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Using e-NRTL framework

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Chemical Engineering
Submission date: July 2012
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dedicated to my Parents,

who struggled to the hardest,
who suffered to the maximus,
who are loved to the deepest,

DECLARATION

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology Trondheim, Norway.

Date and Signature: ______________________

ABSTRACT

Carbon dioxide belongs to the class of greenhouse gases which are highly influential in global warming. Sometime ago, it was also proposed in some circles that Global warming is most like a conspiracy than a reality, but today, it has become a global phenomenon - a crucial fact. Reduction of CO_2 emissions is a priority on international platforms and Sequestration is the only viable solution. Most of the CCS (CO_2 Capture and Storage) is endorsing chemical absorption using amine based solvents. The optimal design of absorber requires a complete and diversified knowledge of Vapor Liquid Equilibrium, the complex phase and chemical equilibria and many more.

For absorber design, the equilibrium stage approach is used, which relates the partial pressure of the acid gas and solubility of the gas in the solution. This factor generates the driving force along the length of the column necessary to evaluate the height. The cyclic capacity of the solution ensures that the system operates at the minimum circulation rate. All these parameter are based upon the properties of the amine under consideration. All amount of experimental data is required to avoid which thermodynamically rigorous model is essentially required which can interpolate and extrapolate confidently. But unfortunately, more we know about amines, less we know about them on the other hand.

In this project, 1,3-Diaminopropane is considered for generating the dissociation constants against different temperatures which tells the story of the two amine groups attached, followed by solubility experimentation which was run for 2M amine concentration by employing the unloaded and loaded solutions. Later on, Vapor liquid equilibrium study was carried out for two concentrations of 2M and 5M. The VLE data was generated at different temperatures against different loadings.

After the experimental analysis, the results were compared with the base case i.e. Monoethanol amine and secondly with the other diamine i.e. Piperazine. Lastly, the modeling was also done using the semi-empirical model of e-NRTL.

ACKNOWLEDGEMENTS

All praise belong to **Allah, the Al-Mighty**, the most Gracious, the most Merciful, who has given me strength and patience during the tough times of completing the experimental work and finalizing it in a reported form. **Hazrat Muhammad**, peace be upon him, following whom makes Islam a lot easier to follow.

I would like to express my deepest gratitude to **Department of Chemical Engineering, Faculty of Natural Sciences, Norwegian University of Science and Technology, Trondheim**, which has given me the opportunity to achieve another level of excellence in my professional career.

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My parents, my grandpa, my brothers, (Simmam, Iatisam, Arsam) and **my sisters (minnie apo)** should know that i really appreciate their love and immense support and the confidence they had in me. I must thank my love and my wife **Rodaba** that you are special and thanks for the understanding. I could not miss more, my beloved uncle, Late **Rana Basit Hussain** (may there be blessings upon him), during my entire stay in Norway.

Finally I must thank my friends who stood like a wall with me through the constant changing phases of my life.

RANA SADDAM HUSSAIN

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INTRODUCTION

Carbon dioxide, a greenhouse gas, Global warming are most commonly used words, now-a-days. Carbon dioxide belongs to the class of greenhouse gases which are highly influential in global warming. Sometime ago, it was also proposed in some circles that Global warming is most like a conspiracy than a reality, but today, it has become a global phenomenon - a crucial fact. If we project CO_2 emission until year 2030 then throughout the period, we observe a rising trend, as shown in Figure 1. Future seems to be promising on two increasing factor i.e. Population and real income of a common man, unfortunately it means more people with more income would need more energy for consumption and production. By the year 2009, more than 80% of the world energy needs were met by fossil fuels (coal, oil & natural gas) which are the major source of CO_2 production in the environment. [International Energy Agency, (2011), CO_2 emissions from fuel combustion: highlights, 123 pp].

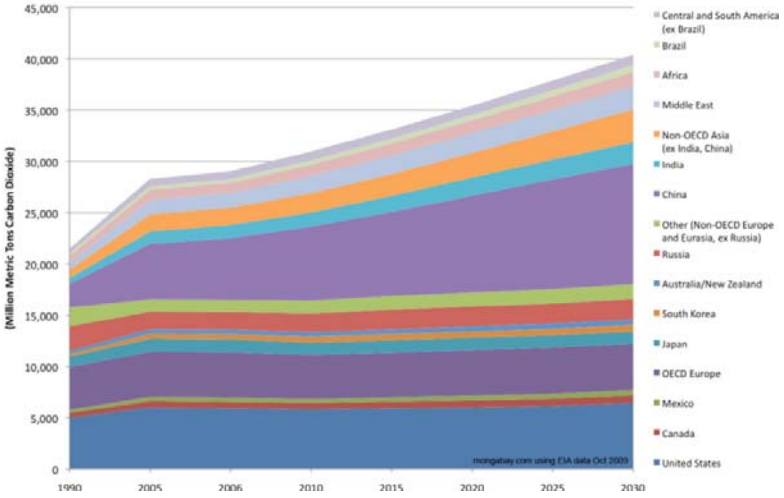


Figure 1:CO2 emission by countries from the year 1990-2030 (Butler, 2006)

