MODELLING OF CO_2 SOLUBILITY IN DIETHANOLAMINE, N-METHYLDIETHANOLAMINE AND THEIR MIXTURES USING ARTIFICIAL NEURAL NETWORK

by

NIK MOHAMAD SYAHROM BIN MD GHAZALI

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

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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(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.

NIK MOHAMAD SYAHROM BIN MD GHAZALI

ABSTRACT

Natural gas has a wide range of acid gas concentrations, from parts per million to 50 volume percent and higher, depending on the nature of the rock formation from which it comes. Because of the corrosiveness of H_2S and CO_2 in the presence of water and because of the toxicity of H_2S and the lack of heating value of CO_2, sales gas is required to be sweetened to contain no more than a quarter grain H_2S per 100 standard cubic feet (4 parts per million) and to have a heating value of no less than 920 to 980 Btu/SCF, depending on the contract. The most widely used processes to sweeten natural gas are those using the alkanolamines, and of the alkanolamines the two most common are n-methyldiethanolamine (MDEA) and diethanolamine (DEA).

In this research, data from Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) will be used to simulate the solubility of CO_2 in MDEA + DEA aqueous solution using ANN model and the performance will be compared to show which model is better for CO_2 absorption. Besides, the study of CO_2 solubility in MDEA and DEA aqueous solution respectively will be using data from Jou et al (1982) and Lee et al (1972) works and simulation of ANN model was used to compare the performance between ANN model and the reference research works mentioned earlier.

Developed model has an absolute relative deviation (δ_{AAD}) of 8.71% while δ_{AAD} for data from Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) are 17.06%, 12.09% and 9.82% respectively. In terms of pure amine prediction, ANN model of CO_2 solubility predicted in pure MDEA has δ_{AAD} of 8.29% while the reference paper which is A. Benamor et al (2005) has absolute relative deviation of 10.76%. For prediction in pure DEA, the model has δ_{AAD} of 3.33% compared to reference paper which is also from A. Benamor et al (2005) with 4.72%.

ANN has great ability to predict CO_2 solubility in pure MDEA, DEA, and their mixtures only by developing models for each situation and condition due to the limitation of ANN itself which cannot simulate the new input data if they do not have same patterns with the one that has been used to develop the model.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The dwindling high quality crude oil reserves around the globe have motivated the oil and gas industry to discover natural gas reservoirs in remote areas. Currently, over 95% of natural gas used in the United States moves from well to market entirely via pipelines (Natural Gas Pipelines, 2012). In order to fulfil the necessities for a clean, dry, completely vaporish fuel appropriate for transmission through pipelines and distribution for burning by end users, the gas should undergo many stages of processes, as well as separation to get rid of greenhouse gas and other impurities.

Dry carbon dioxide (CO_2) is inert and is commonly used as an industrial material. However, CO_2 is an acidic gas when it reacts with water to form carbonic acid (Informative Guide for CO2). Carbonic acid corrosion is a formidable challenge and its effect on carbon steels has been recognized for years as a major source of damage in oil field equipment and gas pipelines. Thus, the formation of carbonic acid and moisture will decrease pipeline flow capacities, even resulting in blockages, and potential harm to valves, filters and compressors that are being used throughout the process. (Koteeswaran, 2010).

Therefore, separation of carbon dioxide from natural gas is needed to meet this requirement. The technologies available in market for natural gas treating may not be ideally suitable for treating highly contaminated natural gas. Current separation techniques in treating natural gas with highly CO_2 namely are absorption, adsorption, membrane, refrigeration and cryogenic (Herzog, 1999).

Absorption is one of the most effective and economic ways of separating carbon dioxide in industries. Although various processes have been proposed for such processes, the gas absorption method with different solvents is the most widely used. In the acid gas absorption process the capacity and the rate of absorption of acid gases are of central importance.

While the CO2 absorption rate of the primary and secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA) is high, in the case of tertiary amines such as triethanolamine (TEA) and n-methyldiethanolamine (MDEA), the CO_2 absorption rate is considerably lower. Thanks to low carbamate stability, the CO_2 absorption capacity of the tertiary amine aqueous solutions is high and due to the formation of stable carbamate, the primary and secondary amines have low capacity of CO_2 absorption (Guevara F.M., 1998).

Sterically hindered amines such as 2-Amino-2-Methyl-1-Propanol (AMP) could be a primary amine in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to secondary or tertiary carbon atoms (Sartori G., 1983). These amines have high capacity absorption and absorption rate as well as selectivity and degradation resistance. Since equilibrium data are indispensable for design of gas absorption units, many researchers have reported the solubility of acid gases in various types of amines.

Solubility of CO_2 in MEA, DEA and MDEA aqueous solutions at various temperatures, amine concentrations and pressures has been reported. Jane et al. (1997) determined the solubility of CO_2, H_2S and their mixtures in the system of DEA+AMP aqueous solution. Teng et al. (1989) measured the solubility of acid gases in AMP at 50^oC and 3.43 $kmol/m^3$ AMP. Roberts et al. (1988) reported the solubility of acid gases in AMP. Tontwachwuthikul et al. (1991) measured the solubility of CO_2 in AMP at various temperatures and AMP concentrations. They also correlated the data with the Modified Kent-Eisenberg model and reported a relation to calculate the equilibrium constant of the protonation reaction.

A number of models such as Kent-Eisenberg, Modified Kent-Eisenberg, Electrolyte-NRTL, Extended Debye-Hückel, Pitzer and Li-Mather models were proposed to correlate the solubility data. Kent & Eisenberg (1976) modelled the solubility of acid gases and their mixtures in MEA and DEA aqueous solutions. They considered equilibrium constants of carbamate formation and protonation of these amines to be temperature-dependent only. Since the Kent-Eisenberg model is an empirical model, in a wide range of temperature, pressure and amine concentrations it cannot properly predict the solubility of acid gases in amine aqueous solutions.

Although the Kent-Eisenberg equilibrium constant of carbamate formation was used in this work, the new correlations for MEA and DEA equilibrium constant of protonation reaction were presented. To increase the accuracy of predicting the solubility of acid gases in amines, the activity coefficients must be considered. To do so, Deshmukh et al. (1981) and Pitzer (1973) proposed the Extended Debye-Hückel and Pitzer models, respectively. It should be noted that application of these models would be more complicated than that of the Kent-Eisenberg and Modified Kent-Eisenberg. In the Pitzer, Extended Debye-Hückel and Li-Mather models the activity coefficients were expressed in terms of long as well as short-range intermolecular forces.

An artificial neural network (ANN) modelling has been used to simulate the experimental results for CO_2 absorption in aqueous solution of MDEA + DEA. The ANN is a powerful modelling method in various scientific fields. The capability of learning from experimental results and the simplicity of implementation are the main advantages of the ANN over the other mathematical modelling methods.

1.2 Problem Statement

Several experiments were done by manipulating temperature, partial pressure of CO_2 and concentration of MDEA + DEA aqueous solution. It was determined that the parameters of activity coefficient model of these systems demonstrated some interactions. But, ANN model has never been developed to study the CO_2 solubility in aqueous solution of MDEA + DEA, MDEA and DEA.

Data from Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) research works will be used to simulate the solubility of CO_2 in MDEA + DEA aqueous solution using ANN model and the performance will be compared to show which model is better for CO_2 absorption.

Besides, the study of CO_2 solubility in MDEA and DEA aqueous solution respectively will be using data from Jou et al (1982) and Lee et al (1972) research works and simulation of ANN model will be used to compare the performance in terms of average absolute relative deviation percent (δ_{AAD}) between ANN model and the reference research works mentioned earlier.

1.3 Objectives

1. To model CO_2 solubility in mixture of MDEA + DEA aqueous solutions using artificial neural network using experimental data of Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) research works.

2. To study the artificial neural network model extrapolation capability by predicting CO_2 loading in MDEA and DEA aqueous solution using experimental data retrieved from Jou et al (1982) and Lee et al (1972) research works.

1.4 Scope of study

The first part of the research focuses on correlation of CO_2 solubility in the mixture of MDEA and DEA aqueous solutions. Artificial neural network model will be developed by using experimental data from Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) research works and will be used to study the relationship mentioned earlier. These three reference papers are chosen because their data consists of various parameters such as temperature, partial pressure of CO_2 and concentration of the mixtures. The second part of the research is the developed ANN model then will be used to predict CO_2 solubility in MDEA aqueous solution and DEA aqueous solution respectively using data from Jou et al (1982) and Lee et al (1972) research works. Difference between reference papers from first part and second part is the first part reference papers only contain data for mixtures of amines while the second part data contain data for pure amines. The deviation of the generated CO_2 loading from both parts will then be compared between the developed neural network models and results from the mentioned experimental works.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon Dioxide

Carbon dioxide is a naturally occurring chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It appears as a gas at standard temperature and pressure. CO_2 is a non-toxic and non-flammable fluid; it has a high chemical stability as it has a very low energy level compared to other carbon compounds. (Refer Appendix I)

Figure 2.1 shows the phase diagram of carbon dioxide. There is no liquid state if carbon dioxide at pressure lowers than 5.11 atm. Above -78.51°C, carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition (Shakhashiri, Carbon Dioxide, CO2, 2008).

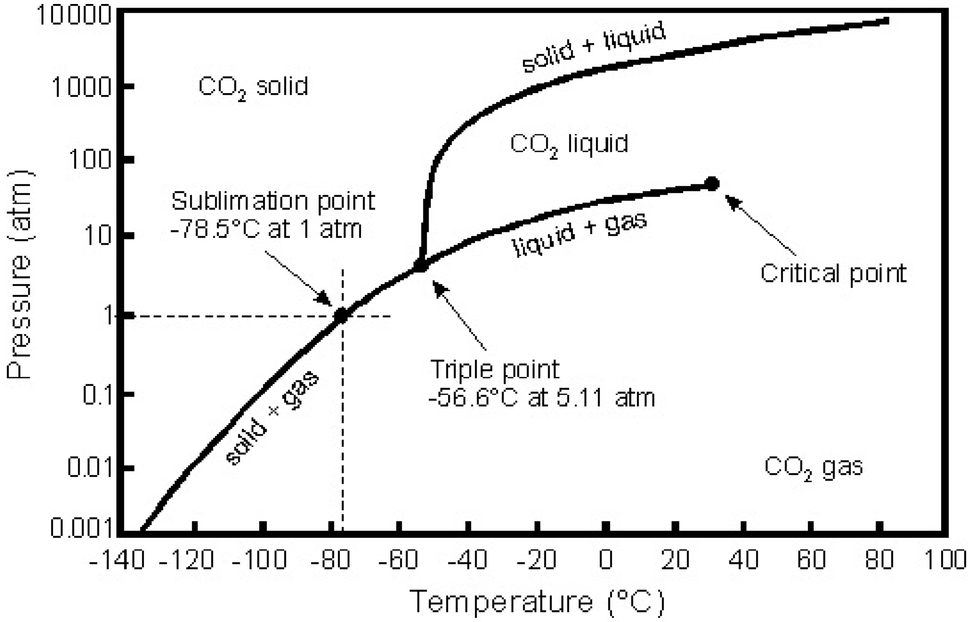


Figure 2.1 Pressure-Temperature phase diagram for CO2

Known as acid gas, CO_2 has to be removed from natural gas to avoid problems such as corrosion, equipment plugging due to the formation of CO_2 solid in the low temperature system and also to maintain the heating value of natural gas. In this context, acid gas removal also can be known as gas treating or gas sweetening. The group of process uses the aqueous solution of various amines to remove CO_2 from natural gas. Removal of acid gas is a common unit process used in refineries, petrochemical plants, and other industries to remove the contaminant in natural gas (Wong & Bioletti, 2002).

Chemical absorption by a solvent is the technique most commonly used to remove acid gas in natural gas flow. The basic principle of this process is illustrated in Figure 2.2.

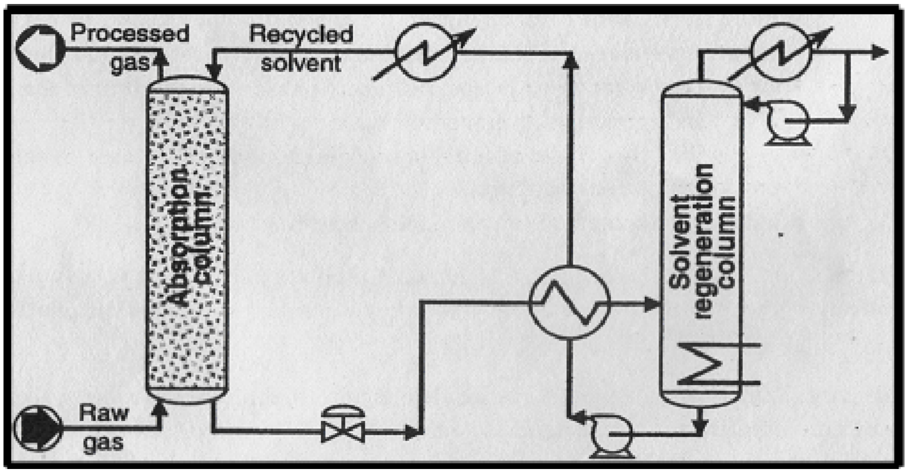


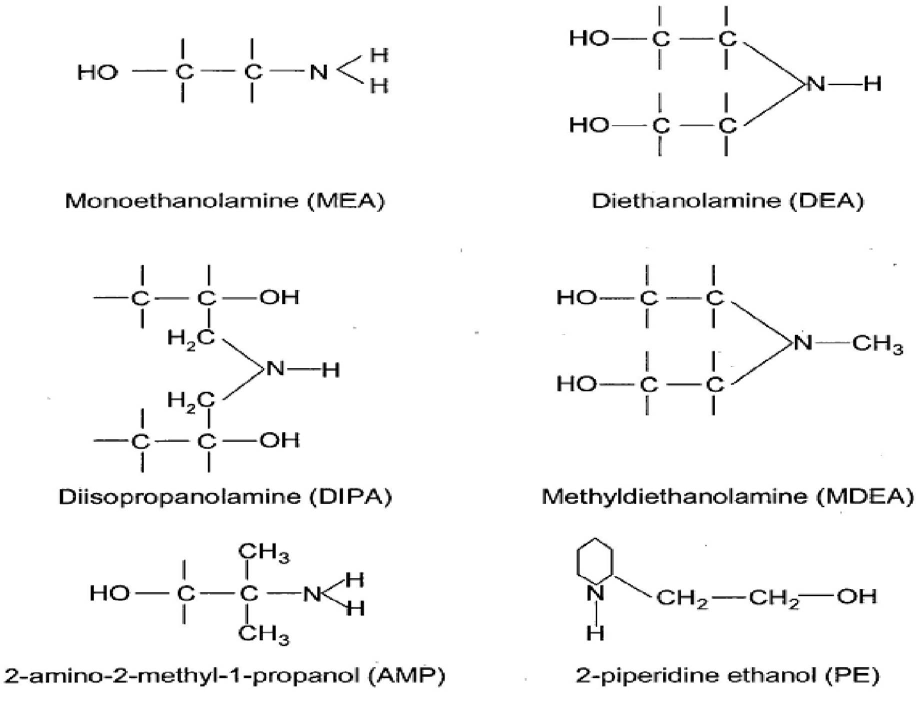
Figure 2.2 Schematic Diagram of Acid Gas Removal Using Chemical Absorption

The gas to be processed is contacted in counter current flow with solvent in a plate or packed column. If the solvent introduced at the top of the column is pure, the solvent circulation rate and the number of plate can be set to obtain gas purity at the exit that corresponds to the specification. The solvent leaving the absorption column is sent to a distillation column for regeneration at lower pressure operating (Alexandre Rojey, 1994).

