

Evaluation of Modified Kent-Eisenberg Model to Predict Carbon Dioxide Solubility in Methyldiethanolamine (MDEA) Under Extended Operating Conditions

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(IR Dr Abdul Halim Shah Maulud)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

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.

ADIFF NAFILLAH AZLIZAH BINTI HAMZAH

ABSTRACT

The aim of this study is to evaluate the reliability of Modified Kent-Eisenberg model for predicting the carbon dioxide (CO₂) solubility in methyldiethanolamine (MDEA) under wider range of carbon dioxide partial pressure. Model from Haji-Sulaiman et. al. (1998) is used as the reference in this work. The model is re-evaluated by re-deriving the equations used in the paper. The re-derived equation is verified by using the equation taken from Pahlavanzadeh et. al. (2010). Data from Haji-Sulaiman et. al (1998) is fitted into the model to validate the model. The modified model is then applied in MATLAB to obtain the solubility data of carbon dioxide in 3.04-4.28 kmol/m³ aqueous MDEA solutions at temperature ranging from 313K to 373K and CO₂ partial pressures ranging from 0.876 to 1013 kPa, with reference to Xu et. al. (1998). The maximum error obtained from the model is 16.585% which is at 4.28M MDEA. The parameters in non-ideality equation are re-regressed and the new values for the parameters g and k generated are -0.0458 and 0.6772 respectively. The new model which use the new parameters are fitted once again to the experimental data and the results shows decrease in errors with maximum error of 14.739% at 3.46M MDEA. Data from Jou et. al. (1982) which range from 2-4M aqueous MDEA solution, temperature from 298K to 393K, and CO₂ partial pressure from 0 to 6630 kPa are fitted to both models to further test their performance. The results once again show that the new model performs better in predicting the CO₂ solubility in aqueous MDEA solution.

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ABBREVIATION AND NOMENCLATURES

Abbreviation

CO ₂	Carbon dioxide
MDEA	Methyldiethanolamine

Nomenclature

α	CO ₂ loading (mol CO ₂ /mol MDEA)
F	Factor in apparent equilibrium constant
H	Henry's constant
K	Equilibrium constant
K'	Apparent equilibrium constant
M	Molarity (mol/L or kmol/m ³)
P	Partial pressure (kPa)
T	Temperature (K)

CHAPTER 1

INTRODUCTION

1.1 Background Study

Raw natural gases extracted from oil well contain primarily different types of hydrocarbon as well as contaminants. Carbon dioxide (CO₂) and hydrogen sulfide (H₂S) content in raw natural gas makes the gas become an acid gas. The raw natural gas must be treated to reduce impurities to acceptable level before it can be use.

The process of removing CO₂ and H₂S from natural gas is called sweetening process because the odour of the processed products is improved by the absence of hydrogen sulfide. The most common method used for sweetening process is amine gas treating. Amine has a natural affinity for both CO₂ and H₂S allowing this process to be a very efficient and effective removal process. Alkanolamine can be 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 as well as a new class of amines known as sterically hindered amines that have been introduces a few years ago. Monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanolamine (AMP) are the examples of these amines respectively.

Several models have been developed to analyze the solubility of CO₂ in aqueous solution of alkanolamine and to predict the total CO₂ loading. Some of the well-known models that have been used widely are the electrolyte-NTRL model of Chen and Evans (1986), Deshmukh and Mather model (1981) and also Kent and Eisenberg model (1976). The first two models were developed based on sound thermodynamic principles. Non idealities of solution are taken into consideration by allowing long and short range interactions between the different species that are

present. The Kent and Eisenberg model is the simplest among these where the non idealities that are present in the system are lumped together into the K values.

Haji-Sulaiman, Aroua & Benamor (1998) used Modified Kent-Eisenberg model to make an analysis of equilibrium data on CO₂ in aqueous solutions of DEA, MDEA and their mixtures of various temperature and low CO₂ pressure (0.09-100 kPa). Following Hu & Chakma (1990), the apparent equilibrium constant, K_i' are taken to be dependent on the partial pressure of CO₂ and the amine concentration in the solution. A factor F_i is introduced which takes into account the effects of CO₂ partial pressure and the amine concentration. The Modified Kent-Eisenberg model has been proved to give relatively good prediction on the total CO₂ loading in the solution. However, there is no modeling prediction was developed using this model to predict the solubility of CO₂ at higher operating pressure around 100 – 1000 kPa.

The purpose of this paper is to apply the Modified Kent-Eisenberg model to predict CO₂ solubility in MDEA at higher operating pressure and evaluate the performance of the established model with other available data such as Xu, Zhang, Qin, Gao & Liu (1998) based on error analysis.

1.2 Problem Statement

Haji-Sulaiman et. al.(1998) used Modified Kent-Eisenberg model to predict the CO₂ loading in aqueous solutions of DEA, MDEA and their mixtures on various temperature and low CO₂ pressure (0.09 – 100kPa). Referring to the same equations of equilibrium, it is observed that total CO₂ loading equation in the work showed some discrepancy with the total CO₂ loading equation in Pahlavanzadeh, Jahangiri & Noshadi (2011). The motivation of the studied system is to evaluate the Modified Kent-Eisenberg model by deriving the total CO₂ loading equation as well as predict and analyze the CO₂ solubility in MDEA at higher operating pressure (100 – 1000 kPa). In order to improve the Modified Kent-Eisenberg model, the parameters of non-idealities equation will be regressed again if necessary.

1.3 Objectives

1. To predict the CO₂ solubility at higher operating pressure around 100 – 1000 kPa based on the revised model.
2. To improve the model by re-regressing the parameters of non-ideality equation.

1.4 Scope of Study

This research paper mainly emphasizes on the solubility of CO₂ in MDEA solution. The total CO₂ loading equation will be derived by using the Modified Kent-Eisenberg model. The modified model will be evaluated in order to study the total CO₂ loading in the solution. Error analysis is used to evaluate the modified model by comparing the calculated total CO₂ loading data with the experimental data. Regression of parameters of non-ideality equation will be done by using MATLAB software.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide

Carbon dioxide (CO₂) is a chemical molecule consisting of one carbon atom covalently bonded to two oxygen atoms. At atmospheric pressure and temperature, CO₂ is a colourless, odourless gas that exists naturally as a trace gas in the Earth's atmosphere. Carbon dioxide is produced by combustion of coal or hydrocarbons, the fermentation of sugars in beer and winemaking and by respiration of all living organisms. It is exhaled in the breath of humans and land animals. It is emitted from volcanoes, hot springs, geysers and other places where the earth's crust is thin and is freed from carbonate rocks by dissolution. CO₂ is also found in lakes at depth under the sea, and commingled with oil and gas deposits. (Energy Institute, Global Carbon Capture and Storage Institute, 2010)

At standard temperature and pressure, the density of CO₂ is around 1.98 kg/m³, about 1.5 times that of air. Figure 1 shows the phase diagram of CO₂. Pure CO₂ exhibits triple point behaviour dependent on the temperature and pressure. The point at the pressure 5.11 atm and temperature -56.7°C is called the triple point; the temperature and pressure where three phases (gas, liquid and solid) can exist simultaneously in thermodynamic equilibrium. The solid-gas phase boundary is called the sublimation line, as a solid changing state directly into a gas is called sublimation. Physically, this boundary implies that the gas and solid can co-exist and transform back and forth without the presence of liquid as an intermediate phase at -78.5°C. In its solid state, CO₂ is commonly called dry ice. Above the critical point (73.8 atm and 31.1°C), the liquid and gas phases cannot exist as separate phases, and liquid phase CO₂ develops supercritical properties, where it has some characteristics of a gas and others of a liquid.

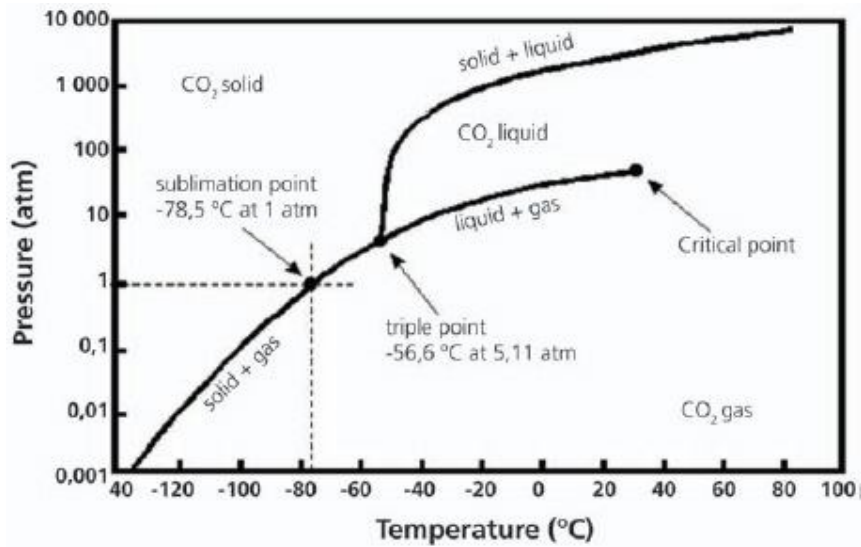


Figure 1 Carbon dioxide phase diagram

CO₂ is widely used commercially by the food industry, oil industry and chemical industry. In the food and beverage industries, CO₂ is used for carbonation of fizzing beverages, for packaging of foodstuffs, as a cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the distribution of foodstuffs. It is also commonly used as the most commonly used compressed gases for pneumatic (pressurized gas) systems in portable pressure tools. CO₂ uses in the chemicals processing industries includes reactor temperatures controlling, alkaline effluents neutralization and also for purifying or dyeing polymer, animal or vegetal fibres.

Despite its wide applications, CO₂ is an important greenhouse gas, warming the Earth's surface to a higher temperature by reducing outward radiation. Burning of carbon-based fuels since the industrial revolution has rapidly increased concentrations of atmospheric carbon dioxide, increasing the rate of global warming and causing anthropogenic climate change. It is also a major source of ocean acidification since it dissolves in water to form carbonic acid, which is a weak acid as its ionization in water is incomplete (National Research Council, 2010).

Removal of carbon dioxide from natural gas or flue gas (also called carbon dioxide removal) is an important process in gas processing plants. CO₂ 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 (Astarita, Savage, & Longo, 1981). Natural gas pipelines usually permit from 1% to 2% of CO₂ and sometimes as high as 5% (Buckingham, 1964). The process of removing CO₂ and H₂S from acid gas is called sweetening process as it removes the sour odour of the gas due to the presence of H₂S. On the other hand, CO₂ capture in the flue gas is significant to reduce the amount of CO₂ emission to the atmosphere and consequently reduce the greenhouse effect.

2.2 Alkanolamines and methyldiethanolamine (MDEA)

Alkanolamine; a sub-classification of amine is a chemical compound made of hydroxyl functional group (-OH) and amino (-NH₂, -NHR, and -NR₂) functional groups attached on an alkane backbone. Depending on the number of alkyl group(s) attached to the nitrogen atom in the structure of the molecule, alkanolamine can be classified into primary, secondary and tertiary amine. In addition to the classes, a new class of amine known as sterically hindered amine has been introduced afterwards. Monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and 2-amino-2-methyl-1-propanolamine (AMP) are the examples of these amines respectively.

Aqueous solutions of alkanolamines have been the main choice in the industries to remove CO₂ from process streams. Primary and secondary amines generally exhibit low CO₂ loadings (mol of captured CO₂/mol of amine) and high rate of absorption. In contrast, tertiary amine such as MDEA shows high CO₂ loadings and low rate of absorption. Among all the alkanolamines, MDEA is the most common amine used in sweetening process, largely because of its high capacity and excellent flexibility to meet process requirement. In addition, due to the lower heat of reaction with CO₂, MDEA has been the alternative to MEA for bulk CO₂ removal (Kohl & Nielsen, 1998).

MDEA is a clear, colourless or pale yellow liquid with an ammonia odour. MDEA is also known as N-Methyl diethanolamine and has the formula of CH₃N(C₂H₄OH)₂. Figure 2 shows the molecular structure of MDEA.

