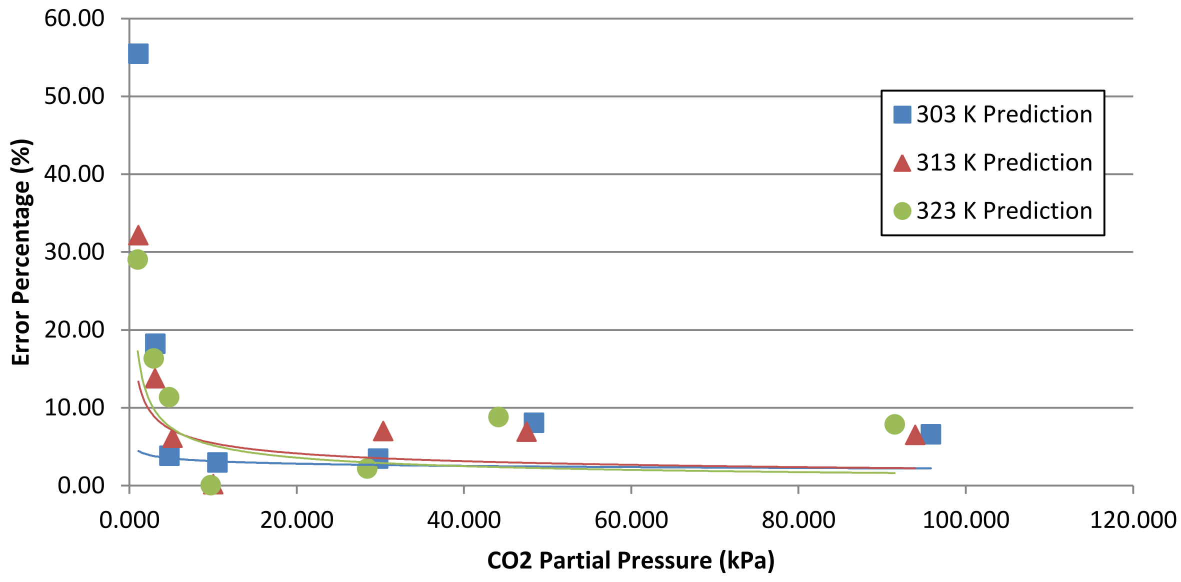


Figure 4.1: Error percentage of CO_2 loading, at 0.01 – 100 kPa CO_2 partial pressure, in aqueous 2M MDEA solution

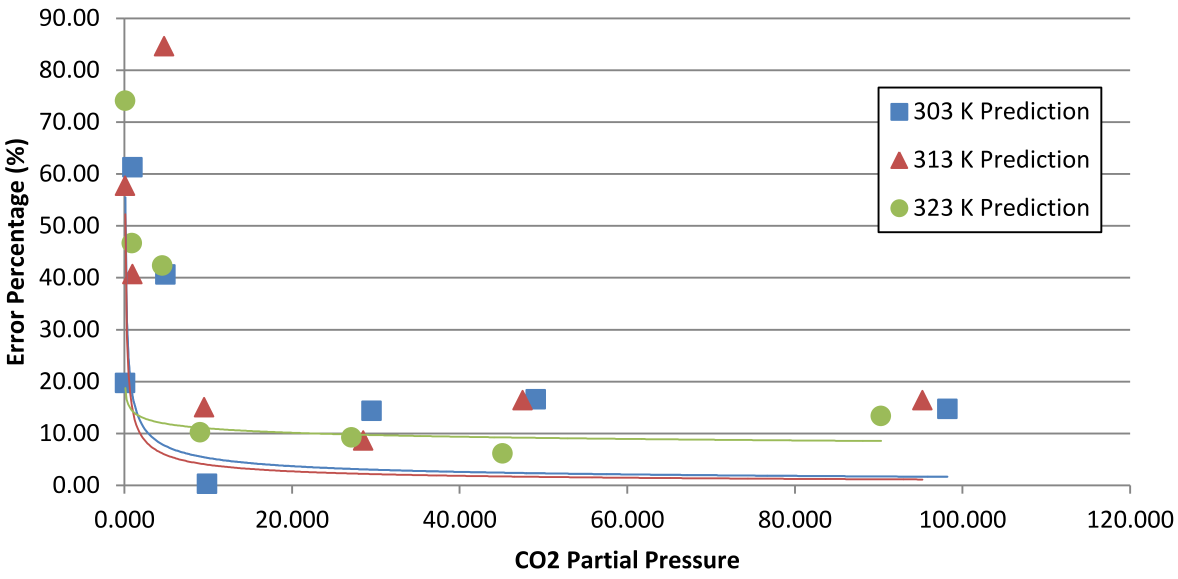


Figure 4.2: Error percentage of CO_2 loading, at 0.01 – 100 kPa CO_2 partial pressure, in aqueous 4M MDEA solution

With the aforementioned findings, it can be concluded that the newly derived Modified Kent-Eisenberg model has a better and improved performance compared to the model of the Haji-Sulaiman paper. Therefore, the former was selected as the prediction model for Modified Kent-Eisenberg model and used for the next modelling, using Xu et al. (1998) paper.

