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Determination of the mechanism of the reaction between CO2 and alkanolamines.

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I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU)

Date and signature: …….

Dedicated to

My Parents for their endless prayers
My uncle and aunt for their moral support
&
My institute NFC institute of Engineering &
Technological training, Multan

ABSTRACT

Emission control of greenhouse gases especially CO_2 has become an environmental challenge. CO_2 capture by absorption in amine is so far the only CCS technique that has been industrially acknowledged. Chemical absorption of CO_2 in amine solution is a complex process and needs investigation for better understanding.

An experimental study has been conducted to understand the kinetics of CO_2 absorption in non-aqueous DEA solution at 293K in a stirred cell reactor with a smooth and flat gas liquid interface. Experiments were repeated to ensure the reproducibility of data and the results were compared with literature to ensure the validity of this work. Physio-chemical properties of all chemicals like density, diffusivity and viscosity were taken from literature whereas solubility data was generated by experimentation. Solubility data was also validated by comparison with literature.

Experimental data for reaction kinetics was treated with both zwitterion and termolecular mechanism. Based on the findings from this work, the order of reaction is 1.78 with respect to amine. Furthermore, Parity plot between calculated and experimental CO_2 fluxes have been generated to elaborate the argument and it could be concluded that for non-aqueous system both studied mechanisms shows less than 10% deviation and hence can give satisfactory results. It is recommended to continue this work at different temperatures for better understanding.

ACKNOWLEDGEMENT

"All praise goes to **Almighty Allah,** Who is the creator of this universe"

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Muhammad Awais

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LIST OF SYMBOLS

C	Concentration *(mol/L)*
D	Diffusivity (m^2/s)
Ha	Hatta number
N	Flux *(mol/m^2s)*
M	Molar concentration *(mol/L)*
V	Volume (cm^3/m^3)
P	Total pressure *(Pa)*
$E_{A\infty}$	Infinite enhancement factor
μ	Viscosity
E	Activation energy
E_A	Enhancement factor
$E_{A,pen}$	Enhancement factor for penetration theory
k_{app}	Apparent rate constant
k_B	Rate constant of base
K_G	Mass transfer coefficient
K_l	Liquid mass transfer coefficient
k_{obs}	Observed rate constant
N_{CO2}	Flux of CO_2
K	Kelvin scale
R	Universal gas constant
Re	Reynold number
t	time
m	mass of solvent

Greek Letters

α	Loading (*mol.mol*-1)
μ	Viscosity ($Pa \times s$)
ρ	Density

Subscripts

Ab	Absorbed
Am	Amine
B	Bulk
calc	Calculated
exp	Experimental
g	Gas phase
i	Interface ; Species *i*
k	Species *k*
l	Liquid phase
obs	Observed
±	Mean

Superscripts

Am	Amine
E	Excess
In	Inlet
out	Outlet
T	Termolecular mechanism; Total
Z	Zwitterion mechanism
o	Initial condition

Abbreviations

B	Base
CO_2	Carbon Dioxide
DEA	Diethanolamine
L	Liter
M	Molarity
H_2O	Water
H_2SO_4	Sulfuric acid
N_2	Nitrogen
N_2O	Nitrous oxide

1 INTRODUCTION

1.1 BACKGROUND

Climate change is one of the major challenges of 21st century. Greenhouse gases (GHS) i.e. carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), per fluorocarbons PFCs, hydro fluorocarbons (HFCs) and sulphur hexafluoride (SF_6) in addition to ozone-depleting substances (ODS, chlorofluorocarbons (CFCs), hydro chlorofluorocarbons (HCFCs) are considered to be responsible for global warming and climate change. Out of these greenhouse gases Carbon dioxide contributes about 76.7%, methane about 14.3%, nitrous oxide about 7.8% and rest by F-gases to the greenhouse effect [1]. Over the last three decades GHG emissions have increased by an average of 1.6% per year with carbon dioxide (CO_2) emissions from the use of fossil fuels growing at a rate of 1.9% per year [1]. Mostly CO_2 emission is produced from the fossil fuel use (74%) while 22.6% from the feedstock emission and the rest from the cement industry and natural gas flaring. Fossil fuel comprises 80% of total world energy demand [2]. With increase in CO_2 emissions, the CO_2 concentration in atmospheric has reached 379 ppm in 2005. This is about 100 ppm higher compared to the pre-industrial level [1].Increase in greenhouse gas contributes to raise global mean temperature and global average sea level and to lessen the Northern hemisphere snow cover [3]. These trends underline the demand to develop technologies to reduce CO_2 emission associated with the use of fossil fuels. Carbon dioxide Capture and Storage (CCS) offers this opportunity to reduce CO_2 emission.

1.2 CARBON CAPTURE AND STORAGE (CCS)

CCS is defined as a system of technologies that integrates CO_2 capture, transportation and geological storage. Each stage of CCS is in principle technically available and has been used commercially for many years [4].

To capture CO_2, different technologies are being used by the industry from gas streams, where it could be an undesirable contaminant or is needed to be separated as a product gas. There are three primary methods for CO_2 capture; pre-combustion capture, post-combustion capture and oxy-fuel processes. Post-combustion capture involves scrubbing of CO_2 from flue gas of a combustion process. Oxy fuel combustion refers to combustion of fuel in pure oxygen, thereby produce a CO_2-rich gas. In a pre-combustion process, gasification is followed by CO_2 separation prior to the use of produced hydrogen as a fuel gas.

CO_2 transport is done for over 30 years in North America; over 30 metric tons of CO_2 from natural and anthropogenic sources are transported per year through 6200 km of CO_2 pipelines in the USA and Canada, mainly for enhanced oil recovery [5]. CO_2 is transported at high pressure through a network of pipeline. Ships, trucks and trains have also been used for CO_2 transportation in early CCS demonstration projects and in regions with inadequate storage.

CO_2 storage involves injection of supercritical CO_2 into a geologic formation. On geological timescales this CO_2 will partly be fixed in minerals by carbonation reactions. There are three common options for geological CO_2 storage; saline aquifers, oil and gas reservoirs, and deep unminable coal seams [4]. It is expected that saline aquifer formations provide the largest storage capacities for CO_2, followed by oil and gas reservoirs. A number of projects involving the injection of CO_2 into oil reservoirs have been conducted in the USA and Canada. Most of these projects use CO_2 for enhanced oil recovery.

1.3 CO_2 CAPTURE TECHNOLOGIES

There are four basic methods for CO_2 capture methods are from fossil fuels as shown in figure 1.1.

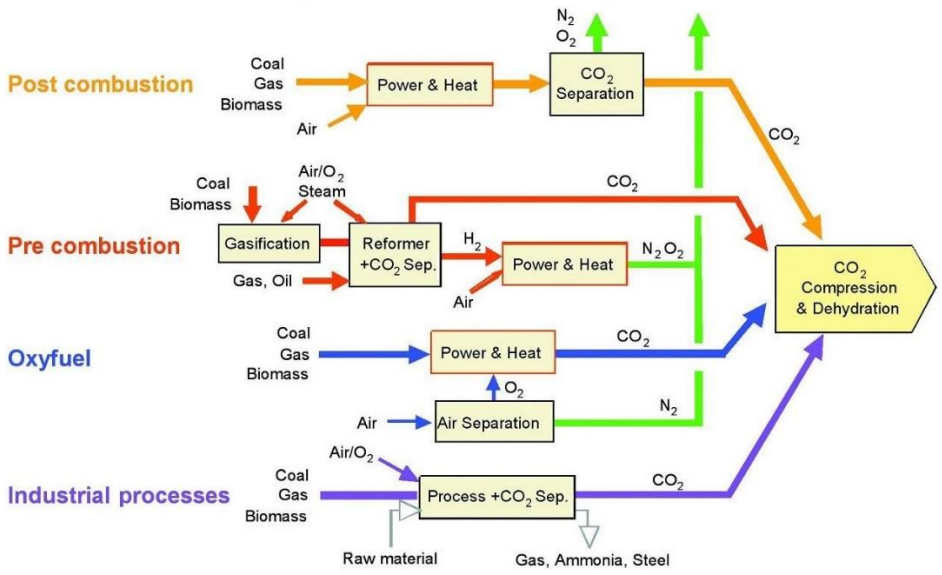


Figure 1. 1 CO_2 Capture techniques [3]

1.3.1 Pre-combustion capture

In pre-combustion carbon dioxide capture, CO_2 is separated from the fossil fuel (coal or natural gas) before combustion. In this process, fossil fuel is converted into synthesis gas, a mixture of CO and H_2. This synthesis gas is then sent to a water gas shift reactor where it reacts with steam to produce a mixture of CO_2 and H_2. CO_2 is then separated from the (high pressure) gas mixture and H_2 is send to the turbine to be combusted.

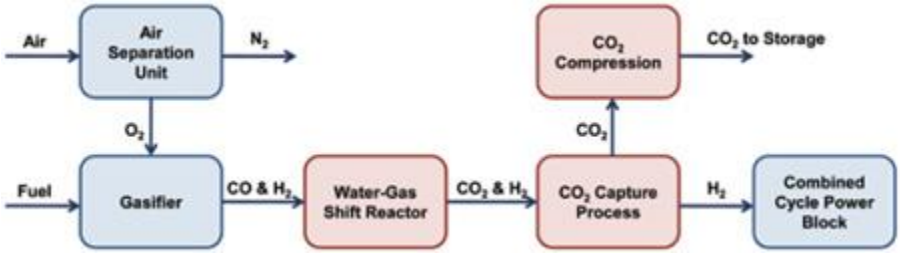


Figure 1. 2 Systematic diagram for pre combustion capture [6]

Separation of CO_2 from H_2 is less energy and cost effective than post combustion capture due to the higher concentration and partial pressure of CO_2. Development is ongoing in this technology to reduce the amount of steam for water gas shift reaction. Combining CO_2 sorption with water-gas shift activity is an alternative promising technology under development.

1.3.2 Post-combustion capture

Carbon dioxide post-combustion capture is one of the most mature capture technologies due to its reputation and implementation within many other industrial applications [7].

Separation of CO_2 from gas mixtures is a commercially applied technology which is in use at hundreds of locations around the world. There are many small facilities in operation today which use amine based solvents to capture significant flows of CO_2 from flue gas. The general chemical absorption process of CO_2 from flue gas is shown schematically in Figure 1.3.

In the absorber, the gas is contacted with a liquid phase amine, and the component to be absorbed normally called the solute, in which the CO_2 is transferred to the liquid phase. The liquid containing CO_2, the "rich" liquid, is sent to a desorber stage where the absorption equilibrium is reversed, normally by increasing the temperature or reducing the pressure, and the solute, CO_2 is released together with water vapor. The gas mixture is cooled and water is condensed out and returned to the desorber top as recycle. The CO_2 is then compressed where more water condensate and sent out for storage. Heat from the CO_2-lean solvent is then

transferred to the CO_2 rich solvent in a heat exchanger referred as a lean-rich heat exchanger.

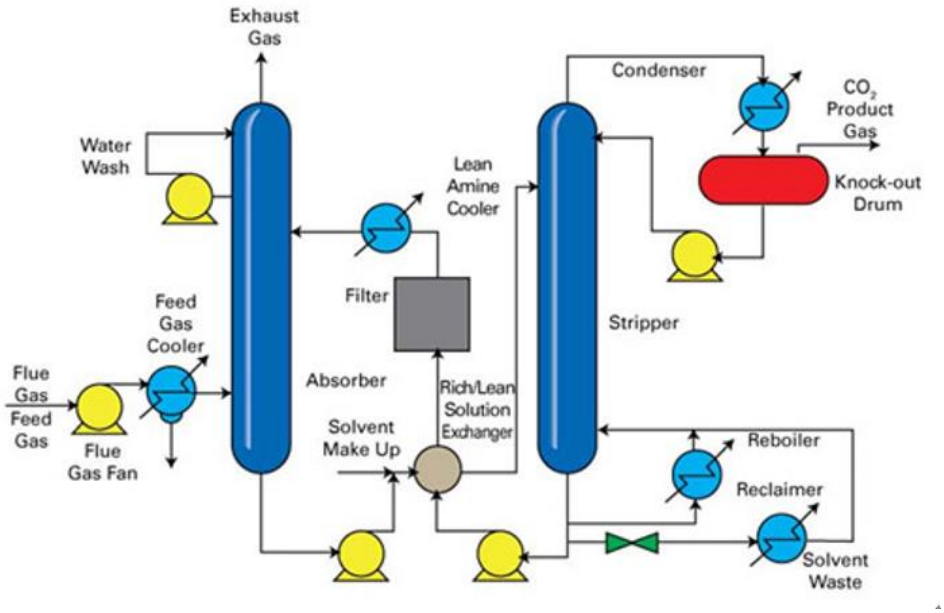


Figure 1. 3 Basic flow diagram for CO_2 absorption from flue gas with chemical solvent [8]

Post-combustion capture is a mature technology, though considerable R&D efforts are undertaken, as there is a need for new solvents which require less energy for regeneration, less corrosive, lower solvent loss rates via degradation and evaporation. Alternative means of capturing CO_2, such as Solid adsorption, membrane separations and chemical looping processes are also being studied which may be able to improve the overall efficiency of the process in near future.

1.3.3 Oxy fuel-combustion capture

In traditional power plants, fuel combustion is carried out using air, and the nitrogen (N_2) in the air ends up in the flue gas. However in oxy-fuel combustion process nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that mainly contains CO_2 and H_2O that can easily be separated by cooling. The water is condensed and after phase separation a gas stream rich with CO_2 is obtained. In this, Oxygen separation unit is the most expensive part which is

usually done by low temperature (cryogenic) air separation. Systematic flow diagram for oxy fuel combustion is shown in figure 1.4. Oxy-fuel processes have a further disadvantage that they are difficult to implement as a retrofit option for existing installations.

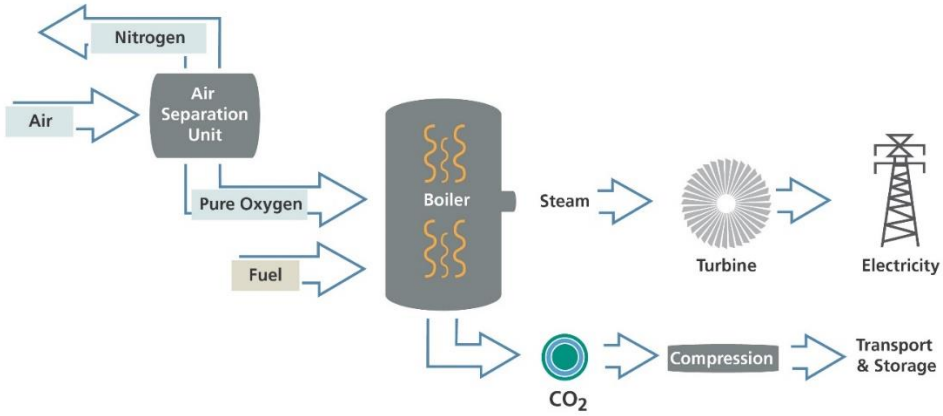


Figure 1. 4 Systematic flow diagram for oxy fuel combustion [6]

1.4 COMMERCIAL SOLVENTS FOR CO_2 POST COMBUSTION CAPTURE PROCESS

The development of aqueous amine solutions as acid gas absorption liquid started with the work of R.R. Bottoms for which a patent was also granted in 1930 [9]. Triethanolamine (TEA) was the first alkanolamine to be used commercially in early gas-treating plants. Monoethanolamine (MEA), Diethanolamine (DEA), and Methyldiethanolamine (MDEA) were also proved to be of principal commercial interest for gas purification [9]. Triethanolamine (TEA) was found to be less attractive mainly due to its low absorption capacity, lower reactivity and relatively poor stability. Diisopropanolamine (DIPA) [10] was used in the Adip process, in the Sulfinol process, as well as in the SCOT process for Claus plant tail gas purification but gradually replaced by Methyldiethanolamine (MDEA). Although MDEA was described by Kohl and coworkers at Fluor Daniel as a selective absorbent for H_2S in the presence of CO_2 as early as 1950, its use

in industrial processes has only become important in recent years. [9] A different type of alkanolamine, 2-(2-aminoethoxy) ethanol, commercially known as Diglycolamine (DGA), was first proposed by Blob and Riesenfeld (1955). This compound couples the stability and reactivity of mono ethanolamine with the low vapor pressure of di-ethyleneglycol therefore, can be used in more concentrated solutions than mono ethanolamine first proposed by Blob and Riesenfeld (1955) [9].