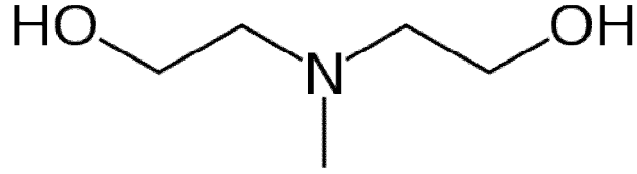


Figure 2 Molecular structure of MDEA

The absorption of CO_2 in aqueous solution of alkanolamine involves physical absorption together with chemical reaction which fixed the CO_2 in the solution as carbonates, bicarbonates and carbamates depending on the type of amine being used (Danckwerts & McNeil, 1967). An equilibrium solution of CO_2 in aqueous MDEA solution is governed by the following set of equations (Kohl & Nielsen, 1998):

Protonation of amine:



Ionization reaction:



In addition, the following balances must hold:

Amine balance:

$$[\text{MDEA}]_t = [\text{MDEA}] + [\text{MDEAH}^+] \quad (5)$$

CO_2 balance:

$$\alpha [\text{MDEA}]_t = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] \quad (6)$$

Charge balance:

$$[\text{H}^+] + [\text{MDEAH}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (7)$$

where α is the gas loading.

In addition, the concentration of CO₂ in liquid phase can be estimated from Henry's Law, i.e

$$P_{CO_2} = H_{CO_2}[CO_2] \quad (8)$$

2.3 Modified Kent-Eisenberg model

Vapor-liquid equilibrium (VLE) modeling of gas-aqueous amine systems is critical for synthesis, design and analysis of gas sweetening plant. Existing VLE models can be broadly divided into two main classes: empirical models based on the model of Kent and Eisenberg and activity coefficient-based models (Patil, Malik, & Jobson, 2006). The simplest model is Kent and Eisenberg (1976) where the non-idealities that are present in the CO₂ – aqueous amine system are lumped together into pseudo equilibrium constants for the main reaction as a function of temperature. This model assumes that all the activity coefficients and fugacity coefficients to be unity and forces a fit between experimental and predicted values by treating the main reaction equilibrium constants as variables. However, the developed model is only applicable to primary and secondary amine. Jou et. al. (1982) later reported that the equilibrium constants depend on temperature, concentration of amine and also the amine loading.

Hu & Chakma (1990) used Kent-Eisenberg model to analyze the solubility of CO₂ in AMP solution, in which case no carbamate ions are formed. However, the Kent-Eisenberg model used in the paper is modified by including the free gas concentration in the solution and the amine concentration in the expression for the equilibrium constant for the protonation of amine. Kritpiphat & Tontiwachwuthikul (1996) also proved that the hydrolysis of carbamate ion is not important by performing sensitivity analysis using this model, hence ignored the reaction in the system. Haji-Sulaiman et. al. (1998) also use Modified Kent-Eisenberg model to analyze the equilibrium data on the absorption of CO₂ in aqueous solutions of DEA, MDEA and their mixtures at various temperature (303 – 323 K) and CO₂ partial pressure (0.09 – 100 kPa).

In Haji-Sulaiman et. al. (1998), the apparent equilibrium constants, K_i' for protonation of amine and hydrolysis of carbamate are taken to be dependent on the

partial pressure of CO₂ and the amine concentration in the solution. To accommodate this equilibrium constant, a factor F_i is introduced which takes into account the effects of CO₂ partial pressure and the amine concentration. Thus

$$K_i' = K_i F_i \quad (9)$$

where K_i is the equilibrium constant at infinite dilution

The dependency of K_i and Henry's constant, H with temperature is expressed as

$$K_i \text{ (or } H) = e^{(a_i/T + b_i \ln T + c_i T + d_i)} \quad (10)$$

where a_i to d_i are constants. Table 1 shows the values of these constants for all the reactions (1) to (4) and that for the Henry's constant taken from Little, Bos, & Knoop (1990) and Edwards, Maurer, Newman, Prausnitz (1978).

Table 1 Values of constants used in equation (10)

Parameter	a	b	c	d	Range of validity (°C)
K₁	-8483.95	-13.8328	0	-48.7594	20-60
K₂	-12092.1	-36.7816	0	235.482	0-225
K₃	-12431.7	-35.4819	0	220.067	0-225
K₄	-13445.9	-22.4773	0	140.932	0-225
H_{CO2}	-6789.04	-11.4519	-0.010454	94.4914	0-225

According to Haji-Sulaiman et. al.(1998), F is defined in a general form as

$$F_i = e^{\left(\frac{f_i}{P_{CO_2}} + g_i P_{CO_2} + h_i P_{CO_2} + \frac{j_i}{[RR'NH]} + k_i \ln[RR'NH] + m_i [RR'NH] \right)} \quad (11)$$

In order to derive the total CO₂ loading equation, all the unknowns $[MDEAH^+]$, $[MDEA]$, $[H^+]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[OH]$, $[CO_2]$, and K_i' must be determined first. Equations (1) to (8) are reduced, for aqueous solution of MDEA, to a single polynomial equation in terms of the concentration of hydrogen ion, H^+ . Haji-Sulaiman et. al. (1998) expresses the equation as

$$A[H^+]^4 + B[H^+]^3 + C[H^+]^2 + D[H^+] + E = 0 \quad (12)$$

where

$$A = 1$$

$$B = [MDEA] = K'_1$$

$$C = -(K_2 P_{CO_2} + K_4)$$

$$D = \left(2K_2 K_3 \frac{P_{CO_2}}{H_{CO_2}} + K'_1 K_4 + K'_1 K_2 \frac{P_{CO_2}}{H_{CO_2}} \right)$$

$$E = -2K'_1 K_2 \frac{P_{CO_2}}{H_{CO_2}}$$

There are four possible roots of equation (12). However, only one value of $[H^+]$ is valid and this can be obtained by limiting the range of $[H^+]$ between 10^{-6} and 10^{-12} kmol/m³ which corresponds to the pH of 7 and 11 respectively for the aqueous solutions of carbonated and fresh amine. In addition, the total CO₂ loading is expressed as

$$\alpha = \frac{([MDEA] + K'_1) \left(1 - \frac{K_2 P_{CO_2} + K_4}{[H^+]} \right) \frac{P_{CO_2}}{[H^+] H_{CO_2}} + \frac{P_{CO_2}}{H_{CO_2}}}{[MDEA]} \quad (13)$$

Finally, they showed that only g and k are important parameters in F for the protonation of amine equilibrium. Based on their analyses, F is finally expressed as

$$F = g \ln P_{CO_2} + k \ln [RR'NH] \quad (14)$$

for the protonation of amine.

The values of these parameters that best fit the observed data with mean residual squares equal to 6.3×10^{-4} for aqueous solutions of MDEA are given in Table 2.

Table 2 Generated parameter for equation (14)

Parameter	g	k
F_{1,MDEA}	-0.03628	0.6262

Referring to Pahlavanzadeh et. al. (2010), the amine used for the modeling is 2-amino-2-methyl-1-propanol (AMP). However, the derivation of equation in this paper can also be used as reference as there is also no formation of carbamate in AMP-CO₂ equilibrium reaction. Despite the same procedures used in determining the total CO₂ loading equation, the polynomial equation used in the work is different

compared to Haji-Sulaiman et. al. (1998). In Pahlavanzadeh's paper, the parameters A to E for equation (12) are stated as follow:

$$A = 1$$

$$B = [AMP] + K'_1$$

$$C = -\left(K_2 \frac{P_{CO_2}}{H_{CO_2}} + K_4\right)$$

$$D = -\left(2K_2K_3 \frac{P_{CO_2}}{H_{CO_2}} + K'_1K_4 + K'_1K_2 \frac{P_{CO_2}}{H_{CO_2}}\right)$$

$$E = -2K'_1K_2K_3 \frac{P_{CO_2}}{H_{CO_2}}$$

The discrepancies in the equation as compared to Haji-Sulaiman (1998) can be found in the C, D and E terms. Finally, the total CO₂ loading equation is shown as:

$$\alpha = \frac{[CO_2] + [HCO_3^-] + [CO_3^{2-}]}{[AMP]} \quad (15)$$

2.4 Experimental data of gas-liquid equilibrium in CO₂-MDEA-H₂O system

The experimental data used in this work to validate the developed model is taken from Haji-Sulaiman et. al. (1998). The data used for the model validation are obtained from their experiments in 2M and 4M aqueous MDEA solutions at temperature ranging from 303 to 323K and CO₂ partial pressures ranging from 0 to 100 kPa.

In order to estimate the reliability of developed model at extended operating pressure, the experimental data from Xu, Zhang, Qin, Gao & Liu (1998) is used. The solubility data of CO₂ from Xu et. at (1998) are obtained from their experiment in 3.04-4.28 kmol/m³ aqueous MDEA solutions at temperature ranging from 313K to 373K and CO₂ partial pressures ranging from 0.876 to 1013 kPa.

For further research to evaluate the performance of the developed model using the current parameters taken from Haji-Sulaiman et. al (1998) compared to the new regressed parameters in this paper, wider range of data is used with reference to Jou, Mather and Otto (1982). The paper provides the experimental data for CO₂

solubility in 2M and 4M aqueous MDEA solutions at temperature ranging from 298 to 393K and CO₂ partial pressure ranging from 0 to 6630 kPa.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

3.1.1 Programming Software

The project is only related to theoretical work with no experimental work to be conducted and focuses on programming activities. The main programming software used for the development of Modified Kent-Eisenberg model and the re-regression of parameters in this project is MATLAB R2011.

For the development of Modified Kent-Eisenberg model, the derived equation obtained will be coded in the MATLAB. Given the concentration of MDEA, CO₂ partial pressure and temperature as the input parameters, the MATLAB will generate the possible $[H^+]$ and total CO₂ loading values. However, the valid value of $[H^+]$ can be obtained by limiting the range of $[H^+]$ between 10^{-6} and 10^{-12} kmol/m³.

The re-regression of parameters for equation (14) will use the optimization command in MATLAB software as well. The command that will be use is *fminunc* which usually used for unconstrained nonlinear optimization.

3.1.2 Program Development

The first phase in this project is to derive the total CO₂ loading equation by using Modified Kent-Eisenberg model. The equations used to derive the total CO₂ loading equation are equation (1) to (7) as described in literature review section. In order to derive the total CO₂ loading equation, a polynomial equation in terms of the concentrations of hydrogen ions, $[H^+]$ need to be derived first. The main reference for the equations derivation is Haji-Sulaiman et. al. (1998). However, the derived

equation is also compared to other paper which is Pahlavanzadeh et. al. (2010) to ensure the derivation is valid. To develop the Modified Kent-Eisenberg model, the derived equation will be programmed in MATLAB software.

3.1.3 Model Validation

After the model is developed, the validation of model is done by using experimental data from Haji-Sulaiman et. al (1998). The input data are fitted into the developed model and the predicted CO₂ loading will be compared to the experimental CO₂ loading. The developed model is accepted if it yields less than 30% of error percentage. The calculation of error percentage is shown as below:

$$Error (\%) = \left| \frac{\alpha_{pi} - \alpha_{expi}}{\alpha_{expi}} \right| \times 100\%$$

where,

α_{exp} = experimental CO₂ loading

α_p = predicted CO₂ loading

If the average error obtained is greater than 30%, the developed model will be revised and improved until the error percentage is within accepted range; i. e less than 30%.

3.1.4 Model performance for extended operating parameters

The validated model will be used in predicting the solubility of CO₂ at higher temperature and CO₂ partial pressure with reference to Xu et. al. (1998). The solubility data of CO₂ from Xu et. at (1998) are obtained from their experiment in 3.04 to 4.28 kmol/m³ aqueous MDEA solutions at temperature ranging from 313 to 373K and CO₂ partial pressures ranging from 0.876 to 1013 kPa. The calculated data will be compared to the experimental data in order to determine the performance of the model at extended operating conditions. The error analysis will be the same as the described in part 3.1.3.

3.1.5 Re-regression of parameters

To improve the model, re-regression of the parameters in equation (14) will be done. The regression will be done using optimization command in MATLAB software where the calculated data will be fitted together with the experimental data. Command *fminunc* will be used to minimize the difference between the calculated data and the experimental data by manipulating the parameters in equation (14). *fminunc* command is widely used for unconstrained linear optimization with purpose to find minimum of unconstrained multivariable function, in this case the sum square error between the experimental data and calculated data. 107 experimental data are collected from Haji-Sulaiman et. al. (1998) and Xu et. al. (1998) for the regression purpose.