4.2 Modelling of Solubility Data at Higher Pressure

The MATLAB coding of Modified Kent-Eisenberg model was modelled at 3.04M, 3.46M, 4.28M concentration of aqueous MDEA solution, 313 – 373 K temperature and 10 – 1000 kPa CO_2 partial pressures. Table 4.2 shows the data generated from the modelling.

Table 4.2: Experimental and calculated CO_2 loading, based on Xu et al (1998)

M	**T (K)**	**$P_{CO2,e}$ (kPa)**	**$P_{CO2,c}$ (kPa)**	**Error percentage (%)**	**α_{expt} (mol/mol)**	**α_{calc2} (mol/mol)**	**Error percentage (%)**
4.28	313	15.40	19.50	26.62	0.269	0.258	3.93
		30.11	36.83	22.32	0.365	0.344	5.92
		203.00	221.90	9.31	0.705	0.661	6.13
		393.00	384.40	2.19	0.795	0.768	3.36
		838.00	772.40	7.83	0.881	0.864	1.94
	328	8.92	9.94	11.42	0.125	0.139	11.29
		32.12	35.78	11.39	0.248	0.252	1.52
		133.00	126.40	4.96	0.450	0.451	0.30
		301.00	297.40	1.20	0.618	0.594	3.81
		603.00	572.10	5.12	0.739	0.716	3.14
		855.00	725.30	15.17	0.778	0.771	0.81
		1013.00	921.50	9.03	0.813	0.796	2.05
	343	9.22	8.97	2.71	0.074	0.099	33.34
		29.32	28.15	3.99	0.140	0.172	23.08
		174.00	164.70	5.34	0.351	0.378	7.82
		389.00	388.70	0.08	0.509	0.512	0.55
		754.00	754.00	0.00	0.641	0.632	1.39
	353	3.27	3.32	1.62	0.030	0.047	53.91
		47.31	50.03	5.75	0.139	0.174	24.64
		207.80	211.00	1.54	0.299	0.338	12.88
		522.80	573.30	9.66	0.474	0.495	4.53
		867.80	890.40	2.60	0.561	0.577	2.78
	373	0.88	1.35	53.88	0.009	0.015	67.64
		11.87	16.01	34.88	0.037	0.058	57.15
		159.00	174.00	9.43	0.142	0.206	44.90
		519.00	590.40	13.76	0.274	0.349	27.32
		824.00	972.30	18.00	0.351	0.422	20.13
		Average		**10.73**	**Average**		**15.79**
3.46	328	115.00	113.10	1.65	0.502	0.486	3.25
		389.00	354.40	8.89	0.721	0.701	2.83

		401.00	396.40	1.15	0.741	0.706	4.67
		782.00	663.20	15.19	0.820	0.808	1.37
		992.00	832.70	16.06	0.849	0.839	1.14
	343	173.50	120.90	30.32	0.358	0.434	21.13
		278.50	278.80	0.11	0.512	0.515	0.62
		388.50	443.50	14.16	0.604	0.575	4.76
		608.50	703.00	15.53	0.693	0.657	5.23
		808.50	989.80	22.42	0.753	0.707	6.15
	353	169.80	106.60	37.22	0.251	0.359	43.23
		254.80	230.00	9.73	0.366	0.423	15.59
		364.80	324.10	11.16	0.427	0.484	13.39
		599.80	605.90	1.02	0.549	0.574	4.56
		794.80	1052.00	32.36	0.658	0.626	4.87
	363	147.50	98.67	33.11	0.174	0.282	61.84
		247.50	175.00	29.29	0.236	0.352	49.17
		357.50	317.90	11.08	0.319	0.409	28.23
		552.50	499.40	9.61	0.395	0.483	22.32
		737.50	758.00	2.78	0.473	0.535	13.19
		Average		**15.14**	**Average**		**15.38**
3.04	328	10.74	13.98	30.17	0.209	0.197	5.61
		18.85	17.11	9.23	0.232	0.255	9.86
		42.57	38.88	8.67	0.347	0.361	4.07
		85.57	75.51	11.76	0.464	0.473	1.87
		200.50	242.60	21.00	0.690	0.624	9.56
		288.50	409.90	42.08	0.779	0.688	11.68
		395.50	580.00	46.65	0.829	0.740	10.69
		595.50	956.00	60.54	0.886	0.802	9.53
		806.50	1286.00	59.45	0.911	0.841	7.71
	343	6.15	4.45	27.75	0.069	0.106	53.42
		12.33	8.39	31.95	0.098	0.149	52.13
		23.79	17.86	24.93	0.149	0.203	36.53
		70.17	57.01	18.75	0.274	0.329	20.42
		206.80	199.60	3.48	0.484	0.502	3.79
		281.80	328.20	16.47	0.582	0.558	4.12
		376.80	485.80	28.93	0.659	0.611	7.28
		581.80	759.10	30.47	0.740	0.689	6.89
		806.80	1042.00	29.15	0.791	0.744	5.89
		Average		**27.86**	**Average**		**14.50**