Various types of trays and packing are used. Information on these items and the design methods applicable in different specific cases can be found by referring to the general works already mentioned. There are three types of packing elements that are widely used such as Raschig ring, Pall ring and Beri saddle. The use of so-called "structure" packing made of modular elements occupying the entire cross-section of the column and helps to reconcile good efficiency with low pressure drop (Branan, 2002).

2.2 Alkanolamines

Figure 1.1 shows some of the common alkanolamines used in gas treating applications. These solvents can be thought of as substituted ammonia molecules. The number of substitutions on the nitrogen atom determines the type of alkanolamine. In primary amines, one hydrogen atom on the nitrogen is replaced with a functional group, in secondary amines two hydrogen atoms are replaced and in tertiary amines all three hydrogen atoms are replaced. The chemical structure of alkanolamines is ideally suited for acid gas removal. The amine group provides the required basicity that allows it to react with acid gases reversibly and the hydroxyl group makes the amine more water-soluble (Jamal, 2002).



Monoethanolamine (MEA)

Diethanolamine (DEA)

Diisopropanolamine (DIPA)

Methyldiethanolamine (MDEA)

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

2-piperidine ethanol (PE)

Figure 2.3 Molecular structures of commonly used alkanolamines

The reaction rates of hydrogen sulphide (H_2S) and CO_2 differ greatly in alkanolamine solutions because of the difference in their structure. As a Bronsted acid, H_2S reacts directly with the amine function in the acid-base neutralization step. This neutralization is much faster than the time it takes for H_2S to diffuse into the bulk liquids.

The reaction of CO_2 with a basic solvent is much slower than that of H_2S. The slower reaction rate of CO_2 is due to its nature as a Lewis acid, which must hydrate before it can react by acid-base neutralization. It may also react directly with the amine to form a carbamate. The rate of hydration and carbamation are both slow and can be comparable to the rate of diffusion of CO_2 (Zare Aliabad & Mirzaei, 2009).

Aqueous MEA and DEA solutions are generally used for bulk CO_2 removal when the partial pressure of CO_2 is relatively low and the product purity requirement is high. DIPA is used primarily in special applications where it is necessary to preferentially absorb H_2S over CO_2. Both primary and secondary amines react strongly with CO_2 to form stable carbamates and their heats of reactions are substantial (Polasek & Bullin, 1994).

2.3 Methyldiethanolamine (MDEA)

MDEA which stands for N-methyldiethanolamine is a psychedelic hallucinogenic drug and empathogen-entactogen of the phenethylamine family. It is a tertiary amine and act as a solvent. It has a greater capacity to react with acid gases because it can be used in higher concentrations. This advantage is enhanced by the fact that it is reacting with all of the H_2S and only part of CO_2.

MDEA is a clear, water-white, hygroscopic liquid with an ammoniacal odour (Methyldiethanolamine (MDEA), 2005). It also delivers energy savings by reducing reboiler duties and lowering overhead condenser duties. It has proved to be highly selective for absorption of H_2S when compared to CO_2 resulting in even lower circulation rates and higher quality acid gases for recycle to sulphur recovery unit. It will absorb carbon dioxide and hydrogen sulphide at lower temperatures and release the hydrogen sulphide at higher temperatures. It is used for selectively remove hydrogen sulphide from gas streams containing carbon dioxide (Methyl Diethanolamine (MDEA)).

According to Kohl and Nielsen (1997), MDEA selectively removes H_2S from natural gas streams while piperazine acts mainly as a corrosion inhibitor and surfactant. A corrosion inhibitor is a chemical compound that, when added in small concentration stops or slows down corrosion (rust) of metals and alloys. The slower rate of reaction of CO_2 with MDEA is compensated through the addition of small amounts of rate-promoting agents such as DEA or PZ.

During the gas sweetening process of absorption and desorption non-reclaimable contaminants (exhausted amines) tend to accumulate in the system and can cause both major reductions in efficiency and operational problems due to the closed loop nature of the system. Therefore, wastewater from gas sweetening units frequently becomes contaminated with raw amine-solutions, amine degradation products, thermal stable salts, heavy hydrocarbons and particulates (M. Fürhacker, 2003).

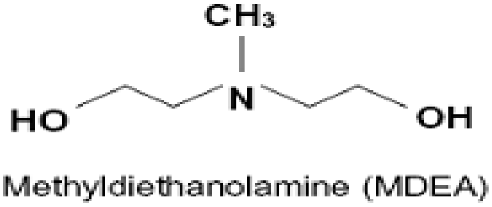


Figure 2.4 Chemical structures of MDEA

MDEA is considered moderately irritating to the eyes, but only slightly irritating to the skin. The product is not corrosive under the conditions of the corrosivity test and is not regulated as a hazardous material for transportation purposes. Because of the low vapour pressure of MDEA, exposure to vapours is not expected to pose significant hazard under normal workplace conditions (Huntsman, 2007). (Refer Appendix II)

MDEA as an absorption solvent of removing acid gases is widely used today in natural gas processing because it possesses the characteristics such as higher hydrogen sulphide selectivity, bigger absorption capacity, lower regeneration energy, smaller hot degradation and lesser corrosive. The basic properties of MDEA are shown in Table 2.1.

Table 2.1 Physical properties of MDEA [Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)]

Methyldiethanolamine (MDEA)	
Molecular formula	$CH_3N(C_2H_4OH)_2$
Molar mass	119.2 g/mol
Appearance	Clear, colourless, 150 APHA max.
Density	1.040 g/mL
Melting point	-21^oC
Boiling point	247^oC @ 760mmHg
Solubility in water	complete
Solubility	Benzene, alcohol
Refractive index (n_D)	1.4694
Viscosity	101cP @ 20^oC
Flash point	135^oC pmcc
Auto ignition temperature	265^oC
Explosive limits	0.9-8.4 vol % in air

2.4 Diethanolamine (DEA)

Diethanolamine, often abbreviated as DEA or DEOA, is an organic compound with the formula $HN(CH_2CH_2OH)_2$. This colorless liquid is polyfunctional, being a secondary amine and a diol. Like other organic amines, diethanolamine acts as a weak base. Reflecting the hydrophilic character of the alcohol groups, DEA is soluble in water, and is even hygroscopic. Amides prepared from DEA are often also hydrophilic.

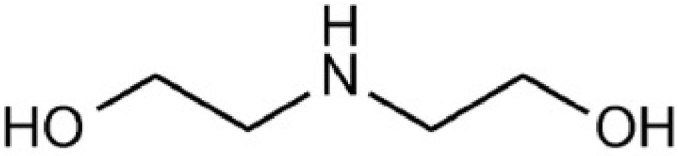


Figure 2.5 Chemical structures of DEA

DEA is used as a surfactant and a corrosion inhibitor. It is used to remove hydrogen sulfide and carbon dioxide from natural gas. In oil refineries, a DEA in water solution is commonly used to remove hydrogen sulfide from various process gases. It has an advantage over a similar amine ethanolamine in that a higher concentration may be used for the same corrosion potential. This allows refiners to scrub hydrogen sulfide at a lower circulating amine rate with less overall energy usage.

Diethanolamine helps to overcome the limitation of MEA, and can be use in the present of COS and CS2. The application of DEA to natural gas processing was described by Berthier in 1959 (Kohl and Riesenfeld, 1985). Operating with solutions containing 25-30% by weight of DEA can be use to process Natural gas with even High acid gases contents.

The solvent apply (DEA) is considered to be chemically stable; DEA can be heated to its normal boiling point (269 ^{o}C at 760mmHg) before decomposition. Therefore reduce the solvent degradation during stripping and reduce solvent loss and accumulation in the units.

The heat of reaction of DEA with CO_2 is low compared to other amines hence the heat generated in the absorber during CO_2 absorption process is low which increases the solvent loading capacity in the absorber as solubility or loading of CO_2 increases at low temperature. The basic properties of DEA are shown in Table 2.2.

Table 2.2 Physical properties of DEA [Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)]

Diethanolamine (DEA)	
Molecular formula	$C_4H_{11}NO_2$
Molar mass	105.14 g/mol
Appearance	Clear, colourless
Density	1.097 g/mL
Melting point	$28^{o}C$
Boiling point	$271^{o}C$ @ 760mmHg
Solubility in water	complete
Solubility	Benzene, alcohol
Refractive index (n_D)	1.477
Viscosity	351cP @ $20^{o}C$
Flash point	$138^{o}C$ pmcc
Auto ignition temperature	$365^{o}C$
Explosive limits	1.6-10.6 vol % in air

2.5 Artificial Neural Network (ANN)

Artificial neural networks as the name suggests are inspired by the biology of a brain's neuron. Human beings can perform a wide range of complex tasks in a relatively easier way as compared to computers. So the researchers are looking for ways in which human intelligence can be incorporated into machines so that they can also perform certain complex tasks easily. Artificial neurons have the characteristics of a biological neuron and these neurons are organized in a way that is reminiscent of the human brain. ANN also display a striking number of brain's properties like learning from experience, generalization from previous instances and apply to new data, etc.

The theorem proved by Hornik et al. (1989) and Cybenko (1989) states that a multilayered feedforward neural network with one hidden layer can approximate any continuous function up to a desired degree of accuracy provided it contains a sufficient number of nodes in the hidden layer. This means that conceptually, feedforward neural networks approximate unknown functions which means, they can be considered as universal approximators.

2.5.1 Characteristics of Neural Network

The first model of an artificial neuron was proposed by McCulloch and Pitts (1943). It was a binary device with a binary input, binary output, and fixed activation threshold. In the Figure 2.6 below, an artificial neuron is shown along with the tasks performed by it.

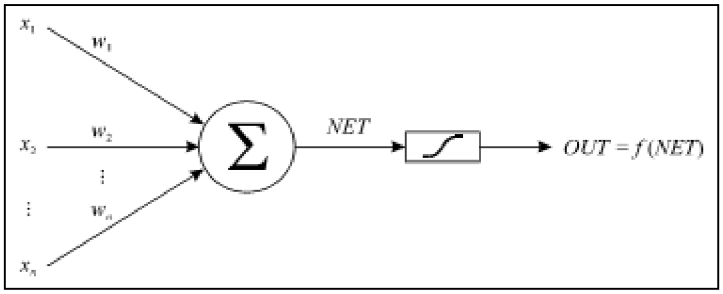


Figure 2.6 Schematic of an artificial neuron with activation function (Teodorović & Vukadinovic, 1998)

The input signals x1, x2 …xn representing the output signals of other neurons, are multiplied by the associated connection strengths w1, w2 ….wn (also called weights). The output signal NET is equal to the weighted sum of input signals. The range of the weighted sum of input signals, NET, is compressed by an 'S' curve such that the value of the output signal, OUT, never exceeds a relatively low level regardless of the value of NET. Most commonly used activation functions are step function, sigmoid function, hyper tangent function and identity function.

The transformation of input signals by a logistic curve enables the receiving and processing of very weak and very strong signals. The present neural network architecture is based on a simplified model of the brain, the processing task being distributed over numerous neurons (nodes or processing elements).

Any neural network has the following characteristics:

a) A set of processing elements,
b) Connectivity of those elements,
c) The rule of signal propagation through the network,
d) Activation or transfer functions,
e) Training algorithms (learning rules or learning algorithms),
f) Environment in which the network functions.

These characteristics can be better understood with the help of the following example shown in Figure 2.7 below.

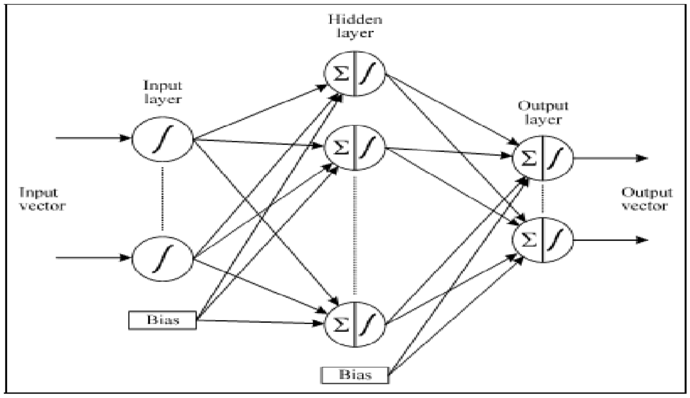


Figure 2.7 Two-layered feedforward neural network (Teodorović & Vukadinovic, 1998)

In this network we can see three layers through which the input signal has to pass through. Each layer has a certain number of processing elements (nodes) as shown in the figure. The number of nodes varies depending on the problem that is being addressed. Any neural network has three types of nodes – input, output and hidden. Input nodes receive input signals from sources outside the network. Output nodes transmit signals that is, output values outside the network. All other nodes not belonging to the input/output layers belong to the hidden layers. The nodes of one layer are connected to the nodes of the adjacent layer. This connectivity can be partial or full connectivity. Each node transmits signals of different strengths to its neighbouring nodes.

The connection strengths are also called as weights of the connections. The propagation of input signal usually follows certain rules; in this case since it is a multilayered feed forward network, the input signal extends forward through several layers, while it is being processed to estimate the network's output signal. Each node is a processing element associated with the corresponding activation function by which the weighted sum of input values is transformed to determine the output value. To each node's input only the outputs of nodes from a previous layer are supplied and the output signal is transmitted to the nodes of the next layer.