3.1.6 Evaluation of new regressed parameters

By fitting the new regressed parameters into the developed model, the improved model is used to determine the CO₂ loading with reference to Haji-Sulaiman et. al (1998) and Xu et. al. (1998) once again. The evaluation of the improved model is done by comparing the error percentage of the improved model to the error percentage of the previous model (which use the old parameters).

For further performance evaluation, both previous and improved model are applied to experimental data from Jou et. al. (1982). The error percentage are once again calculated to compare the performance of both models.

Overall, Figure 3 shows the flow chart of the project.

3.2 Gantt Chart

Table 3 explains the timelines for Final Year Project 1 (FYP1) with several milestones are expected to be achieved during the end of FYP1.

The first two weeks of the semester is allocated for the student to select and finalize the title of the project. Literature review will be done after the title is finalized until week 5. By the end of week 5, the objectives and problem statement of the project must be clearly identified.

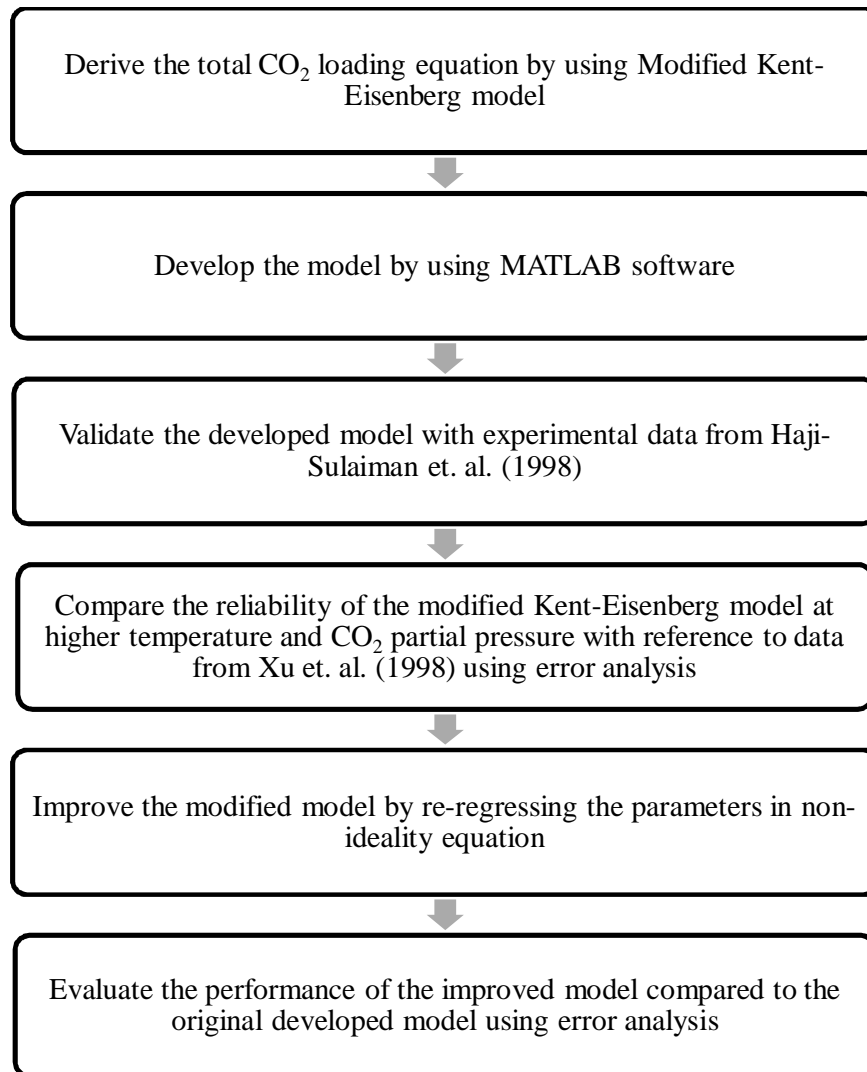


Figure 3 Flow chart of the project

The first phase of this project is expected to be done starting week 5 and finished in week 7. Two weeks allocation for the derivation of total CO₂ loading equation is reasonable as the reference of the equation derivation need to be obtained from different work.

The second phase of the project will be conducted from the 8th week until the 12th week. The period allocated for the development of model is 5 weeks as the student need to enhance the capability and skills of using MATLAB.

By the end of FYP1 period, the student is expected to complete two out of six phases of the project. The rest of the project shall be continued during Final Year Project 2 (FYP2) period.

Table 4 shows the timeline for FYP2. The third phase of the project which is model validation will be conducted on the first and second week of the semester. Then, the project continues with the next phase which is prediction of CO₂ solubility at higher temperature and partial pressure together with the error analysis to compare the reliability of the modified Kent-Eisenberg model. By the end of the 7th week, the first objective of the project is expected to be achieved.

The fifth and sixth phases of the project which is the re-regression of parameters and improved model evaluation will be done on the 8th and 9th week. Two weeks allocated for the phase are considered reasonable as the student will have ample time to learn about the command *fminunc* during the development of model in FYP1. After the project is completed, the final report will be prepared as well as the technical paper.

Table 3 Gantt Chart of FYP1

NO	DETAIL	WEEK															
		1	2	3	4	5	6	7	Mid Semester Break	8	9	10	11	12	13	14	
1	Selection of Project Title	■	■														
2	Literature Review		■	■	■	■											
3	Submission of Extended Proposal Defence							●									
4	Derivation of Equation					■	■		●								
5	Proposal Defence										■	■					
6	Development of Model										■	■	■	■	●		
7	Submission of Interim Draft Report															●	
8	Submission of Interim Final Report																●

● Suggested Milestone
 ■ Process

Table 4 Gantt Chart for FYP2

NO	DETAIL	WEEK																					
		1	2	3	4	5	6	7	Mid Semester Break							8	9	10	11	12	13	14	
1	Validation of Developed Model	■	■	●					Mid Semester Break														
2	Prediction of CO2 Solubility at Extended Condition				■	■			Mid Semester Break														
3	Error Analysis						■	●	Mid Semester Break														
4	Submission of Progress Report								Mid Semester Break							●							
5	Re-regression of Parameters								Mid Semester Break							■	●						
6	Pre-EDX								Mid Semester Break									●					
7	Submission of Draft Report								Mid Semester Break										●				
8	Submission of Dissertation (soft bound)								Mid Semester Break											●			
9	Submission of Technical Paper								Mid Semester Break											●			
10	Oral Presentation								Mid Semester Break													●	
11	Submission of Project Dissertation (Hard Bound)								Mid Semester Break														●

● Suggested Milestone
 ■ Process

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Equation Derivation

The equation derivation for the single polynomial equation in terms of the concentrations of hydrogen ions (12) and the total carbon dioxide loading equation (13) is done. The equation derived is as following:

4.1.1 Single polynomial equation

$$\begin{aligned} & [H^+]^4 + ([MDEA]_t + k_1)[H^+]^3 - \left(k_2 \frac{P_{CO_2}}{H_{CO_2}} + k_4\right)[H^+]^2 \\ & - \left(k_1 k_2 \frac{P_{CO_2}}{H_{CO_2}} + k_1 k_4 + 2k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}\right)[H^+] - \left(2k_1 k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}\right) = 0 \end{aligned} \quad (16)$$

This equation can be rewritten in form of equation (12) as follow:

$$A[H^+]^4 + B[H^+]^3 + C[H^+]^2 + D[H^+] + E = 0$$

where

$$A = 1$$

$$B = [MDEA]_t + k_1$$

$$C = -\left(k_2 \frac{P_{CO_2}}{H_{CO_2}} + k_4\right)$$

$$D = -\left(2k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}} + k_1 k_4 + k_1 k_2 \frac{P_{CO_2}}{H_{CO_2}}\right)$$

$$E = -2k_1 k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}$$

There are several discrepancies detected while comparing the coefficients of the derived equation with coefficients of equation (12) from Haji-Sulaiman et. al

(1998). However, the coefficients of the derived equation are consistent to the coefficients of the same equation from Pahlavanzadeh et. al. (2010). This consistency can be interpreted as the validation of the derived equation.

Full equation derivation for single polynomial equation is attached in Appendix 1.

4.1.2 Total carbon dioxide loading equation

$$\alpha = \frac{\left([H^+]^2 + k_2[H^+] + k_2k_3\right)\frac{P_{CO_2}}{H_{CO_2}}}{\left(\frac{k_1}{[H^+]} + 1\right)\left([H^+]^3 + \left(k_2\frac{P_{CO_2}}{H_{CO_2}} + k_4\right)[H^+] + 2k_2k_3\frac{P_{CO_2}}{H_{CO_2}}\right)} \quad (17)$$

This equation is inconsistent with equation (13). The main reason behind the discrepancies is that the polynomial equation derived earlier is already inconsistent with equation (12). Unfortunately, as shown in equation (15); Pahlavanzadeh et. al. (2010) does not provide the extended total carbon dioxide loading equation but only the basic equation based on the amine balance expression.

Full equation derivation for total carbon dioxide loading equation is attached in Appendix 2.

4.2 Development of model

The model is coded in MATLAB software to obtain the CO₂ loading in aqueous solutions of MDEA provided the concentration of MDEA, temperature and CO₂ partial pressure as the input parameters.

The coding is attached in Appendix 3.

4.3 Validation of Model

After the model has been developed, the solubility data of CO₂ taken from Haji-Sulaiman et. al. (1998) were generated by fitting the data into the model. Table 5 shows the data generated from the developed model.

Table 5 Experimental and calculated CO₂ loading data, based on Haji-Sulaiman et. al. (1998)

M	T	P_{CO2}	α_{exp}	α_{calc}	Error (%)
2	303	1.064	0.114	0.184	61.579
		3.130	0.244	0.301	23.443
		4.802	0.333	0.362	8.559
		10.535	0.483	0.491	1.677
		29.756	0.673	0.682	1.352
		48.370	0.793	0.767	3.291
		95.830	0.880	0.869	1.273
	313	1.064	0.103	0.140	36.214
		3.069	0.197	0.232	17.716
		5.176	0.267	0.294	9.963
		10.029	0.374	0.389	3.957
		30.349	0.603	0.584	3.184
		47.520	0.688	0.668	2.922
		93.956	0.805	0.788	2.087
	323	0.997	0.079	0.104	31.899
		2.938	0.148	0.177	19.392
		4.761	0.194	0.222	14.433
		9.725	0.298	0.307	2.987
		28.435	0.471	0.476	1.040
		44.136	0.590	0.557	5.661
		91.514	0.726	0.695	4.325
Average					12.236
4	303	0.099	0.027	0.033	21.481
		0.984	0.061	0.101	65.082
		4.918	0.149	0.215	44.497
		9.853	0.284	0.293	3.169
		29.509	0.516	0.456	11.686
		49.100	0.633	0.545	13.902
		98.200	0.761	0.672	11.761
	313	0.095	0.015	0.024	59.333
		0.954	0.052	0.075	43.269
		4.762	0.086	0.162	88.488
		9.523	0.190	0.224	17.632
		28.521	0.384	0.360	6.354
		47.535	0.513	0.440	14.269
		95.234	0.654	0.562	14.037
	323	0.090	0.010	0.018	76.000
		0.901	0.037	0.055	48.649
		4.514	0.084	0.122	44.643
		9.028	0.151	0.169	12.053
		27.084	0.251	0.279	11.315
		45.139	0.363	0.347	4.298
		90.279	0.516	0.457	11.434
Average					29.683

α_{exp} are the CO₂ loading experimental data published by Haji-Sulaiman et. al. (1998) while α_{calc} are the CO₂ loading data generated using the developed Modified Kent-Eisenberg model.

As observed in the table, the average error for calculated data of CO₂ loading at 2M is 12.236% while at 4M is 29.683%. Since the average errors are less than 30%, the model is accepted and will be evaluated at extended operating conditions. Figure 4 and 5 below show the graphical comparison between the generated CO₂ loading and the experimental data from Haji-Sulaiman et. al. (1998) in 2M and 4M aqueous MDEA solution respectively.