With the solubility data of CO_2 generated by the modelling, graphs of error percentage versus CO_2 partial pressures at different concentration and temperature were plotted for comparison and further discussion.

As in Haji-Sulaiman et al. (1998) paper, Modified Kent-Eisenberg model was fitted at lower CO_2 partial pressures, which ranged between 0.09 to 100 kPa. Therefore, it was expected for the model to be having higher relative error as the partial pressure increases.

In contrast, Figure 4.3, 4.4 and 4.5 clearly indicate that as the CO_2 partial pressure increases from 0.1 kPa to 1000 kPa, the error percentage of the modelling decreases significantly. Although it is a simple model, Modified Kent-Eisenberg model is considered good because it is able to extrapolate the prediction of solubility data at higher pressure with relatively low percentage of error.

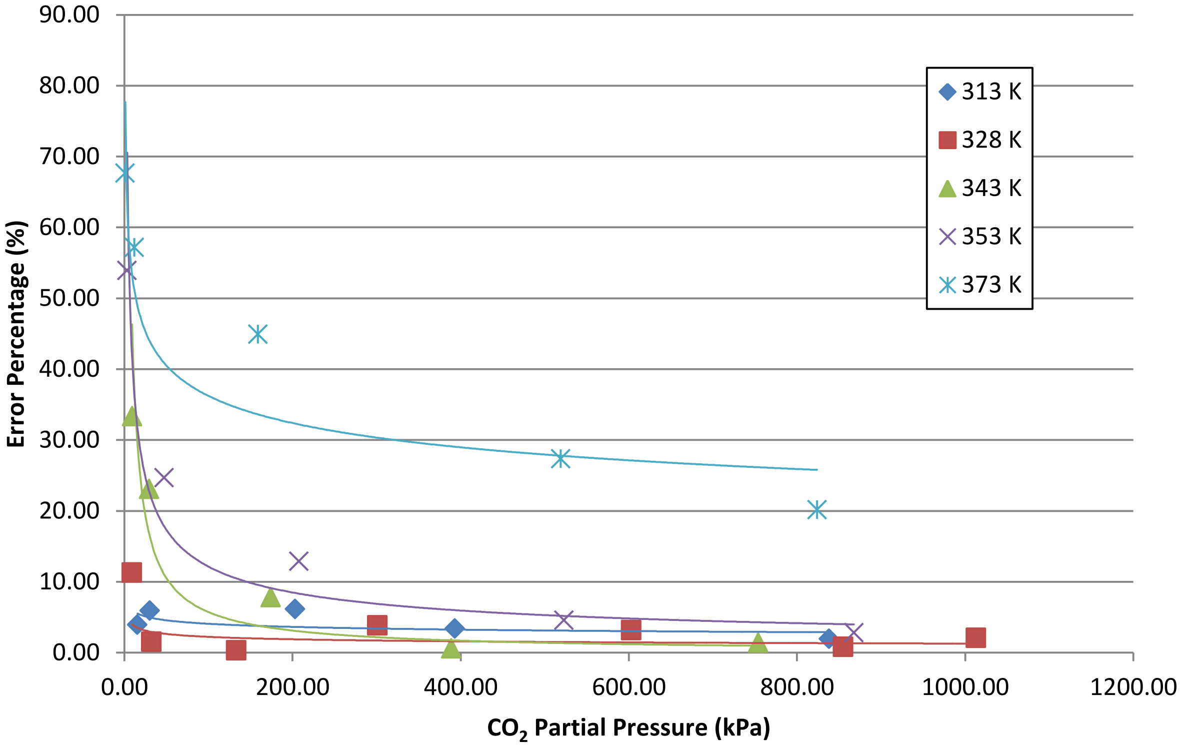


Figure 4.3: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, in 4.28 M aqueous MDEA solution