1.1 CO_2 Capture and Storage (Sequestration)

There is more CO_2 present in atmosphere then it should be and as CO_2 stores heat quite well, hence the increment in average temperature of the Earth surface is an obvious reality. There are two ways for restoring the mean surface temperature of Earth which is increasing with every passing moment. Either we reduce the CO_2 production which means that we have to change the entire industrial set up, globally and this is totally out of the chart or the second option is by capturing the produced CO_2 either on its way to atmosphere or before it could ever be produced. Any method that stops the CO_2 entering in the atmosphere and revert it to the carbon viable sinks, is regarded as CO_2 Capture and Storage or Sequestration.

Following are the methods through which we can proceed with Sequestration:

i. Pre-combustion: CO_2 is captured prior to combustion by using gasification with air or oxygen. The fuel is gasified under a known pressure through a water-gas shift to produce CO_2 and H_2 (syngas). The CO_2 is captured later on.
ii. Oxy-fuel combustion: Fuel is being reacted with oxygen instead of air producing primary products of CO_2, H_2O and O_2. CO_2 is extracted later on from water.
iii. Post-combustion: CO_2 is captured anywhere along the product processing to exhaust stream. The mole fraction of CO_2 in the flue gas stream lies in the range of 4-15%, which means that for the Natural gas combined cycle plant exhaust, gas contains up to 4% CO_2 and for Coal fired power plants, the amount is around 15%.

1.1.1 Post-Combustion: A better choice

Among the three ways to sequestration, post-combustion seems to be more promising than the rest. The benefits we have in capturing CO_2 from the exhaust stream are quite significant. It is obvious that the post-combustion CO_2 capture systems are installed in the downstream of the process which makes them highly compatible without changing the process which is already having enormous amount of investment in fossil fuel infrastructure, around the world. The existing plants could be retrofitted without any special issues regarding the post-combustion systems. It is worth mentioning here that if the CO_2 capture system encounters a problem then the plant will continue to operate as normal even CO_2 could be vented to the atmosphere in drastic conditions as well.

1.1.2 Physical Processes in the fore-front of CO2 Capture

There is a list of technologies that are not only evident in helping the carbon dioxide separation but also involved simple physical processes [GCEP Energy Assessment Analysis, 2005].

Chemical Solvents

This technique is majorly used for CO_2 capture but at low concentrations by involving chemical solvents. This process consumes huge amount of material, experience a lot of changes which compromises the energy consumption and investment cost of the system. These changes include oxidation of solvent and degradation resulting in products that could be corrosive or hazardous in nature.

Amine Solvents

Solvents involving amine are most commonly used examples in CO_2 capture systems employing chemical solvents. The major names in this field are monoethanol amine (MEA) & diglycolamine (DGA) which constitutes under Primary amines, while the others include diethanol amine (DEA) & diisopropyl amine (DGA) making a part in secondary amines and lastly, the tertiary amine includes Triethanol amine (TEA) & methyldiethanol amine (MDEA).

Physical Absorption

This method uses the mechanism of absorption to capture CO_2 followed by desorption or stripping. Both sets of mechanism requires different set of temperatures and pressures, so, smaller the difference in operating conditions, smaller would be the energy expense but greater would be the consumption of absorbents for CO_2 capture.

Physical Solvents

The examples of physical solvents used these days are Selexol, Rectisol and Glycerol carobonate which are working well under physical solvent scrubbing as far as CO_2 is concerned.

Mixed Chemical-Physical Solvents

In this category a hybrid of physical and chemical solvents are used employing the positive qualities of every constituent under the governing conditions. Example include Sulfinol which contains sulfolane a physical solvent and the amines like DIPA or MDEA.

Physical Adsorption

Carbon dioxide, being attached on the surface of the material without forming any chemical bond, is described by physical adsorption. Usually, the physical adsorption takes place at high pressure by involving the van der Waals forces.

Regenerable Physical Adsorbents

The adsorption is reversible in a sense that the adsorbed gas i.e. CO_2 could be stripped just by changing the conditions and hence improve the efficiency of the adsorbent running for a longer time. Major adsorbents are activated carbon and zeolites.

Membrane Separation Processes

Membrane separation processes are a steady state blend of absorption and adsorption. Molecules gets adsorbed at high pressure side of the membrane and desorbed at the other low pressure side. Different membranes are used to separate CO_2 from H_2 and N_2. From the mixture of H_2 and CO_2, palladium membrane but for the CO_2 capture from the blend of CO_2 and N_2 polysulfone are considered efficient.

Chemisorption

The material that is to be used for the adsorption is chemically bound to the gas molecules of the process stream.