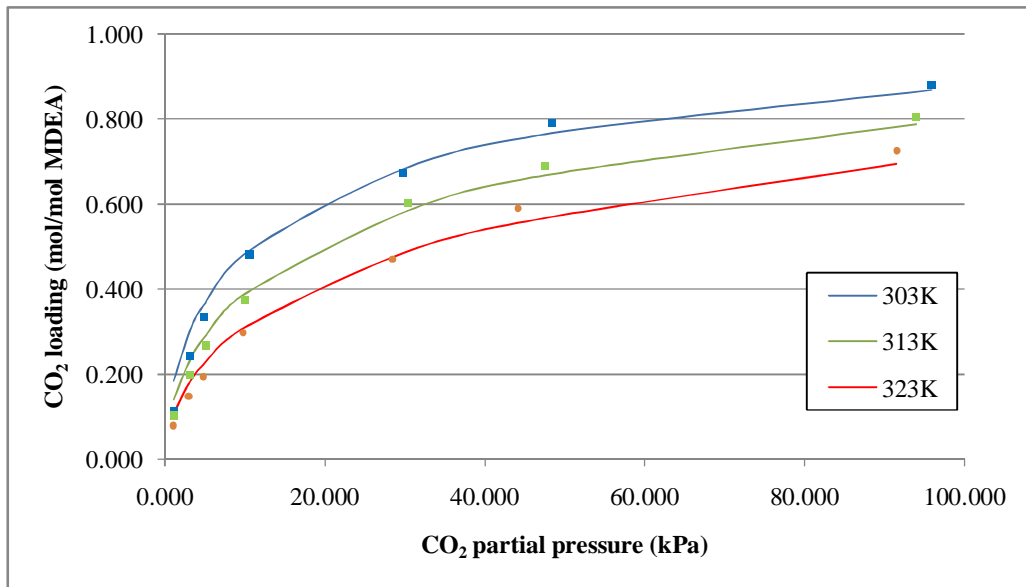


Figure 4 Comparison between generated CO₂ loading and data of Haji-Sulaiman et. al. (1998) in 2M MDEA; solid line: model, point: experimental data

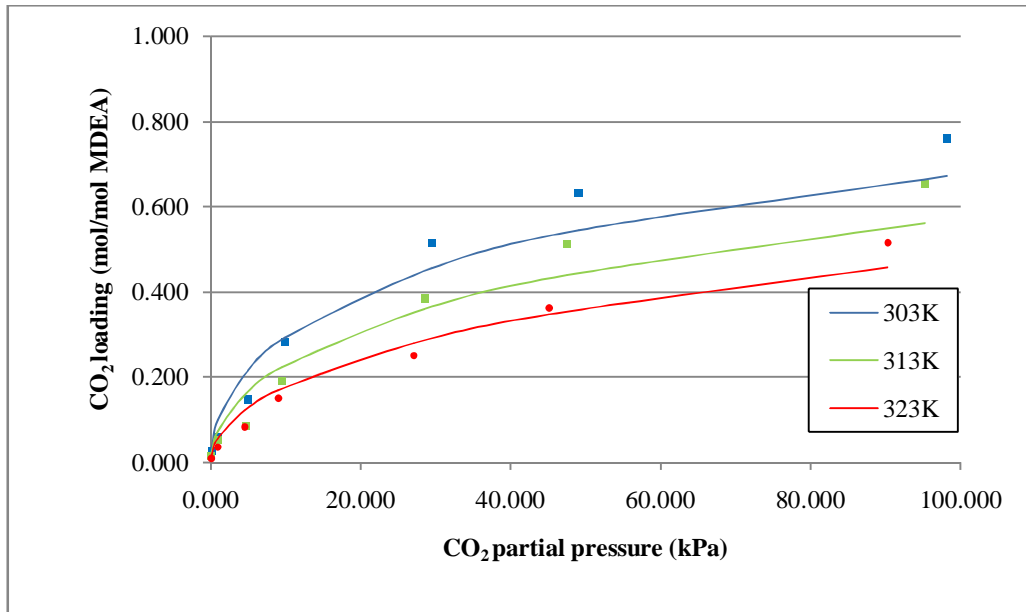


Figure 5 Comparison between generated CO₂ loading and data of Haji-Sulaiman et. al. (1998) in 4M MDEA; solid line: model, point: experimental data

For better error analysis, Figure 6 and 7 show the percentage error of the calculated data referring to Haji-Sulaiman et. al (1998) data at 2M and 4M of aqueous MDEA solution respectively. Based on Figure 6, it is shown that the largest error occurs at the low partial pressure which is due to the inconsistency of the MDEA solution concentration during the experiment.

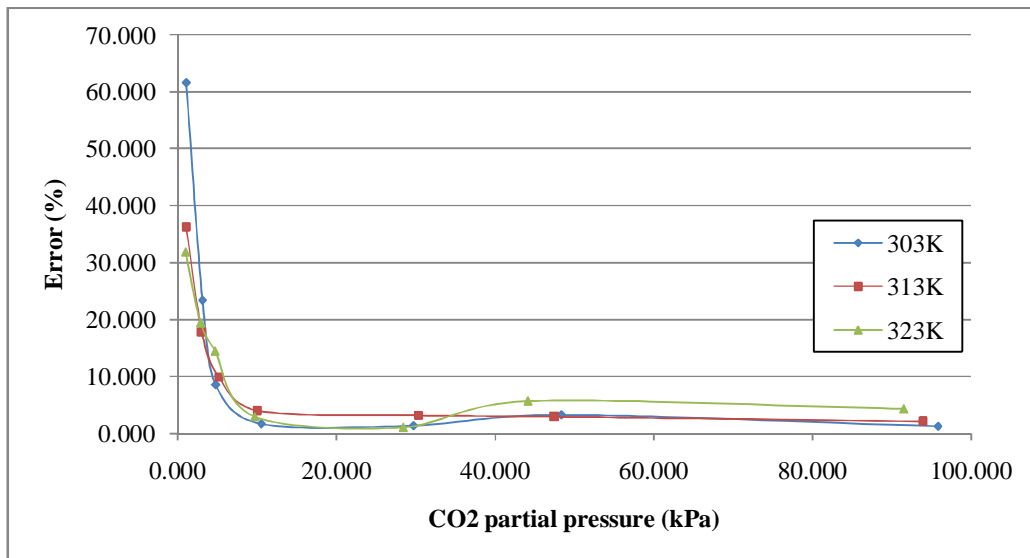


Figure 6 Percentage error of CO₂ loading at 0.01 - 100 kPa CO₂ partial pressure, in aqueous 2M MDEA solution, based on Haji-Sulaiman et. al. (1998)

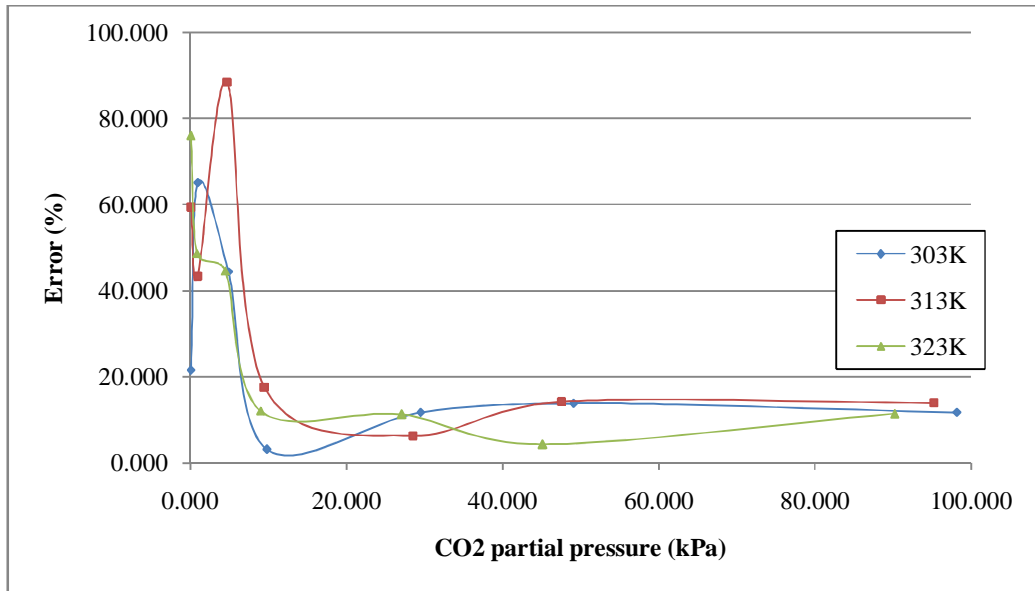


Figure 7 Percentage error of CO₂ loading at 0.01 - 100 kPa CO₂ partial pressure, in aqueous 4M MDEA solution, based on Haji-Sulaiman et. al. (1998)

From Figure 7, the deviation of calculated data from the experimental data at 4M of MDEA is inconsistent as the pressure increases. Further evaluation is performed and as tabulated in Figure 8, it is shown that the experimental data for CO₂ loading does not produce smooth trendline especially between 0 to 20 kPa of CO₂ partial pressure. This phenomena thus indicating that the experimental data from Haji-Sulaiman et. al. (1998) are not so reliable at very low pressure. Hence, it is concluded that the calculated data is acceptable for the model validation.

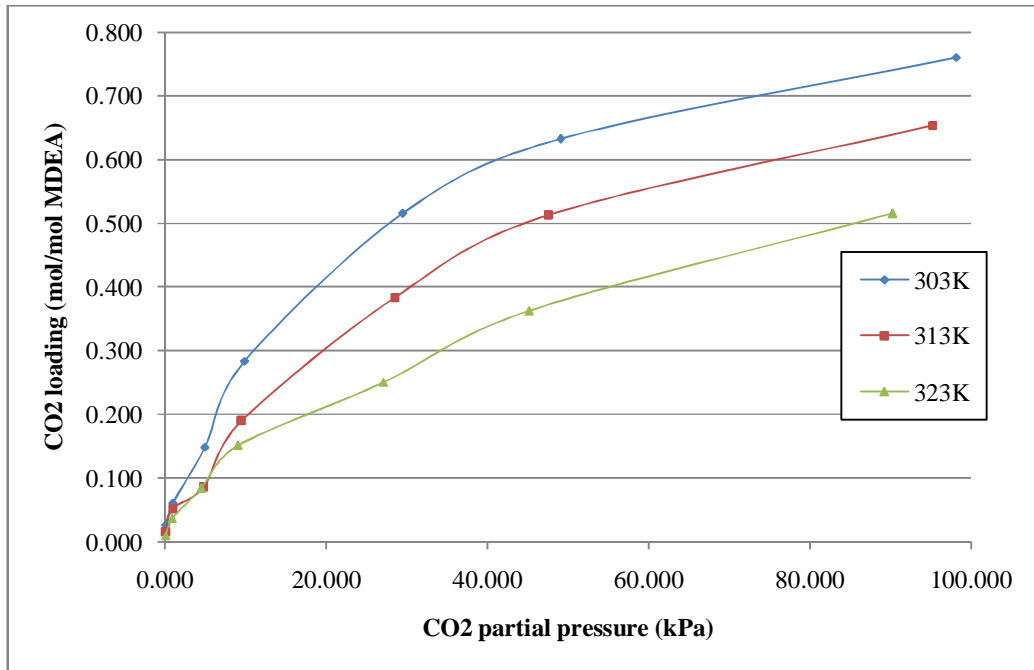


Figure 8 Experimental CO₂ loading data in aqueous 4M MDEA solution, based on Haji-Sulaiman et. al. (1998)

4.4 Evaluation of Model Performance at Extended Operating Conditions

The developed Modified Kent-Eisenberg model is fitted to the experimental data from Xu et. al. (1998) to evaluate its performance at extended operating conditions (particularly at higher CO₂ partial pressure). The generated CO₂ loading data is compared to the experimental data at 3.04M, 3.46M, and 4.28M concentration of aqueous MDEA solution, at 313-373 K temperature and 10-1000 kPa CO₂ partial pressure. Table 6 below shows the comparison between the generated data and the experimental data.