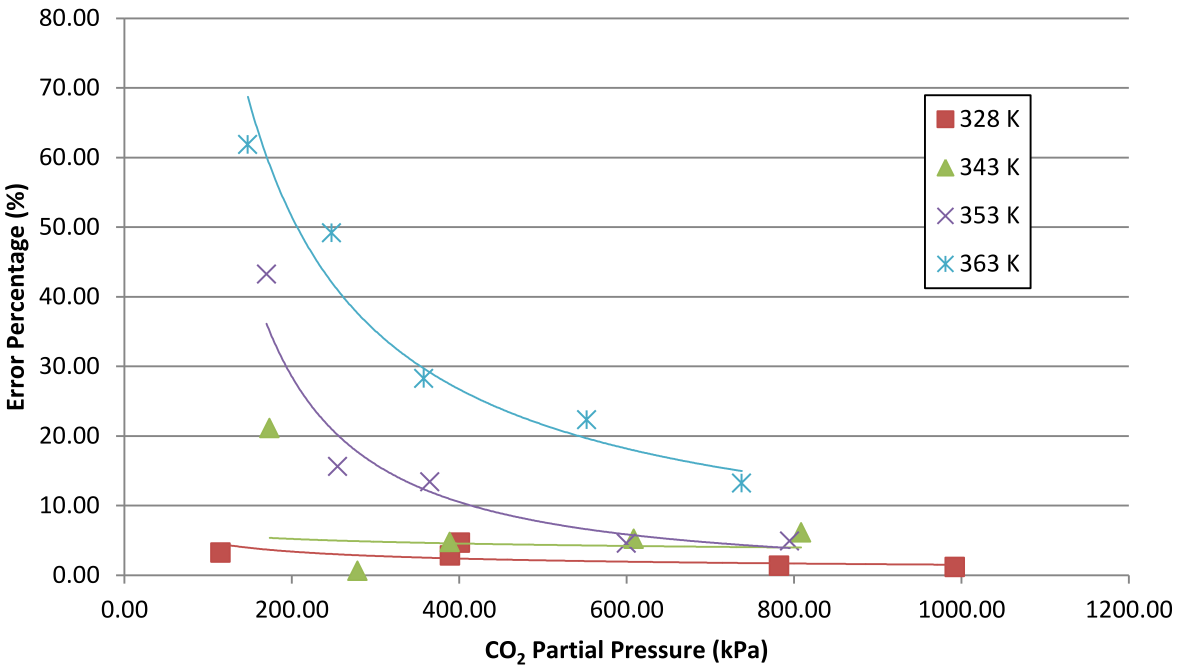


Figure 4.4: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, in 3.46 M aqueous MDEA solution