Commercially available solvents are continuously being improved for better CO_2 absorption performance. The most important characteristics for a solvent are CO_2 loading (cyclic capacity), absorption rate, chemical binding energy, and absorption and desorption temperatures [11].

A low binding energy comes together with a low reactivity for CO_2 and similarly high absorption rate is usually accompanied by high binding energy. The absorption rate determines the dimensions of the absorber and the capital costs of absorber make up about 40% of the total costs of the amine-based CO_2 capture plant [12].

The cyclic loading of the solvent is the difference of CO_2 loading between lean and rich in terms of mole of CO_2 per kilogram of solvent. A high cyclic loading will result in lower solvent circulation flow rate in the amine plant, which will lower the dimensions of the solvent heat exchanger, reboiler, amine pumps, absorber, and piping. It will also decrease the electricity consumption of pumps and the energy required for solvent heating. In addition, a smaller absorber will lower the flue gas blower energy requirements and dimensions.

The absorption temperature determines the costs and the energy requirements of the flue gas coolers. By bringing the absorption temperature closer to desorption will decrease the costs of the solvent heat exchanger. For CO_2 capture in a power-plant setting, the desorption temperature determines the temperature of the steam that has to be extracted from the steam turbine. Bolland and Undrum (2003), showed that there is a strong dependency between the energy output of the steam cycle and the steam temperature [13]. For specific solvents, lowering desorption

temperature will mean a higher lean CO_2 loading and thus a smaller cyclic loading.

Higher solvent concentrations is not always possible, due to the corrosive nature of amine based solvents. The stability of the amine based solvent and the specific solvent costs are also important characteristics when it comes to the operational cost, influencing solvent make-up and replacement costs. Furthermore, evaporative losses, associated health risks and the impact on the environment are also becoming increasingly important. Formation of degradation products also play an essential role in the corrosion [14]. The corrosion mainly affects the stripper, reboiler and lean-rich heat exchangers. Reducing the degradation rate will result in lowering the Operational and the Capital of the critical parts in the CO_2 capture plant. Despite several studies on each aqueous amine based solvents in past, the above mentioned aspects are still not entirely met by the current commercial solvents for CO_2 absorption.

1.5 MOTIVATION AND SCOPE OF THIS WORK

The interest in the study of reaction between CO_2 and alkanolamine has been growing for past two decades. Several amine based solvents (Individual and mixed amine systems) for their enhancement for CO_2 capture have been proposed. Usually gas treating processes are operated with aqueous amine solutions but non aqueous solvents and their mixture with water are also used due to their lower energy requirements in regeneration. A detailed knowledge of the reaction kinetics between CO_2 and these solvents is needed in order to deepen fundamental understanding of the reaction, to describe the effect of chemical reaction on mass transfer rates and to represent the reaction rate as function of process variables (e.g. temperature, pressure and reactant concentration) [15]. Such information is useful for reactor designing and performance prediction.

Primary and secondary alkanolamine react with CO_2 to form carbamate. MEA and DEA are extensively studied amines and kinetic behavior of large number of

such amines in aqueous and non-aqueous amines is well established. For MEA general agreement exist for rate constants and reaction order because various techniques have been used e.g. the rapid mixing method, wetted wall, stopped flow technique, tracer diffusion method and continuously stirred cell [16]. For DEA there is no general agreement on reaction order and reaction rate constants and some researchers suggest first or second order kinetics while other report as fractional order between one and two with respect to amine concentration in both aqueous and non-aqueous solvents [15].

The zwitterion mechanism is extensively used to describe chemical reaction kinetics. A single step termolecular (direct) mechanism is also presented. Sada [17] investigated the reaction between CO_2 and MEA at 303 in both aqueous and non-aqueous solvents and found a gradual change in reaction order from 1 to 1.90. Sada [17] also studied DEA in water, ethanol, methanol and 2-propanol solution and found reaction order changing from 1.42 to 2. Alvaraz-Fuster [18] reported reaction order 2 for MEA in both ethanol and ethylene glycol; however these authors were not able to find reaction order other than whole number due to used interpretation method. Versteeg and van Swaaij [19] also studied reaction kinetics between CO_2 and DEA in ethanol and butanol solutions and they found reaction order between 1 and 2 in ethanol while for butanol it was found to be second order. Crooks and Donnellan [20] also reported second order reaction between DEA and CO_2 in anhydrous ethanol. Comparison made on these results in aqueous and non-aqueous solutions, Versteeg [21] concluded that occurrence of reaction order in amine varied between 1 and 2 which can only be explained satisfactory by zwitterion mechanism. Da Silva and Svendsen [22] studied the mechanism for carbamate formation from CO_2 and alkanolamine in aqueous solutions by Ab Initio Study and suggested a single step, third order reaction is the most likely which is in good agreement with experimental data. The validity of termolecular molecular is said to be questionable by Versteeg [21] because it not able to explain the occurrence of broken order kinetics as was observed by

Sada [23], Versteeg and Van Swaaij [19] and Crooks and Donnellan [20] for non-aqueous systems [21]. Moreover, the experimental data presented by Little [24] for blends of secondary amines cannot be understood by termolecular mechanism whereas it can be profoundly explained by zwitterion mechanism [24].

Based on the literature review above, the objective of this work is to characterize the kinetics and mechanism of CO_2 absorption into non aqueous solvent. Experiments were performed for DEA-Ethanol solution using continuously stirred cell for different concentration in range of 0.2-3.2 mole/m^3 at 20^oC temperature. This work equally aims at applying the zwitterion and termolecular mechanism in the interpretation of experimental data.

2 THEORETICAL BACKGROUND

2.1 REACTION MECHANISM FOR PRIMARY AND SECONDARY AMINES

The overall forward reaction between CO2 and primary or secondary amines is being represented as:

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH \qquad 2.1$$

$$R_1R_2NCOOH + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \qquad 2.2$$

The first step being bimolecular, second order and rate determining, while second step is supposed to take place instantaneously. However this scheme is substantial simplification for the reaction mechanism that actually occurs [21].

1.1.1 Zwitterion Mechanism

Zwitterion mechanism was originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979). It consists of a two-step mechanism, i.e. the reaction between CO2 and the amine proceeds through the formation of an intermediate called zwitterion (reaction 2.3) and the deprotonation of the zwitterion by a base B (reaction 2.4).

$$CO_2 + R_1R_2NH \underset{K_{-1}}{\overset{K_2}{\rightleftharpoons}} R_1R_2NH^+COO^- \qquad 2.3$$

$$R_1R_2NH^+COO^- + B \underset{K_{-b}}{\overset{K_b}{\rightleftharpoons}} R_1R_2NCOO^- + BH^+ \qquad 2.4$$

R_1 and R_2 represents substituted group attached to the amine group; B represents a base molecule which may be a hydroxyl ion, water or an amine-functionality. In this work only DEA will be considered and solvent will be pure ethanol.

By applying the pseudo-steady-state condition for the zwitterion concentration, the overall forward reaction rate can be expressed as:

$$-r^{z}_{CO_2-R_1R_2NH} = \frac{k_2[CO_2][R_1R_2NH]}{1+\frac{k_{-1}}{\sum k_b[B]}} \qquad 2.5$$

$\sum K_b[B]$ Represents deprotonation of the zwitterion by any base such as CO_3^{-2}, HCO_3^-, H_2O, OH^- or R_1R_2NH, as well as by combination of bases.

If the zwitterion formation is the rate determining step i.e. $1 \geq K_{-1} / \sum K_b[B]$, then equation 2.5 can be simplified to:

$$-r^{z}_{CO_2-R_1R_2NH} = k_2[CO_2][R_1R_2NH] \qquad 2.6$$

Equation 2.6 shows a first order rate dependency with respect to both amine and CO_2 concentration.

If the deprotonation of the zwitterion is the rate determining step i.e. $K_{-1} / \sum K_b[B] \geq 1$ then equation 2.5 becomes:

$$-r^{z}_{CO_2-R_1R_2NH} = \frac{k_2 \sum k_b[B]}{k_{-1}}[CO_2][R_1R_2NH] \qquad 2.7$$

For this work amine is the only reacting base B, this suggest a broken order dependency from one to two with respect to amine concentration. For this case the forward reaction can be expressed as:

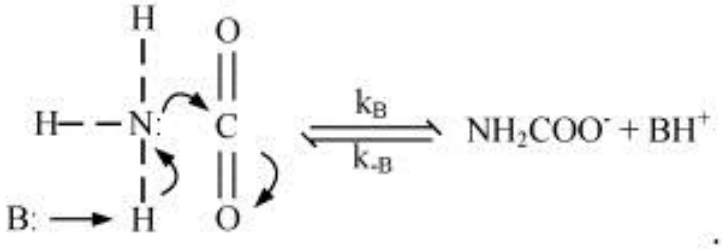
$$-r^{z}_{CO_2-R_1R_2NH} = \frac{[CO_2][R_1R_2NH]}{\frac{1}{k_2}+\frac{1}{k^{z}_{R_1R_2NH}[R_1R_2NH]}} \qquad 2.8$$

2.1.2 Single-step termolecular mechanism (Direct mechanism)

Termolecular mechanism was originally proposed by Crooks and Donnellan (1989) [20] who suggested that the bonding of amine to CO_2 and

proton transfer take place simultaneously and the initial product is loosely bound encounter complex. Most of these complexes break up to give reagent molecules again but a few react with a second amine molecule to give an ionic product.

Da Silva and Svandsen [22] have reviewed this mechanism by using ab-initio calculations and a solvation model and suggested that most probable mechanism was similar to one proposed by Crooks and Donnellan [20]. Any zwitterion like intermediate would be likely to have a very short lifetime. They concluded that in any case, the single step mechanism was the most suited to describe the nature of reaction taking place between amine and CO_2. An important observation from that work was that termolecular mechanism could explain broken order kinetics too, it had previously been argued that termolecular mechanism could not account for this observation by Versteeg et al. [21].



2. 9

In reaction 2.9, if amine and water are dominating bases the forward reaction rate for termolecular mechanism can be written as:

$$-r^{T}_{CO_2-R_1R_2NH} = \left\{k^{T}_{R_1R_2NH}[\mathrm{R_1R_2NH}] + k^{T}_{H_2O}[\mathrm{H_2O}]\right\}[CO_2][R_1R_2NH] \qquad 2.\ 10$$

For zwitterion mechanism, equation 2.6 and equation 2.8 will be the same if the deprotonation of zwitterion is rate determining step.

For this work where the only base is amine, the forward rate equation 2.10 can be written as:

$$-r^{T}_{CO_2-R_1R_2NH} = \left\{k^{T}_{R_1R_2NH}[\mathrm{R_1R_2NH}]\right\}[CO_2][R_1R_2NH] \qquad 2.\ 11$$

2.1.3 Reaction mechanism for tertiary alkanolamines

Donaldson and Nguyen suggested the mechanism in which tertiary alkanolamines cannot react directly with CO_2. These amines have a base-catalytic effect in the hydration of CO_2. This was also confirmed by Versteeg and Van Swaaij by the absorption of CO_2 into a water free solution of MDEA and ethanol [19]. They concluded that CO_2 was only physically absorbed and also agreed with the proposed reaction mechanism [25].

$$R_1R_2R_3N + H_2O + CO_2 \xrightarrow{K'} R_1R_2R_3NH^+ + HCO_3^- \qquad 2.\ 12$$

At higher pH values (pH =13), a direct reaction between CO_2 and tertiary amine has been reported by Jørgensen and Faurholt [26]. However, the rate of this reaction can be neglected at lower pH values (pH < 11) [19].
Versteeg and Swaaij [27] showed that the rate of absorption of CO_2 into an MDEA-ethanol solution could be described as physical absorption which was almost identical to absorption of N_2O in the same solution.
The overall rate of reaction for all CO_2 reaction in aqueous amine solutions can be represented as follows:

$$r_{overall} = \left\{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k'[R_1R_2R_3N]\right\}[CO_2] \qquad 2.\ 13$$

k_{ov} is given by:

$$r_{ov} = \left\{k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k'[R_1R_2R_3N]\right\} \qquad 2.\ 14$$

And k_{app} is:

$$k_{app} = k'[R_1R_2R_3N] \qquad 2.\ 15$$

2.1.4 Determination of kinetic rate constant

For the absorption of CO_2 into aqueous amine solution, the overall reaction rate can be expressed as follows:

$$r_{ov} = r_{CO_2-R_1R_2NH} + r_{CO_2-OH^-} \quad 2.16$$

The apparent kinetic rate constant (k_{app}) can be defined as:

$$k_{app} = k_{ov} - k^*_{OH^-}[OH^-] \quad 2.17$$

In this case where no water is present it can be modified to:

$$k_{app} = k_{ov} \quad 2.18$$

A graphical method can be used, i.e. by plotting ($k_{app}/[R_1R_2NH]$) against the $[R_1R_2NH]$ value for termolecular mechanism according to equation 2.11, value of slope is $k^T_{R_1R_2NH}$ itself. If equation 2.5 for zwitterion mechanism holds, then the plot between $[R_1R_2NH]/k_{app}\ and\ 1/[R_1R_2NH]$ should yield a straight line with slope $\frac{k_2k_b}{k_{-1}}$ and intercept k_2. This method was used by Versteeg and van Swaaij [25], Crooks and Donnellan [20].

2.2 MASS TRANSFER WITH A CHEMICAL REACTION

In chemical absorption, the reaction rate is an important feature of the mass transfer. The absorption flux is enhanced by the chemical reaction and can be expressed as:

$$N_A = \frac{1}{\frac{1}{E_A k_l} + \frac{RT}{Hk_g}}(C^*_A - C_{A,b}) \quad 2.19$$

Where E_A is the enhancement factor, i.e. the ratio of the liquid side mass transfer coefficient in the presence of chemical reaction to the physical

coefficient under the conditions of equal mass transfer driving force. Two simplifications can be incorporated with equation 2.19 as:

1. If the experiments are performed under conditions of very low loading (zero loading assumption), the concentration of solute (CO_2) in the bulk ($C_{A,b}$) liquid is zero and equation 2.19 reduces to:

$$N_A = \frac{C_A^*}{\frac{1}{E_A k_l} + \frac{RT}{H k_g}} \qquad 2.20$$

2. If the experiments are performed with pure CO_2, then the gas-side mass transfer resistance can be omitted and equation becomes:

$$N_A = E_A k_l C_A^* \qquad 2.21$$

Thus in reactive absorption information on enhancement factor E_A is necessary. However a large number of enhancement factor equations exist based on a variety of mass transfer models, from the well-known two film model (Lewis and Whitman) [28] to the penetration and surface renewal model (Higbie) [29] If irreversible or reversible reactions are assumed then expression for E_A will also vary.

The complexity of choosing a model can be simplified by using the pseudo-first order irreversible approach. As mentioned previously, the reaction order with respect to the amine concentration varies from 1 to 2 and the concentration of amine is normally in relatively large excess compared to the concentration of CO_2 in liquid phase.

2.2.1 Two film model

Two film model initially proposed by Whitman and Lewis and Whitman in 1924 [28] aims at developing a description of the mass transfer process when a gas phase is in contact with a liquid phase. In this model the assumption was

made that a stagnant film of thickness (δ) exists at the gas/liquid interface while the bulk liquid is well-mixed. Mass transport was assumed to take place by steady state molecular diffusion through the film while mass transfer by convection within this layer was assumed to be insignificant. Beyond the thin layers, mixing is sufficient to eliminate concentration gradients (as can be seen in Figure 2.1).