Figure 9, 10 and 11 shows the graphical comparison between the generated CO₂ loading data with the experimental data from Xu et. al. (1998). The obvious error between the generated and experimental data at the higher CO₂ partial pressure is expected as the constant values in the factor F used in the model are regressed by using data within the range of 0.09 and 100 kPa CO₂ partial pressure.

Table 6 Experimental and calculated CO₂ loading data, based on Xu et. al. (1998)

M	T	P_{CO2}	α_{exp}	α_{calc}	Error (%)
3.04	328	10.740	0.209	0.201	3.971
		18.850	0.232	0.260	11.897
		42.570	0.347	0.369	6.254
		85.570	0.464	0.484	4.289
		200.500	0.690	0.643	6.884
		288.500	0.779	0.712	8.652
		395.500	0.829	0.770	7.105
		595.500	0.886	0.843	4.898
		806.500	0.911	0.894	1.888
	343	6.150	0.069	0.107	55.652
		12.330	0.098	0.151	53.878
		23.790	0.149	0.206	38.255
		70.170	0.274	0.335	22.153
		206.800	0.484	0.514	6.095
		281.800	0.582	0.572	1.684
		376.800	0.659	0.629	4.537
		581.800	0.740	0.716	3.297
		806.800	0.791	0.781	1.315
				Average	13.484
3.46	328	115.000	0.502	0.497	1.056
		389.000	0.721	0.726	0.680
		401.000	0.741	0.732	1.269
		782.000	0.820	0.853	4.000
		992.000	0.849	0.894	5.277
	343	173.500	0.358	0.442	23.380
		278.500	0.512	0.527	2.910
		388.500	0.604	0.591	2.185
		608.500	0.693	0.680	1.876
		808.500	0.753	0.737	2.098
	353	169.800	0.251	0.365	45.378
		254.800	0.366	0.431	17.678
		364.800	0.427	0.495	15.855
		599.800	0.549	0.591	7.668
		794.800	0.658	0.649	1.398
	363	147.500	0.174	0.285	63.736
		247.500	0.236	0.357	51.271
		357.500	0.319	0.417	30.564
		552.500	0.395	0.495	25.291
		737.500	0.473	0.551	16.575
				Average	16.007

4.28	313	15.400	0.269	0.264	1.784
		30.110	0.365	0.352	3.644
		203.000	0.705	0.682	3.234
		393.000	0.795	0.800	0.579
		838.000	0.881	0.919	4.359
	328	8.920	0.125	0.141	12.880
		32.120	0.248	0.256	3.185
		133.000	0.450	0.461	2.356
		301.000	0.618	0.610	1.246
		603.000	0.739	0.743	0.582
		855.000	0.778	0.809	3.933
		1013.000	0.813	0.840	3.284
	343	9.220	0.074	0.100	34.595
		29.320	0.140	0.174	24.429
		174.000	0.351	0.384	9.516
		389.000	0.509	0.524	2.849
		754.000	0.641	0.653	1.872
	353	3.270	0.030	0.047	56.667
		47.310	0.139	0.175	26.115
		207.800	0.299	0.342	14.515
		522.800	0.474	0.496	4.662
		867.800	0.561	0.595	6.078
	373	0.880	0.009	0.015	70.000
		11.870	0.037	0.058	56.486
		159.000	0.142	0.208	46.197
		519.000	0.274	0.355	29.635
		824.000	0.351	0.432	23.105
					Average

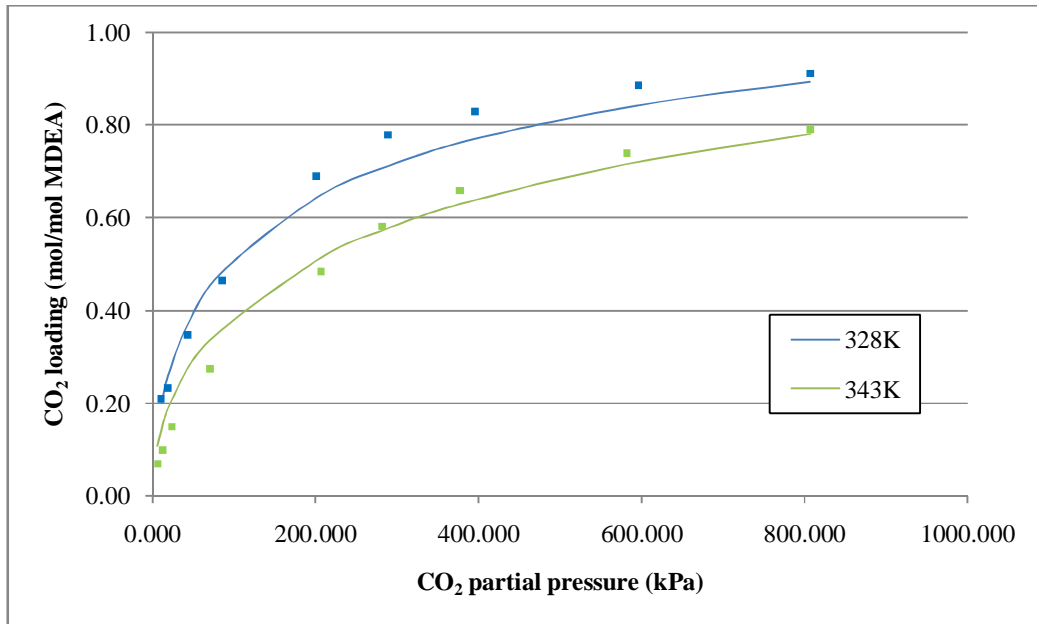


Figure 9 Comparison between generated CO₂ loading and data of Xu et. al. (1998) in 3.04M MDEA; solid line: model, point: experimental data

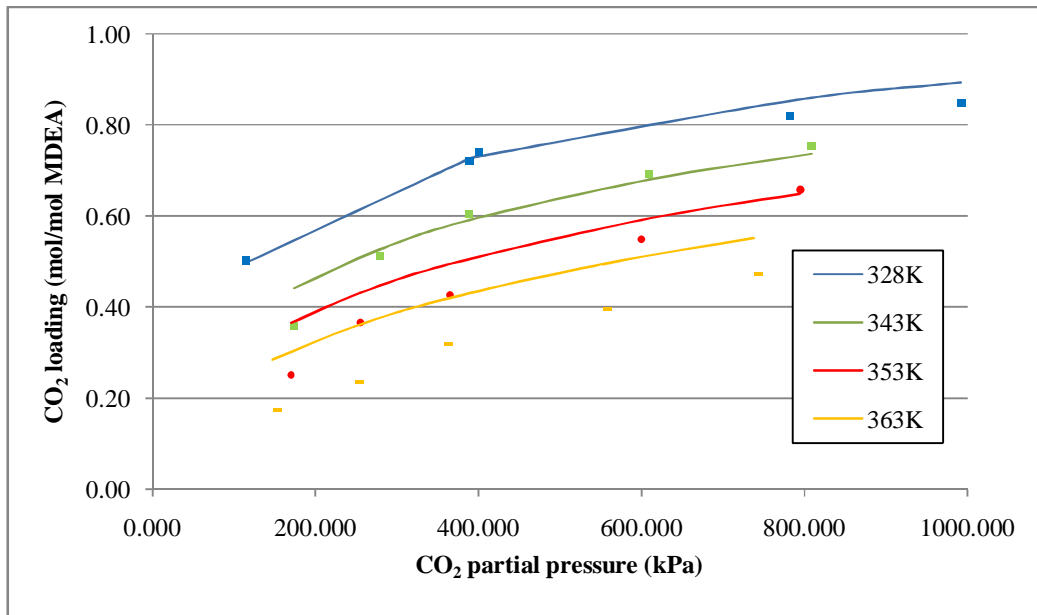


Figure 10 Comparison between generated CO₂ loading and data of Xu et. al. (1998) in 3.46M MDEA; solid line: model, point: experimental data

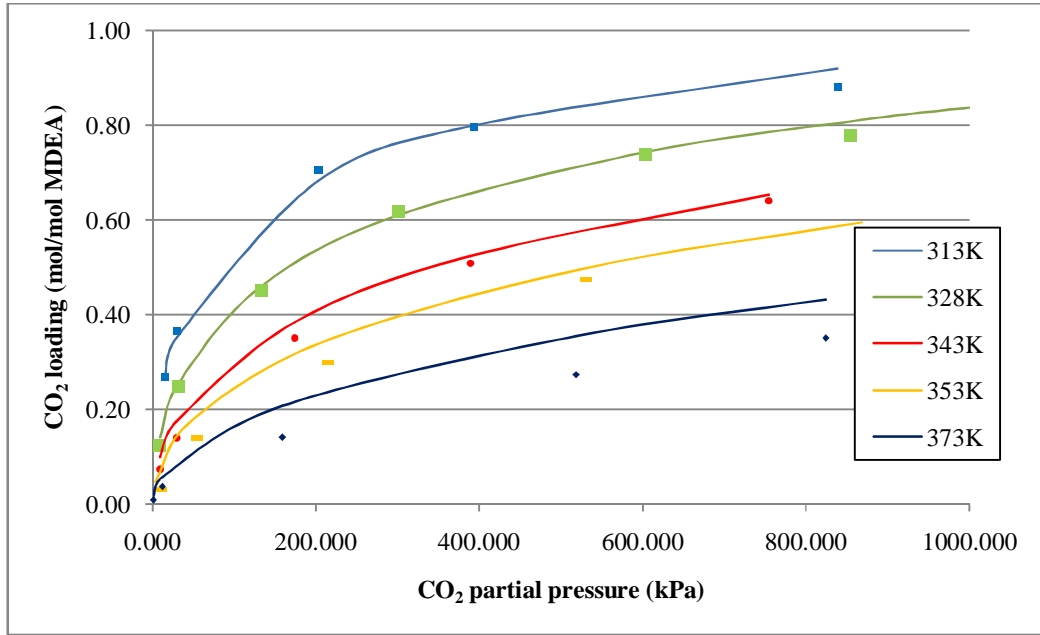


Figure 11 Comparison between generated CO₂ loading and data of Xu et. al. (1998) in 4.28M MDEA; solid line: model, point: experimental data

4.5 Regression of Parameters

Section 4.4 discussed the performance of the Modified Kent-Eisenberg model at higher operating pressure. The results show that the performance is not satisfying at high pressure. Hence, the parameter g and k in equation (14) is re-regressed in order to improve the performance of the model. The values of the re-regressed parameters are shown in Table 7 below.

The complete coding is shown in Appendix 4.

Table 7 Values for regressed parameters for equation (14)

Parameter	g	k
$F_{1,MDEA}$	-0.0458	0.6772

The re-regressed parameters are used to substitute the original parameters into the model to test the performance of the new parameters in predicting the CO₂ loading at high pressure. Table 8 and 9 below shows the comparison of the predicted CO₂ loading data between the original parameters and new parameters. α_{calc2} are the CO₂ loading data generated using the new parameters.