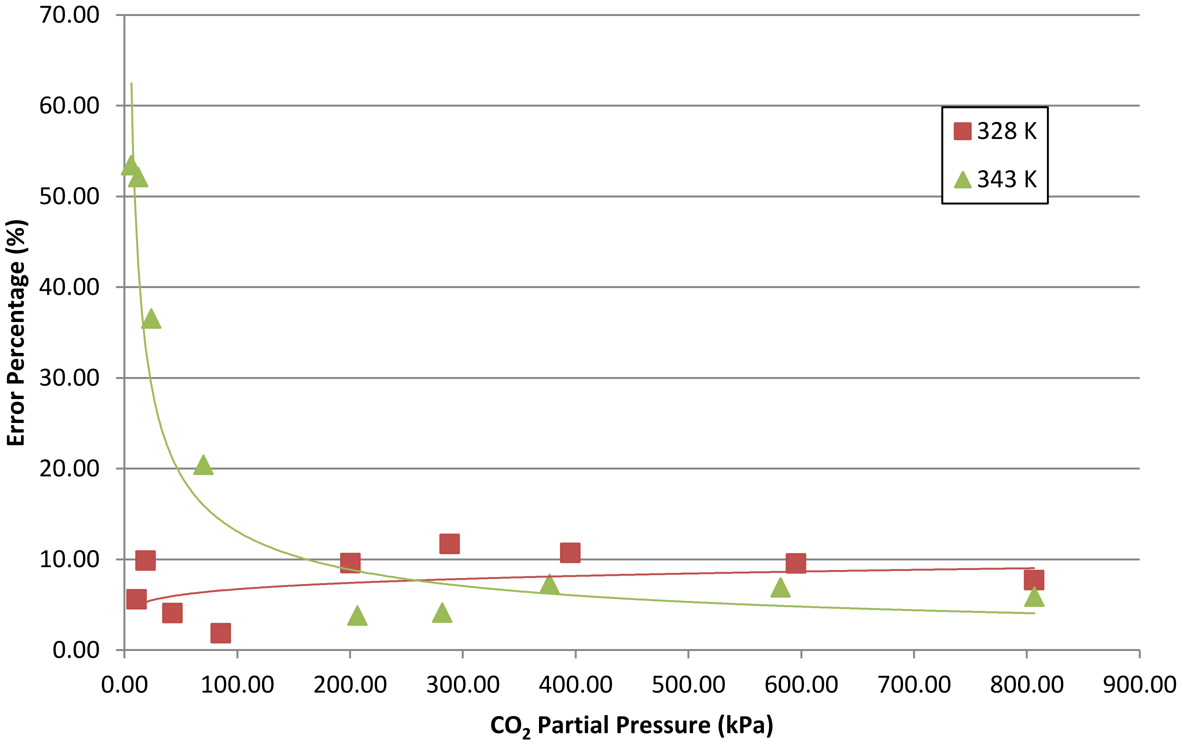


Figure 4.5: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, in 3.04 M aqueous MDEA solution

From the observation and findings, it is recommended that the refitting of the model with more data is conducted at higher CO_2 partial pressure. This is to give the modelling a better and improved accuracy of the prediction data.

From the observation of Figure 4.6, 4.7 and 4.8, it is interesting to note that the error percentage increases substantially as the temperature increases from 328 K to 353 K. Therefore, it is recommended that the model shall be reassessed to improve the prediction under higher temperature.

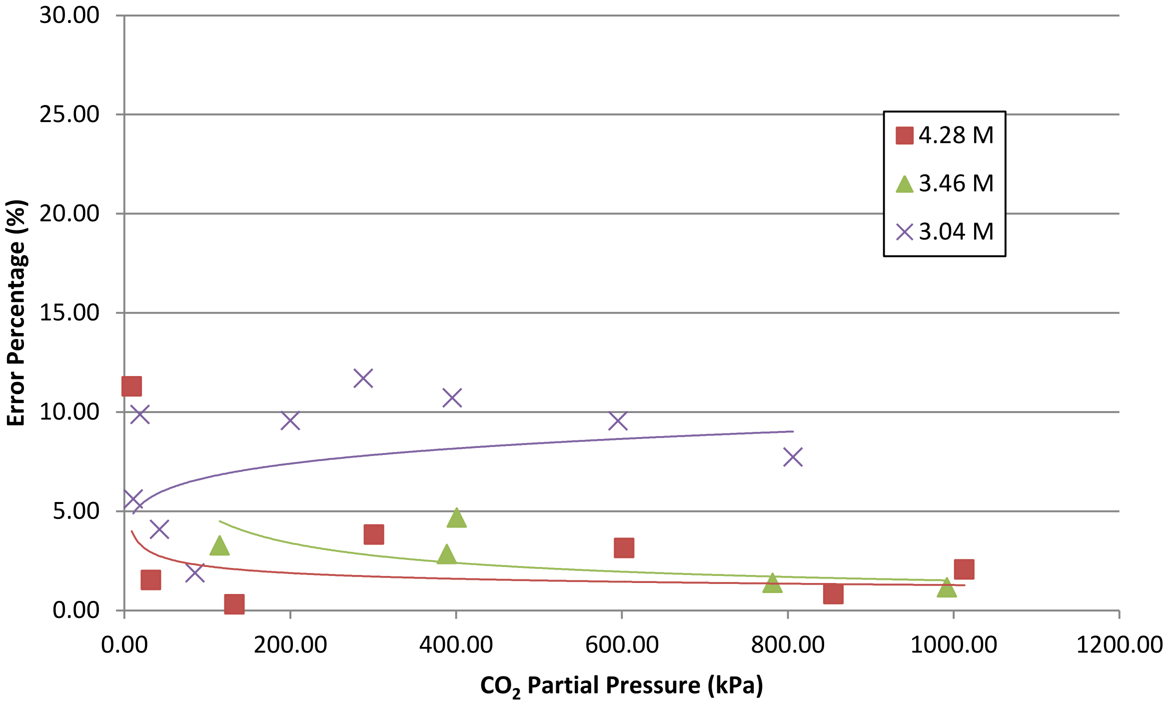


Figure 4.6: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, at temperature of 328 K