2.5.2 Training Algorithm

The most important ANN characteristic is its ability to learn from its environment. This ability of ANN to learn results from the process by which the connection weights are updated. The process of weight updating is called learning or training. The training process is achieved by applying a backpropagation (BP) procedure. The BP is a gradient descent optimization procedure in which the mean square error performance index is minimized. Several training algorithms use the BP procedure, and although each one has its own advantages, such as calculation rate and computation and storage requirements, no single algorithm is best suited to all problems. The performance of each algorithm depends on the process to be modelled and on the learning sample and training mode used.

Table 2.3 List of Training Algorithms in MATLAB

Training Algorithms	description
BFGS quasi-Newton backpropagation (TRAINBFG)	BFGS quasi-Newton method. It requires storage of approximate Hessian matrix and has more computation in each iteration than conjugate gradient algorithms, but it usually converges in fewer iterations.
Bayesian regularization backpropagation (TRAINBR)	Bayesian regularization. Modification of the Levenberg−Marquardt training algorithm to produce networks that generalizes well. It reduces the difficulty of determining the optimum network architecture.
Conjugate gradient backpropagation with Powell-Beale restarts (TRAINCGB)	Powell−Beale conjugate gradient algorithm. Slightly larger storage requirements than TRAINCGP. Generally faster convergence.
Conjugate gradient backpropagation with Fletcher-Reeves updates (TRAINCGF)	Fletcher−Reeves conjugate gradient algorithm. It has the smallest storage requirement of the conjugate gradient algorithms.
Conjugate gradient backpropagation with Polak-Ribiére updates (TRAINCGP)	Polak−Ribiere conjugate gradient algorithm. Slightly larger storage requirements than TRAINCGF. Faster convergence on some problems.
Gradient descent backpropagation (TRAINGD)	Basic gradient descent. Slow response; it can be used in incremental-mode training.
Gradient descent with adaptive learning rate backpropagation (TRAINGDA)	A network training function that updates weight and bias values according to gradient descent with adaptive learning

	rate
Gradient descent with momentum backpropagation (TRAINGDM)	Gradient descent with momentum. Generally faster than TRAINGD. TRAINGDM can be used in incremental-mode training.
Gradient descent with momentum and adaptive learning rate backpropagation (TRAINGDX)	Adaptive learning rate. Faster training than TRAINGD, but it can be used only in batch-mode training.
Levenberg-Marquardt backpropagation (TRAINLM)	Levenberg−Marquardt algorithm. It is the fastest training algorithm for networks of moderate size. It has memory reduction feature for use when the training set is large.
One-step secant backpropagation (TRAINOSS)	One-step secant method. Compromise between conjugate gradient methods and quasi-Newton methods.
Resilient backpropagation (TRAINRP)	A network training function that updates weight and bias values according to the resilient backpropagation algorithm
Scaled conjugate gradient backpropagation (TRAINSCG)	Scaled conjugate gradient algorithm. The only conjugate gradient algorithm that requires no line search. Very good general-purpose training algorithm.

2.5.3 Levenberg-Marquardt Backpropagation

`trainlm` is a network training function that updates weight and bias values according to Levenberg-Marquardt optimization. It is often the fastest backpropagation algorithm in the toolbox, and is highly recommended as a first-choice supervised algorithm, although it does require more memory than other algorithms.

Like the quasi-Newton methods, the Levenberg-Marquardt algorithm was designed to approach second-order training speed without having to compute the Hessian matrix. When the performance function has the form of a sum of squares (as is typical in training feedforward networks), then the Hessian matrix can be approximated as

$$\mathbf{H} = \mathbf{J}^{T}\mathbf{J}$$

and the gradient can be computed as

$$\mathbf{g} = \mathbf{J}^{T}\mathbf{e}$$

where **J** is the Jacobian matrix that contains first derivatives of the network errors with respect to the weights and biases, and **e** is a vector of network errors. The Jacobian matrix can be computed through a standard backpropagation technique that is much less complex than computing the Hessian matrix.

The Levenberg-Marquardt algorithm uses this approximation to the Hessian matrix in the following Newton-like update:

$$\boldsymbol{x}_{k+1} = \boldsymbol{x}_{k} - (\boldsymbol{J}^{\boldsymbol{T}}\boldsymbol{J} + \mu\boldsymbol{I})^{-1}\boldsymbol{J}^{\boldsymbol{T}}\boldsymbol{e}$$

When the scalar μ is zero, this is just Newton's method, using the approximate Hessian matrix. When μ is large, this becomes gradient descent with a small step size. Newton's method is faster and more accurate near an error minimum, so the aim is to shift toward Newton's method as quickly as possible. Thus, μ is decreased after each successful step (reduction in performance function) and is increased only when a tentative step would increase the performance function. In this way, the performance function is always reduced at each iteration of the algorithm.

2.5.4 Training of A Neural Network

After the building of neural network, the input data is fed into the network through the input nodes, along with the desired output data. The neural networks self-adapt to the data and incite appropriate responses. This process of making the network adapt to the data is known as training of a neural network and the algorithms used for this purpose renown as training algorithms. These algorithms can be classified according to their modelling, learning, and validation properties. The modelling abilities of an algorithm determine the range of nonlinear functions that it is able to precisely reproduce. The chosen structure of a neural network model can influence the convergence rate of a training algorithm and even determine the type of learning to be used.

The multilayered neural networks have come into use after the development of an error backpropagation algorithm, which was used for training a network. Various researches have independently developed a suitable and currently most popular algorithm for training a multilayered feedforward neural network (Rumelhart and McClelland (1986), Le Cun (1985), Parker (1985). The proposed backpropagation algorithm is a gradient procedure. The activation functions of nodes are bounded, continuous, monotonously increasing, nonlinear, differentiable functions. The output function of the network is a continuous, differentiable weight function enabling the search of the extremum by the "gradient descent" algorithm.

The optimal weights, w_{ij}, are determined by the rule of gradient descent (delta rule, generalized delta rule) minimizing the criterion function or error. Each iteration of the algorithm (cycle or epoch defined as the process of transmission of one or a few training pairs through the network whereby the error is calculated) contains two passes (Figure 2.8):

- Propagation of one or a set of input signals forward to the output layer (in the original algorithm input signals were brought to the network individually)
- Backward pass where the computed error extends backward in order to calculate the changes of parameters (weight of the network's branches).

The procedure is performed in numerous iterations using the same training pairs until the error becomes “sufficiently” small.

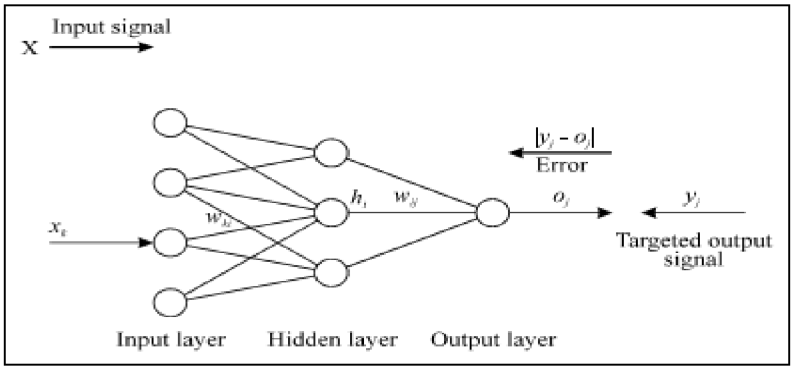


Figure 2.8 Taxonomy of training a multilayered perceptron: the input signal extends forward and the computed error backward (Teodorović & Vukadinovic, 1998)

2.5.5 Testing of A Neural Network

Any model has to be validated using some data. A trained neural network is validated using testing data. The available data is always divided into three parts prior to the training – training data, cross-validation data, and testing data. The training data is used during the training purposes; the cross-validation data is also used during the training but not to train the network, instead to check the learning of the network during the training process. The testing data is totally a different set of data that the network is unaware of; this data is used for validation of the trained network. If the network is able to generalize rather precisely the output for this testing data, then it means that the neural network is able to predict the output correctly for new data and hence the network is validated. The amount of data that is to be used for training and testing purposes is dependent on the availability of the data, but in general the training data is 2/3rd of the full data and the remaining is used for testing purposes. The cross-validation data can be 1/10th of the training data.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

There are a total of five steps or phase of activities will be carried out to complete this project. Figure 3.1 depicts the methodology employed in all phases of the project.

The first step was several literature reviews had been done on every component related to the project such as carbon dioxide, acid gases, alkanolamines, MDEA, DEA and Artificial Neural Network.

Next, data collection from several journals and research papers from previous experimental works on CO_2 solubility using MDEA and DEA. These data had been selected based on several parameters such as concentration of alkanolamines, operating temperatures and partial pressures of CO_2. For data from Zhang et al (2002), the data can be classified as low pressure data as the partial pressure of CO_2 is from 1 – 75 kPa while the temperature ranging from 313K to 343K. Second set of data is taken from A. Benamor et al (2005) which consists of CO_2 partial pressure ranging from 0.09 – 100 kPa and temperature from 303 – 323 K. The partial pressure from this set of data is slightly higher than the first one. The third set of data which taken from Khalid et al (2012) is considered high pressure because the partial pressure of CO_2 ranging from approximately 500 to 1500 kPa and the temperature is from 362.1 – 412.1 K. All the data are normalized from 0 to 1 due to restriction in MATLAB. Data can be obtained from Appendix III.

The third phase was developing Artificial Neural Network model using the mentioned computer software which is MATLAB. There has been several lecture sessions conducted by supervisor in order to master the skills of using MATLAB. There were a lot of trials and errors have been performed in order to get an ANN model with the lowest error and highest performance. At the end of the day, an ANN model has been developed and can be used in the next phase. The first step of developing ANN is by randomizing the input data. All the data from the three reference papers will be randomize and divided into three parts:

a) 60% of data will be used for training of the neuron.

b) 5% of data will be used for validation of the neuron.

c) 35% of data will be used for testing of the neuron.

The trial and error method will then be used to determine number of nodes for the neuron. Every number of neuron will give different results in term of Mean Square Error (MSE) and Regression. The trial and error process has been performed by setting the number of nodes as 1 and the results are recorded. Number of nodes is increased from 3, 5, 7, 9, 15, 20, 25, 30 and the process stops at 35. The results from each iteration are recorded and number of nodes that shown lowest MSE and highest Regression will be the optimal number of nodes for the neural network model. The basis is at MSE equals to zero means no error and Regression equals to one means no deviation of generated output data from targeted data.

The fourth step was to predict CO_2 solubility at different concentration of MDEA and DEA. There were three different ways of predicting CO_2 solubility in both pure MDEA and DEA. Predictions were done using totally different data input. New data input consists of experimental data for MDEA and DEA which was taken from Jou et al (1982) and Lee et al (1972) respectively. The important point for this part was the condition of the amines. Previously, the model was developed using mixtures of MDEA and DEA. However, for this part, pure amines were used instead of mixtures.

The first prediction method was done by simulating the previously developed model using the new data. The importance of this simulation was to evaluate the ability of the neural network either it still can predict the CO_2 loading correctly or not after input data was changed from mixtures of MDEA and DEA into individual solutions of MDEA and DEA.

The second prediction method was done by developing a new artificial neural network model using data that was mentioned earlier in second phase together with Jou et al (1982) data. So, the data that had been used for this part were the combination of mixtures of both amines and pure MDEA. The purpose for this part was to compare the performance of this method with the first method in predicting CO_2 solubility in pure MDEA.

The third prediction method is basically the same with second method but for this time the principle was to compare the performance of this method with the first method in predicting CO_2 loading in pure DEA. Data for pure DEA was taken from Lee et al (1972) and it was combined together with mixtures of MDEA and DEA data.

Generated CO_2 loading from these three methods of prediction were then recorded and prepared for the next phase which was error analysis.

The fifth phase was done by performing error analysis on the results obtained by comparing the generated CO_2 loading with the experimental data from the reference paper. Error calculated in the form of average absolute relative deviation percent, δ_{AAD} using the following equation:

$$(\delta_{AAD}) = \frac{\sum_{i=1}^{N} \frac{|\alpha_{calc} - \alpha_{exp}|}{\alpha_{exp}}}{N} \times 100\%$$

Where

α_{calc} = generated CO_2 loading

α_{exp} = experimental CO_2 loading

N = number of data points

Several graphs of generated CO_2 loading and experimental CO_2 loading were plotted to show the differences between the developed ANN model and the experimental results from previous research works.

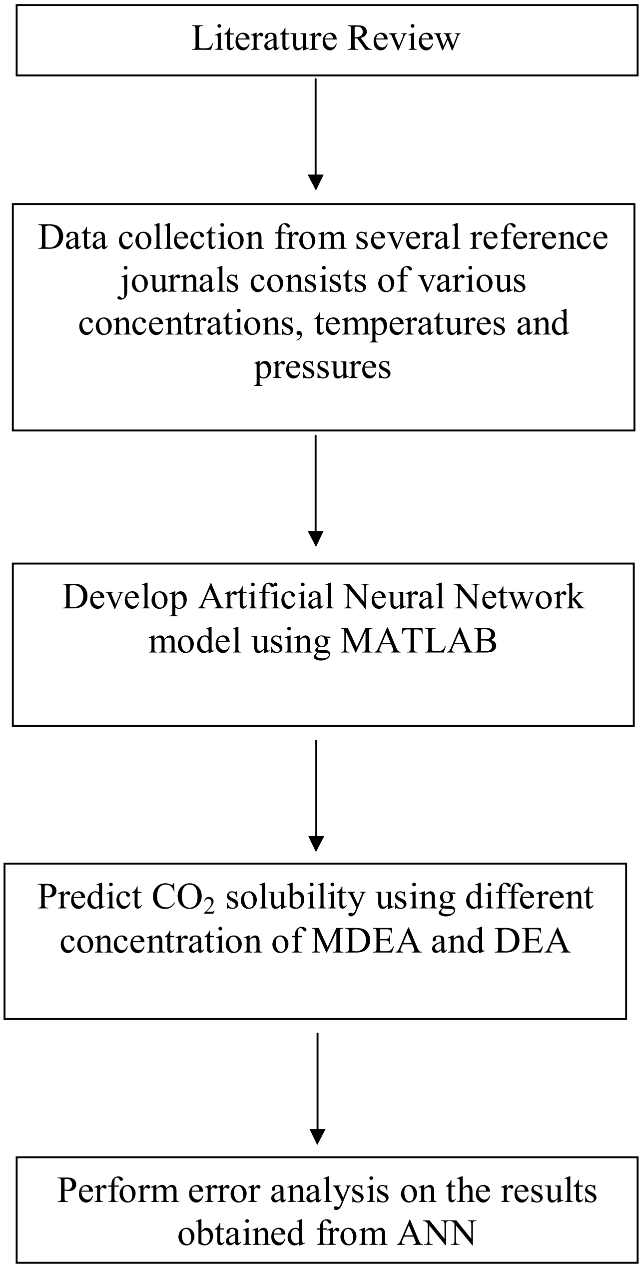


Figure 3.1 Project Flow Chart

3.2 Gantt Chart

There are a total of 9 processes that has been decided in order to make sure the research work can be done within given time frame. 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-EDX 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)																●

● Suggested milestone

🟪 Process

3.3 Software Required

In this project, there are two main softwares will be used to develop the mentioned Artificial Neural Network models which are:

a) Microsoft Excel
  - This software will be used in data collection and error analysis

b) MATLAB
  - This software will be used in developing Artificial Neural Network model, performing complex calculation related to the model and increasing the accuracy of calculated data.