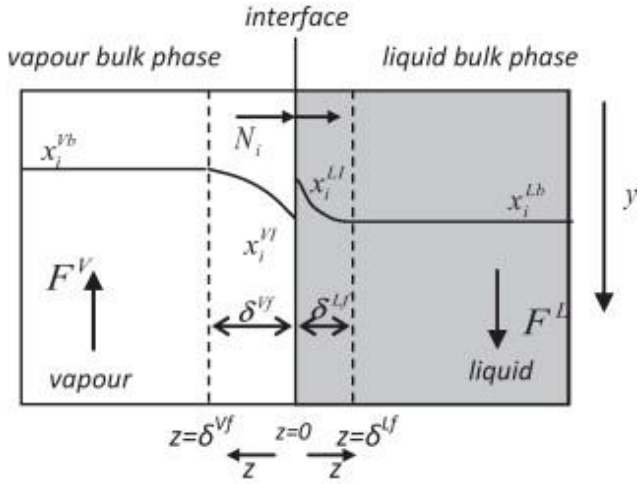


Figure 2. 1 Two film model for mass transfer between liquid and gas phases [30]

The mass transfer from gas phase to liquid phase without any reaction is determined at steady state from the mass balance of the solute (CO_2=A) as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} = 0 \quad \text{For } 0 \le x \le \delta \qquad 2.\ 22$$

With boundary conditions:

$$\begin{aligned} x = 0, C_A &= C_{A,i} \\ x = \delta, C_A &= C_{A,b} \end{aligned} \qquad 2.\ 23$$

The solution will give the flux of solute through the gas-liquid interface as:

$$N_A = k_l (C_{A,i} - C_{A,b}) \qquad 2.\ 24$$

Where the mass transfer coefficient k_l is equal to D_A/δ.

For a pseudo-first order irreversible reaction, Hatta (1932) presented the analytical solution for the mass transfer for the film model. Starting from the mass balance for the solute:

$$D_A \frac{\partial^2 C_A}{\partial x^2} = k_1 C_A \text{ For } 0 \leq x \leq \delta \qquad 2.25$$

Inserting two boundary conditions given below, resulted in an enhancement factor as:

$$x = 0, C_A = C_{A,i}$$
$$x = \delta, D_A \left(\frac{\partial C_A}{\partial x} \right)_\delta = k_1 C_A V_b \qquad 2.26$$

$$E_{A,\,film} = \frac{Ha}{\tanh(Ha)} \qquad 2.27$$

A further simplification can be made if Ha >>1, then $E_{A,\,film} \approx$ Ha where $Ha = \frac{\sqrt{k_{ov} D_A}}{k_l}$

2.2.2 Penetration theory

The penetration theory was proposed by Higbie in 1935 [29]. It is assumed that the gas-liquid interface is made up of a variety of small liquid elements, which are continuously brought to the surface from the bulk of the liquid by the motion of the liquid phase itself. Each liquid element is considered to be stagnant, and the concentration of the dissolved gas in the element is considered equal to the bulk liquid concentration when the element reaches the surface. The residence time at the phase interface is the same for all elements. Mass transfer takes place by unsteady molecular diffusion in the various elements of the liquid surface.

The mass transfer from gas phase to liquid phase is determined as an unsteady state condition from the mass balance of the solute as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} = \frac{\partial C_A}{\partial t} \qquad 2.\ 28$$

With initial and boundary conditions:

$$\begin{aligned} &C_A(x,0) = 0 \\ &C_A(0,\mathrm{t}) = C_{A,i} \\ &C_A(\infty,\mathrm{t}) = C_{A,\mathrm{b}} \end{aligned} \qquad 2.\ 29$$

The solution will lead to an average rate of mass transfer over the time interval 0 to t^* as:

$$N_A = k_l (C_{A,i} - C_{A,b}) \qquad 2.\ 30$$

Where the mass transfer coefficient k_l is equal to $k_l = \sqrt[2]{\frac{D_A}{\pi t^*}}$

For a pseudo-first order irreversible reaction, the enhancement factor can be expressed as (reported in van Swaiij & Versteeg (1993) and from Danckwerts (1970)).

$$E_{A,pen} = Ha\left[\left\{1+\frac{\pi}{8Ha^2}erf\left[\sqrt{\frac{4Ha^2}{\pi}}\right]+\frac{1}{2Ha}\exp\left(\frac{4Ha^2}{\pi}\right)\right\}\right] \qquad 2.\ 31$$

As for the film model, if $Ha >> 1$, then the simplification for the enhancement factor derived from the penetration model is $E_{A,pen} \approx Ha$.

2.2.3 Surface renewal model

Danckwerts in 1951 [31] proposed the surface renewal model which is an extension of the penetration theory where it was assumed that the liquid elements stay the same time at the phase interface. In the surface renewal model

the liquid elements do not stay the same time at the phase interface. The distribution of surface element contact times is described by a distribution function $\Psi(t) = se^{-st}$, where

$$\Psi(t) = \frac{1}{t^*} for\ t < t^*\ and\ \Psi(t) = 0\ for\ t > t^* \qquad 2.\ 32$$

The rate of absorption at the surface is then the average of the rates of absorption in each element and can be expressed as:

$$N_A = \int_0^\infty N_{A,inst}(t)\psi(t)dt = \sqrt{\frac{D_A}{\pi}}(C_{A,i} - C_{A,b})\int_0^\infty \frac{se^{-st}}{\sqrt{t}}dt = k_l(C_{A,i} - C_{A,b}) \qquad 2.\ 33$$

The mass transfer coefficient resulting from this model is then $k_l = \sqrt{D_A s}$

In both the penetration and surface renewal models, the unknown thickness of the film has vanished and been replaced by an unknown contact time t^* or an unknown retention time distribution parameters. For a pseudo-first order irreversible reaction, the mass balance for the solute for the diffusion, reaction and accumulation can be written as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A = \frac{\partial C_A}{\partial t} \qquad 2.\ 34$$

With boundary conditions:

$$\begin{aligned} &C_A(x,0) = 0 \\ &C_A(0,\mathrm{t}) = C_{A,i} \\ &C_A(\infty,\mathrm{t}) = 0 \end{aligned} \qquad 2.\ 35$$

Implementing the Laplace transform and inserting the boundary conditions, Equation 2.34 can be rewritten as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - k_1\left(\frac{k_1 + s}{D_A}\right)\overline{C_A} = 0 \qquad 2.\ 36$$

By using inverse transformation, the solution of Equation 2.36 can be written as the distribution of concentration $C_A(x,t)$ as:

$$\frac{C_A}{C_{A,i}} = \frac{1}{2}\exp\left(-x\sqrt{\frac{k_1}{D_A}}\right)erfc\left(\frac{x}{2D_A t} - \sqrt{k_1 t}\right) + \frac{1}{2}\exp\left(x\sqrt{\frac{k_1}{D_A}}\right)erfc\left(\frac{x}{2D_A t} + \sqrt{k_1 t}\right)$$

2. 37

Equation 2.37 can be simplified for large value of $k_1 t$ to:

$$\frac{C_A}{C_{A,i}} = \exp\left(-x\sqrt{\frac{k_1}{D_A}}\right) \qquad 2.\ 38$$

The rate of absorption in an element having a surface age t can be calculated as:

$$N_A(t) = \sqrt{k_1 D_A C_{A,i}}\left[erfc(\sqrt{k_1 t} + \frac{e^{-k_1 t}}{\sqrt{\pi k_1 t}}\right] \qquad 2.\ 39$$

The average absorption rate at the surface can be determined using Danckwert's age function as:

$$N_A(t) = \sqrt{D_A(k_1 + s)C_{A,i}} = \sqrt{D_A\left(k_1 + \frac{k_l^2}{D_A}\right)C_{A,i}} = k_l C_{A,i}\sqrt{1 + \frac{k_l D_A}{k_l^2}} \qquad 2.\ 40$$

Then the enhancement factor for this model can be expressed as:

$$E_{A,surf} = \sqrt{1 + \frac{k_l D_A}{k_l^2}} = \sqrt{1 + Ha^2} \qquad 2.\ 41$$

For $Ha >> 1$, the enhancement factor $E_{A,surf} \approx Ha$.

The conclusion can be made that the enhancement factors derived from the three different models for mass transfer for the pseudo-first order irreversible reaction

are very similar. The largest deviation among the model is found to be 7.6% for Ha =1 (van Swaiij & Versteeg, 1992).

The regime of the reaction can be determined from the absolute value of *Ha* and the ratio between *Ha* and $E_{A\infty}$ (the infinite enhancement factor), i.e.:

1. Slow reaction regime ($Ha < 0.3$), no enhancement caused by the chemical reaction. The absorption flux depends on the physical mass transfer coefficient and since the mass transfer coefficient is strongly liquid flow rate dependent, the absorption flux will also be liquid flow rate dependent.
2. Fast reaction/ pseudo-first order regime ($3 < Ha \ll E_{A\infty}$), gives weak to strong enhancement of the mass transfer rate due to the reaction. In this regime the absorption flux is independent of the physical mass transfer coefficient and, hence independent of liquid flow rate.
3. Instantaneous reaction regime ($3 < E_{A\infty} \ll Ha$), the reaction is said to be instantaneous with respect to the mass transfer and the absorption flux is limited by diffusion of the reactants.

A transition regime for ($0.3 < Ha < 3$) also exists. Expressions for the infinite enhancement factor for the different mass transfer models can be found in van Swaaij and Versteeg 1992.

Astarita et al. (1983) uses a term called the ratio of the diffusion time (t_D) over the reaction time (t_R), denoted $\Theta = t_D/t_R$, to classify the reaction regimes based on the film model. The diffusion time (t_D) is the time needed for molecular diffusion to make the concentration uniform, and the reaction time (t_R) is a required time for the chemical reaction to proceed to such an extent that the concentration of the limiting reactant is changed significantly. Three different regimes can be represented as:

1. Slow reaction if ($\theta \ll 1$), the reaction is too slow to have any significant influence on the diffusion phenomena and no enhancement will take place.
2. Fast reaction if ($\theta \gg 1$), the reaction is fast enough to result in a significant change in limiting reactant concentration and rate enhancement results.
3. Instantaneous reaction if ($\theta \to \infty$), the reaction is infinitely fast and chemical equilibrium is established instantaneously.

3 MATERIALS AND METHODS

3.1 MATERIALS

Chemicals used for this work with their physical properties and purity are listed in the table below:

Table 1 Specifications of chemicals used in this work

Chemical	CAS No.	Manufacturer	Molecular Formula (g/g mole)	Mol. weight	Purity
Di-ethanolamine	111-42-2	Sigma Aldrich	$HN(CH_2CH_2OH)_2$	105.14	>99%
Tetra-butyl ammonium hydroxide solution	2052-49-5	Sigma Aldrich	$(CH_3CH_2CH_2CH_2)_4N(OH)$	259.47	>99%
Ethanol		Assink Chemie	C_2H_6O	46.068	>99.8%
Nitrous oxide	10024-97-2	Air Liquide BV	N_2O	44	>99%
Carbon dioxide	124-38-9	Air Liquide BV	CO_2	44	>99.9 %
Molecular sieves, 3 Å	308080-99-1	Sigma Aldrich	$K_nNa_{12-n}[(AlO_2)_{12}(SiO_2)_{12}].xH_2O$		

Solutions of different molarities were prepared using di-ethanolamine (DEA) and ethanol listed above. DEA was used as provided by sigma Aldrich. 99.8% denatured ethanol was provided by Assink Chemie BV with small fraction of water as main impurity. To achieve highest purity, calculated amount of molecular sieves 8-12 mesh were added in ethanol to further remove water contents. Enough time was given for molecular sieves to absorb water contents

to their capacity before using ethanol for experimentation. All other chemicals were used as received.

3.1.1 Experimental Section

All experiments were carried out in closed stirred cell contractor with smooth gas-liquid interface and was operated batch wise with respect to liquid and gas phases. A schematic drawing of the set-up is presented in Fig. 3.1 below.

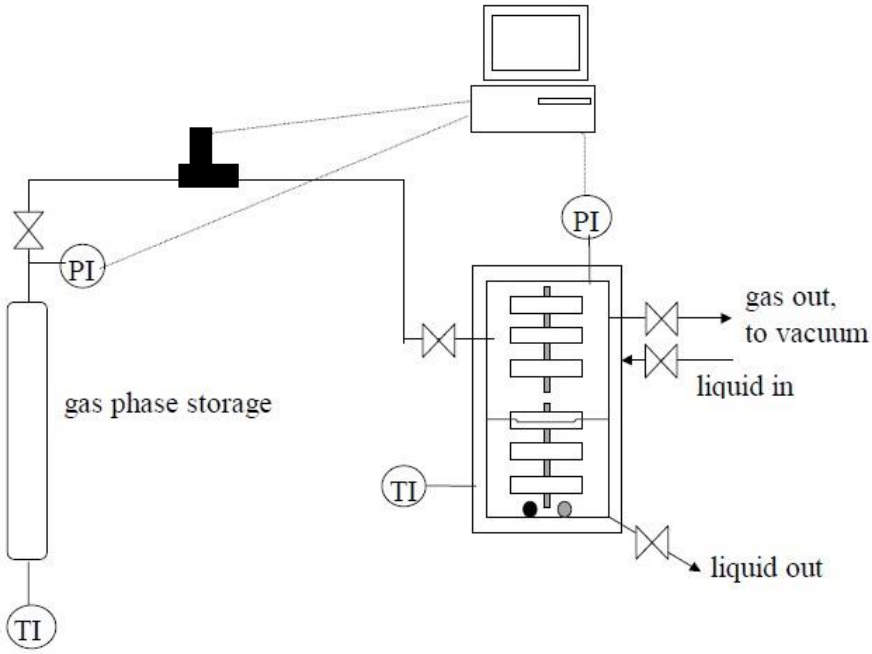


Figure 3. 1 Stirred cell experimental setup [32]

Absorption experiments were carried out at 20^{o}C. The reactor consists of jacketed glass (ID = 15.02cm) with upper and lower parts which seal on ground flanges giving total interfacial area of 177.1861cm^{2}. There were two set of stirrer in the reactor which were equipped with molten in magnets and was driven externally. For this work only one stirrer was used because the reactor was half full and also the stirrer position doesn't have any effect on

mass transfer for ethanol [33]. The stirrer speed is always set at constant value of 157 rpm for each experiment which was the maximum speed that could be setup for that apparatus because of the maximum output of the power supply attached with the stirrer and stirring beyond this limit may disturb smooth interface for gas-liquid contact. Total volume of the reactor was 4335cm^3 out of which 2050cm^3 was filled with the solution for each experiment. This specific volume of the solution was selected in order to dip stirrer support completely and to give a flat horizontal gas–liquid interface which was possible only in the middle of the reactor as shown in figure 3.2. Hence total volume available for gas phase inside the reactor was 2285cm^3.

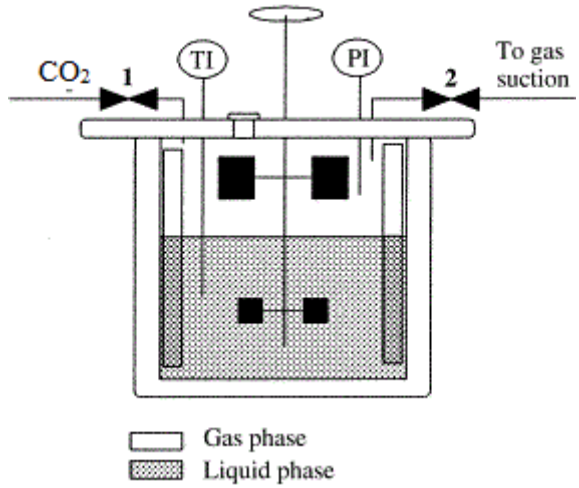


Figure 3. 2 Stirred cell reactor

The reactor was connected to a gas supply vessel (gas bomb) filled with carbon dioxide or nitrous oxide from gas cylinders. Total volume of gas bomb was 583.2652cm^2 including lines connecting with the reactor. Both reactor and gas bomb were equipped with digital pressure transducers and thermocouples. The pressure transducers connected to the stirred cell reactor and gas bomb are HEISE DXD pressure transducers (range 0–30 psi or 0-2 bar absolute, error ±0.02%). The measured signals were recorded with a computer using labVIEW.

A text file is then generated by labVIEW giving total pressure in reactor (mbar), pressure in gas bomb (mbar) with their temperatures as well as the temperature of the gas above the liquid in the reactor with respect to time of gas absorption into the solution.