Table 8 Comparison between the calculated CO₂ loading data using original and new parameters, based on Haji-Sulaiman et. al. (1998)

M	T	P_{CO2}	α_{exp}	α_{calc}	Error(%)	α_{calc2}	Error(%)
2	303	1.064	0.114	0.184	61.579	0.174	52.982
		3.130	0.244	0.301	23.443	0.288	17.828
		4.802	0.333	0.362	8.559	0.346	3.994
		10.535	0.483	0.491	1.677	0.474	1.781
		29.756	0.673	0.682	1.352	0.667	0.892
		48.370	0.793	0.767	3.291	0.754	4.893
		95.830	0.880	0.869	1.273	0.860	2.227
	313	1.064	0.103	0.140	36.214	0.133	28.641
		3.069	0.197	0.232	17.716	0.221	12.030
		5.176	0.267	0.294	9.963	0.281	5.056
		10.029	0.374	0.389	3.957	0.374	0.053
		30.349	0.603	0.584	3.184	0.568	5.771
		47.520	0.688	0.668	2.922	0.653	5.029
		93.956	0.805	0.788	2.087	0.777	3.466
	323	0.997	0.079	0.104	31.899	0.098	24.430
		2.938	0.148	0.177	19.392	0.168	13.378
		4.761	0.194	0.222	14.433	0.212	9.021
		9.725	0.298	0.307	2.987	0.294	1.309
		28.435	0.471	0.476	1.040	0.461	2.144
		44.136	0.590	0.557	5.661	0.542	8.186
		91.514	0.726	0.695	4.325	0.682	6.102
Average					12.236	Average	9.963
4	303	0.099	0.027	0.033	21.481	0.031	14.815
		0.984	0.061	0.101	65.082	0.096	57.049
		4.918	0.149	0.215	44.497	0.206	38.523
		9.853	0.284	0.293	3.169	0.282	0.669
		29.509	0.516	0.456	11.686	0.442	14.302
		49.100	0.633	0.545	13.902	0.531	16.098
		98.200	0.761	0.672	11.761	0.659	13.456
	313	0.095	0.015	0.024	59.333	0.023	50.667
		0.954	0.052	0.075	43.269	0.071	36.154
		4.762	0.086	0.162	88.488	0.155	80.349
		9.523	0.190	0.224	17.632	0.215	13.000
		28.521	0.384	0.360	6.354	0.348	9.453
		47.535	0.513	0.440	14.269	0.427	16.784
		95.234	0.654	0.562	14.037	0.549	16.070
	323	0.090	0.010	0.018	76.000	0.017	66.000
		0.901	0.037	0.055	48.649	0.052	41.081
		4.514	0.084	0.122	44.643	0.116	38.214
		9.028	0.151	0.169	12.053	0.162	7.483
		27.084	0.251	0.279	11.315	0.270	7.371
		45.139	0.363	0.347	4.298	0.336	7.383
		90.279	0.516	0.457	11.434	0.445	13.837
Average					29.683	Average	26.608

Table 9 Comparison between the calculated CO₂ loading data using original and new parameters, based on Xu et. al. (1998)

M	T	P_{CO2}	α_{exp}	α_{calc}	Error(%)	α_{calc2}	Error(%)
3.04	328	10.740	0.209	0.201	3.971	0.192	7.943
		18.850	0.232	0.260	11.897	0.250	7.672
		42.570	0.347	0.369	6.254	0.357	2.824
		85.570	0.464	0.484	4.289	0.471	1.530
		200.500	0.690	0.643	6.884	0.630	8.638
		288.500	0.779	0.712	8.652	0.701	10.077
		395.500	0.829	0.770	7.105	0.760	8.299
		595.500	0.886	0.843	4.898	0.835	5.801
		806.500	0.911	0.894	1.888	0.887	2.602
	343	6.150	0.069	0.107	55.652	0.103	48.551
		12.330	0.098	0.151	53.878	0.144	47.347
		23.790	0.149	0.206	38.255	0.198	32.953
		70.170	0.274	0.335	22.153	0.324	18.248
		206.800	0.484	0.514	6.095	0.502	3.657
		281.800	0.582	0.572	1.684	0.561	3.694
		376.800	0.659	0.629	4.537	0.618	6.237
		581.800	0.740	0.716	3.297	0.706	4.649
		806.800	0.791	0.781	1.315	0.772	2.427
Average					13.484	Average	12.397
3.46	328	115.000	0.502	0.497	1.056	0.484	3.566
		389.000	0.721	0.726	0.680	0.715	0.804
		401.000	0.741	0.732	1.269	0.721	2.699
		782.000	0.820	0.853	4.000	0.845	3.049
		992.000	0.849	0.894	5.277	0.887	4.499
	343	173.500	0.358	0.442	23.380	0.430	20.196
		278.500	0.512	0.527	2.910	0.515	0.625
		388.500	0.604	0.591	2.185	0.579	4.073
		608.500	0.693	0.680	1.876	0.669	3.405
		808.500	0.753	0.737	2.098	0.728	3.373
	353	169.800	0.251	0.365	45.378	0.355	41.315
		254.800	0.366	0.431	17.678	0.420	14.727
		364.800	0.427	0.495	15.855	0.484	13.279
		599.800	0.549	0.591	7.668	0.580	5.719
	363	794.800	0.658	0.649	1.398	0.639	2.964
		147.500	0.174	0.285	63.736	0.276	58.736
		247.500	0.236	0.357	51.271	0.348	47.288
		357.500	0.319	0.417	30.564	0.406	27.398
		552.500	0.395	0.495	25.291	0.485	22.658
	737.500	0.473	0.551	16.575	0.541	14.397	
	Average					16.007	Average

4.28	313	15.400	0.269	0.264	1.784	0.254	5.428	
		30.110	0.365	0.352	3.644	0.340	6.795	
		203.000	0.705	0.682	3.234	0.670	4.950	
		393.000	0.795	0.800	0.579	0.790	0.642	
		838.000	0.881	0.919	4.359	0.913	3.655	
	328	8.920	0.125	0.141	12.880	0.135	8.160	
		32.120	0.248	0.256	3.185	0.247	0.484	
		133.000	0.450	0.461	2.356	0.449	0.333	
		301.000	0.618	0.610	1.246	0.598	3.188	
		603.000	0.739	0.743	0.582	0.733	0.812	
		855.000	0.778	0.809	3.933	0.800	2.789	
		1013.000	0.813	0.840	3.284	0.831	2.263	
	343	9.220	0.074	0.100	34.595	0.095	28.919	
		29.320	0.140	0.174	24.429	0.168	19.714	
		174.000	0.351	0.384	9.516	0.374	6.467	
		389.000	0.509	0.524	2.849	0.512	0.589	
		754.000	0.641	0.653	1.872	0.642	0.203	
	353	3.270	0.030	0.047	56.667	0.045	49.333	
		47.310	0.139	0.175	26.115	0.169	21.511	
		207.800	0.299	0.342	14.515	0.333	11.271	
		522.800	0.474	0.496	4.662	0.485	2.363	
		867.800	0.561	0.595	6.078	0.585	4.189	
	373	0.880	0.009	0.015	70.000	0.015	62.222	
		11.870	0.037	0.058	56.486	0.055	49.730	
		159.000	0.142	0.208	46.197	0.201	41.479	
		519.000	0.274	0.355	29.635	0.346	26.350	
		824.000	0.351	0.432	23.105	0.423	20.456	
	Average					16.585	Average	14.233

Overall, based on Table 8 and 9, it is clearly proved that the new regressed parameters have enhanced the performance of the model. Referring to Table 8, the new model provides better estimation at CO₂ partial pressure less than 10 kPa, and especially better estimation at high temperature and high concentration of MDEA as well. Based on Table 9, less error is calculated at CO₂ partial pressure less than 200 kPa and more than 800 kPa. At high temperature and high concentration of MDEA, the model is able to improve the CO₂ loading prediction up to 7% error reduction. Hence, it can be concluded that the new regressed parameters are more reliable compared to the old parameters in predicting the CO₂ loading in MDEA solution at high CO₂ partial pressure, temperature, and concentration of MDEA.

To further demonstrate that the new model can provide better estimation of CO₂ loading compared to the old model, both model are fitted into experimental data taken from Jou et. al (1982). Although this paper is not written recently, it provides wide range of temperature and CO₂ partial pressure, thus make it the most suitable reference to compare the reliability of the model. Table 10 below shows the comparison between the calculated CO₂ loading data using old and new model with the experimental data from Jou et. al. (1982).

Table 10 Comparison between the calculated CO₂ loading data using old and new model, based on Jou et. al. (1982)

M	T	P_{CO2}	α_{exp}	α_{calc}	Error(%)	α_{calc2}	Error(%)
2	298	0.001	0.005	0.008	58.000	0.007	44.000
		0.007	0.017	0.019	13.855	0.017	4.819
		0.022	0.033	0.033	1.216	0.030	8.511
		1.550	0.334	0.251	24.760	0.239	28.503
		4.220	0.452	0.386	14.513	0.371	18.031
		9.260	0.638	0.520	18.495	0.503	21.191
		181.000	1.025	0.967	5.678	0.963	6.049
		698.000	1.146	1.104	3.639	1.104	3.700
		2040.000	1.308	1.348	3.028	1.348	3.020
		3550.000	1.479	1.611	8.925	1.611	8.925
		4570.000	1.587	1.788	12.665	1.788	12.672
		5260.000	1.676	1.908	13.825	1.908	13.825
		6380.000	1.833	2.102	14.659	2.102	14.659
	313	0.002	0.003	0.007	133.333	0.006	113.333
		0.003	0.004	0.008	91.142	0.008	74.825
		0.013	0.012	0.016	35.833	0.015	25.000
		0.184	0.068	0.059	12.722	0.055	18.343
		2.380	0.224	0.206	8.036	0.196	12.634
		11.200	0.441	0.407	7.823	0.391	11.270
		101.000	0.866	0.800	7.633	0.789	8.857
		294.000	0.990	0.946	4.444	0.942	4.899
		640.000	1.083	1.034	4.506	1.032	4.681
		2360.000	1.204	1.271	5.523	1.270	5.507
		3200.000	1.268	1.374	8.320	1.374	8.320
		4800.000	1.467	1.567	6.810	1.567	6.810
		6330.000	1.639	1.750	6.797	1.751	6.803
	6630.000	1.682	1.786	6.207	1.786	6.207	
	343	0.002	0.001	0.003	188.889	0.002	166.667
		0.003	0.001	0.003	163.566	0.003	140.310
		0.048	0.006	0.013	139.286	0.013	123.214
		0.305	0.021	0.034	65.385	0.032	54.808
		0.951	0.044	0.062	40.091	0.058	31.891
		40.900	0.369	0.375	1.599	0.362	1.843
		447.000	0.841	0.820	2.485	0.813	3.365

		993.000	1.011	0.958	5.262	0.954	5.598	
		2320.000	1.147	1.112	3.051	1.111	3.121	
		2730.000	1.182	1.148	2.868	1.148	2.902	
		4230.000	1.235	1.268	2.688	1.268	2.696	
		6020.000	1.397	1.402	0.322	1.402	0.336	
	373	0.047	0.002	0.006	179.817	0.006	161.468	
		0.128	0.004	0.011	184.574	0.010	163.298	
		30.800	0.130	0.184	41.154	0.176	35.385	
		373.000	0.502	0.551	9.681	0.541	7.749	
		573.000	0.564	0.641	13.688	0.633	12.199	
		2600.000	1.009	0.989	1.982	0.988	2.131	
		4200.000	1.161	1.120	3.575	1.120	3.566	
	5530.000	1.218	1.209	0.772	1.209	0.722		
	393	0.073	0.001	0.005	270.968	0.004	246.774	
		0.116	0.002	0.006	273.494	0.006	249.398	
		3.840	0.013	0.043	221.805	0.041	204.511	
		57.700	0.097	0.173	77.595	0.166	70.915	
		493.000	0.336	0.469	39.435	0.460	36.994	
		1930.000	0.689	0.786	14.035	0.782	13.527	
		3380.000	0.910	0.945	3.813	0.944	3.725	
		4660.000	1.043	1.048	0.479	1.048	0.518	
	5490.000	1.152	1.106	4.002	1.107	3.915		
					Average	44.195	Average	40.090
	4.28	298	0.004	0.006	0.008	28.824	0.008	20.773
			0.009	0.010	0.012	11.650	0.011	4.854
			0.034	0.019	0.022	14.136	0.021	7.330
			0.086	0.031	0.034	11.111	0.032	4.575
			0.384	0.072	0.070	2.361	0.067	7.361
5.300			0.318	0.243	23.491	0.234	26.541	
48.100			0.784	0.576	26.582	0.562	28.367	
111.000			0.930	0.726	21.925	0.714	23.237	
235.000			0.996	0.846	15.030	0.838	15.914	
1190.000			1.115	1.054	5.516	1.051	5.731	
3939.000			1.300	1.305	0.408	1.305	0.354	
5430.000			1.370	1.429	4.336	1.429	4.299	
6370.000		1.381	1.507	9.102	1.506	9.080		
313		0.002	0.002	0.004	98.020	0.004	83.168	
		0.008	0.004	0.007	81.102	0.007	70.604	
		0.011	0.006	0.008	42.105	0.008	33.333	
		0.030	0.010	0.013	25.962	0.012	18.269	
		0.703	0.061	0.061	0.000	0.058	5.090	
		2.670	0.136	0.117	14.044	0.112	17.941	
		13.300	0.285	0.248	12.970	0.238	16.274	
		83.400	0.700	0.518	25.957	0.505	27.829	
		106.000	0.710	0.562	20.859	0.549	22.718	
	413.000	0.936	0.808	13.686	0.799	14.690		
1420.000	1.100	0.998	9.291	0.994	9.664			
2800.000	1.170	1.113	4.915	1.110	5.094			