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 ANN Model Development

Artificial Neural Network model has been successfully developed using MATLAB. The modelling procedure basically is trial and error concept. Data is set at 60% : 5% : 35% for training, validating and testing. The optimal number of nodes for the model is 5 with the MSE (Testing) of 0.004947 and Regression (Testing) of 0.948546. The results of simulation are tabulated below.

Table 4.1 Simulation Results

No of nodes	MSE (Training)	Regression (Training)	MSE (Validating)	Regression (Validating)	MSE (Testing)	Regression (Testing)
1	0.038527	0.614555	0.056611	0.535754	0.023074	0.832425
3	0.049714	0.534522	0.024847	0.848392	0.050896	0.387476
5	0.005976	0.956102	0.000968	0.993102	0.004947	0.948546
7	0.024236	0.774147	0.014569	0.938196	0.043194	0.568845
9	0.048722	0.449111	0.029824	0.806270	0.051635	0.535453
15	0.019612	0.843014	0.052344	0.339451	0.017002	0.837862
20	0.186283	0.705789	0.098656	0.170069	0.258710	0.562405
25	0.001792	0.983866	0.001789	0.980234	0.097779	0.691668
30	0.010654	0.906327	0.006593	0.949663	0.040117	0.740795
35	0.008478	0.927138	0.016194	0.835601	0.032470	0.778969

From the results above, 5 nodes is the best even though the value of MSE for each function is not the lowest and value for Regression for each function is not the highest. However, same as optimization concept, there will be trade off between Training, Validating and Testing. For example, value of Regression (Training) for nodes 25 is higher than nodes 5 but nodes 5 has higher value than nodes 25 for Regression (Validating) and Regression (Testing). Hence, nodes 5 has been chosen as the optimal no of nodes for the artificial neural network model of CO_2 solubility in mixture of MDEA + DEA aqueous solution.

Graphs of mean square error and regression versus number of nodes are plotted below.

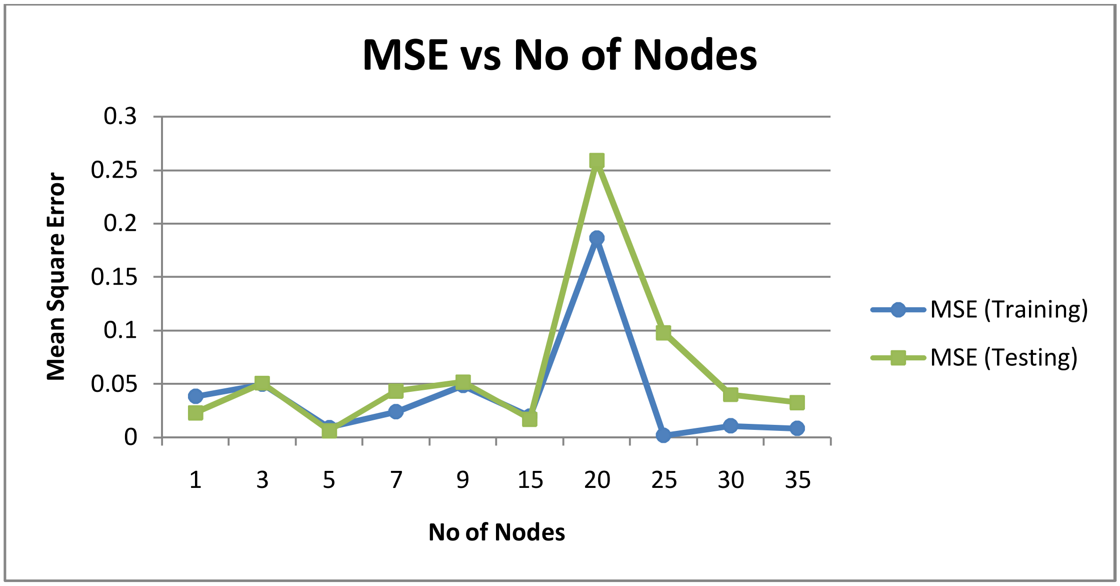


Figure 4.1 Graph of MSE vs No of Nodes

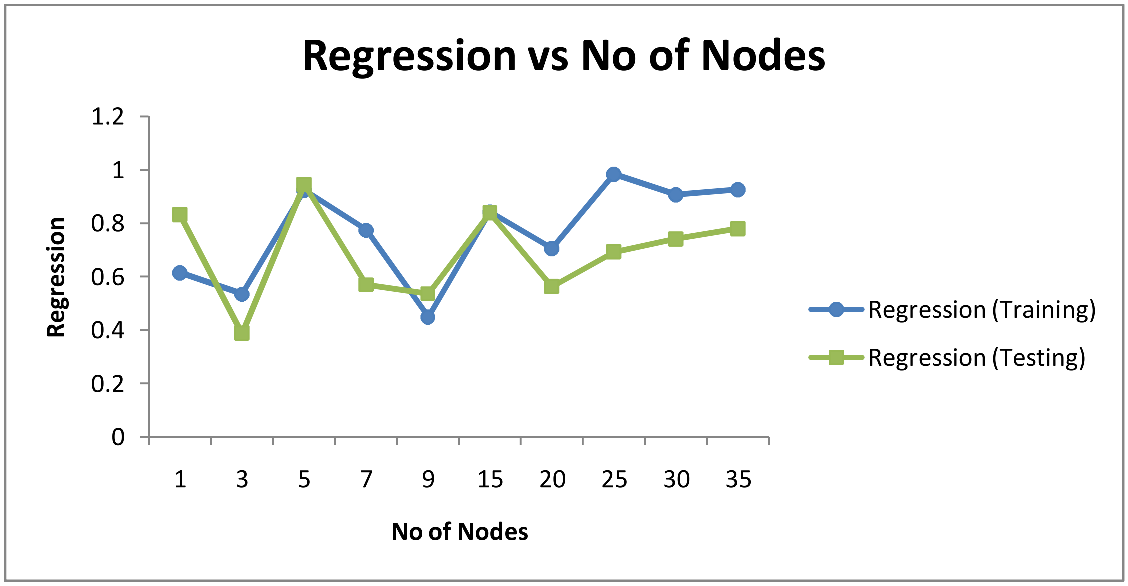


Figure 4.2 Graph of Regression vs No of Nodes

Besides MSE and Regression, there are also generated output data as a part of the results. The output data was simulated as a result of the training and testing by the neuron. However, there are small deviations of the generated output from the target data. Generated output and calculated error are tabulated in the Appendix IV. Error is calculated using the following equation:

$$Error = Target\ Data - Output\ Data$$

Deviation between generated CO_2 loading and experimental CO_2 loading were plotted below. Results were divided into 6 parts based on concentration of amines.

- 1.5M MDEA + 0.5M DEA
- 1.0M MDEA + 1.0M DEA
- 0.5M MDEA + 1.0M DEA
- 3.0M MDEA + 1.0M DEA
- 2.0M MDEA + 2.0M DEA
- 1.0M MDEA + 3.0M DEA