For first experiment a certain amount of CO_2 in gas bomb is collected from the main supply source and let the pressure be stable for a while inside the gas bomb. First set of absorption study at any concentration in unloaded solution is named as α_1. Figure 3.3 below shows a typical absorption measurement curve:

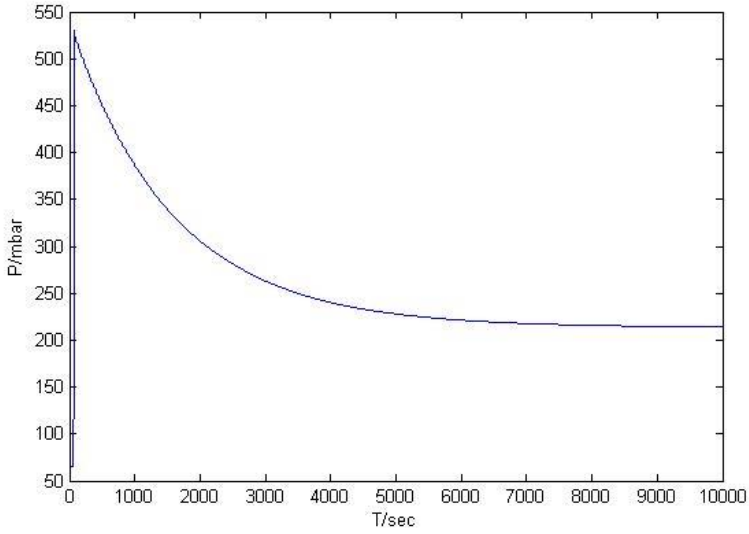


Figure 3. 3 Typical absorption curve

At first the reactor is at vapor pressure of the solution. When CO_2 is injected, it goes to the maximum pressure and then start decreasing with the absorption of CO2 into the amine solution. After some time when almost all CO2 is absorbed, it reaches to steady state pressure in the reactor. For each concentration, after achieving steady end pressure, more CO_2 gas at higher CO_2 pressure in gas bomb than α_1 was added to reactor and reaction conditions were verified (Equation 3.5). Results obtained from second loading were named as α_2 and this procedure

continued till α_9 in the same solution with higher CO_2 pressure in the reactor each time. It should be noted that at the end of every experimental stage the pressure in the reactor is either equal (for first two, three sets for higher concentrations) or greater than initial vapor pressure due to presence of un-absorbed CO_2 in the solution which is resulted due to decrease in free amine with increase in loading.

A typical curve at the end of one set of experiments at one concentration is shown in figure 3.4.

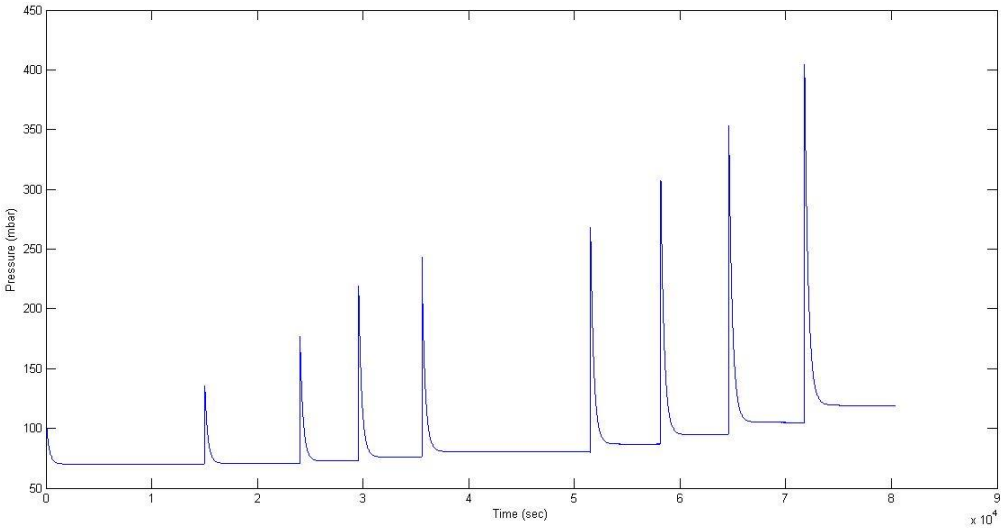


Figure 3. 4 typical curves at the end of one set of experiments for 0.8M DEA in ethanol

Total amount of CO_2 absorbed into the amine solution, for each value of α, was calculated theoretically using a real gas law where the gas compressibility factor was calculated based on 2nd viral coefficient. No sample was drawn in between but after completing experiments till α_9, the end solution was analyzed for total CO_2 by non-aqueous titration according to method described by Jonnes et al. [34], Verbrugge [35] to verify the amount of CO_2 absorbed with theoretically calculated.

3.1.2 Determination of Carbon Dioxide

The equipment for the determination of carbon dioxide is presented in Fig. 3.3 below.

Figure 3. 5 Metrohm 716 DMS titrino setup for CO2 analysis

It consists of round a bottom flask with 2M boiling sulphuric acid with sufficient nitrogen supply. Small amount of sample is injected into the acid using syringe through a septum. Carbon dioxide that is physically and chemical bonded to the solution, sulphuric acid and ethanol evaporated are directed to titration flask through a condenser. Water at 2^{o}C is passed continuously through the condenser to condense ethanol and sulphuric acid vapors back into the round bottom flask. Carbon dioxide is transferred to the titration vessel with a nitrogen flow of 50 ml/min. The titration flask having 3 volume % MEA in dimethyl form amide

(DMF) and thymolphtalein, as an indicator, is stirred sufficiently and specific nitrogen flow ensured that all carbon dioxide is reacted with primary amine MEA. The solution is kept on constant pH by maintaining constant blue color in the flask.

Standardization of titrant is performed for 0.1M sodium carbonate standard solution used as sample. Initial pH was noted before the sample was injected into boiling acid, after some time, the solution in titration flask became more acidic. The blue color disappeared and pH started to decrease till all carbon dioxide is absorbed. An automatic Metrohm 716 DMS Titrino was used to carry out the titration. Using correct setting and feeding initial pH, the solution was titrated against 0.1M Tetra-butyl ammonium hydroxide (TBAH) provided by sigma Aldrich. The addition of titrant continued till the pH of the initial conditions is reached. This was also verified by color transition to blue. Two consecutive titration results giving less than 2.5% error were taken as final amount of TBAH solution used against injected amount of solution.

Amount of carbon dioxide present in the solution can be calculated by:

$$Amount\ of\ CO_2(mole/kg) = \frac{Amount\ of\ TBAH\ used \times Concentration\ of\ TBAH}{Amount\ of\ sample\ added} \quad 3.1$$

3.1.3 Physico-chemical parameters

3.1.3.1 Physical solubility and liquid side mass transfer coefficient:

In order to verify the conditions of pseudo first order absorption experiments, $m_{CO_2}.\sqrt{D_{CO_2}}$ and mass transfer coefficient k_l are the most important physicochemical parameters (equation 3.5, 3.6). As CO_2 reacts with alkanolamines, so it is not possible to determine physical solubility (m_{CO_2}) or diffusivity (D_{CO_2}) of carbon dioxide in alkanolamine solutions directly. These parameters were measured using CO_2-N_2O analogy [36] [37] as N_2O is almost identical in configuration, molecular volume and electronic structure. It was concluded that the ratio of CO_2 solubility to N_2O solubility remained constant for

the various solutions and that the "N_2O analogy" could be applied to estimate the solubility of CO_2 in alkanolamine solutions according to the given equation [36]:

$$m_{i,CO_2} = \frac{m^E_{CO_2}}{m^E_{N_2O}} m_{i,N_2O} \qquad 3.2$$

And:

$$k_{l,CO_2} = \frac{k^E_{l,CO_2}}{k^E_{l,N_2O}} k_{l,N_2O} \qquad 3.3$$

Where superscript E refers measurements in pure ethanol.

3.1.3.2 Diffusivity and viscosity:

Diffusivity of CO_2 and N_2O in pure ethanol solvent, solution viscosity and density have been reported by Alvarez-fuster [18], Sada [17] [23], Versteeg [19] and Little [33] at different concentration and temperature conditions. Snjgder [38] presented following temperature based relation for CO_2 and N_2O diffusivity in ethanol [38].

For CO_2 in ethanol:

$$D_{CO_2}(m^2/s) = 336.5\times10^{-9}\exp\left(-\frac{1314.7}{T/K}\right) \qquad 3.4$$

For N_2O in ethanol:

$$D_{N_2O}(m^2/s) = 345.0\times10^{-9}\exp\left(-\frac{1310.4}{T/K}\right) \qquad 3.5$$

3.2 METHODS

In each set of experiments freshly prepared solution was fed into the reactor and was degassed using vacuum pump to strip off all inert gas

contaminants present in the solution. After degassing, the pressure in the reactor was almost the same with the vapor pressure of the solution in the reactor at that temperature. A vapor liquid equilibrium was allowed to establish before starting the experiments. The pressure recorded in the reactor before starting the experiment is the vapor pressure of the solution P_{vap} and was used to calculate actual pressure of CO_2 in the reactor by subtracting from total pressure in the reactor:

$$P_{CO_2} = P_{tot} - P_{vap} \qquad 3.6$$

After equilibrium has achieved, pure CO_2 (for kinetics experiments) was introduced into the reactor. The initial pressure $P_{CO2}\big|_{t=0}$ and average loading for each experiment could be adjusted by means of amount of CO_2 added to the reactor. The decrease in pressure with time due to absorption of pure CO_2 into solutions was studied and called α_1. Reaction kinetics were studied in first order reaction regime where following condition was satisfied as stated in equation 3.7. The decrease in P_{CO2} during these experiments caused E_∞ to increase steadily, therefore condition in 3.7 were always satisfied in time-pressure curve.

$$2 < Ha \ll E_{CO_2,\infty} \qquad 3.7$$

Where:

$$Ha = \frac{\sqrt{k_{ov} . D_{CO_2}}}{K_l} \qquad 3.8$$

And:

$$E_{CO_2,\infty} = \sqrt{\frac{D_{CO_2}}{D_{DEA}}} + \sqrt{\frac{D_{DEA}}{D_{CO_2}}} . \frac{[DEA].R.T}{\nu_{CO_2} m_{CO_2} P_{CO_2}} \qquad 3.9$$

Transient absorption rates were thus given by:

$$V_g \frac{dC_g^b}{dt} = -k_l a(mC_g^b - C_l^b) \qquad 3.\ 10$$

Where:

$$m = \frac{C_l^i}{C_g^i} \qquad 3.\ 11$$

The superscripts *b* and *i* refers to the bulk and interface and *m* can be regarded as a distribution coefficient. The conservation of mass gives:

$$V_g C_g^o + V_l C_l^o = V_g C_g^b + V_l C_l^b \qquad 3.\ 12$$

$$C_g^\infty = \frac{V_g C_g^o + V_l C_l^o}{mV_l + V_g} \qquad 3.\ 13$$

Where the superscripts 0 and ∞ refers to the initial and infinite time. Solving Equations (3.10), (3.12) and (3.13) with respect to C_g^b and t using the following initial condition:

$$C_g^b = C_g^o \ \ at \ \ t = 0 \qquad 3.\ 14$$

Which gives:

$$\ln\left[\frac{C_g^b - C_g^\infty}{C_g^o - C_g^\infty}\right] = \frac{(mV_l + V_g)(k_l a)t}{V_g V_l} \qquad 3.\ 15$$

For our case of partial pressure it could be modified as:

$$\ln\left[\frac{P(t) - P^\infty}{P^o - P^\infty}\right] = \frac{(mV_l + V_g)}{V_g V_l} k_L A t \qquad 3.\ 16$$

From this relation between pressure decrease and time the liquid phase mass transfer coefficient k_L can be calculated by plotting the left side of Equation (3.16) versus the time t and finding the slope (see figure 3.6).

The absorption experiments for determining k_L value were allowed to reach equilibrium in order to obtain dimensionless solubility:

$$\mathrm{m} = \frac{(P^o - P^\infty)\,\mathrm{V}_g}{(P^\infty - P_{vap})V_l} \qquad 3.\ 17$$

For our closed reactor with gas volume V_g, from a mass balance (equation 3.12), the pressure-time relation (equation 3.16) can be rearranged as:

$$ln\, P_{CO_2|\,t} = -\frac{m_{CO_2}.A}{V_g}.\sqrt{k_{ov}\, D_{CO_2}}.t + ln\, P_{CO_2|\,t=0} \qquad 3.\ 18$$

The overall reaction rate constant k_{ov} was determined from the slope in lnP_{CO_2} and time graph in the region where conditions in equation 3.7 was met. A typical pressure-time curve is shown in figure 3.6.

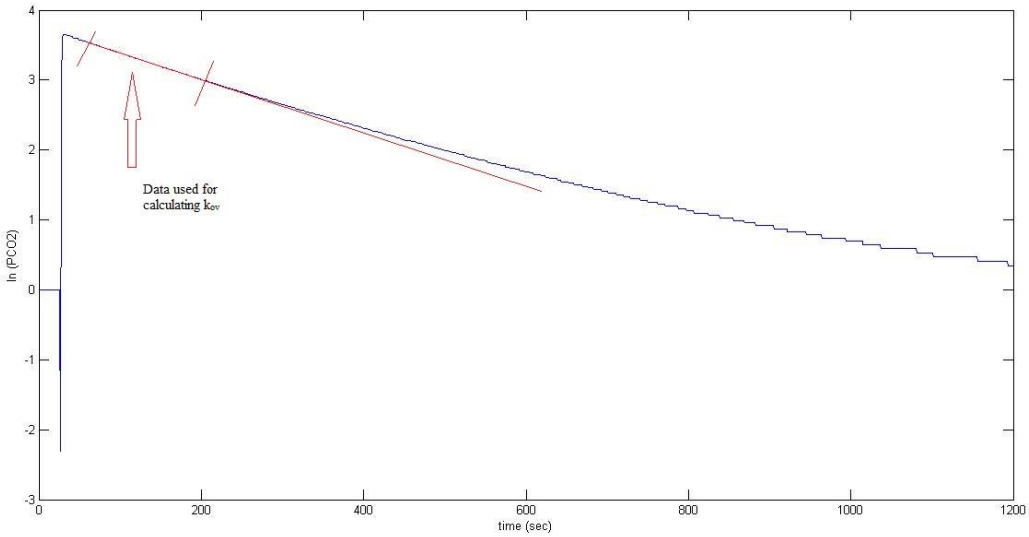


Figure 3. 6 Typical plot between time and ln(P_{CO2}) showing data used for k_{ov} calculation

It can be seen in figure 3.6 that $ln(P_{CO_2})$and time plot is not straight which goes down until reached to steady state so we have to take the straight line region where slope is almost constant.

If condition (3.7) is fulfilled then the reaction is regarded as pseudo first order. The CO_2 absorption rate into the solution is described by:

$$J_{CO_2}.A = \sqrt{k_{ov}\, D_{CO_2}}\; m_{CO_2} P_{CO_2} \frac{A}{RT} \quad (\text{mole.m}^{-2}.\text{s}^{-1}) \qquad 3.\ 19$$

The apparent reaction rate k_{app} for carbamate formation for this system was calculated from overall rate constant k_{ov} as:

$$K_{app} = K_{ov} - K^*_{OH^-}[OH^-] \qquad 3.\ 20$$

For our case, without presence of OH^- it would be as:

$$K_{app} = K_{ov} \qquad 3.\ 21$$

On the basis of zwitterion and termolecular (direct) mechanism respectively, k_{app} can then be expressed as:

$$k_{app} = \frac{[DEA]}{\frac{1}{k_2} + \frac{1}{k^z_{DEA}[DEA]}} \qquad 3.\ 22$$

And:

$$k_{app} = \{k^T_{DEA}[DEA]\}[\text{DEA}] \qquad 3.\ 23$$

4 RESULTS AND DISCUSSION

4.1 PHYSICAL SOLUBILITY AND MASS TRANSFER COEFFICIENT

In table 4.1 the values of the term $m\sqrt{D}$ and mass transfer coefficient (k_L) for CO_2 in ethanol and N_2O in both ethanol and DEA in ethanol solutions are presented.