		4070.000	1.218	1.196	1.773	1.195	1.888
		5550.000	1.272	1.287	1.164	1.286	1.085
		6570.000	1.290	1.347	4.419	1.346	4.357
	343	0.002	0.000	0.001	251.351	0.001	224.324
		0.005	0.001	0.002	161.364	0.002	150.000
		0.010	0.001	0.003	157.813	0.003	134.375
		0.018	0.002	0.005	97.368	0.004	84.211
		0.170	0.008	0.014	73.077	0.013	62.821
		0.918	0.021	0.031	49.524	0.030	41.905
		40.300	0.189	0.202	6.984	0.195	3.069
		705.000	0.740	0.640	13.581	0.629	15.054
		1620.000	0.941	0.810	13.921	0.802	14.825
		2890.000	1.110	0.932	16.045	0.926	16.595
		4300.000	1.159	1.022	11.855	1.017	12.252
		5590.000	1.187	1.087	8.408	1.084	8.711
		6280.000	1.232	1.119	9.180	1.116	9.448
	373	0.040	0.001	0.003	200.000	0.003	180.000
		0.055	0.001	0.004	166.667	0.003	151.852
		0.071	0.002	0.004	171.523	0.004	158.278
		0.174	0.003	0.007	126.804	0.006	113.058
		0.277	0.004	0.008	123.404	0.008	112.766
		7.690	0.028	0.047	68.478	0.044	60.870
		63.100	0.095	0.133	40.655	0.128	35.480
		331.000	0.256	0.291	13.711	0.283	10.547
		1310.000	0.532	0.521	2.105	0.511	3.929
		2680.000	0.784	0.680	13.214	0.671	14.362
		4010.000	0.941	0.783	16.823	0.775	17.673
		5590.000	1.096	0.875	20.146	0.868	20.785
	393	0.143	0.001	0.004	252.381	0.004	233.333
		0.183	0.001	0.004	233.333	0.004	210.078
		0.479	0.002	0.007	224.444	0.007	206.667
		14.300	0.019	0.043	129.032	0.041	119.355
		69.100	0.055	0.095	71.429	0.091	65.099
		248.000	0.128	0.179	39.531	0.173	35.156
		857.000	0.279	0.322	15.305	0.314	12.545
		2920.000	0.525	0.554	5.429	0.545	3.790
5290.000	0.743	0.709	4.576	0.701	5.653		
Average				53.874	Average	49.021	

From Table 10, it can be deduced that the new model does a better job in predicting the CO₂ loading data as compared to the old model. The comparison between generated CO₂ loading and experimental data from Jou et. al. (1982) in 2M MDEA using old model and new model are plotted as shown in Figure 12 and 13 respectively.

At extremely low pressure, the new model gives less error in the CO₂ loading prediction than the old model while their performance is quite similar at very high pressure. However, as the temperature increases, the performance of new model increases and it certainly able to predict the data better than the old model.

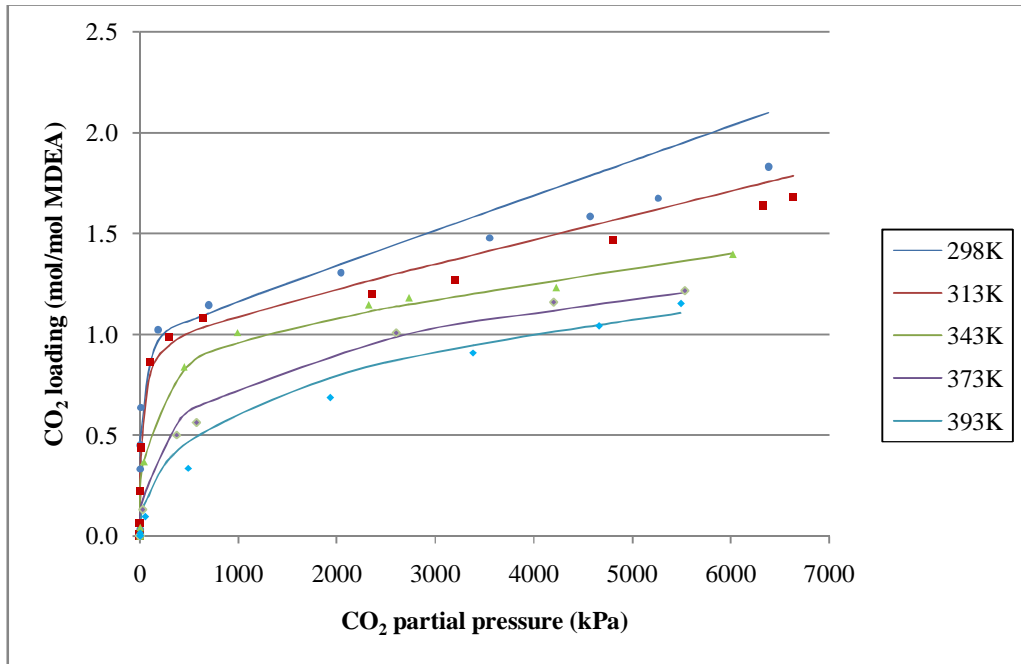


Figure 12 Comparison between generated CO₂ loading and data of Jou et. al. (1982) in 2M MDEA using original model; solid line: model, point: experimental data

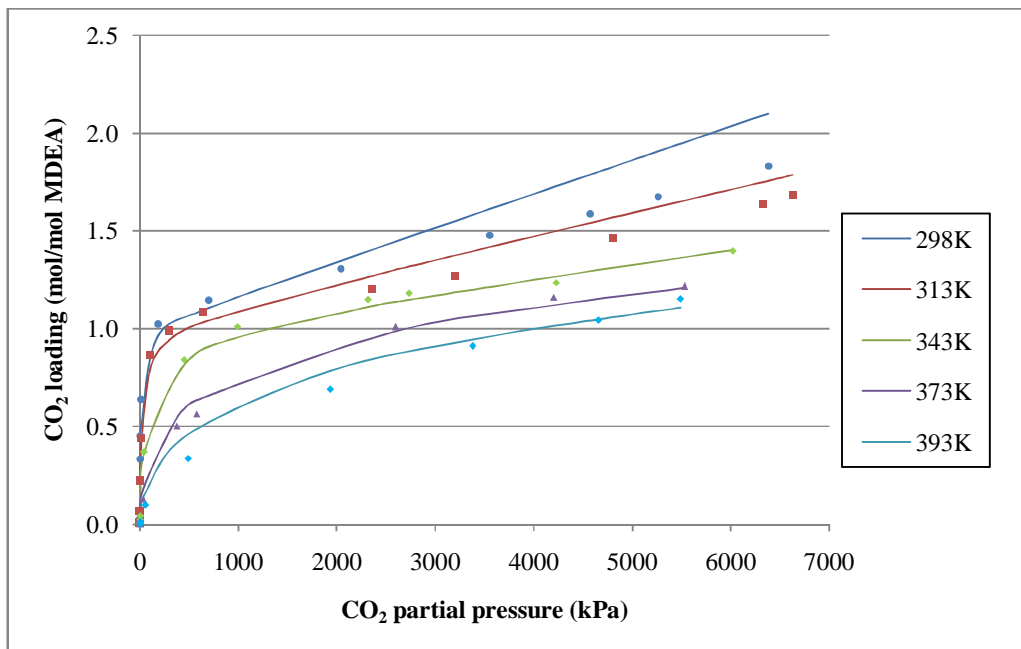


Figure 13 Comparison between generated CO₂ loading and data of Jou et. al. (1982) in 2M MDEA using new model; solid line: model, point: experimental data

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

By using the model taken from Haji-Sulaiman et. al. (1998) as reference, a new Modified Kent-Eisenberg model has been successfully developed to determine the solubility of carbon dioxide in MDEA at CO₂ partial pressure between 0 to 1000 kPa. Equation taken from the paper is revised and modified to suit in the model and the model is validated by using the experimental data from the paper itself. For the model performance evaluation purpose, experimental data from Xu et. al. (1998) is used as the range of the data is wider. With the errors less than 27%, the new model is proven to be more reliable in predicting the carbon dioxide solubility in MDEA at wide range of CO₂ partial pressure (between 0 to 1000 kPa) especially at very low and very high partial pressure compared to the original model.

In this paper, 107 data from Haji-Sulaiman et. al. (1998) and Xu et. al. (1998) are taken for the regression of parameters in the non-ideality equation purpose. For future research, it is advised for the researcher(s) to use more experimental data with wider range of CO₂ partial pressure during the regression of parameters to get better results. It is also recommended to add other parameters in the non-ideality equation in terms of concentration of MDEA or CO₂ partial pressure to produce more accurate model.

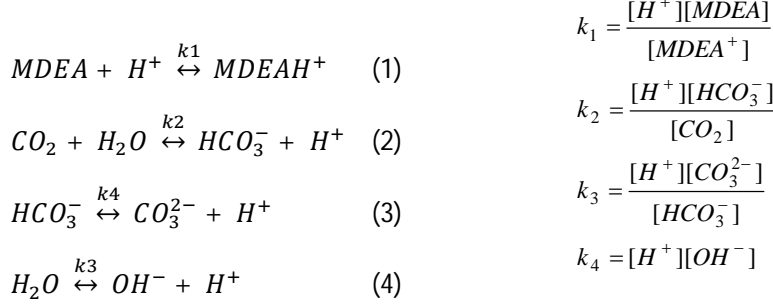
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APPENDIX 1

An equilibrium solution of CO₂ in aqueous solution of MDEA is governed by the following set of equations:



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

$$[\text{MDEA}]_t = [\text{MDEA}] + [\text{MDEAH}^+] \quad (5)$$

$$\alpha[\text{MDEA}]_t = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (6)$$

$$[\text{H}^+] + [\text{MDEAH}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (7)$$

where α is gas loading

$$\text{Henry's Law; } P_{\text{CO}_2} = H_{\text{CO}_2}[\text{CO}_2] \quad (8)$$

From equation (6), it can be expanded to:

$$\alpha[\text{MDEA}]_t = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$\alpha[\text{MDEA}]_t = [\text{CO}_2] + [\text{HCO}_3^-] + \frac{k_3[\text{HCO}_3^-]}{[\text{H}^+]}$$

$$\alpha[\text{MDEA}]_t = [\text{CO}_2] + \frac{k_2[\text{CO}_2]}{[\text{H}^+]} + \frac{k_2 k_3[\text{CO}_2]}{[\text{H}^+]^2} \quad (9)$$

The unknowns of the equations are:

$$[MDEAH^+], [MDEA], [HCO_3^-], [CO_3^{2-}], [OH^-], [CO_2], k_1, H^+$$

From equation (1) to (8), the unknowns can be expressed as:

$$[MDEAH^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [H^+]$$

$$[MDEA] = \frac{k_1[MDEAH^+]}{[H^+]}$$

$$[HCO_3^-] = k_2 \frac{P_{CO_2}}{H_{CO_2}} \frac{1}{[H^+]}$$

$$[CO_3^{2-}] = k_3 \frac{[HCO_3^-]}{[H^+]}$$

$$[OH^-] = \frac{k_4}{[H^+]}$$

$$[CO_2] = \frac{P_{CO_2}}{H_{CO_2}}$$

$$k_1 = \frac{[MDEA][H^+]}{[MDEAH^+]}$$

To solve the unknowns, first solving for [H+]:

$$[MDEA]_t = [MDEA] + [MDEAH^+]$$

Replace [MDEA]:

$$[MDEA]_t = \frac{k_1[MDEAH^+]}{[H^+]} + [MDEAH^+]$$

Replace [MDEAH⁺]:

$$[MDEA]_t = \frac{k_1}{[H^+]} ([HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]) + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

Expand, replace [CO₃²⁻]:

$$[MDEA]_t = \frac{k_1[HCO_3^-]}{[H^+]} + \frac{2k_1k_3[HCO_3^-]}{[H^+]^2} + \frac{k_1[OH^-]}{[H^+]} - k_1 + [HCO_3^-] + \frac{2k_3[HCO_3^-]}{[H^+]} + [OH^-] - [H^+]$$