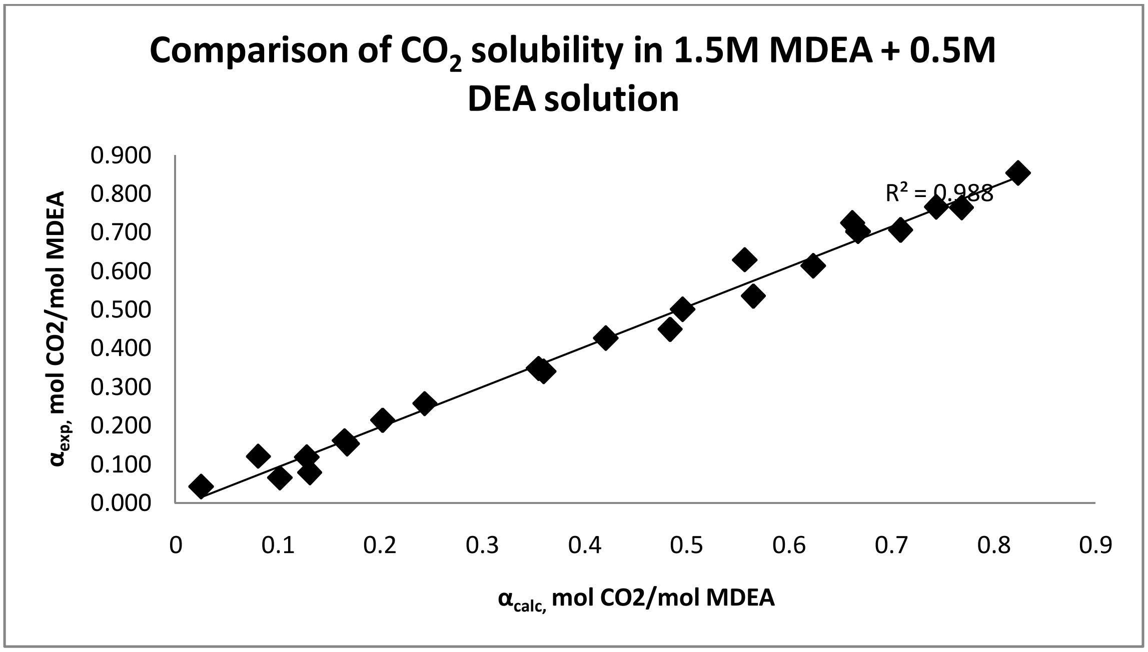


Figure 4.3 Comparison of CO_2 solubility in 1.5M MDEA + 0.5M DEA solution

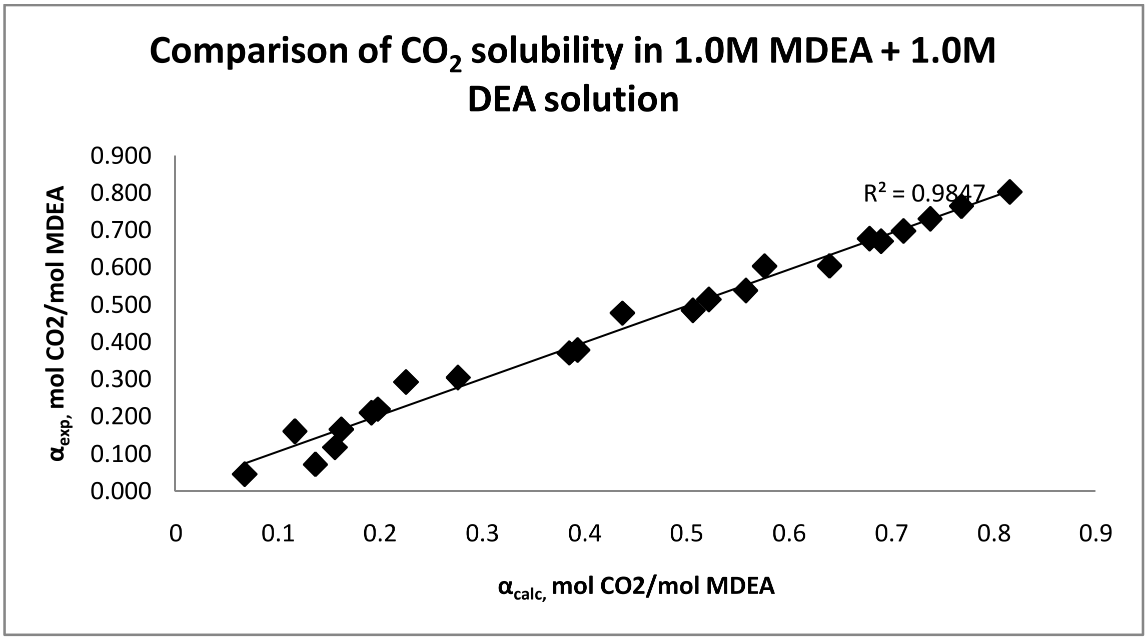


Figure 4.4 Comparison of CO_2 solubility in 1.0M MDEA + 1.0M DEA solution

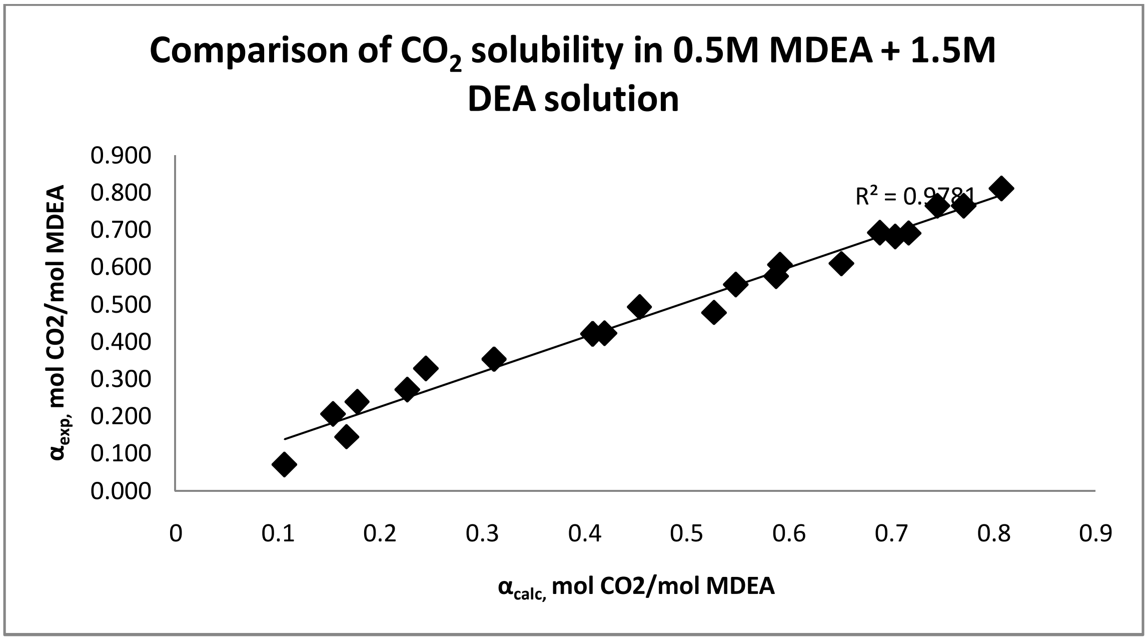


Figure 4.5 Comparison of CO_2 solubility in 0.5M MDEA + 1.5M DEA solution

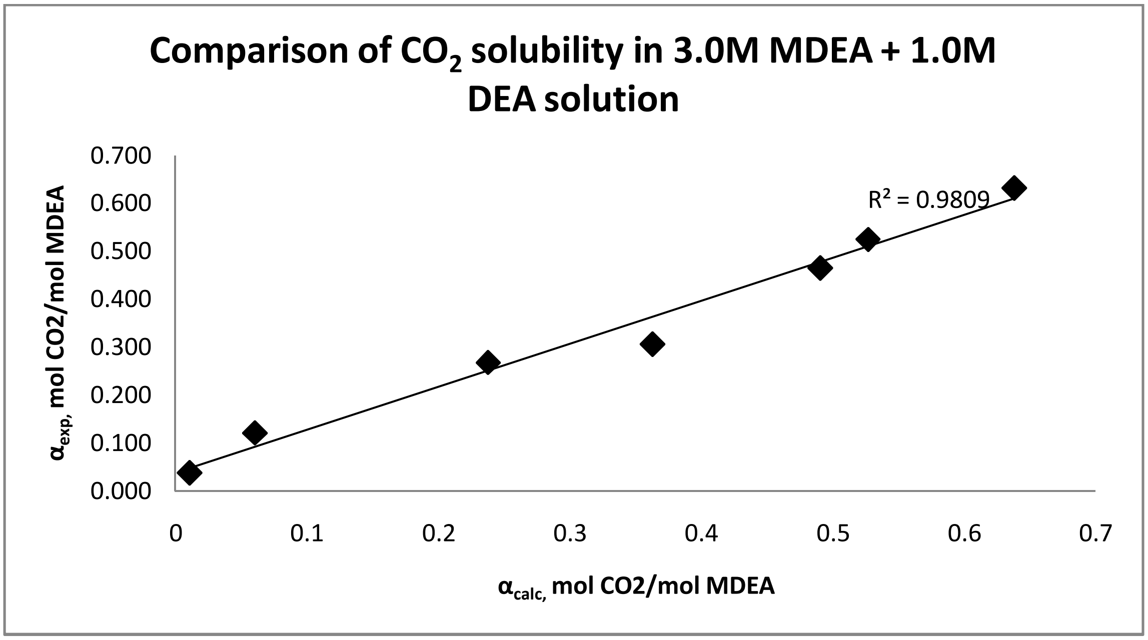


Figure 4.6 Comparison of CO_2 solubility in 3.0M MDEA + 1.0M DEA solution

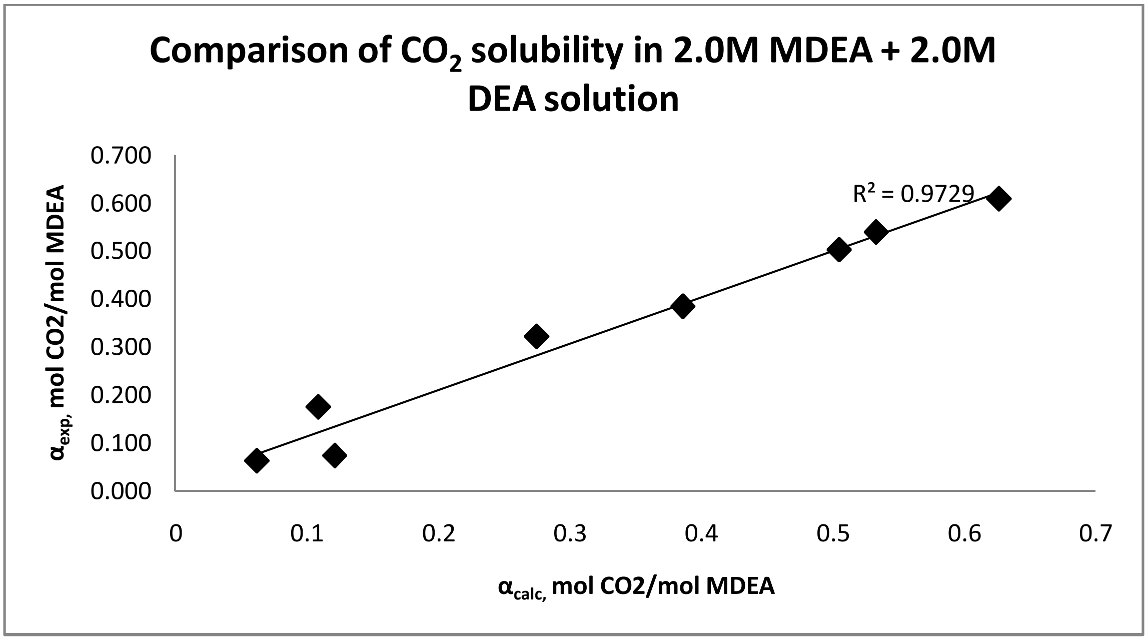


Figure 4.7 Comparison of CO_2 solubility in 2.0M MDEA + 2.0M DEA solution

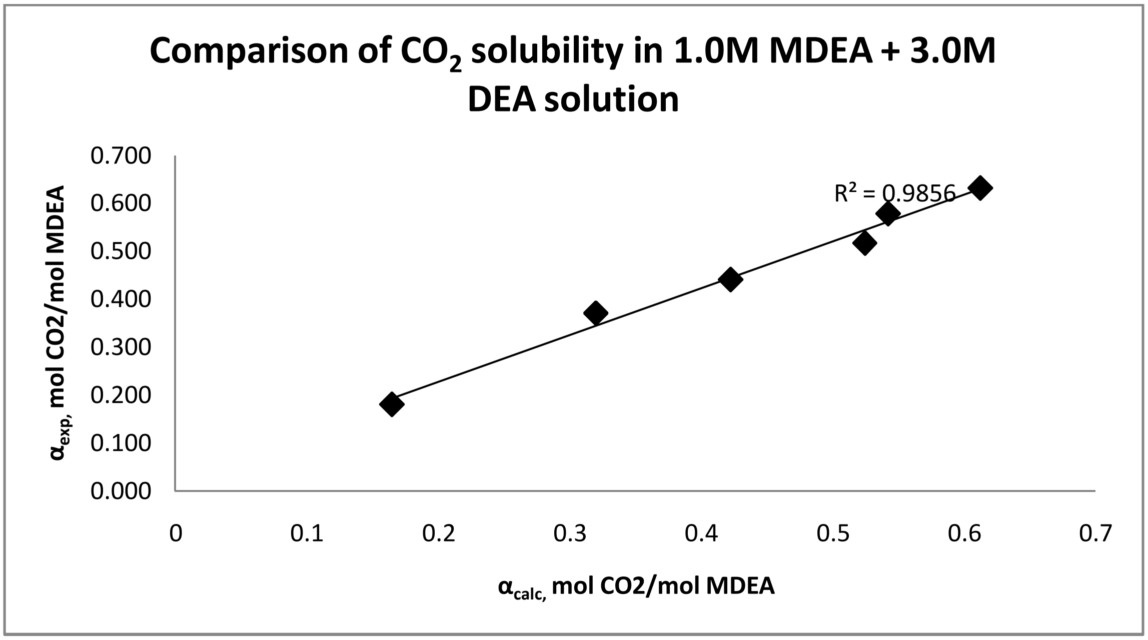


Figure 4.8 Comparison of CO_2 solubility in 1.0M MDEA + 3.0M DEA solution

From the graphs, all of the generated data followed the same pattern as the experimental data with the presence of some deviation. However, the deviation is very small since the average absolute relative deviation percent δ_{AAD} calculated is 8.71% while δ_{AAD} for data from Khalid Osman et al (2012), A. Benamor et al (2005) and Zhang et al (2002) are 17.06%, 12.09% and 9.82% respectively. From the value of δ_{AAD}, the model was considered as valid and has the ability to predict CO_2 loading in mixtures of MDEA and DEA since deviation is the smallest among other previous works that have been done before.

4.2 Prediction of CO_2 Loading

As mentioned earlier, there are three methods that have been used for predicting CO_2 solubility in individual amines. All of the predictions were done using concentration of 2.0M and 4.0M for both amines.

4.2.1 First Prediction Method

From the deviation graphs below, CO_2 loading cannot be predicted at all. δ_{AAD} for pure MDEA is 566.08% while for DEA is 71.20%. The errors are too high due to failure of ANN model to learn the new data input. When predicting using pure MDEA, concentrations of MDEA were set at 2.0M and 4.0M while concentration of DEA was set at 0. Since ANN was developed with the presence of DEA, the model cannot interpret the changes occurred in DEA concentration.

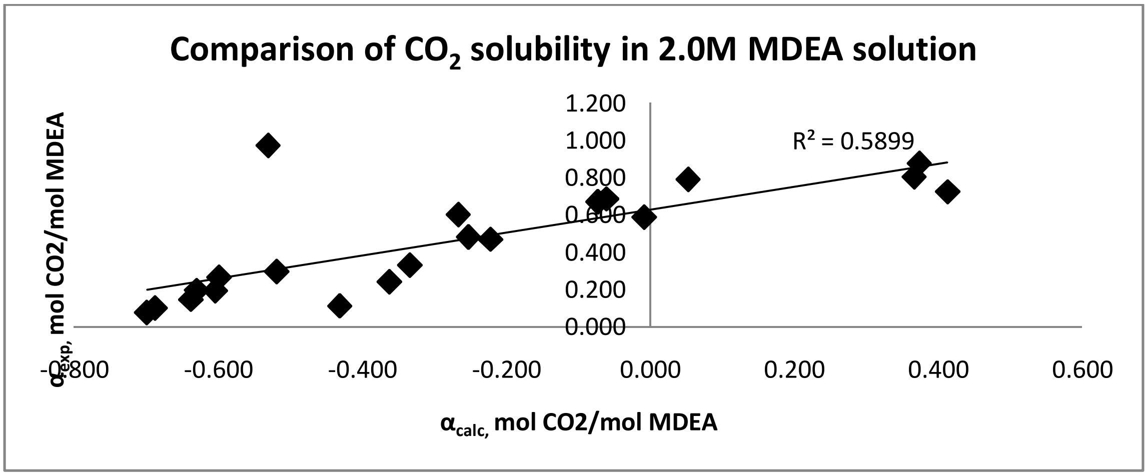


Figure 4.9 Comparison of CO_2 solubility in 2.0M MDEA solution

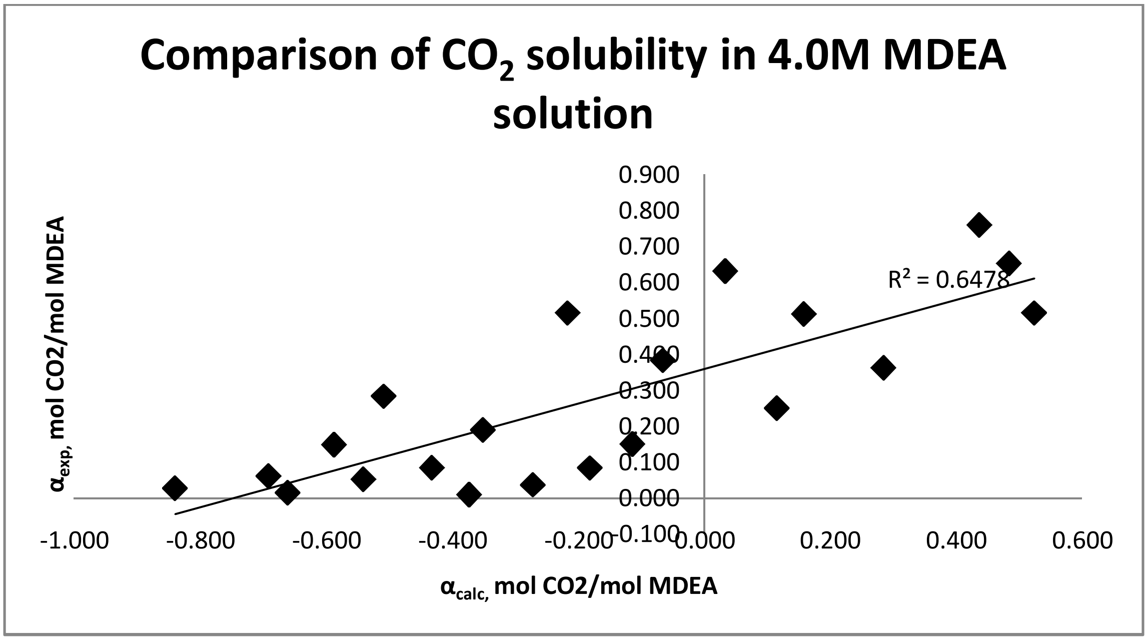


Figure 4.10 Comparison of CO_2 solubility in 4.0M MDEA solution

The same situation happened when prediction was done using pure DEA. The model cannot simulate the input data. Hence, this method of prediction cannot be used to predict CO_2 solubility in pure MDEA and DEA.