Table 4. 1 $m\sqrt{D}$ for N_2O and CO_2 in DEA-ethanol solutions at 293K

[DEA] mole/m^3	Gas	$m\sqrt{D}\times10^{-4}$ m.s$^{-1/2}$	$K_L\times10^5$ m/sec	Reference
0	CO_2	1.37	-	Versteeg and Swaaij 1988
0	CO_2	1.64	-	Alvarez-Fuster et al. 1981
0	CO_2	1.73	-	Little et al. 1991
0	CO_2	1.77	-	William Kunerth
0	CO_2	1.75	6.85	This work
0	N_2O	1.44	-	Versteeg and Swaaij 1988
0	N_2O	1.88	-	William Kunerth 1921
0	N_2O	1.82	7.79	This work
201	N_2O	1.72	7.36	This work
401	N_2O	1.51	6.85	This work
805	N_2O	1.14	5.60	This work
1602	N_2O	1.00	4.31	This work
3201	N_2O	0.7	2.20	This work

Solubility of CO_2 in solvent does not seem to be dependent on amine concentration [39] [40] however diffusivity of CO_2 is much dependent on amine concentration which can be concluded from table 4.1 and appendix. The solubility

of CO_2 and N_2O in the solvents for zero loading are well in line with values previously reported [19] [18] [33] [41]. The only difference is with Versteeg [25] whose value is much lower than this work but also with other references as well. The mass transfer coefficients are specific to the gaseous component, the solvent, and the type/geometry of the reactor applied, thus cannot be compared directly to values from other sources [41].

4.2 APPARENT RATE OF REACTION

In Fig 4.1 the apparent kinetic rate constant based on equation 3.18 and 3.20 from this work is shown as function of DEA concentration. The apparent rate constant k_{app} from Versteeg 1988 [25] and Crooks and Donnellan 1988 [20] (stopped flow) are also shown for comparison. The absorption results are well in line with the literature date presented in figure below.

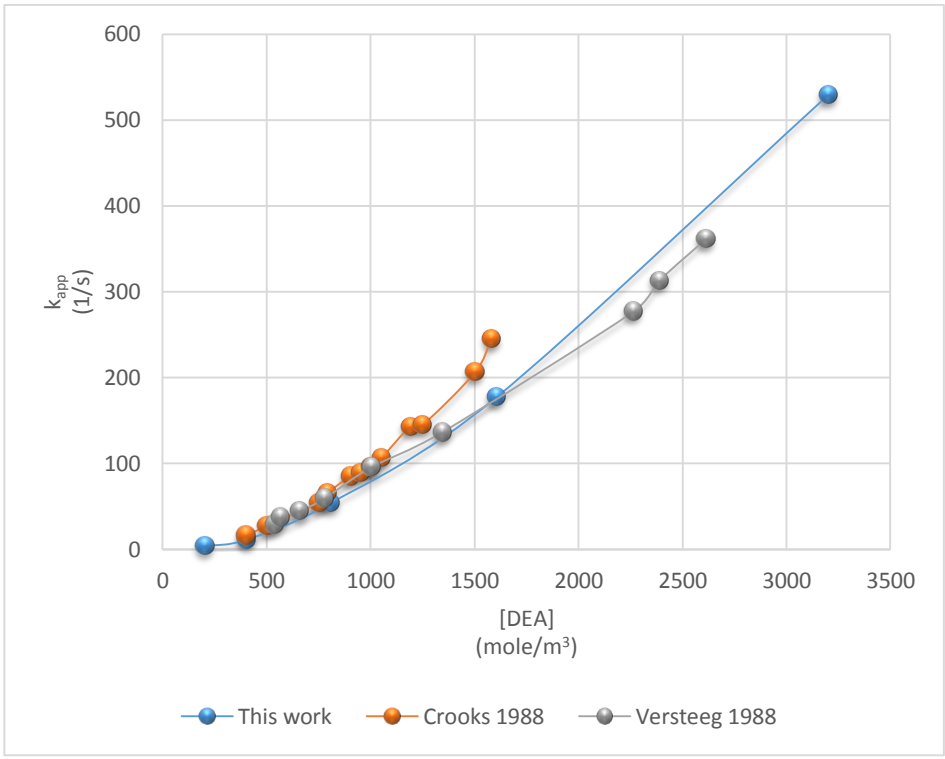


Figure 4. 1 k_{app} with concentration of DEA in ethanol at 293K

From figure 4.1, it could be concluded that the results obtained from this work are in agreement with Crooks [20] and Versteeg [25] at lower concentrations. As the concentration increases more than 1000 mole/m^3 the literature data and current start deviating. The data of crooks [20] at higher concentration shower higher k_{app} values while Versteeg [25] show otherwise with comparison to this work. The reason of this difference is due to the values used for physical properties as can be seen in table 4.1.

By assuming $k_{app} = k'[DEA]^n$ and fitting the points with power correlation, the obtained order of the reaction is presented in table 4.2. The agreement on reaction order from this work is found with Alvarez-Fuster [18] and Sada [17] with values 2.0 and 1.74 respectively and Versteeg [25] suggested that it varies between 1.5 and 2 for high and lower amine concatenation respectively.

Table 4. 2 Order of the reaction with respect to amine for reaction between CO_2 and DEA in ethanol solution

Reference	Order of reaction (n)
Alvarez-Fuster [18]	2.0
E. Sada [17]	1.74
Versteeg [25]	1.54
Crook [20]	1.93
This work	1.78

There is some discrepancy in the results for absorption at $[DEA] = 0.2M$ in this work where the condition of pseudo-first order (equation 3.7) is not fulfilled as obtained *Ha* number was 1.88 due to low concentration of amine. This discrepancy for lower amine concentration (less than 0.4M) can be overcome by carrying out experimentation at lower stirrer speed.

Another problem which is observed at higher amine concentration is interfacial turbulence during absorption at higher CO_2 partial pressures. In this work

experiments carried out at higher P_{CO_2} values were not used for calculating reaction rate constants and order of the reaction, however this does not mean that the influence was completely excluded.

4.3 INITIAL/FORWARD REACTION RATE CONSTANTS

The initial reaction rate constant can be determined in the first run of the experiment, i.e when the loading of the solution was nearly zero. The proposed method by Danckwerts (1979) was used to estimate the initial/forward kinetic rete constants for both mechanisms i.e the reaction rate constant is function of amine concentration having second and third order reaction rate constants k_2, k_{DEA}^z. The reaction rate constants can be calculated by plotting $\frac{[DEA]}{k_{app}}$ against $\frac{1}{[DEA]}$ (equation 2.8) which should yield a straight line with slope $\frac{1}{k_{DEA}^z}$ and intercept $\frac{1}{k_2}$. Such plot is shown in figure 4.2 below.

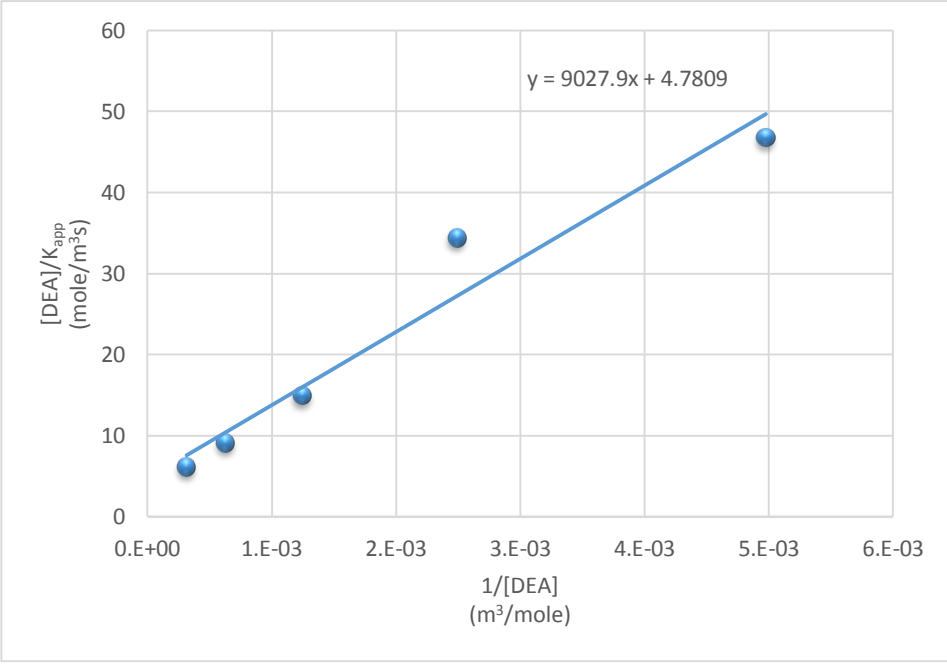


Figure 4. 2 The Zwitterion mechanism plot for DEA-ethanol at 293K

When the intercept of equation is set to zero then the Termolecular kinetic rate constant can be determined, as seen in figure 4.3.

According to equation 2.11 if termolecular (direct) mechanism holds then the plot of $\frac{k_{app}}{[DEA]}$ against $[DEA]$ should also yield a straight line passing through the origin i.e intercept=0; slope of the line gives the value of k_2 as shown if figure 4.3.

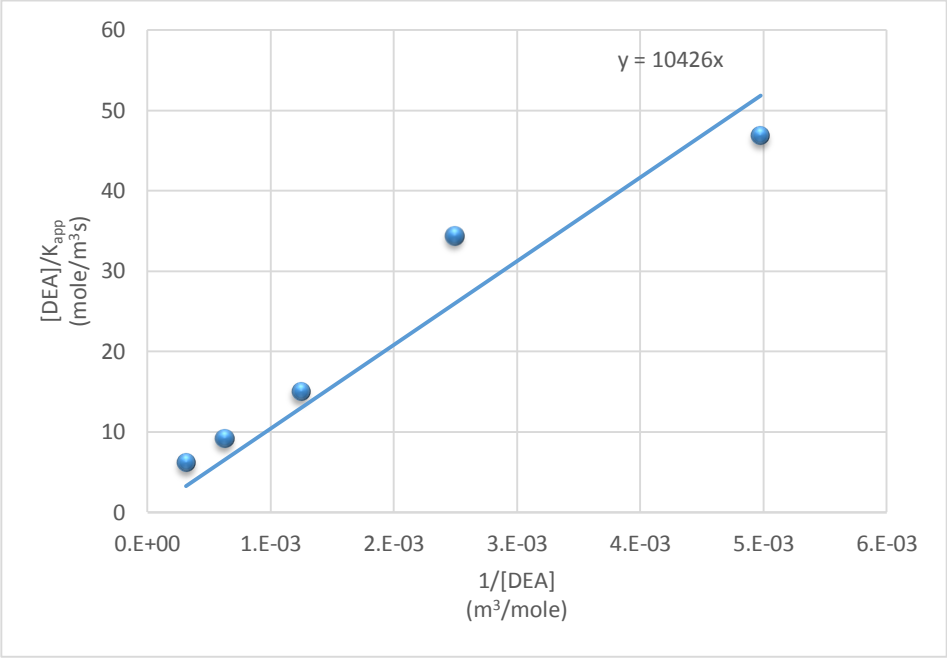


Figure 4. 3 Termolecular mechanism plot for DEA-ethanol at 293K

The derived rate constants according to zwitterion and termolecular mechanism are shown in table 4.3 below for DEA ethanol solutions and for sake of comparison, the reaction rate constants from earlier works for the same system are also listed in the same table.

From the comparison made in table 4.3, it can be seen that for zwitterion mechanism both k_2 *and* k_{DEA} seems to agree with the previous work of Versteeg (1988), however the deviation reaches to 26% for k_{DEA} and less than 5% for k_2.

Agreement for k_{DEA} is also found with Alvarez's work however they did not reported the k_2 value.

The k_2 value is much larger than k_{DEA} which means that the zwitterion has faster kinetic rate than k_{DEA}. The process of zwitterion in the system was expected to be very short thus the life time is very short [42]. When $\frac{1}{k_2}$ was set to zero, the existing of the zwitterion is most likely extremely short and cannot be observed. The kinetic rate constant (k_{DEA}) for termolecular is found to agree with zwitterion within 15% which is smaller than that of the suggested value of Versteeg 1988 [25].

Table 4. 3 Fitted rate parameters for reaction between carbon dioxide and di-ethanolamine in ethanol at 293K

Amine Conc. Mole/m^3	**T (K)**	**k_2 m^3/mol.s**	**k_{DEA}×10^{-4} m^6/mol^2.s**	**Reference**	**Mechanism Adopted**
0.3 – 2.2	293	-	1.3	Alveraz 1981 [18]	Zwitterion
0.5 – 1.5	303	0.29	2.0	E. Sada 1985 [17]	Zwitterion
0.49 – 2.937	293	0.215	1.5	Versteeg 1988 [19]	Zwitterion
0.2 – 3.2	293	0.209	1.11	This work	Zwitterion
0.2 – 3.2	293	-	0.959	This work	Termolecular

The kinetic rate constants of both mechanism were used to recalculate the experimental CO_2 flux observed from the experiments as seen in figure 4.4.

It is seen that the suggested kinetic rate constants gave a similar deviation (within 10%) of the predicted CO_2 flux similar. The reported k_2 value could also be associated with the experimental error, hence both mechanisms are practically similar.

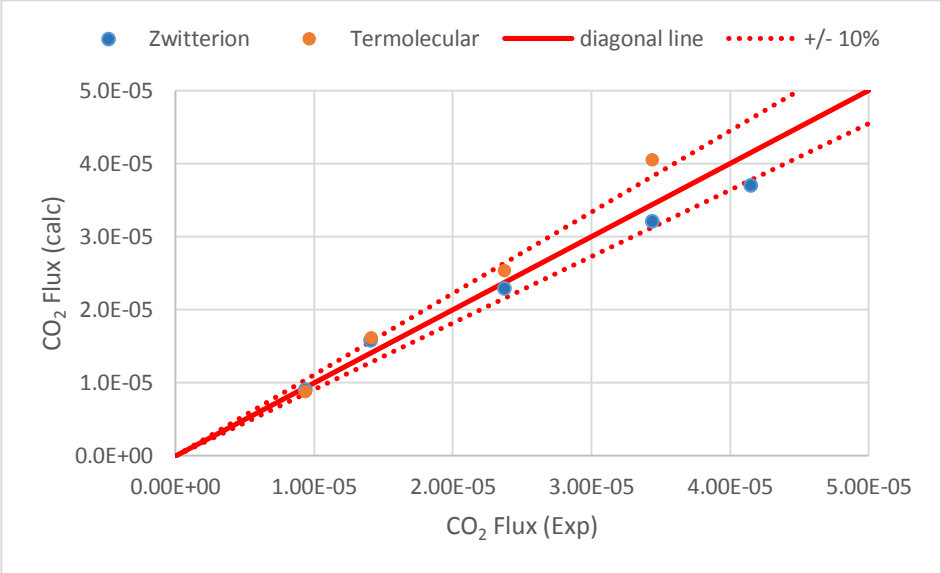


Figure 4. 4 Parity plot of experimental and calculated CO_2 flux

4.4 MASS TRANSFER IN THE DEA/CO_2/ETHANOL SYSTEM

For calculation of absorption experiments it was assumed that the reaction between DEA and CO_2 can be described by an irreversible pseudo first order reaction whereas at higher loading the actual reaction is not irreversible (equation 2.1 and 2.2). So the influence of its reversibility is neglected. The backward reaction can be determined from the experimental data at higher loading.

The apparent kinetic rate constant for loaded system as function of loading at different concentration can be seen in figure 4.5. It can been seen from above figure that CO_2 loading has inverse effect on the apparent kinetic rate constant for all concentrations except for 3.2M DEA. For 3.2M the apparent kinetic rate constant first increases with CO_2 loading and then start decreasing after loading of 0.05 mole CO_2/mole amine. The reason for this behavior could be that for same P_{CO_2} the solution has more free amine present to absorb CO_2 at higher concentrations than that of lower concentration for the same P_{CO_2} . Same amount

of CO_2 absorbed in higher concentration will reflect less loading than that of lower concentrations which results into higher kinetic rate.