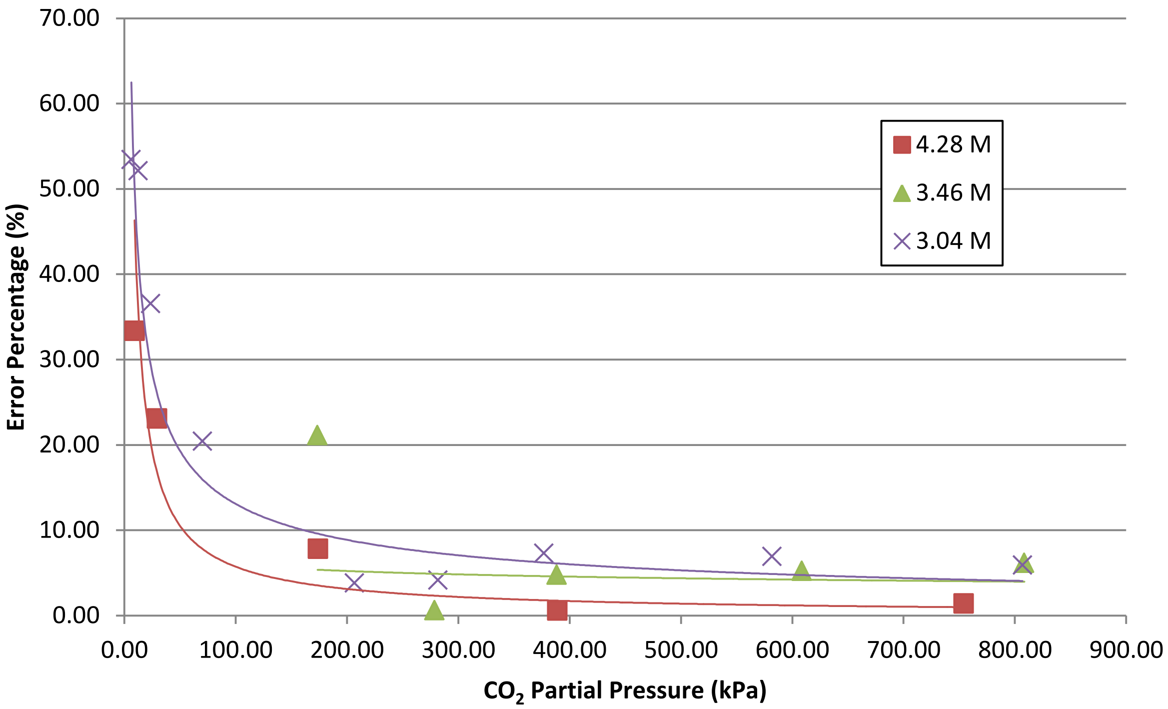


Figure 4.7: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, at temperature of 343 K