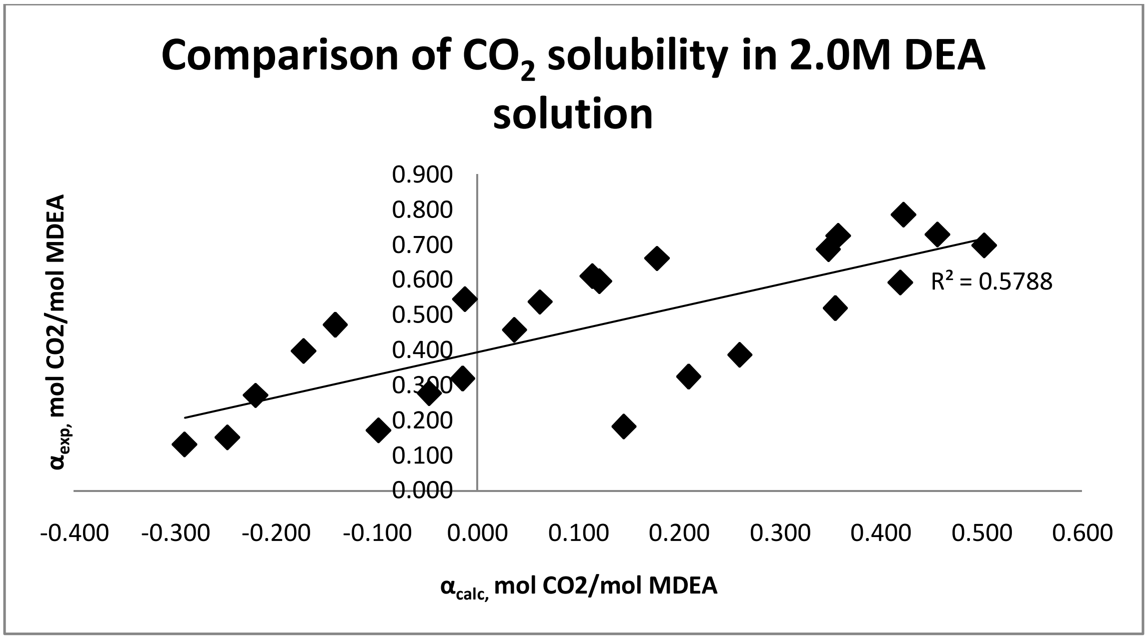


Figure 4.11 Comparison of CO_2 solubility in 2.0M DEA solution

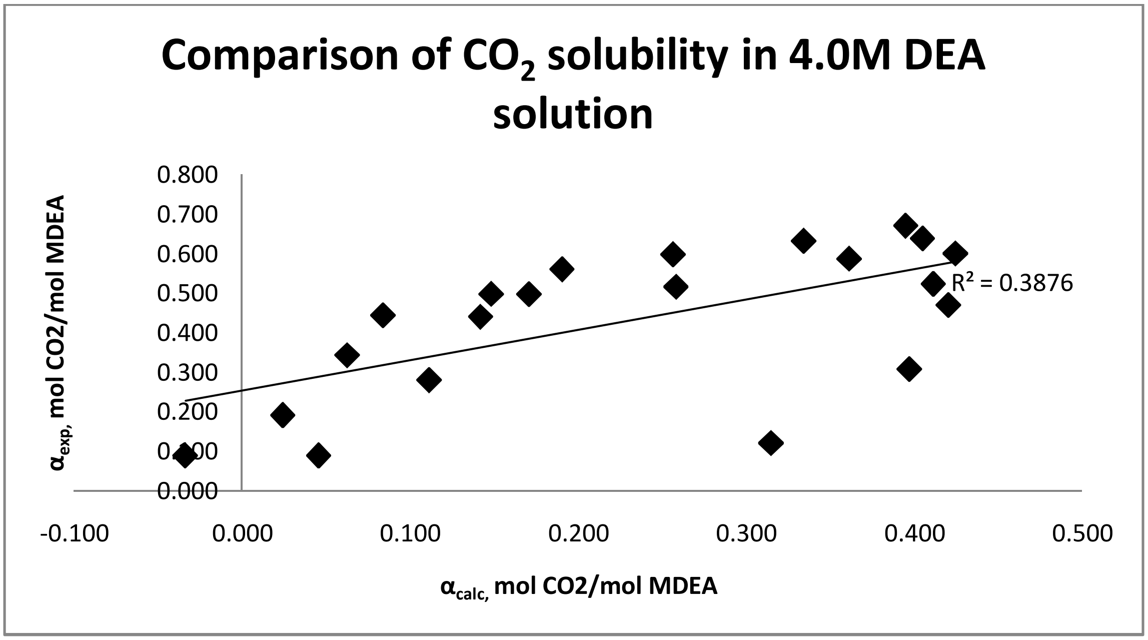


Figure 4.12 Comparison of CO_2 solubility in 4.0M DEA solution

4.2.1 Second & Third Prediction Method

Since the first prediction method cannot be used to predict CO_2 loading, second method have to be developed in order to perform the prediction. In this method, only pure MDEA is used while pure DEA is used in the next method. The concentration for both amines are maintained the same as the first method. Comparisons of generated data and experimental data of CO_2 loading are plotted below.

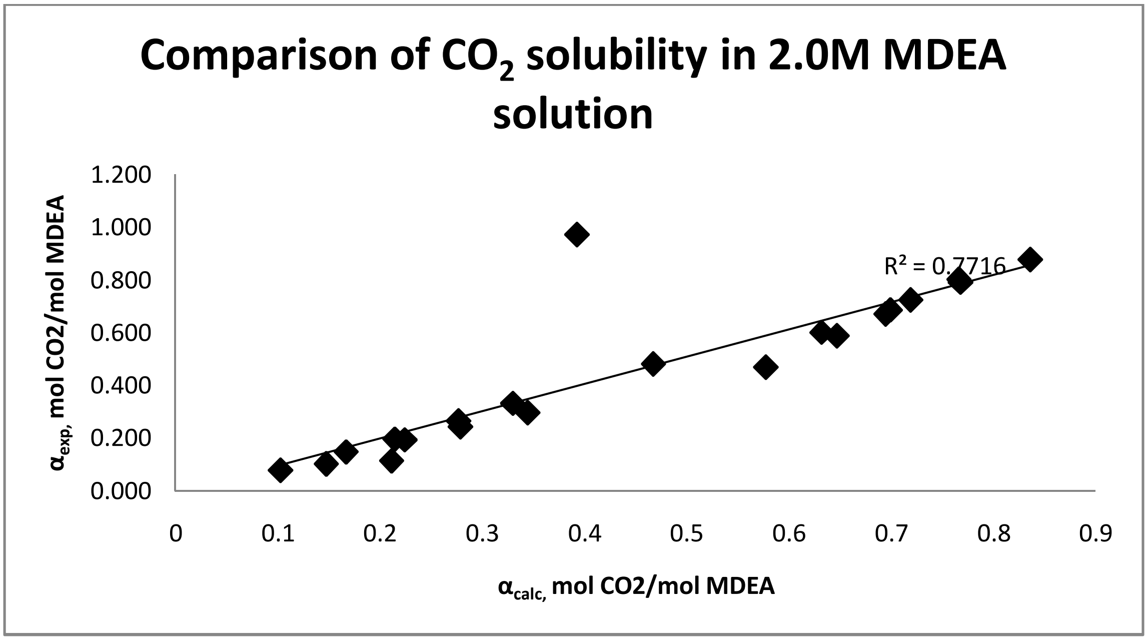


Figure 4.13 Comparison of CO_2 solubility in 2.0M MDEA solution

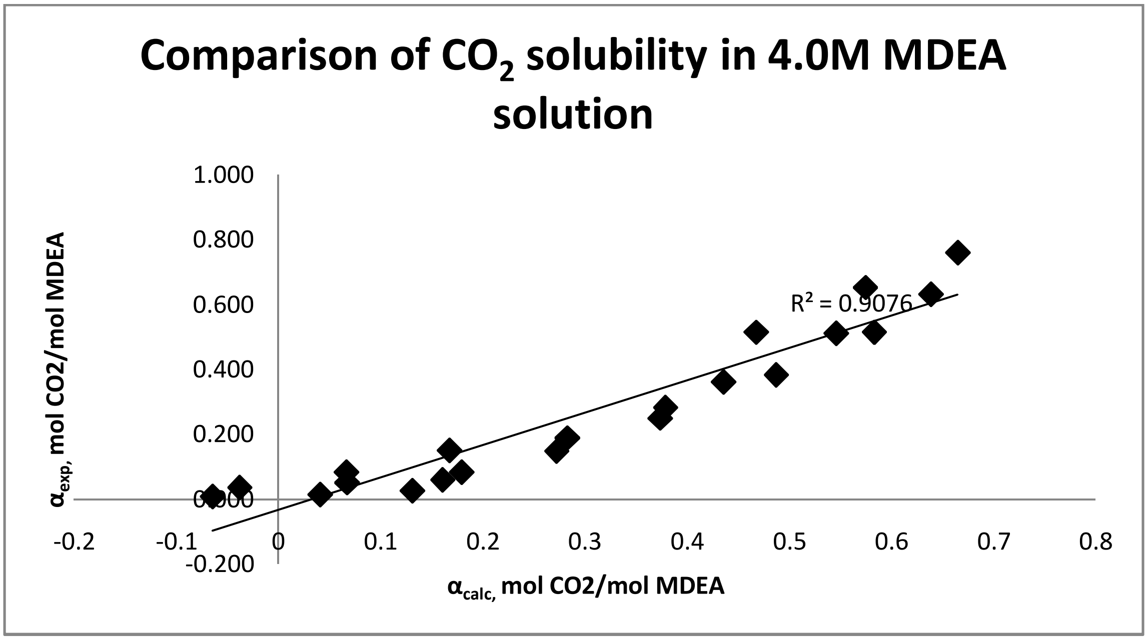


Figure 4.14 Comparison of CO_2 solubility in 4.0M MDEA solution

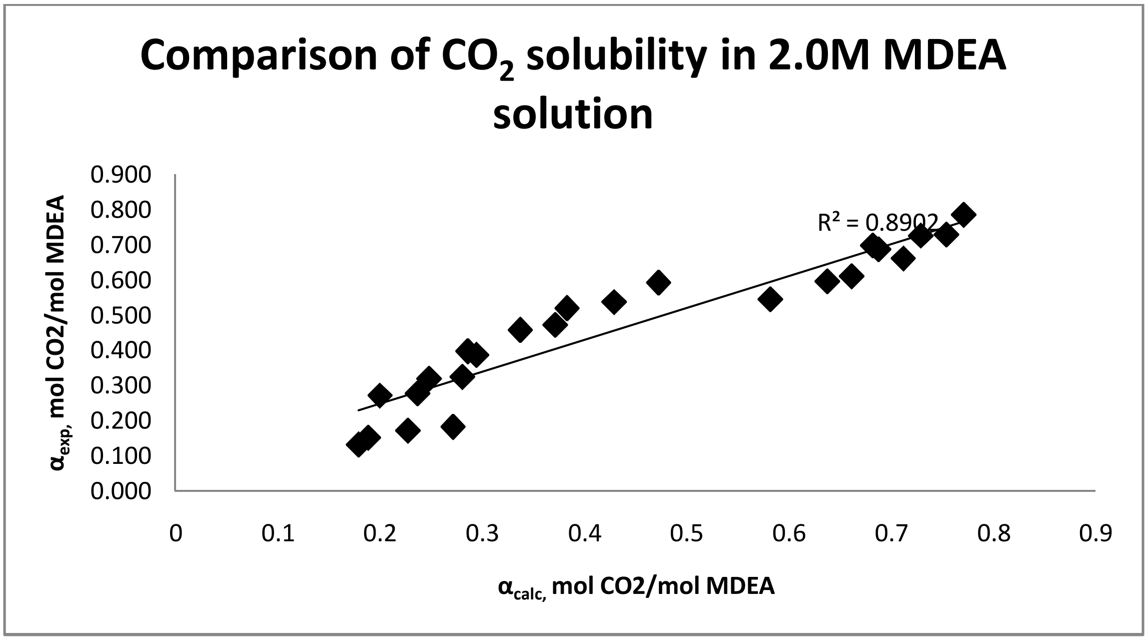


Figure 4.15 Comparison of CO_2 solubility in 2.0M DEA solution

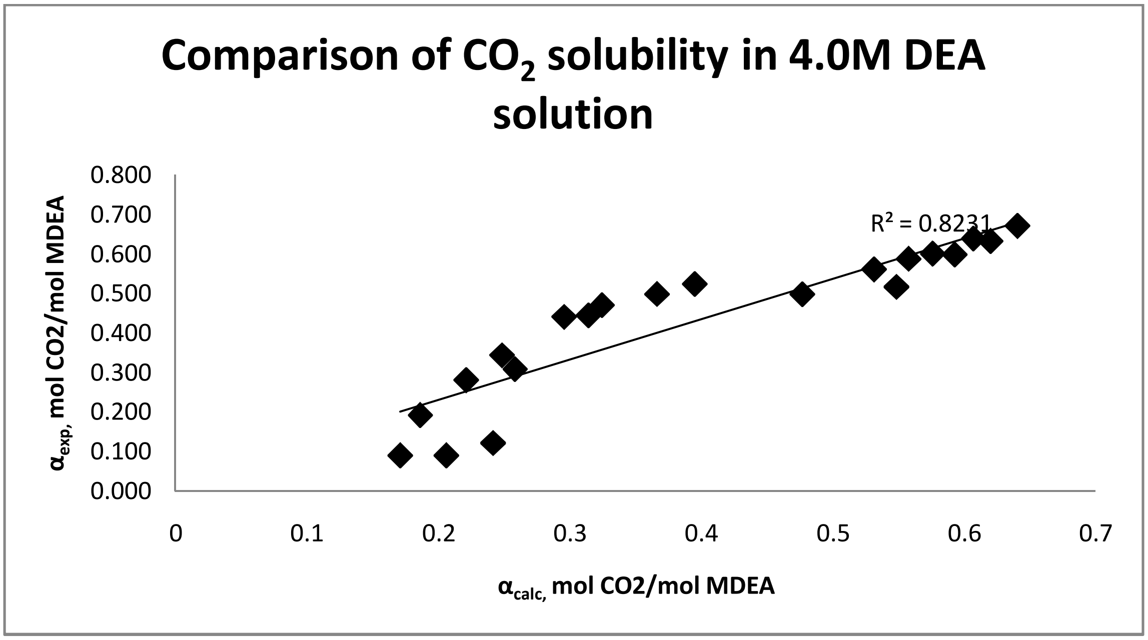


Figure 4.16 Comparison of CO_2 solubility in 4.0M DEA solution

In terms of pure amine prediction, ANN model of CO_2 solubility predicted in pure MDEA has δ_{AAD} of 8.29% while the reference paper which is A. Benamor et al (2005) has absolute relative deviation of 10.76%. For prediction in pure DEA, the model has δ_{AAD} of 3.33% compared to reference paper which is also from A. Benamor et al (2005) with 4.72%.

The error or deviations are very small since new models were developed for each method. ANN models can learn the pattern from data input and the accuracy were great as the deviations are small.