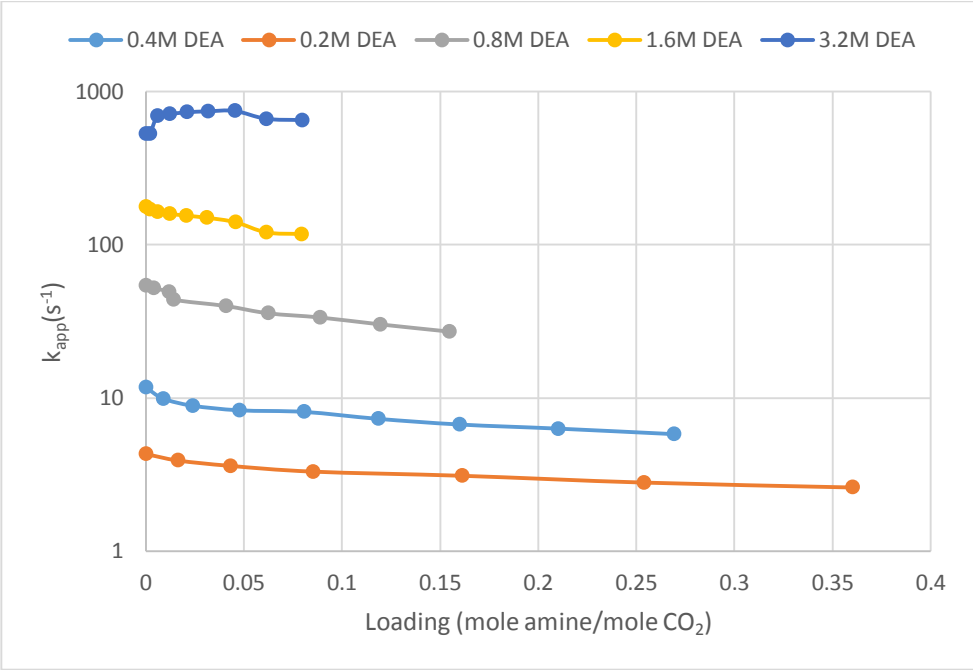


Figure 4.5 k_{app} with loading in different DEA concentrations in ethanol at 293K

4.5 SENSITIVITY ANALYSIS

The data for physical properties is scarcely available in literature. Most of the physical properties (solubility, diffusivity, viscosity and density) varied ±10% in the literature. The parameter sensitivity test for only 0.8M DEA-ethanol at 293K is applied and physical properties (solubility and diffusivity) are varied ±10% and the deviation between calculated apparent rates as well as order of the reaction and their original values caused by the variation were shown in table 4.4.

Table 4. 4 Parameter sensitivity for 0.8M DEA apparent kinetic rate constant at 273K

Parameter	k_{app}		Order of reaction (n)	
	+10%	-10%	+10%	-10%
m_{CO_2}	-17.4%	+23.5%	+0.1%	-0.1%
D_{CO_2}	-9.2%	+11.3%	+0.1%	-0.1%

At lower DEA-ethanol lack of data for these physical properties exist so large variation in final results can be expected at lower concentrations. From the physical properties test, it can be seen that the kinetic rate constant are sensitive to solubility and CO_2 diffusivity in amine solutions and hence these are the key physical properties in the kinetic experiments. Sample of raw data of CO_2 absorbed by unloaded DEA-ethanol solution from the experiments in stirrer cell can be seen in the appendix.

5 CONCLUSIONS

The kinetics of carbon dioxide absorption into non aqueous amine solution (DEA-ethanol) were performed in a stirrer contactor at different amine concentrations at 293K. Two reaction mechanisms, i.e. the termolecular and zwitterion mechanisms were implemented to interpret the experimental data.

The physical solubility for N_2O and CO_2 in pure ethanol and for N_2O at different concentrations was also studied at this temperature which is found to be with line with literature data. The apparent rate of reaction increases with concentration while has inverse relation with CO_2 loading at all concentrations. The reaction order with respect to amine concentration was found to be 1.78 which vary with concentration.

The reaction rate constant for DEA was calculated based on zwitterion and termolecular mechanism and the values obtained were found to be in agreement with the literature. Parity plots for calculated and experimental flux was also plotted for comparison. Practically both mechanism are similar.

6 FUTURE RECOMMENDATIONS

- To verify the results presented in this work, experimental work should also be done at different temperatures.
- The degassing of the solution in the reactor should be done at a very lower temperature to avoid loss of volatile solvent at experimental temperatures.
- CO_2 or N_2O gases should be cooled to the liquid temperature before injection into the reactor. The gas is observed at higher temperature even after giving some time to settle down. For this purposes water bath is suggested for gas bomb.
- The cooling system installed for the apparatus is not much efficient in controlling the temperature. The temperature of the liquid inside the reactor is dependent to the ambient temperature which varies with the temperature in the lab during the experiments.
- Physical properties (density, viscosity and diffusivity of CO_2) should be estimated by experimentation rather than to have the data from literature because there is not much data available at very low amine concentration and data interpolation in between two points cannot be relayed due to large variations.

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APPENDIX

- **List of figures**
- **Calculation sheets**
- **Risk assessment**
- **Safety data sheets**

LIST OF FIGURES

Physical solubility and liquid side mass transfer K_L for N_2O in 0.2M DEA-Ethanol at 20C

Calculation of "m"

P_{end}	189.2	mbar	Total Reactor Volume	4335	ml	Diameter of Reactor	15.02cm
P_{vap}	66.6	mbar	Volume of Liquid	2050	ml		
$P_{initial}$	520	mbar	Volume of Gas	2285	ml		

$$m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}$$

* Always remember to subtract P_{vap} from all pressure values

m = 3.007512

Calculation of "K_L"

Slope from graph = -0.0024

Area of Reactor = 177.1866

K_L = 0.007508329 cm/sec

$$KL = \frac{(-slope*Vg*Vl)}{((m*Vl) + Vg)*A}$$

K_L = 7.50833E-05 m/sec

Physical solubility and liquid side mass transfer K_L for N_2O in 0.4M DEA-Ethanol at 20C

Calculation of "m"

P_{end}	186.4	mbar	Total Reactor Volume	4335	ml	Diameter of Reactor	15.02cm
P_{vap}	69.4	mbar	Volume of Liquid	2050	ml		
$P_{initial}$	499	mbar	Volume of Gas	2285	ml		

$$m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}$$

* Always remember to subtract P_{vap} from all pressure values

m = 2.97807

Calculation of "K_L"

Slope from graph = -0.0022

Area of Reactor = 177.1866

K_L = 0.006932141 cm/sec

$$KL = \frac{(-slope*Vg*Vl)}{((m*Vl) + Vg)*A}$$

K_L = 6.93214E-05 m/sec

Physical solubility and liquid side mass transfer K_L for N_2O in 0.8M DEA-Ethanol at 20C

Calculation of "m"

P_{end}	201.1	mbar	Total Reactor Volume	4335	ml	Diameter of Reactor	15.02cm
P_{vap}	79.7	mbar	Volume of Liquid	2050	ml		
$P_{initial}$	499	mbar	Volume of Gas	2285	ml		

$$m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}$$

* Always remember to subtract P_{vap} from all pressure values

m = 2.90043

Calculation of "K_L"

Slope from graph = -0.0018

Area of Reactor = 177.1866

K_L = 0.005781424 cm/sec

$$KL = \frac{(-slope*Vg*Vl)}{((m*Vl) + Vg)*A}$$

K_L = 5.78142E-05 m/sec

Physical solubility and liquid side mass transfer K_L for N_2O in 1.6M DEA-Ethanol at 20C

Calculation of "m"

P_{end}	195	mbar	Total Reactor Volume	4335	ml	Diameter of Reactor	15.02cm
P_{vap}	70.5	mbar	Volume of Liquid	2050	ml		
$P_{initial}$	497	mbar	Volume of Gas	2285	ml		

$$m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}$$

* Always remember to subtract P_{vap} from all pressure values

m = 2.70377

Calculation of "K_L"

Slope from graph = -0.0013

Area of Reactor = 177.1866

K_L = 0.004390528 cm/sec

$$KL = \frac{(-slope*Vg*Vl)}{((m*Vl) + Vg)*A}$$

K_L = 4.39053E-05 m/sec

Physical solubility and liquid side mass transfer K_L for N_2O in 3.2M DEA-Ethanol at 20C

Calculation of "m"

P_{end}	213.2	mbar	Total Reactor Volume	4335	ml	Diameter of Reactor	15.02cm
P_{vap}	65.1	mbar	Volume of Liquid	2050	ml		
$P_{initial}$	523	mbar	Volume of Gas	2285	ml		

$$m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}$$

* Always remember to subtract P_{vap} from all pressure values

m = 2.331625

Calculation of "K_L"

Slope from graph = -0.00062

Area of Reactor = 177.1866

K_L = 0.00232006 cm/sec

$$KL = \frac{(-slope*Vg*Vl)}{((m*Vl) + Vg)*A}$$

K_L = 2.32006E-05 m/sec

Kinetics of 0.2M DEA in Ethanol at 20C

Liquid Volume	2050.0	cm^3
Gas Volume Reactor	2285.0	cm^3
Surface Area	177.2	cm^2
Physical Solubility of CO_2	2.98	
Diffusivity of CO_2	3.14E-9	m^2/sec

Exp. No.	Vapor Pressure (mbar)	Initial Pressure (mbar)	Equilibrium Pressure (mbar)	Slope	k_{app} (sec^{-1})	Ha	P_{CO2} (mbar)	E_∞
1	67.1	104.2	67.8	-0.00269	4.3	1.93	37.1	131.83
2	68.1	128.4	71.2	-0.002547	3.9	1.83	60.3	81.11
3	71.2	168.8	77.4	-0.002442	3.6	1.75	97.6	50.11
4	77.4	253.0	89.5	-0.002366	3.3	1.70	175.6	27.85
5	89.5	304.9	108.1	-0.002264	3.1	1.62	215.4	22.71
6	108.1	356.6	133.6	-0.002174	2.8	1.56	248.5	19.68
7	133.6	418.9	166.4	-0.002105	2.6	1.51	285.3	17.14

Kinetics of 0.4M DEA in Ethanol at 20C

Liquid Volume	2050.0	cm^3
Gas Volume Reactor	2285.0	cm^3
Surface Area	177.2	cm^2
Physical Solubility of CO_2	2.955	
Diffusivity of CO_2	2.49E-9	m^2/sec

Exp. No.	Vapor Pressure (mbar)	Initial Pressure (mbar)	Equilibrium Pressure (mbar)	Slope	k_{app} (sec^{-1})	Ha	P_{CO2} (mbar)	E_∞
1	69.3	107.7	69.6	-0.003904	11.7	2.83	38.4	254.44
2	69.6	135.7	70.8	-0.003597	9.9	2.60	66.1	147.81
3	70.8	177.1	72.7	-0.003407	8.9	2.47	106.3	91.91
4	72.7	219.0	75.9	-0.003302	8.3	2.39	146.3	66.78
5	75.9	243.5	80.1	-0.003247	8.1	2.35	167.6	58.30
6	80.1	268.0	87.0	-0.003083	7.3	2.23	187.9	52.00
7	87.0	306.9	94.6	-0.00295	6.7	2.14	219.9	44.43
8	94.6	353.2	104.9	-0.002877	6.3	2.08	258.6	37.78
9	104.9	404.8	118.9	-0.002747	5.8	1.99	299.9	35.58

Kinetics of 0.8M DEA in Ethanol at 20C

Liquid Volume	2050.0	cm^3
Gas Volume Reactor	2285.0	cm^3
Surface Area	177.2	cm^2
Physical Solubility of CO_2	2.878	
Diffusivity of CO_2	1.49E-9	m^2/sec

Exp. No.	Vapor Pressure (mbar)	Initial Pressure (mbar)	Equilibrium Pressure (mbar)	Slope	k_{app} (sec^{-1})	Ha	P_{CO2} (mbar)	E_∞
1	67.8	103.8	67.8	-0.006336	54.1	4.71	36.0	544.91
2	67.8	134.0	68.1	-0.006216	52.1	4.62	66.2	296.33
3	68.1	174.1	68.7	-0.006036	49.1	4.49	106.0	185.06
4	68.7	215.4	69.5	-0.005706	43.9	4.24	146.7	133.72
5	69.5	254.8	70.7	-0.005432	39.8	4.04	185.3	105.86
6	70.7	290.4	71.8	-0.005147	35.7	3.83	219.7	89.29
7	71.8	336.7	74.2	-0.004987	33.5	3.71	264.9	74.05
8	74.2	374.4	76.9	-0.004736	30.2	3.52	300.2	65.35
9	76.9	419.0		-0.004481	27.1	3.33	342.1	57.34

Kinetics of 1.6M DEA in Ethanol at 20C

Liquid Volume	2050.0	cm^3
Gas Volume Reactor	2285.0	cm^3
Surface Area	177.2	cm^2
Physical Solubility of CO_2	2.683	
Diffusivity of CO_2	1.31E-9	m^2/sec

Exp. No.	Vapor Pressure (mbar)	Initial Pressure (mbar)	Equilibrium Pressure (mbar)	Slope	k_{app} (sec^{-1})	Ha	P_{CO2} (mbar)	E_∞
1	67.8	104.4	68.0	-0.010013	176.9	12.69	36.6	1066.8
2	68.0	132.8	68.2	-0.09805	169.6	12.43	64.8	602.6
3	68.2	174.6	68.4	-0.009622	163.3	12.20	106.4	367.0
4	68.4	212.9	68.5	-0.009502	159.3	12.04	144.5	270.2
5	68.5	250.1	68.8	-0.009367	154.8	11.87	181.6	215.0
6	68.8	285.6	69.3	-0.009221	150.0	11.69	216.8	180.1
7	69.3	324.0	69.6	-0.008918	140.3	11.30	254.7	153.3
8	69.6	361.5	70.1	-0.008262	120.4	10.47	291.9	133.8
9	70.1	405.2	70.6	-0.008161	117.5	10.35	335.1	116.5

Kinetics of 3.2M DEA in Ethanol at 20C

Liquid Volume	2050.0	cm^3
Gas Volume Reactor	2285.0	cm^3
Surface Area	177.2	cm^2
Physical Solubility of CO_2	2.313	
Diffusivity of CO_2	0.858E-9	m^2/sec

Exp. No.	Vapor Pressure (mbar)	Initial Pressure (mbar)	Equilibrium Pressure (mbar)	Slope	k_{app} (sec^{-1})	Ha	P_{CO2} (mbar)	E_∞
1	63.9	101.2	63.9	-0.012087	529.1	17.77	37.3	2091.6
2	63.9	132.0	64.2	-0.012114	531.5	17.81	68.1	1145.6
3	64.2	170.2	64.3	-0.013854	695.1	20.36	106.0	736.0
4	64.3	209.2	64.4	-0.014036	713.5	20.63	144.9	538.4
5	64.4	248.8	64.5	-0.014223	732.6	20.91	184.4	423.1
6	64.5	292.1	64.6	-0.014329	743.6	21.06	227.6	342.8
7	64.6	329.0	64.7	-0.014373	748.2	21.13	264.4	295.1
8	64.7	363.6	64.8	-0.013548	664.7	19.91	298.6	261.3
9	64.8	410.5	65.1	-0.013423	625.5	19.73	345.7	225.7

CO_2 Loading calculation with 2nd varial coefficient for 0.2M DEA-Ethanol solution