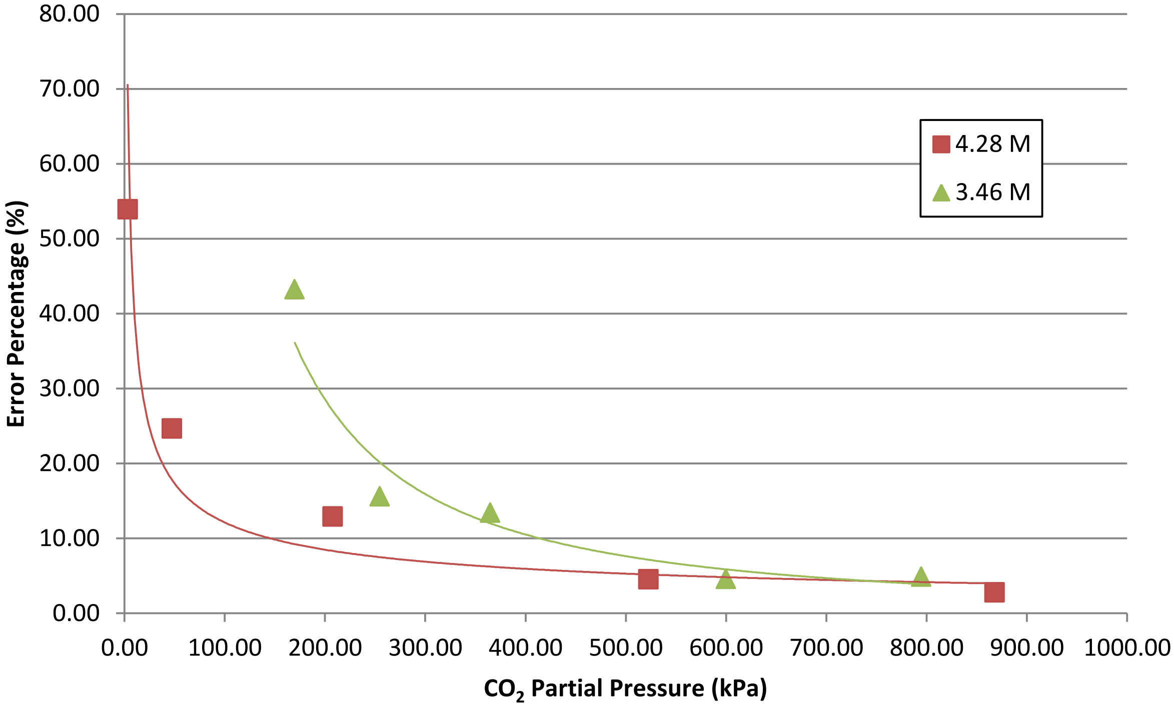


Figure 4.8: Error percentage of CO_2 loading, at 10 – 1000 kPa CO_2 partial pressure, at temperature of 353 K

From the results, it is more appropriate for the Modified Kent-Eisenberg model to be reassessed to improve its accuracy under higher temperature. Besides that, the regression for the parameters of g_i and k_i shall include the effect of temperature into the analysis of factor F_i.

In comparison with the thermodynamics model of Xu et al. (1998), the performance of Modified Kent-Eisenberg at higher pressure is considered better than the model as its average error of 15.22% is lower than Xu et al (1998), which yields 17.91% average error.

CHAPTER 5

CONCLUSION

The Modified Kent-Eisenberg model is considered able to give a good prediction of CO_2 solubility data in aqueous MDEA solution at 313 – 373 K, at higher CO_2 partial pressure ranged between 0.1 kPa – 1000 kPa. As the pressure increases from 0.1 kPa to 1000 kPa, the percentage of error decreases. It is recommended that the model is refitted with more solubility data at higher pressure in order to give a better and improved accuracy.

Besides that, it is interesting to note that Modified Kent-Eisenberg model gives higher percentage of error as the temperature increase from 328 K to 353 K. It is recommended that the model is reassessed in order to improve the accuracy of the prediction under higher temperature. Besides that, the regression for the parameters of g_i and k_i shall include the effect of temperature into the analysis of factor F_i.

In comparison with the thermodynamics model of Xu et al. (1998), the performance of Modified Kent-Eisenberg at higher pressure is considered better than Xu et al. (1998) as its average error of 15.22% is lower than Xu et al (1998), which yields 17.91% average error.

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APPENDIX I: MATLAB CODING OF MODIFIED KENT-EISENBERG MODEL

```
%function [alpha] = co2mdea(PCO2, T, RRNH)
%co2mdea calculates CO2 loading in aqueous MDEA
%   alpha = CO2 Loading (mol/mol)
%   PCO2 = CO2 Partial Pressure (kPa)
%   T = temperature (K)
%   RRNH = MDEA concentration (mol/L)

%   Reference: Haji-Sulaiman et al (1998) Analysis of Equilibrium Data of
%   CO2 in Aqueous Solutions of DEA, MDEA and Their Mixtures using the
%   Modified Kent-Eisenberg Model, Trans IChemE, Vol 76, Part A, 961-968.

%   Inputs
% Data Lee 12 13
clc

PCO2=91.514/101.32;       % CO2 Partial Pressure (atm/101.32kPa)
T= 323;                   % temperature in Kelvin
RRNH= 2;                  % RR'NH


% Constants
a1=-8483.95;
b1=-13.8328;
c1=0;
d1=87.39717;

a3=-12092.1;
b3=-36.7816;
c3=0;
d3=235.482;

a4=-12431.7;
b4=-35.4819;
c4=0;
d4=220.067;

a5=-13445.9;
b5=-22.4773;
c5=0;
d5=140.932;

a6=-6789.04;
b6=-11.4519;
c6=-0.010454;
d6=94.4914;

g=-0.03628;
j=0;
k=0.6262;
```

```
%   Equations
K1=exp((a1/T)+(b1*log(T))+(c1*T)+d1);
K3=exp((a3/T)+(b3*log(T))+(c3*T)+d3);
K4=exp((a4/T)+(b4*log(T))+(c4*T)+d4);
K5=exp((a5/T)+(b5*log(T))+(c5*T)+d5);
HCO2=exp((a6/T)+(b6*log(T))+(c6*T)+d6);

F1=(g*log(PCO2))+(k*log(RRNH));
K1p=K1*F1;

A=1;
B=RRNH+K1p;
C=(K3*PCO2/HCO2+K5);% change sign and divide with HCO2
D=-(2*K3*K4*(PCO2/HCO2)+K1p*K5+K1p*K3*(PCO2/HCO2)); % change sign
E=-2*K1p*K3*K4*(PCO2/HCO2); % add K4

PN=[A B C D E];
HR=roots(PN);   % [H+]

for i=1:4;
H=HR(i);
alpha=(PCO2/HCO2)*((H.^2)+(K3*H)+K3*K4)/((H.^2)*RRNH+(K3*H*(PCO2/HCO2))+2*K3*
K4*(PCO2/HCO2));
alphar(i)=alpha;
end

H=HR'
alphar
```