CHAPTER 5

CONCLUSION

Acid gas removal is an important gas treatment in natural gas process. It is because CO_2 can cause global warming beside, if more than 3% of CO_2 composition in natural gas, it is unmarketable. CO_2 also cause corrosion to the pipeline because it can react with water vapour to form a carbonic acid. Nowadays, among the most effective and economic acid gas removal is by using aqueous amine solutions, for example MDEA and DEA in aqueous solution. This research focuses on performance of CO_2 solubility in MDEA + DEA, MDEA and DEA aqueous solutions by using artificial neural network model approach. Data for the model development are taken from several previous research works which consists of various set of parameters such as temperature, partial pressure of CO_2 and concentration of amines. An Artificial Neural Network model has been successfully developed and is ready to be simulated.

Overall, ANN model performance was great as long as it is given chance to train and validate the input data. This can be proven from δ_{AAD} of those developed models. However, prediction by simulating the developed model by changing the input data cannot be done since the patterns of the data are not same. Simulation of ANN model can only be done as long as the input data has the same patterns. This is due to limitation possessed by the model itself. Since ANN was developed by learning the input data as well as the patterns of the input, it cannot interpret the data once the new input does not happen to have the same pattern with the previous input. To conclude, ANN has great ability to predict CO_2 solubility in pure MDEA, DEA, and their mixtures only by developing models for each situation and condition due to the limitation of ANN itself which cannot simulate the new input data if they do not have same patterns with the one that has been used to develop the model.

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APPENDICES

MATERIAL SAFETY DATA SHEET Carbon Dioxide

SECTION 1: IDENTIFICATION OF THE MATERIAL AND SUPPLIER

Product Name	Carbon Dioxide	Other Names	None
Recommended Use	Fire protection agent for total flooding of rooms containing electrical equipment such as computer rooms as well as flammable liquid storage and Class A risks such as records rooms and libraries.		
Supplier Name	Wormald	Address	Unit 1, 2-8 South Street Rydalmere, NSW 2116 AUSTRALIA
Telephone No.	133 166	Emergency Telephone No.	133 166 or 000
		Date Prepared	February 2008

SECTION 2: HAZARDS IDENTIFICATION

Hazard Classification	DANGEROUS GOODS. NON HAZARDOUS SUBSTANCE		
Safety Phrase(s)	Not available	Risk Phrase(s)	Not available

SECTION 3: COMPOSITION / INFORMATION ON INGREDIENTS

SUBSTANCE

Chemical Identity of the Pure Substance	Common Name / Synonyms	CAS Number
CO_2	Carbon Dioxide	124-38-9

MIXTURE

Chemical Identity of Ingredients	Proportion of Ingredients	CAS Number
Not applicable	Not applicable	Not applicable

SECTION 4: FIRST AID MEASURES

Description of Necessary First Aid Measures	EYE CONTACT	Immediately flush eyes with plenty of water for 15 minutes whilst holding lids open. If redness, itching or burning occurs get medical attention.
	SKIN CONTACT	Wash material off skin wit copious amounts of water and soap for at least 15 minutes. If redness, itching or burning occurs get medical attention.
	INHALATION	Call doctor. If victim is conscious, move to uncontaminated area to breath fresh air. Keep warm and quiet. If victim is unconscious, move to uncontaminated area and give assisted respiration. Continued treatment should be symptomatic and supportive.
	INGESTION	Not applicable.
Medical Attention and Special Treatment	See above.	
Aggravated Medical Conditions Caused by Exposure	Respiratory problems.	

SECTION 5: FIRE FIGHTING MEASURES

Suitable Extinguishing Media	This is an extinguishing agent	Hazards From Combustion Products	None
Special Protective Precautions and Equipment for Fire Fighters	Rescuers should not enter an oxygen deficient atmosphere without using self-contained full face positive pressure breathing equipment.	Hazchem Code	2TE

SECTION 6: ACCIDENTAL RELEASE MEASURES

Emergency Procedures	Evacuate the area and ventilate. Do not enter areas where high concentrations may exist without appropriate protective equipment including a self-contained breathing apparatus.
Methods and Materials for Containment and Clean Up	Not applicable - agent is a gas.

SECTION 7: HANDLING AND STORAGE

Precautions for Safe Handling	Protect the cylinder from damage. Handle in well-ventilated areas.
Conditions for Safe Storage, Including any Incompatibilities	Store in cool, dry, well ventilated areas out of direct sunlight and away from heat and ignition sources. Do not expose ay cylinder part to temperatures about 55°C, store upright on a level, fireproof floor, secure in position and protected from damage. Full cylinders stored separately from empties.

SECTION 8: EXPOSURE CONTROLS / PERSONAL PROTECTION

National Exposure Standards	Substance	ES-TWA		ES-STEL	
		ppm	mg/m^3	ppm	mg/m^3
	Carbon dioxide	5000	9000	30000	54000
Engineering Controls	Keep cylinder in a well ventilated area.	Biological Limit Controls		Not available	
Personal Protection Equipment	Chemical goggles, gloves, full cover overalls and safety footwear.				

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Straw yellow clear liquid	Odour	Mild sweet odour
pH	Not available	Vapour Pressure	5090 kPa @ 15°C
Vapour Density (air = 1)	1.873 kg/m^3	Boiling Point / Range	-78.5°C
Freezing / Melting Point (specify)	Not available	Solubility in Water	1.716 m^3/kg
Specific Gravity or Density	1.53	Flash Point	None
Upper and Lower Flammable (explosive) Limits in Air	Not explosive	Ignition Temperature	Does not ignite

SECTION 10: STABILITY AND REACTIVITY

Chemical Stability	Stable under normal conditions of handling and use.	Conditions to Avoid	None
Incompatible Materials	Not applicable	Hazardous Decomposition Products	None
Hazardous Reactions	None		

SECTION 11: TOXICOLOGICAL INFORMATION

Health Effects From the Likely Routes of Exposure	EYE CONTACT	The liquid form of this material can produce chilling sensations and discomfort and also frostbite.
	SKIN CONTACT	Evaporation of liquid from skin can produce chilling sensations. Frostbite can occur. Avoid carbon dioxide snow (dry ice).
	INHALATION	Carbon dioxide is an asphyxiant. Effects of oxygen deficiency (below 6 %) are as follows: convulsive movements, possible respiratory collapse and death.
	INGESTION	Not a likely route of entry.
Acute Overexposure	Contact can produce chilling sensations, light headedness, giddiness, shortness of breath, muscular tremors and weakness, and acrocyanosis. Also unconsciousness or even death.	
Chronic Overexposure	Prolonged exposure to an oxygen deficient atmosphere (below 18 % oxygen) may affect the heart and nervous system.	

SECTION 12: ECOLOGICAL INFORMATION

Ecotoxicity	Not available	Persistence and Degradability	Not available
Mobility	Not available	Environmental Fate (Exposure)	Not available
Bioaccumulative Potential	Not available		

SECTION 13: DISPOSAL CONSIDERATIONS

Disposal Methods and Containers	Dispose of in compliance with local, state or Commonwealth regulations that may be in force.
Special Precautions for Landfill or Incineration	None

SECTION 14: TRANSPORT INFORMATION

UN Number	UN 1013	UN Proper Shipping Name	Carbon Dioxide
Class and Subsidiary Risk	D. G. Class 2.2	Packing Group	Packing Group III
Special Precautions for User	None	Hazchem Code	2TE

SECTION 15: REGULATORY INFORMATION

The regulatory status of a material (including its ingredients) under relevant Australian health, safety and environmental legislation.	Carbon dioxide is an approved gas which is listed in Australian Standard AS 4214.

SECTION 16: OTHER INFORMATION

Date of Preparation	February 2008

END OF MSDS

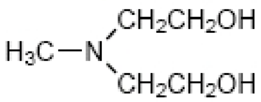
APPENDIX II

HUNTSMAN
Enriching lives through innovation

Technical Bulletin

METHYLDIETHANOLAMINE (MDEA)

Methyldiethanolamine (MDEA) a clear, water-white, hygroscopic liquid with an ammoniacal odor.



APPLICATIONS

The alkanolamines and their aqueous solutions will absorb carbon dioxide and hydrogen sulfide at lower temperatures and release the acid gases at higher temperatures. This forms the basis for processes which separate carbon dioxide and hydrogen sulfide from gas streams.

Methyldiethanolamine is an alkanolamine used in tail gas treating and hydrogen sulfide enrichment units for selectively removing hydrogen sulfide from gas streams containing carbon dioxide. These units will, in most cases, permit 60 to 80% of the carbon dioxide to remain in the treated gas stream. Methyldiethanolamine is also used in natural gas plants for the bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100 scf. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the CO_2:H_2S ratio ranges from 100 to 1,000.

Other suggested uses are urethane catalyst, textile softeners, pH control, and epoxy resin curing agents.

SALES SPECIFICATIONS

Property	Specifications	Test Method*
Appearance	Clear and substantially free of foreign matter	ST-30.1
Color, Pt-Co	150 max.	ST-30.12
Methyldiethanolamine, wt%	99 min.	ST-5.5
Water, wt%	0.5 max.	ST-31.53, 6

*Methods of Test are available from Huntsman Corporation upon request.

ADDITIONAL INFORMATION

Regulatory Information	
DOT/TDG Classification	Not regulated
HMIS Code	1-1-0
WHMIS Classification	D2B
CAS Number	105-59-9

Chemical Control Laws	
US, TSCA	Listed
Canada, DSL	Listed

Typical Physical Properties	
Boiling Range, °C	247 (477)
Flash point, PMCC, °C (°F)	116 (240)
Freezing Point, °C (°F)	-21 (-5.8)
Specific gravity, 20/20°C	1.0431
Vapor pressure, 20°C, mm Hg	<0.01
Viscosity, cSt, 100°F	36.8
Weight, lb/gal, 20°C	8.69
Water solubility	Complete

APPENDIX II

HUNTSMAN

Enriching lives through innovation

TOXICITY AND SAFETY

On the basis of acute studies with laboratory animals, methyldiethanolamine is considered slightly toxic by single oral dose and practically nontoxic by single dermal application. The oral LD_{50} value in the rat is 4.78 g/kg and the dermal LD_{50} value in the albino rabbit is 6.24 g/kg.

Methyldiethanolamine is considered moderately irritating to the eyes, but only slightly irritating to the skin. The product is not corrosive under the conditions of the DOT corrosivity test and is not regulated as a hazardous material for transportation purposes.

Because of the low vapor pressure of methyldiethanolamine, exposure to vapors is not expected to present a significant hazard under normal workplace conditions.

When handling methyldiethanolamine, chemical-type goggles must be worn. In addition, exposed employees should exercise reasonable personal cleanliness, including washing exposed skin areas several times daily with soap and water and laundering soiled work clothing at least weekly.

Should accidental contact with the eyes occur, flush them thoroughly with water for at least 15 minutes and get medical attention. Wash exposed skin areas with soap and water.

For further information on the safe handling of methyldiethanolamine, consult the Material Safety Data Sheet.

HANDLING AND STORAGE

The handling and storage of methyldiethanolamine presents no unusual problems. See the section on toxicity and safety for related additional information.

The solvent properties and alkaline nature of methyldiethanolamine should be considered when installing handling and storage facilities. Methyldiethanolamine will react with copper to form complex salts, so the use of copper and alloys containing copper should be avoided. Carbon steel storage tanks, constructed according to a recognized code, are generally satisfactory.

Carbon steel transfer lines, at least 2 inches in diameter and joined by welds or flanges, are suitable. Screw joints are subject to failure unless back-welded because methyldiethanolamine will leach conventional pipe dopes. U.S. Rubber 899 gasket material or its equivalent is satisfactory for use with flange connections.

Centrifugal pumps are preferred with methyldiethanolamine, although carbon steel rotary pumps can be used. Rotary pumps should be equipped with externally lubricated bearings. A Durametallic Type RO-TT mechanical seal is suitable. Garlock 234, 239, or equivalent can be utilized as pump packing.

AVAILABILITY

Methyldiethanolamine is currently available in 55-gallon drums, tank wagons, and tank cars. Samples are available by contacting our sample department at 1-800-662-0924.

Huntsman Corporation
Business Offices
10003 Woodloch Forest Dr.
The Woodlands, TX 77380
(281) 719-6000

Huntsman Advanced Technology Center
Technical Service
8600 Gosling Rd.
The Woodlands, TX 77381
(281) 719-7780

Samples 1-800-662-0924

www.huntsman.com

APPENDIX III

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
303	0.1	0.5	1.5	0.079	0.131539504	0.053
303	0.6	0.5	1.5	0.153	0.168314432	0.015
303	1.1	0.5	1.5	0.214	0.202812013	-0.011
303	5.4	0.5	1.5	0.426	0.420889765	-0.005
303	10.8	0.5	1.5	0.535	0.565123846	0.030
303	33.2	0.5	1.5	0.706	0.709047032	0.003
303	55.1	0.5	1.5	0.766	0.744027475	-0.022
303	107.1	0.5	1.5	0.853	0.823684959	-0.029
313	0.1	0.5	1.5	0.065	0.102457691	0.037
313	0.5	0.5	1.5	0.119	0.12864836	0.010
313	1.1	0.5	1.5	0.161	0.165391276	0.004
313	5.3	0.5	1.5	0.348	0.354986376	0.007
313	10.6	0.5	1.5	0.449	0.483801684	0.035
313	32.1	0.5	1.5	0.613	0.623633696	0.011
313	53.2	0.5	1.5	0.702	0.667594351	-0.034
313	102.8	0.5	1.5	0.764	0.768564996	0.005
323	0.1	0.5	1.5	0.043	0.025577452	-0.017
323	1.1	0.5	1.5	0.121	0.081373081	-0.040
323	5.1	0.5	1.5	0.257	0.24400502	-0.013
323	10.2	0.5	1.5	0.340	0.360211305	0.020
323	28.9	0.5	1.5	0.501	0.495893727	-0.005
323	50.9	0.5	1.5	0.629	0.556740903	-0.072
323	90.7	0.5	1.5	0.724	0.661999333	-0.062
303	0.1	1.0	1.0	0.116	0.156000458	0.040
303	0.6	1.0	1.0	0.210	0.191732264	-0.018
303	1.1	1.0	1.0	0.292	0.225244173	-0.067
303	5.4	1.0	1.0	0.477	0.436887836	-0.040
303	9.8	1.0	1.0	0.538	0.557657733	0.020
303	32.1	1.0	1.0	0.698	0.711850071	0.014
303	49.3	1.0	1.0	0.730	0.737939646	0.008
303	106.4	1.0	1.0	0.802	0.815695395	0.014
313	0.1	1.0	1.0	0.071	0.136736643	0.066
313	0.5	1.0	1.0	0.165	0.162162849	-0.003
313	1.1	1.0	1.0	0.219	0.197824693	-0.021
313	5.4	1.0	1.0	0.370	0.384845983	0.015
313	10.6	1.0	1.0	0.485	0.506125839	0.021
313	32.3	1.0	1.0	0.604	0.639562449	0.036
313	53.0	1.0	1.0	0.677	0.67855865	0.002
313	102.1	1.0	1.0	0.764	0.768593656	0.005
323	0.1	1.0	1.0	0.045	0.067705067	0.023