2nd virale coefficient for gas (ref DIPPR):															
	A	B	C	D	E										
CO2	5.44E-02	-3.64E+01	-1.50E+06	8.59E+16	-1.40E+19										
N2O	4.34E-02	-3.41E+01	-1.61E+06	-3.20E+16	-4.56E+18										
		Belading		**Meting**											
		Datafile A		**Datafile B**											
CO2-Loading		1/7		2/7		3/7		4/7		5/7		6/7		7/7	
Gasbommetje	N/L/S/LS	LS													
		0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	252.8	106.4	365.6	131.9	551.9	173	950.5	255.1	1155.7	312.4	1353	361.2	1545.6	425.6
T	°C	25	23.11	22.99	23.86	23.75	25.1	25.78	23.75	23.286	25.234	24.865	26.06	26.423	25.45
B		-0.000123	-0.00013	-0.00013	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00013	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012
Z	-	0.9987384	0.999458	0.998133	0.999334	0.997203	0.999138	0.995281	0.998709	0.994094	0.998445	0.9932	0.998218	0.992359	0.997885
n	mol	0.0059558	0.002521	0.008677	0.003118	0.013077	0.004073	0.022412	0.006036	0.027513	0.007356	0.032068	0.008484	0.036474	0.01002
									0.016377						
CO2 in the reactor	mol		0.003435		0.00556		0.009005		0.016377		0.020157		0.023584		0.026453
cum	mol		0.003435		0.008994		0.017999		0.034376		0.054533		0.078117		0.10457
Reactor		0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	67.1	68.1	68.1	71.1	71.1	77.4	77.4	89.4	89.4	108.1	108.1	133.5	133.5	166.4
T	°C	20	20	20	20	20	20	20	20	20	20	20	20	20	20
B		-0.000128	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013
Z	-	0.9996461	0.999641	0.999641	0.999625	0.999625	0.999592	0.999592	0.999528	0.999528	0.99943	0.99943	0.999296	0.999296	0.999122
n	mol	0.0061903	0.006323	0.006325	0.006585	0.006587	0.007139	0.007122	0.008283	0.008296	0.009967	0.009979	0.012277	0.012262	0.015336
					0.000259		0.000551		0.001161						
CO2 in gasphase (cum)	mol		0.000132		0.000394		0.000948		0.002093		0.003777		0.006086		0.009146
CO2 in liquid phase (cum)	mol		0.003303		0.0086		0.017051		0.032283		0.050756		0.072031		0.095424
CO2 loading	mol CO2/mol amine		0.016513		0.043001		0.085254		0.161415		0.25378		0.360154		**0.477122**
CO2 total	mol CO2/kg solution		0.002014		0.005244		0.010396		0.019683		0.030946		0.043918		**0.058181**
P_{CO2}	mbar		1		4		10.3		22.3		41		66.4		99.3

CO_2 Loading calculation with 2nd varial coefficient for 0.4M DEA-Ethanol solution

2de virale coefficient gassen (ref DIPPR):																			
	A	B	C	D	E														
CO2	5.44E-02	-3.64E+01	-1.50E+06	8.59E+16	-1.40E+19														
N2O	4.34E-02	-3.41E+01	-1.61E+06	-3.20E+16	-4.56E+18														
		Belading		**Meting**															
		Datafile A		**Datafile B**															
CO2-belading		1/9		2/9		3/9		4/9		5/9		6/9		7/9		8/9		9/9	
Gasbommetje	N/L/S/LS	LS																	
		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	264.9	109.9	398.2	139.6	598.3	181.5	801.7	224.1	906.3	249.5	1007.7	274.8	1200.5	314.8	1403.9	357.6	1598.8	411.9
T	°C	27.96	25.764	27.152	27.1	28.445	28.172	27.486	27.095	26.54	25.69	25.872	26.692	27.655	27.929	28.627	27.035	27.99	26.74
B		-0.000121	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012
Z	-	0.9987208	0.999457	0.998059	0.99932	0.997122	0.999126	0.996098	0.998908	0.99554	0.998764	0.995001	0.998654	0.994157	0.998479	0.993233	0.998255	0.992232	0.997982
n	mol	0.0061796	0.002581	0.00932	0.003264	0.013957	0.004229	0.018781	0.005242	0.02131	0.005864	0.023761	0.006438	0.028163	0.007346	0.032859	0.008372	0.037537	0.009655
CO2 naar reactor	mol		0.003599		0.006056		0.009728		0.013539		0.015446		0.017322		0.020816		0.024487		0.027882
cum	mol		0.003599		0.009655		0.019383		0.032922		0.048368		0.065691		0.086507		0.110994		0.138876
Reactor		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	69.3	69.6	69.6	70.8	70.8	72.7	72.7	75.9	75.9	80.1	80.1	87	87	94.6	94.6	104.9	104.9	118.9
T	°C	20.0337	19.94	19.94	20.03	20.03	19.95	19.95	19.95	19.95	19.89	19.89	19.993	19.993	20.05	20.05	20.0622	20.0622	20.046
B		-0.000128	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013
Z	-	0.9996346	0.999633	0.999633	0.999627	0.999627	0.999616	0.999616	0.999599	0.999599	0.999577	0.999577	0.999541	0.999541	0.999501	0.999501	0.999447	0.999447	0.999373
n	mol	0.0065017	0.006532	0.006532	0.006643	0.006643	0.006823	0.006823	0.007123	0.007123	0.007519	0.007519	0.008164	0.008164	0.008876	0.008876	0.009843	0.009843	0.011158
					0.000111		0.00018		0.0003										
CO2 in gasfase (cum)	mol		3.02E-05		0.000141		0.000321		0.000621		0.001017		0.001663		0.002374		0.003341		0.004656
CO2 in vloeistof (cum)	mol		0.003569		0.009515		0.019062		0.032301		0.047351		0.064028		0.084133		0.107653		0.13422
CO2 belading	mol CO2/mol amine		0.008922		0.023786		0.047655		0.080752		0.118378		0.160071		0.210332		0.269133		**0.335551**
[CO2]t	mol CO2/kg solution		0.002165		0.005772		0.011565		0.019596		0.028727		0.038845		0.051042		0.065311		**0.081429**
P_{CO2}	mbar		0.3		1.5		3.4		6.6		10.8		17.7		25.3		35.6		49.6

CO_2 Loading calculation with 2nd varial coefficient for 0.8M DEA-Ethanol solution

2de virale coefficient gassen (ref DIPPR):																			
	A	B	C	D	E														
CO2	5.44E-02	-3.64E+01	-1.50E+06	8.59E+16	-1.40E+19														
N2O	4.34E-02	-3.41E+01	-1.61E+06	-3.20E+16	-4.56E+18														
		Belading		**Meting**															
		Datafile A		**Datafile B**															
CO2-belading		1/9		2/9		3/9		4/9		5/9		6/9		7/9		8/9		9/9	
Gasbommetje	N/L/S/LS	LS																	
		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	250.3	106.5	401.7	138.6	599.3	178	804.6	220.1	1001.2	261.3	1210.4	295.7	1398.2	347.2	1598.5	383.4	1801.2	430.9
T	°C	30.41	27.28	28.43	27.17	28.49	28.42	29.05	28.61	29.36	28.58	29.04	27.67	28.56	29.19	29.49	30.15	31.44	31.78
B		-0.000118	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012
Z	-	0.9988237	0.999482	0.998069	0.999325	0.997118	0.999145	0.996151	0.998945	0.995223	0.998747	0.994198	0.998567	0.993256	0.998345	0.992362	0.998192	0.991569	0.998004
n	mol	0.0057913	0.002488	0.009362	0.00324	0.013978	0.004144	0.01875	0.005122	0.02333	0.006083	0.028264	0.006906	0.032732	0.00807	0.037339	0.008884	0.041838	0.009933
CO2 naar reactor	mol		0.003303		0.006123		0.009834		0.013628		0.017247		0.021358		0.024662		0.028455		0.031905
cum	mol		0.003303		0.009426		0.01926		0.032888		0.050135		0.071492		0.096154		0.12461		0.156514
Reactor		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	67.8	67.8	67.8	68.1	68.1	68.7	68.7	69.5	69.5	70.7	70.7	71.8	71.8	74.2	74.2	76.9	76.9	79.6
T	°C	20.091	19.88	19.88	19.94	19.94	19.95	19.95	19.93	19.93	19.97	19.97	19.89	19.89	20.03	20.03	20.005	20.005	20.04
B		-0.000128	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013
Z	-	0.9996428	0.999642	0.999642	0.999641	0.999641	0.999637	0.999637	0.999633	0.999633	0.999627	0.999627	0.999621	0.999621	0.999609	0.999609	0.999594	0.999594	0.99958
n	mol	0.0063597	0.006364	0.006364	0.006391	0.006391	0.006447	0.006447	0.006523	0.006523	0.006635	0.006635	0.00674	0.00674	0.006962	0.006962	0.007216	0.007216	0.007468
					2.69E-05		5.61E-05		7.56E-05										
CO2 in gas phase (cum)	mol		4.59E-06		3.14E-05		8.76E-05		0.000163		0.000275		0.00038		0.000602		0.000856		0.001109
CO2 in liquid phase (cum)	mol		0.003299		0.009394		0.019172		0.032725		0.04986		0.071112		0.095552		0.123754		0.155406
CO2 belading	mol CO2/mol amine		0.004123		0.011743		0.023965		0.040906		0.062325		0.08889		0.119441		0.154692		0.194257
[CO2]t	mol CO2/kg solution		0.001973		0.005619		0.011468		0.019575		0.029825		0.042537		0.057156		0.074025		0.092959
P_{CO2}	mbar		0		0.3		0.9		1.7		2.9		4		6.4		9.1		11.8

CO_2 Loading calculation with 2nd varial coefficient for 1.6M DEA-Ethanol solution

2de virale coefficient gassen (ref DIPPR):																			
	A	B	C	D	E														
CO2	5.44E-02	-3.64E+01	-1.50E+06	8.59E+16	-1.40E+19														
N2O	4.34E-02	-3.41E+01	-1.61E+06	-3.20E+16	-4.56E+18														
		Belading		**Meting**															
		Datafile A		**Datafile B**															
CO2-belading		1/9		2/9		3/9		4/9		5/9		6/9		7/9		8/9		9/9	
Gasbommetje	N/L/S/LS	LS																	
		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	252.3	107.3	401.3	134.8	602.4	180.1	799.2	221.9	992.8	258.8	1200.1	192.5	1405.1	335.8	1605.4	374.3	1811.7	411.9
T	°C	27.725	28.45	28.757	26.7	26.475	28.102	28.67	29.24	30.914	30.39	30.71	28.27	29.14	29.48	31.21	32.04	32.57	30.61
B		-0.000121	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012
Z	-	0.9987786	0.999485	0.998078	0.99934	0.997038	0.999132	0.996161	0.998944	0.995344	0.998783	0.994353	0.999074	0.993266	0.998405	0.992473	0.998271	0.991625	0.998067
n	mol	0.00589	0.002497	0.009343	0.003156	0.014146	0.004198	0.018648	0.005153	0.023013	0.005989	0.027865	0.004484	0.03283	0.007797	0.037284	0.008619	0.041924	0.009531
CO2 naar reactor	mol		0.003393		0.006187		0.009949		0.013494		0.017024		0.02338		0.025033		0.028665		0.032393
cum	mol		0.003393		0.00958		0.019529		0.033023		0.050047		0.073427		0.09846		0.127126		0.159519
Reactor		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	67.8	68	68	68.2	68.2	68.4	68.4	68.5	68.5	68.8	68.8	69.3	69.3	69.6	69.6	70.1	70.1	70.6
T	°C	19.993	19.968	19.968	19.968	19.968	20.09	20.09	19.99	19.99	20.074	20.074	20.1	20.1	20.026	20.026	20.02	20.02	19.98
B		-0.000128	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013
Z	-	0.9996424	0.999641	0.999641	0.99964	0.99964	0.99964	0.99964	0.999639	0.999639	0.999637	0.999637	0.999635	0.999635	0.999633	0.999633	0.99963	0.99963	0.999628
n	mol	0.0063618	0.006381	0.006381	0.0064	0.0064	0.006416	0.006416	0.006428	0.006428	0.006454	0.006454	0.0065	0.0065	0.00653	0.00653	0.006577	0.006577	0.006625
					1.88E-05		1.61E-05		1.16E-05										
CO2 in gas phase (cum)	mol		1.93E-05		3.81E-05		5.42E-05		6.58E-05		9.21E-05		0.000138		0.000168		0.000215		0.000263
CO2 in liquid phase (cum)	mol		0.003374		0.009542		0.019474		0.032957		0.049955		0.073289		0.098292		0.126911		0.159255
CO2 belading	mol CO2/mol amine		0.002108		0.005964		0.012171		0.020598		0.031222		0.045806		0.061433		0.079319		0.099535
[CO2]t	mol CO2/kg solution		0.001961		0.005546		0.011318		0.019154		0.029033		0.042595		0.057126		0.073759		0.092558
P_{CO2}	mbar		0.2		0.4		0.6		0.7		1		1.5		1.8		2.3		2.8

CO_2 Loading calculation with 2nd varial coefficient for 3.2M DEA-Ethanol solution

2de virale coefficient gassen (ref DIPPR):																			
	A	B	C	D	E														
CO2	5.44E-02	-3.64E+01	-1.50E+06	8.59E+16	-1.40E+19														
N2O	4.34E-02	-3.41E+01	-1.61E+06	-3.20E+16	-4.56E+18														
		Belading		**Meting**															
		Datafile A		**Datafile B**															
CO2-belading		1/9		2/9		3/9		4/9		5/9		6/9		7/9		8/9		9/9	
Gasbommetje	N/L/S/LS	LS																	
		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	252.2	103.5	403.7	135.6	603.1	174.2	802.3	215.3	1003.4	250.3	1215.9	299.6	1413	339.9	1620.2	380.2	1847.4	421.9
T	°C	29.88	27.26	26.71	27.71	28.26	28.42	28.81	27.88	28.8	24.54	25.2	26.05	25.93	26.58	25.97	25.53	26.96	25.86
B		-0.000119	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012	-0.00012
Z	-	0.9988078	0.999497	0.998022	0.999344	0.997093	0.999163	0.996152	0.99896	0.995182	0.998744	0.993916	0.998522	0.992981	0.998333	0.991947	0.998113	0.990909	0.997913
n	mol	0.0058456	0.002418	0.009464	0.003164	0.014078	0.004056	0.018712	0.005023	0.023425	0.005906	0.028766	0.007035	0.033378	0.007969	0.038308	0.008947	0.043581	0.009919
CO2 naar reactor	mol		0.003427		0.0063		0.010022		0.013689		0.017519		0.021731		0.02541		0.029361		0.033662
cum	mol		0.003427		0.009727		0.019749		0.033438		0.050958		0.072688		0.098098		0.127458		0.16112
Reactor		0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
P	mbara	63.9	63.9	63.9	64.2	64.2	64.3	64.3	64.4	64.4	64.5	64.5	64.6	64.6	64.7	64.7	64.8	64.8	65.1
T	°C	20.017	20	20	19.99	19.99	20	20	20.01	20.01	20.02	20.02	20.01	20.01	20.03	20.03	20.01	20.01	20.07
B		-0.000128	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013	-0.00013
Z	-	0.9996631	0.999663	0.999663	0.999661	0.999661	0.999661	0.999661	0.99966	0.99966	0.99966	0.99966	0.999659	0.999659	0.999659	0.999659	0.999658	0.999658	0.999657
n	mol	0.0059952	0.005996	0.005996	0.006024	0.006024	0.006033	0.006033	0.006042	0.006042	0.006051	0.006051	0.006061	0.006061	0.00607	0.00607	0.00608	0.00608	0.006107
					2.84E-05		9.18E-06		9.18E-06										
CO2 in gas phase (cum)	mol		3.48E-07		2.87E-05		3.79E-05		4.71E-05		5.63E-05		6.58E-05		7.48E-05		8.46E-05		0.000112
CO2 in liquid phase (cum)	mol		0.003427		0.009698		0.019711		0.033391		0.050901		0.072622		0.098023		0.127374		0.161009
CO2 belading	mol CO2/mol amine		0.002142		0.006061		0.01232		0.020869		0.031813		0.045389		0.061264		0.079609		0.10063
[CO2]t	mol CO2/kg solution		0.001992		0.005636		0.011456		0.019407		0.029583		0.042207		0.05697		0.074028		0.093577
P_{CO2}	mbar		0		0.3		0.4		0.5		0.6		0.7		0.8		0.9		1.2

Flux calculation from Experimental values

[DEA] (mole/m^3)	k_{app} (sec^{-1})	D_{CO2} (m_2/sec)	m_{CO2}	P_{CO2} (mbar)	P_{CO2} (bar)	$\sqrt{K_{app}}*D_{CO2}$ ($m/s^{1/2}$)	Flux J_{CO2} mole/m^2.s
201	4.3	3.14E-09	2.98	37.1	0.0371	0.000116198	9.34E-06
401	11.7	2.49E-09	2.954855	38.4	0.0384	0.000170684	1.41E-05
805	54.1	1.49E-09	2.877822	39.9	0.0399	0.000283917	2.37E-05
1602	176.9	1.31E-09	2.682691	36.6	0.0366	0.000481393	3.44E-05
3201	529.1	8.58E-10	2.313446	36.6	0.0366	0.000673771	4.15E-05