Replace [OH⁻]:

$$[MDEA]_t = \frac{k_1[HCO_3^-]}{[H^+]} + \frac{2k_1k_3[HCO_3^-]}{[H^+]^2} + \frac{k_1k_4}{[H^+]^2} - k_1 + [HCO_3^-] + \frac{2k_3[HCO_3^-]}{[H^+]} + \frac{k_4}{[H^+]} - [H^+]$$

Replace [HCO₃⁻]:

$$[MDEA]_t = \frac{k_1k_2[CO_2]}{[H^+]^2} + \frac{2k_1k_2k_3[CO_2]}{[H^+]^3} + \frac{k_1k_4}{[H^+]^2} - k_1 + \frac{k_2[CO_2]}{[H^+]} + \frac{2k_2k_3[CO_2]}{[H^+]^2} + \frac{k_4}{[H^+]} - [H^+]$$

Replace [CO₂], rearrange:

$$[H^+] + [MDEA]_t + k_1 - \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} - \frac{k_4}{[H^+]} - \frac{k_1k_2 P_{CO_2}/H_{CO_2}}{[H^+]^2} - \frac{k_1k_4}{[H^+]^2} - \frac{2k_2k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2} - \frac{2k_1k_2k_3 P_{CO_2}/H_{CO_2}}{[H^+]^3} = 0$$

Equation * [H⁺]³:

$$[H^+]^4 + ([MDEA]_t + k_1)[H^+]^3 - (k_2 P_{CO_2}/H_{CO_2} + k_4)[H^+]^2 - (k_1k_2 P_{CO_2}/H_{CO_2} + k_1k_4 + 2k_2k_3 P_{CO_2}/H_{CO_2})[H^+] - (2k_1k_2k_3 P_{CO_2}/H_{CO_2}) = 0$$

Checked with Pahlavanzadeh, Jahangiri & Noshadi (2010)

APPENDIX 2

Equilibrium loading (α) equation:

$$\begin{aligned}
 \alpha[MDEA]_t &= \frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2} \\
 \alpha &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2}}{[MDEA]_t} \\
 &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2}}{[MDEA] + [MDEAH^+]} \\
 &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2}}{\frac{k_1[MDEAH^+]}{[H^+]} + [MDEAH^+]} \\
 &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2}}{\left(\frac{k_1}{[H^+]} + 1\right)[MDEAH^+]} \\
 &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 P_{CO_2}/H_{CO_2}}{[H^+]} + \frac{k_2 k_3 P_{CO_2}/H_{CO_2}}{[H^+]^2}}{\left(\frac{k_1}{[H^+]} + 1\right)\left([HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [H^+]\right)}
 \end{aligned}$$

$$\begin{aligned}
\alpha &= \frac{\frac{P_{CO_2}}{H_{CO_2}} + \frac{k_2 \frac{P_{CO_2}}{H_{CO_2}}}{[H^+]} + \frac{k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}}{[H^+]^2}}{\left(\frac{k_1}{[H^+]} + 1\right) \left(\frac{k_2}{[H^+]} \frac{P_{CO_2}}{H_{CO_2}} + \frac{2k_2 k_3}{[H^+]^2} \frac{P_{CO_2}}{H_{CO_2}} + \frac{k_4}{[H^+]} + [H^+]\right)} \\
&= \frac{[H^+]^2 \frac{P_{CO_2}}{H_{CO_2}} + k_2 [H^+] \frac{P_{CO_2}}{H_{CO_2}} + k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}}{\left(\frac{k_1}{[H^+]} + 1\right) \left(k_2 [H^+] \frac{P_{CO_2}}{H_{CO_2}} + 2k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}} + k_4 [H^+] + [H^+]^3\right)} \\
&= \frac{\left([H^+]^2 + k_2 [H^+] + k_2 k_3\right) \frac{P_{CO_2}}{H_{CO_2}}}{\left(\frac{k_1}{[H^+]} + 1\right) \left([H^+]^3 + \left(k_2 \frac{P_{CO_2}}{H_{CO_2}} + k_4\right) [H^+] + 2k_2 k_3 \frac{P_{CO_2}}{H_{CO_2}}\right)}
\end{aligned}$$

APPENDIX 3

Modified Kent-Eisenberg model code in MATLAB:

```
T=1;
while T~=0;
prompt = 'T(K)=';
T = input(prompt);
prompt = 'PCO2(kPa)=';
PCO2 = input(prompt);
prompt = 'MDEA(mol/L)=';
MDEA = input(prompt);

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

a2=-12092.1;
b2=-36.7816;
c2=0;
d2=235.482;

a3=-13445.9;
b3=-22.4773;
c3=0;
d3=140.932;

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

a5=-6789.04;
b5=-11.4519;
c5=-0.010454;
d5=94.4914;
%end constants

k1=exp((a1/T)+(b1*log(T))+(c1*T)+d1);
k2=exp((a2/T)+(b2*log(T))+(c2*T)+d2);
k3=exp((a3/T)+(b3*log(T))+(c3*T)+d3);
k4=exp((a4/T)+(b4*log(T))+(c4*T)+d4);
HCO2=exp((a5/T)+(b5*log(T))+(c5*T)+d5);

f1=-0.03628*log(PCO2)+0.6262*log(MDEA);
k1p=k1*f1;

A=1;
```

```

B=MDEA+k1p;
C=-(k2*PCO2/HCO2+k3);
D=-((k1p*k2*PCO2/HCO2)+(k1p*k3)+(2*k2*k4*PCO2/HCO2));
E=-2*k1p*k2*k4*PCO2/HCO2;

eq=[A B C D E];
HR=roots(eq);

for i=1:4;
    H=HR(i);
    alpha=((H^2+k2*H+k2*k4)*PCO2/HCO2)/((k1p/H+1)*(H^3+k2*PCO2/HCO2*H+k3*H+2*k2*k4*PCO2/HCO2));
    alphas(i)=alpha;
end

H=HR'
alphas

end

```


APPENDIX 4

Coding for regression of parameters in equation (14):

```
function [sse]=new(xo)
g=xo(1);
k=xo(2);

% 107 data from Haji-Sulaiman et al (1998) and Xu et al (1998)
data=[2 303 1.064 0.114; 2 303 3.13 0.244; 2 303 4.802 0.333; 2 303 10.535 0.483; 2 303 29.756 0.673; 2 303 48.37 0.793; 2
303 95.83 0.88;
 2 313 1.064 0.103; 2 313 3.069 0.197; 2 313 5.176 0.267; 2 313 10.029 0.374; 2 313 30.349 0.603; 2 313 47.52 0.688; 2 313
93.956 0.805;
 2 323 0.997 0.079; 2 323 2.938 0.148; 2 323 4.761 0.194; 2 323 9.725 0.298; 2 323 28.435 0.471; 2 323 44.136 0.59; 2 323
91.514 0.726;
 4 303 0.099 0.027; 4 303 0.984 0.061; 4 303 4.918 0.149; 4 303 9.853 0.284; 4 303 29.509 0.516; 4 303 49.1 0.633; 4 303
98.2 0.761;
 4 313 0.095 0.015; 4 313 0.954 0.052; 4 313 4.762 0.086; 4 313 9.523 0.190; 4 313 28.521 0.384; 4 313 47.535 0.513; 4 313
95.234 0.654;
 4 323 0.09 0.01; 4 323 0.901 0.037; 4 323 4.514 0.084; 4 323 9.028 0.151; 4 323 27.084 0.251; 4 323 45.139 0.363; 4 323
90.279 0.516;
 3.04 328 10.74 0.209; 3.04 328 18.85 0.232; 3.04 328 42.57 0.347; 3.04 328 85.57 0.464; 3.04 328 200.5 0.69; 3.04 328 288.5
0.779; 3.04 328 395.5 0.829;
 3.04 328 595.5 0.886; 3.04 328 806.5 0.911;
 3.04 343 6.15 0.069; 3.04 343 12.33 0.098; 3.04 343 23.79 0.149; 3.04 343 70.17 0.274; 3.04 343 206.8 0.484; 3.04 343
281.8 0.582; 3.04 343 376.8 0.659;
 3.04 343 581.8 0.74; 3.04 343 806.8 0.791;
 3.46 328 115 0.502; 3.46 328 389 0.721; 3.46 328 401 0.741; 3.46 328 782 0.82; 3.46 328 992 0.849;
 3.46 343 173.5 0.358; 3.46 343 278.5 0.512; 3.46 343 388.5 0.604; 3.46 343 608.5 0.693; 3.46 343 808.5 0.753
 3.46 353 169.8 0.251; 3.46 353 254.8 0.366; 3.46 353 364.8 0.427; 3.46 353 599.8 0.549; 3.46 353 794.8 0.658;
 3.46 363 147.5 0.174; 3.46 363 247.5 0.236; 3.46 363 357.5 0.319; 3.46 363 552.5 0.395; 3.46 363 737.5 0.473;
 4.28 313 15.4 0.269; 4.28 313 30.11 0.365; 4.28 313 203 0.705; 4.28 313 393 0.795; 4.28 313 838 0.881;
 4.28 328 8.92 0.125; 4.28 328 32.12 0.248; 4.28 328 133 0.45; 4.28 328 301 0.618; 4.28 328 603 0.739; 4.28 328 855 0.778;
 4.28 328 1013 0.813;
 4.28 343 9.22 0.074; 4.28 343 29.32 0.14; 4.28 343 174 0.351; 4.28 343 389 0.509; 4.28 343 754 0.641;
 4.28 353 3.27 0.03; 4.28 353 47.31 0.139; 4.28 353 207.8 0.299; 4.28 353 522.8 0.474; 4.28 353 867.8 0.561;
 4.28 373 0.88 0.009; 4.28 373 11.87 0.037; 4.28 373 159 0.142; 4.28 373 519 0.274; 4.28 373 825 0.351];

sse=0;

% constants
a1=-8483.95; % for k1 MDEA + H+ <-> MDEAH+
b1=-13.8328;
c1=0;
d1=87.39717;

a2=-12092.1; % for k2 CO2 + H2O <-> HCO3- + H+
b2=-36.7816;
c2=0;
d2=235.482;

a3=-12431.7; % for k3 HCO3- <-> CO32- + H+
b3=-35.4819;
c3=0;
d3=220.067;

a4=-13445.9; % for k4 H2O <-> OH- + H+
b4=-22.4773;
c4=0;
d4=140.932;

a5=-6789.04; % for henry's law
```

```

b5=-11.4519;
c5=-0.010454;
d5=94.4914;

for n=1:107;
    MDEA=data(n,1);
    T=data(n,2);
    PCO2=(data(n,3))/101.3;

    k1=exp((a1/T)+(b1*log(T))+(c1*T)+d1);
    k2=exp((a2/T)+(b2*log(T))+(c2*T)+d2);
    k3=exp((a3/T)+(b3*log(T))+(c3*T)+d3);
    k4=exp((a4/T)+(b4*log(T))+(c4*T)+d4);
    HCO2=exp((a5/T)+(b5*log(T))+(c5*T)+d5);

    f1=g*log(PCO2)+k*log(MDEA);
    k1p=k1*f1;

    A=1;
    B=MDEA+k1p;
    C=-(k2*PCO2/HCO2+k4);
    D=-((k1p*k2*PCO2/HCO2)+(k1p*k4)+(2*k2*k3*PCO2/HCO2));
    E=-2*k1p*k2*k3*PCO2/HCO2;

    eq=[A B C D E];
    HR=roots(eq);
    HA=HR(HR>=1e-12&HR<=1e-6); %select the valid value of [H+]
    H=HA(1); %in case there are 2 values of [H+]
    alpha=(H^2+k2*H+k2*k3)*PCO2/HCO2/((k1p/H+1)*(-H.^3+k2*PCO2/HCO2*H+k4*H+2*k2*k3*PCO2/HCO2)); %calc
    alpha for corresponding H+

    error=alpha-data(n,4);
    sse=sse+(error^2);

end

```

Code in command window:

```

>> xo=[-0.03628 0.6262];
>> fminunc(@new2,xo)

```