APPENDIX III

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
323	1.0	1.0	1.0	0.160	0.11669993	-0.043
323	5.0	1.0	1.0	0.304	0.27631508	-0.028
323	10.3	1.0	1.0	0.378	0.393006502	0.015
323	29.3	1.0	1.0	0.514	0.521601138	0.008
323	50.8	1.0	1.0	0.603	0.575850353	-0.027
323	97.7	1.0	1.0	0.670	0.690164507	0.020
303	0.1	1.5	0.5	0.239	0.177568569	-0.061
303	1.1	1.5	0.5	0.328	0.244843238	-0.083
303	5.5	1.5	0.5	0.493	0.4537688	-0.039
303	10.9	1.5	0.5	0.575	0.587155305	0.012
303	33.2	1.5	0.5	0.691	0.716792718	0.026
303	55.1	1.5	0.5	0.764	0.745175772	-0.019
303	106.4	1.5	0.5	0.810	0.8076068	-0.002
313	0.1	1.5	0.5	0.145	0.167358974	0.022
313	1.1	1.5	0.5	0.271	0.226656691	-0.044
313	5.4	1.5	0.5	0.421	0.407970506	-0.013
313	10.7	1.5	0.5	0.478	0.526756641	0.049
313	31.9	1.5	0.5	0.609	0.651210984	0.042
313	53.9	1.5	0.5	0.692	0.688616231	-0.003
313	103.8	1.5	0.5	0.764	0.770823908	0.007
323	0.1	1.5	0.5	0.071	0.106574384	0.036
323	1.0	1.5	0.5	0.206	0.154082644	-0.052
323	5.1	1.5	0.5	0.353	0.311526314	-0.041
323	10.2	1.5	0.5	0.422	0.419701326	-0.002
323	31.0	1.5	0.5	0.553	0.547792376	-0.005
323	50.1	1.5	0.5	0.606	0.590922512	-0.015
323	101.0	1.5	0.5	0.682	0.703669252	0.022
313	0.1	1.0	3.0	0.038	0.011096368	-0.027
313	0.9	1.0	3.0	0.121	0.06061237	-0.060
313	4.8	1.0	3.0	0.268	0.238017355	-0.030
313	9.8	1.0	3.0	0.306	0.362986017	0.057
313	28.5	1.0	3.0	0.465	0.490365905	0.025
313	47.6	1.0	3.0	0.525	0.52676283	0.002
313	95.1	1.0	3.0	0.632	0.63779886	0.006
313	0.1	2.0	2.0	0.063	0.062215586	-0.001
313	0.9	2.0	2.0	0.175	0.108740434	-0.066
313	4.8	2.0	2.0	0.322	0.274908531	-0.047
313	9.5	2.0	2.0	0.385	0.386053989	0.001
313	28.6	2.0	2.0	0.503	0.504798994	0.002
313	47.4	2.0	2.0	0.540	0.532974469	-0.007

APPENDIX III

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
313	94.1	2.0	2.0	0.609	0.626149373	0.017
313	0.1	3.0	1.0	0.073	0.121292007	0.048
313	0.9	3.0	1.0	0.181	0.164868924	-0.016
313	4.8	3.0	1.0	0.371	0.319842446	-0.051
313	9.5	3.0	1.0	0.441	0.422300007	-0.019
313	28.5	3.0	1.0	0.517	0.524391223	0.007
313	47.4	3.0	1.0	0.579	0.542049704	-0.037
313	95.1	3.0	1.0	0.632	0.612112163	-0.020
313	4.81	0.305	2.695	0.107	0.08952357	-0.017
313	6.10	0.305	2.695	0.137	0.134467709	-0.003
313	8.40	0.305	2.695	0.165	0.19837227	0.033
313	9.61	0.305	2.695	0.189	0.225335817	0.036
313	11.80	0.305	2.695	0.236	0.265103826	0.029
313	16.80	0.305	2.695	0.275	0.326092792	0.051
313	21.40	0.305	2.695	0.319	0.360840535	0.042
313	25.20	0.305	2.695	0.356	0.38147569	0.025
313	29.80	0.305	2.695	0.391	0.401232681	0.010
323	9.01	0.305	2.695	0.135	0.107197677	-0.028
323	11.00	0.305	2.695	0.167	0.143545093	-0.023
323	14.50	0.305	2.695	0.201	0.191107929	-0.010
323	17.10	0.305	2.695	0.223	0.217174925	-0.006
323	23.50	0.305	2.695	0.283	0.262400952	-0.021
323	33.80	0.305	2.695	0.320	0.310867341	-0.009
323	39.10	0.305	2.695	0.359	0.331826542	-0.027
323	44.50	0.305	2.695	0.398	0.352286053	-0.046
323	49.00	0.305	2.695	0.431	0.369047881	-0.062
333	17.90	0.305	2.695	0.128	0.165036425	0.037
333	18.40	0.305	2.695	0.160	0.169003299	0.009
333	21.80	0.305	2.695	0.192	0.192804565	0.001
333	22.80	0.305	2.695	0.218	0.198962241	-0.019
333	33.10	0.305	2.695	0.271	0.250597121	-0.020
333	40.10	0.305	2.695	0.301	0.280209855	-0.021
333	51.20	0.305	2.695	0.334	0.324783413	-0.009
333	57.30	0.305	2.695	0.361	0.348862706	-0.012
333	64.10	0.305	2.695	0.390	0.375581466	-0.014
333	72.10	0.305	2.695	0.427	0.406913728	-0.020
343	21.80	0.305	2.695	0.127	0.15300982	0.026
343	29.00	0.305	2.695	0.194	0.188073688	-0.006
343	40.80	0.305	2.695	0.235	0.233955755	-0.001
343	48.20	0.305	2.695	0.261	0.260356731	-0.001

APPENDIX III

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
343	55.20	0.305	2.695	0.295	0.284688861	-0.010
343	61.00	0.305	2.695	0.317	0.304546342	-0.012
343	63.50	0.305	2.695	0.326	0.313039251	-0.013
333	12.10	0.191	2.809	0.055	0.095148961	0.040
333	15.20	0.191	2.809	0.099	0.131225075	0.032
333	18.90	0.191	2.809	0.130	0.163351768	0.033
333	37.70	0.191	2.809	0.241	0.260300611	0.019
333	42.80	0.191	2.809	0.280	0.281043462	0.001
333	14.60	0.555	2.445	0.111	0.151528141	0.041
333	19.00	0.555	2.445	0.160	0.190453649	0.030
333	27.40	0.555	2.445	0.231	0.241017638	0.010
333	35.50	0.555	2.445	0.280	0.278370998	-0.002
333	46.10	0.555	2.445	0.331	0.322514402	-0.008
333	56.80	0.555	2.445	0.370	0.365702584	-0.004
362.1	150.000	2.4	2.1	0.107	0.3121716	0.205
362.1	450.000	2.4	2.1	0.296	0.326855038	0.031
362.1	105.100	2.4	2.1	0.789	0.293554943	-0.495
362.1	351.000	2.4	2.1	0.297	0.332120294	0.035
362.1	61.000	2.4	2.1	0.043	0.266968131	0.224
362.1	149.000	2.4	2.1	0.101	0.311837648	0.211
412.1	151.000	2.4	2.1	0.098	0.104157836	0.006
412.1	450.000	2.4	2.1	0.304	0.287348753	-0.017
412.1	1153.000	2.4	2.1	0.544	0.497738445	-0.046
412.1	49.000	2.4	2.1	0.042	0.024485112	-0.018
412.1	160.000	2.4	2.1	0.102	0.110746075	0.009
412.1	351.000	2.4	2.1	0.200	0.234560611	0.035
362.1	450.000	1.9	2.5	0.293	0.197467374	-0.096
362.1	1050.000	1.9	2.5	0.301	0.357070384	0.056
362.1	152.000	1.9	2.5	0.117	0.137840777	0.021
362.1	57.000	1.9	2.5	0.046	0.088875041	0.043
362.1	351.000	1.9	2.5	0.344	0.182965509	-0.161
362.1	152.000	1.9	2.5	0.148	0.137840777	-0.010
412.1	153.000	1.9	2.5	0.094	0.116246546	0.022
412.1	1050.000	1.9	2.5	0.301	0.485151758	0.184
412.1	450.000	1.9	2.5	0.236	0.297667768	0.062
412.1	52.000	1.9	2.5	0.043	0.036281041	-0.007
412.1	152.000	1.9	2.5	0.155	0.115503854	-0.039
412.1	352.000	1.9	2.5	0.209	0.246012379	0.037
392.1	1050.000	4.8	0.0	0.416	0.414595065	-0.001
392.1	450.000	4.8	0.0	0.281	0.285883341	0.005

APPENDIX IV

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
303	1.1	0.0	2.0	0.114	-0.197	0.311
303	3.1	0.0	2.0	0.244	0.168	0.076
303	4.8	0.0	2.0	0.333	0.038	0.295
303	10.5	0.0	2.0	0.483	-0.006	0.489
303	29.8	0.0	2.0	0.673	0.017	0.656
303	48.4	0.0	2.0	0.793	-0.018	0.811
303	95.8	0.0	2.0	0.880	0.008	0.872
313	1.1	0.0	2.0	0.103	0.208	0.105
313	3.1	0.0	2.0	0.197	0.064	0.133
313	5.2	0.0	2.0	0.267	0.011	0.256
313	10.0	0.0	2.0	0.974	-0.608	1.582
313	30.3	0.0	2.0	0.603	-0.037	0.640
313	47.5	0.0	2.0	0.688	-0.010	0.698
313	94.0	0.0	2.0	0.805	0.036	0.769
323	1.0	0.0	2.0	0.079	0.099	0.020
323	2.9	0.0	2.0	0.148	0.026	0.122
323	4.8	0.0	2.0	0.194	-0.005	0.199
323	9.7	0.0	2.0	0.298	-0.075	0.373
323	28.4	0.0	2.0	0.471	-0.033	0.504
323	44.1	0.0	2.0	0.590	-0.064	0.654
323	91.5	0.0	2.0	0.726	0.009	0.717
303	0.1	0.0	4.0	0.027	0.000	0.027
303	1.0	0.0	4.0	0.061	0.383	0.322
303	4.9	0.0	4.0	0.149	0.281	0.132
303	9.8	0.0	4.0	0.284	-0.031	0.315
303	29.5	0.0	4.0	0.516	-0.074	0.590
303	49.1	0.0	4.0	0.633	-0.042	0.675
303	98.2	0.0	4.0	0.761	0.045	0.716
313	0.1	0.0	4.0	0.015	0.325	0.310
313	0.9	0.0	4.0	0.052	0.187	0.135
313	4.8	0.0	4.0	0.085	0.630	0.545
313	9.5	0.0	4.0	0.190	0.062	0.128
313	28.5	0.0	4.0	0.384	-0.058	0.442
313	47.5	0.0	4.0	0.513	-0.076	0.589
313	95.2	0.0	4.0	0.654	0.021	0.633
323	0.1	0.0	4.0	0.010	0.487	0.477
323	0.9	0.0	4.0	0.037	0.211	0.174
323	4.5	0.0	4.0	0.084	0.197	0.113
323	9.0	0.0	4.0	0.151	-0.032	0.183
323	27.1	0.0	4.0	0.251	0.058	0.193
323	45.1	0.0	4.0	0.363	-0.024	0.387

APPENDIX V

T/K	P_{CO2}/kPa	DEA/ (kmol/m^3)	MDEA/ (kmol/m^3)	α_{co2}(exp)	α_{co2}(calc)	deviation
303	0.1	2.0	0.0	0.183	0.146	0.037
303	0.5	2.0	0.0	0.325	0.210	0.115
303	1.1	2.0	0.0	0.388	0.261	0.127
303	5.4	2.0	0.0	0.521	0.355	0.166
303	10.7	2.0	0.0	0.593	0.420	0.173
303	32.5	2.0	0.0	0.699	0.503	0.196
303	54.2	2.0	0.0	0.730	0.456	0.274
303	100.9	2.0	0.0	0.786	0.423	0.363
313	0.1	2.0	0.0	0.172	-0.098	0.270
313	0.5	2.0	0.0	0.278	-0.047	0.325
313	1.0	2.0	0.0	0.320	-0.014	0.334
313	5.3	2.0	0.0	0.459	0.037	0.422
313	10.7	2.0	0.0	0.538	0.063	0.475
313	32.1	2.0	0.0	0.597	0.121	0.476
313	53.8	2.0	0.0	0.662	0.178	0.484
313	104.7	2.0	0.0	0.727	0.358	0.369
323	0.1	2.0	0.0	0.133	-0.290	0.423
323	0.5	2.0	0.0	0.152	-0.248	0.400
323	1.0	2.0	0.0	0.272	-0.219	0.491
323	5.1	2.0	0.0	0.398	-0.172	0.570
323	10.0	2.0	0.0	0.473	-0.141	0.614
323	30.4	2.0	0.0	0.546	-0.012	0.558
323	50.8	2.0	0.0	0.611	0.114	0.497
323	98.2	2.0	0.0	0.688	0.348	0.340
303	0.1	4.0	0.0	0.122	0.315	0.193
303	1.0	4.0	0.0	0.309	0.397	0.088
303	4.9	4.0	0.0	0.471	0.420	0.051
303	9.9	4.0	0.0	0.524	0.411	0.113
303	29.4	4.0	0.0	0.588	0.361	0.227
303	48.9	4.0	0.0	0.633	0.334	0.299
303	98.6	4.0	0.0	0.671	0.395	0.276
313	0.1	4.0	0.0	0.091	0.046	0.045
313	0.9	4.0	0.0	0.281	0.111	0.170
313	5.3	4.0	0.0	0.441	0.142	0.299
313	10.4	4.0	0.0	0.499	0.148	0.351
313	31.0	4.0	0.0	0.561	0.190	0.371
313	52.6	4.0	0.0	0.599	0.257	0.342
313	102.1	4.0	0.0	0.639	0.405	0.234
323	0.1	4.0	0.0	0.091	-0.034	0.125
323	0.9	4.0	0.0	0.193	0.024	0.169
323	4.5	4.0	0.0	0.344	0.063	0.281