APPENDIX II: RE-DERIVATION OF MODIFIED KENT-EISENBERG MODEL

In understanding the Modified Kent-Eisenberg model, it is important to have overview knowledge on the mechanism of the process. An equilibrium solution of CO_2 in aqueous solution of alkanolamine is governed by the following set of equations:

$$RR'NH_2^+ \overset{K_1}{\Leftrightarrow} RR'NH + H^+ \qquad (1)$$

$$RR'NCOO^- + H_2O \overset{K_2}{\Leftrightarrow} RR'NH + HCO_3^- \qquad (2)$$

$$CO_2 + H_2O \overset{K_3}{\Leftrightarrow} HCO_3^- + H^+ \qquad (3)$$

$$HCO_3^- \overset{K_4}{\Leftrightarrow} CO_3^= + H^+ \qquad (4)$$

$$H_2O \overset{K_5}{\Leftrightarrow} OH^- + H^+ \qquad (5)$$

Equation (1) represents the protonation of amine, equation (2) corresponds to the hydrolysis of carbamate and is only considered in systems consisting of primary and secondary amines. Equations (3), (4) and (5) are the ionization reactions for the different species in the solutions.

In addition to the above equations, the following set of conditions must also be satisfied:

Amine balance:

$$[RR'NH]_t = [RR'NH]_e + [RR'NH^+_2]_e + [RN'NCOO^-]_e \qquad (6)$$

CO_2 balance:

$$\alpha[RR'NH]_t = [HCO^-_3]_e + [RR'NCOO^-]_e + [CO^=_3] + P_{CO_2}/H_{CO_2} \qquad (7)$$

Charge balance:

$$[RR'NH^+_2]_e = [HCO^-_3]_e + [RR'NCOO^-]_e + 2[CO^=_3]_e \qquad (8)$$

where α is the gas loading. The concentration of carbon dioxide in the liquid phase can be estimated from Henry's law, i.e.

$$P_{CO_2} = H_{CO_2}[CO_2] \qquad (9)$$

For MDEA solutions, no stable carbamates are formed. Thus, reaction (2) does not exist in the system and $RR'NCOO^-$ was omitted in the charge and mass balance equations. Thus for this system, equation (1) – (9) can be reduced to a single polynomial equation in terms of the concentrations of hydrogen ions, $[H^+]$, and the equilibrium constants as follows:

$$A'[H^+]^4 + B'[H^+]^3 + C'[H^+]^2 + D'[H^+] + E' = 0 \qquad (13)$$

where

$A' = 1$

$B' = [RR'NH] + K'_{1,MDEA}$

$C' = K_3\,(P_{CO2}/H_{CO2}) + K_5$

$D' = -\,(2K_3K_4\,(P_{CO2}/H_{CO2}) + K'_{1,MDEA}\,K_5 + K_{1,MDEA}\,K_3\,(P_{CO2}/H_{CO2}))$

$E' = -\,2K'_{1,MDEA}\,K_3\,K_4\,(P_{CO2}/H_{CO2})$

Consequently, the total CO_2 loading, α, can be expressed as:

$$\alpha = \frac{\frac{P_{CO2}}{H_{CO2}}\left([H^+]^2+K_3[H^+]+K_3K_4\right)}{[H^+]^2[RR'NH]+K_5[H^+]-[H^+]^3+K_3[H^+]\left(\frac{P_{CO2}}{H_{CO2}}\right)+2K_3K_4\left(\frac{P_{CO2}}{H_{CO2}}\right)} \qquad (14)$$