Flux calculation from zwitterion mechanism

k^{z}_{DEA} =1.11E-4 $m^6/mole^2.s$

k_2 = 0.209166 $m^2/mole.s$

[DEA] ($mole/m^3$)	k_{app} (sec^{-1})	D_{CO2} (m_2/sec)	m_{CO2}	P_{CO2} (mbar)	P_{CO2} (bar)	$\sqrt{K_{app}}*D_{CO2}$ ($m/s^{1/2}$)	Flux J_{CO2} $mole/m^2.s$
201	4.052269676	3.14E-09	2.98	37.1	0.0371	1.13E-04	9.07054E-06
401	14.71708242	2.49E-09	2.954855	38.4	0.0384	1.91E-04	1.57982E-05
805	50.40004718	1.49E-09	2.877822	39.9	0.0399	2.74E-04	2.28862E-05
1602	153.9719448	1.31E-09	2.682691	36.6	0.0366	4.49E-04	3.20728E-05
3201	421.443313	8.58E-10	2.313446	36.6	0.0366	6.01E-04	3.70325E-05

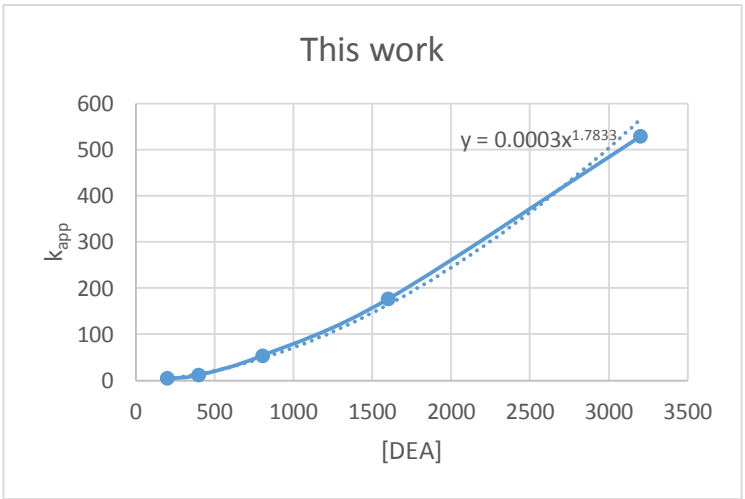
Flux calculation from termolecular mechanism

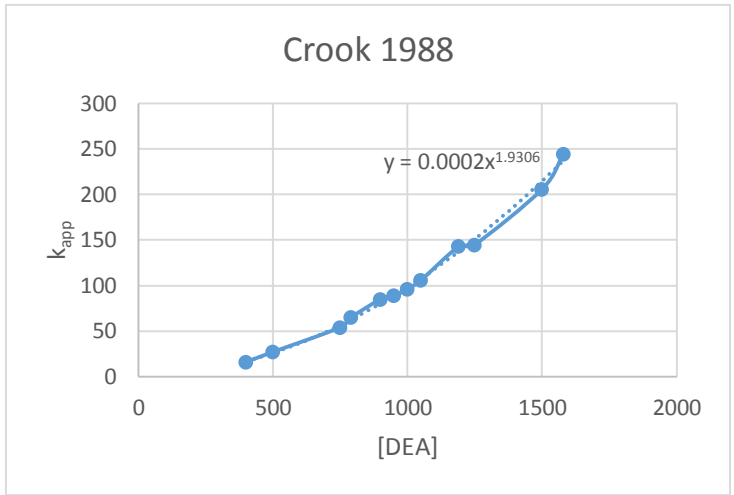
k_{DEA}^{T} =9.59E-5 $m^6/mole^2.s$

[DEA] ($mole/m^3$)	k_{app} (sec^{-1})	D_{CO2} (m_2/sec)	m_{CO2}	P_{CO2} (mbar)	P_{CO2} (bar)	$\sqrt{K_{app}}*D_{CO2}$ ($m/s^{1/2}$)	Flux J_{CO2} $mole/m^2.s$
201	3.8744559	3.14E-09	2.98	37.1	0.0371	1.10E-04	8.8693E-06
401	15.4208159	2.49E-09	2.954855	38.4	0.0384	1.96E-04	1.61715E-05
805	62.1455978	1.49E-09	2.877822	39.9	0.0399	3.04E-04	2.54135E-05
1602	246.1181436	1.31E-09	2.682691	36.6	0.0366	5.68E-04	4.05497E-05
3201	982.6298559	8.58E-10	2.313446	36.6	0.0366	9.18E-04	5.65468E-05

Order of the reaction calculation and literature comparison

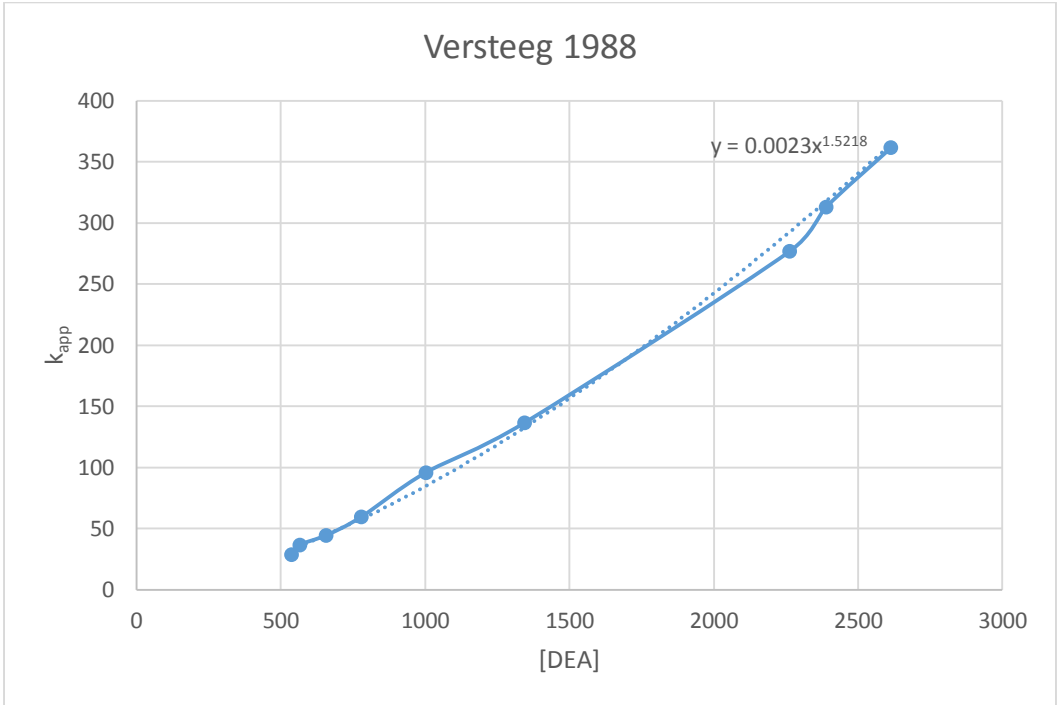
This work		Crook		Versteeg 1988	
[DEA] mole/m^3	k_{ov} / k_{app} sec^{-1}	[DEA] mole/m^3	k_{obs} sec^{-1}	[DEA] mole/m^3	k_{app} sec^{-1}
201	4.3	400	16	536.25	28.7
401	11.7	500	27	566.47	36.68
805	54.1	750	54	657.98	44.57
1602	176.9	790	65	778.41	59.49
3201	529.1	900	85	1001.86	95.8
		950	89	1343.42	136.45
		1000	96	2262.58	276.81
		1050	106	2388.55	312.95
		1190	143	2613.48	361.55
		1250	145		
		1500	206		
		1580	245		





Oerder of reaction, n = 1.7833

Order of reaction, n = 1.9306



Order of reaction, n = 1.5218

NTNU	Hazardous activity identification process	Risikovurdering	Nummer	Dato
		HMS-avd.	HMSRV2601	
		Godkjent av	Side	Erstatter
HMS				

Unit:	*Kjemisk prosessteknologi*	**Date:**	23-01-2013
Line manager:	*Naveen Ramachandran / Greet Versteeg (Procede Group BV, The Netherlands)*		
Participants in the identification process (including their function):	Muhammad Awais (Operator), Naveen Ramachandran (Co supervisor)		

Short description of the main activity/main process:

ID no.	Activity/process	Responsible person	Laws, regulations etc.	Existing documentation	Existing safety measures	Comment
1	Cleaning of equipment	Operator			Wearing Proper PPE	Exhaust Valve is very important for volatile chemicals
2	Preparation of sample	Operator			Wearing Proper PPE	To be prepared in specified chamber where air flow is availible
3	Sample loading in equipment	Operator			Wearing Proper PPE	
4	Sample taking from equipment	Operator			Wearing Proper PPE	
5	Draining of chemical from equipment	Operator			Wearing Proper PPE	waste container to be disposed properly or recycled
6	Cleaning of equipment after experiment	Operator			Wearing Proper PPE	Vent valve should be open during cleaning and drying period
7						

NTNU	Risk assessment	Utarbeidet av	Nummer	Dato
		HMS-avd.	HMSRV2603	04-02-2011
		Godkjent av	Side	Erstatter
HMS /KS				

Unit: *Kjemisk prosessteknologi* **Date:** 23-01-2013

Line manager: *Naveen Ramachandran / Greet Versteeg (Procede Group BV, The Netherlands)*

Participants in the identification process (including their function): *Muhammad Awais (Operator), Naveen Ramachandran (Co Supervisor)*

Signatures:

ID no.	Activity from the identification process form	Potential undesirable incident/strain	Likelihood:	Consequence:				Risk value	Comments/status Suggested measures
			Likelihood (1-5)	Human (A-E)	Environment (A-E)	Economy/ material (A-E)	Reputation (A-E)	Human	
1	Cleaning of equipment	breakage of glass ware, Chemcial fumes	3	A	A	A	A	A3	
2	Preparation of sample	spillage of amines, Alcohol	4	B	B	B	A	B4	Use of fume cupboard
3	Sample loading in equipment	spillage of chemical	4	B	A	B	A	B4	Fume mask is mandatory
4	Sample taking from equipment	spillage of chemical	4	B	A	A	A	B4	
5	Draining of chemical from equipment	spillage of chemical	4	B	A	A	A	B4	
6	Cleaning of equipment after experiment	breakage of glass ware	3	A	B	A	A	A3	Exhaust value should be open
7									

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.2 Revision Date 02.08.2012
Print Date 01.07.2013
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name : Diethanolamine

Product Number : D8885
Brand : Sigma-Aldrich
Index-No. : 603-071-00-1
CAS-No. : 111-42-2

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie BV
Stationsplein 4
3331 LL ZWIJNDRECHT
NETHERLANDS

Telephone : +31 78-620-5411
Fax : +31 78-620-5421
E-mail address : eurtechserv@sial.com

1.4 Emergency telephone number

Emergency Phone # : 112

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Acute toxicity, Oral (Category 4)
Specific target organ toxicity - repeated exposure (Category 2)
Skin irritation (Category 2)
Serious eye damage (Category 1)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Harmful if swallowed. Harmful: danger of serious damage to health by prolonged exposure if swallowed. Irritating to skin. Risk of serious damage to eyes.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008 [CLP]
Pictogram

Signal word Danger

Hazard statement(s)
H302 Harmful if swallowed.
H315 Causes skin irritation.
H318 Causes serious eye damage.
H373 May cause damage to organs through prolonged or repeated exposure.

Precautionary statement(s)
P280 Wear protective gloves/ eye protection/ face protection.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove

contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements: none

According to European Directive 67/548/EEC as amended.

Hazard symbol(s)

R-phrase(s)

R22	Harmful if swallowed.
R38	Irritating to skin.
R41	Risk of serious damage to eyes.
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed.

S-phrase(s)

S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S46	If swallowed, seek medical advice immediately and show this container or label.

2.3 Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Synonyms : Bis(2-hydroxyethyl)amine
2,2'-Iminodiethanol

Formula : $C_4H_{11}NO_2$

Molecular Weight : 105,14 g/mol

Component		Concentration
Diethanolamine		
CAS-No.	111-42-2	-
EC-No.	203-868-0	
Index-No.	603-071-00-1	

4. FIRST AID MEASURES

4.1 Description of first aid measures

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

4.3 Indication of any immediate medical attention and special treatment needed
no data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture
Carbon oxides, nitrogen oxides (NOx)
Nature of decomposition products not known.

5.3 Advice for firefighters
Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information
no data available

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures
Use personal protective equipment. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas.

6.2 Environmental precautions
Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

6.3 Methods and materials for containment and cleaning up
Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections
For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling
Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.

7.2 Conditions for safe storage, including any incompatibilities
Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Air sensitive.

7.3 Specific end uses
no data available

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

8.2 Exposure controls

Appropriate engineering controls
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection
Tightly fitting safety goggles. Faceshield (8-inch minimum). Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Immersion protection
Material: Nature latex/chloroprene
Minimum layer thickness: 0,6 mm
Break through time: > 480 min
Material tested:Lapren® (Aldrich Z677558, Size M)

Splash protection
Material: Nitrile rubber
Minimum layer thickness: 0,11 mm
Break through time: > 30 min
Material tested:Dermatril® (Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 873000, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an Industrial Hygienist familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection
Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a)	Appearance	Form: viscous liquid
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	11,0 - 12 at 105 g/l at 25 °C
e)	Melting point/freezing point	Melting point/range: 28 °C
f)	Initial boiling point and boiling range	217 °C at 200 hPa
g)	Flash point	138 °C - closed cup
h)	Evaporation rate	no data available
i)	Flammability (solid, gas)	no data available
j)	Upper/lower flammability or explosive limits	Upper explosion limit: 10,6 %(V) Lower explosion limit: 1,6 %(V)
k)	Vapour pressure	no data available
l)	Vapour density	3,63 - (Air = 1.0)

m)	Relative density	1,097 g/mL at 25 °C
n)	Water solubility	105 g/l at 20 °C - completely soluble
o)	Partition coefficient: n-octanol/water	log Pow: -2,18
p)	Autoignition temperature	no data available
q)	Decomposition temperature	no data available
r)	Viscosity	no data available
s)	Explosive properties	no data available
t)	Oxidizing properties	no data available

9.2 Other safety information
no data available

10. STABILITY AND REACTIVITY

10.1 Reactivity
no data available

10.2 Chemical stability
no data available

10.3 Possibility of hazardous reactions
no data available

10.4 Conditions to avoid
no data available

10.5 Incompatible materials
Oxidizing agents, Copper, Zinc, Iron

10.6 Hazardous decomposition products
Other decomposition products - no data available

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - rat - 710 mg/kg

LD50 Dermal - rabbit - 12.200 mg/kg

LD50 Intraperitoneal - rat - 120 mg/kg

LD50 Intravenous - rat - 778 mg/kg

Skin corrosion/irritation
Skin - rabbit - Mild skin irritation - 24 h - Draize Test

Serious eye damage/eye irritation
Eyes - rabbit - Severe eye irritation - 24 h

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: 3 - Group 3: Not classifiable as to its carcinogenicity to humans (Diethanolamine)

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	Harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	Causes eye burns.

Signs and Symptoms of Exposure
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: KL2975000

12. ECOLOGICAL INFORMATION

12.1 Toxicity

Toxicity to fish	mortality NOEC - Cyprinodon variegatus (sheepshead minnow) - 540 mg/l - 96 h
	LC50 - Pimephales promelas (fathead minnow) - 1.460 mg/l - 96 h
Toxicity to daphnia and other aquatic invertebrates	mortality NOEC - Daphnia magna (Water flea) - < 4,2 mg/l - 11 d
	EC50 - Daphnia magna (Water flea) - 55 mg/l - 48 h

12.2 Persistence and degradability
Biodegradability — Result: > 90 % - Readily biodegradable.

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
no data available

12.6 Other adverse effects
Harmful to aquatic life.
no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

14.1 UN number
ADR/RID: - IMDG: - IATA: -

14.2 UN proper shipping name

ADR/RID: Not dangerous goods
IMDG: Not dangerous goods
IATA: Not dangerous goods

14.3 Transport hazard class(es)

ADR/RID: - IMDG: - IATA: -

14.4 Packaging group

ADR/RID: - IMDG: - IATA: -

14.5 Environmental hazards

ADR/RID: no IMDG Marine pollutant: no IATA: no

14.6 Special precautions for user

no data available

15. REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

no data available

15.2 Chemical Safety Assessment

no data available

16. OTHER INFORMATION

Further information

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