Metal Oxide Air Separation

Air is used to separate the pure stream of O_2 which then oxidizes the fuel under an exothermic reaction resulting in CO_2, H_2O and other products like H_2. With the current present technological state it is easy to separate CO_2 from H_2O. Models predict that for power generation this methodology has significant advantages, but no large scale demonstration plants exists in the world, today.

Dry Chemical Absorbents

A dry absorbent can go under a reversible chemical reaction with CO_2, if the conditions are changed then it could produce the CO_2. Sodium carbonate is an important example in dry chemical absorbents along with lithium zirconate.

Chemical Bonding

There is a list of materials that have the capability to form thermodynamically favored, stable chemical bonds with the gas (in the solution or mixture). Later on these stable materials could be stored as waste, but large volumes could induce handling and transportation problems.

CO_2 Mineralization

Limestone, $CaCO_3$ react with CO_2 to form carbonate and bicarbonate ions which could be stored in the ocean. Other example is Magnesium Silicate which produces Magnesium carbonate and silicate on reaction with CO_2.

Phase Separation

Phase separation is easily achievable when we approach below a certain temperature making the gas molecules to move significantly slower and hence settling them into a distinct layer with a distinct composition, if comparing to the vapor phase composition.

Cryogenics

If, the temperature is lowered in order to separate gases according to their boiling points, then we could have a very pure stream of individual gases. But it would increase the energy penalty as well i.e. loss of resources employing a particular process instead of not using it.

CO_2Clathrate

Clathrate is special phase of water in which the gas molecules are entrapped by the Hydrogen bonded structures. CO_2 could be produced by dissociating the CO_2 Clathrate. But the formation of CO_2 Clathrate need 140 atm and 273 K which makes it a bit hard to implement in an economic spirit.GCEP Energy Assessment Analysis, (2005).

1.2 Motivation for this work

With the passage of time, we are becoming more civilized and more industrialized, which is just one side of the frame. While on the other, we are producing more CO_2 which means higher magnitude in global warming gas potential. To reduce the post combustion CO_2, we need absorbers and stripper columns which could be accomplished by applying equilibrium stage approach. Here comes the reason for this entire work which is producing the equilibrium data for an amine system i.e. in my case is 1,3-Diaminopropane. Equilibrium data actually relates the partial pressure of the acid gas with the solubility of the amine under consideration.

This work focuses on characterizing 1,3-Diamionopropane and model it through e-NRTL by using the activity co-efficient and total pressure.

1.3 Scope of this report

1.3.1 Physicochemical Properties

The density experiment was conducted on 1,3-Diaminopropane (DAP) which is unloaded and loaded. The loaded solutions of DAP were having the CO_2 content upto 0.1, 0.3 and 0.5 mol/ mol of amine. 1^{st} and 2^{nd} Dissociation constants were also determined for DAP to find the relation of the pKa with reaction rates and examining how the structure was being justified by the Dissociation constant values. Later on solubility data was also generated to help in establishing base for the main aim of this work i.e. VLE data for DAP.

1.3.2 Vapor Liquid Equilibrium

VLE experiment for low and high temperatures was conducted for two different molarities of DAP (2M and 5M). This data with the physicochemical properties along with the critical properties (taken from literature) was used to model the activity coefficient ,P_{CO2} and P_{Total} by employing e-NRTL.

2

THEORETICAL BACKGROUND

2.1 Alkanolamines, the chronicles

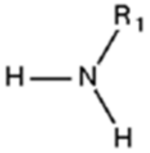
The major names of the Alkanolamine which are highly commercial in use are Monoethanolamine (MEA), Diethanolamine (DEA) and Methyldiethanolamine (MDEA). It was not until 1930, when the alkanolamines were first used for the acid gas treatment method as absorbents. The first amine ever run as an absorbent on commercial scale was Triethanolamine (TEA). But it was having some serious drawbacks which involved its being low in capacity and reactivity, but also attributed of having poor stability. Diisopropanolamine (DIPA) was used instead of TEA in processes like SCOT,Adip and Sulfinol. Later on, Methyldiethanolamine (MDEA) was considered to be the best candidate for the acid gas absorption systems but it was used in 1953 by Kohl & coworkers in Fluor Daniel as selective absorbent for H_2S in CO_2 presence.Blohm&Riesenfeld proposed a different type of Alkanolamine known as Diglycolamine (DGA) which is having a blend of properties of MEA and Diethylene glycol, hence being used in more complex systems.

Furthermore, not only the aqueous solutions of alkanolamines were used but mixture of different alkanolamines along with some additives are widely used that were offered by Dow Chemical Company (GAS/SPEC), UOP (and/or Union Carbide Corp.) (Amine Guard and UCARSOL), Huntsman Corporation (TEXTREAT) and BASF Aktiengesellschaft (activated MDEA). The concept of tailored amines mixtures was a dramatic step in acid gas treatment. They are having MDEA, other amines, corrosion inhibitors, buffers, promoters and foam depressants, under specific concentrations. They are selective in their application but highly goal oriented. In early 1980s, EXXON Research and Engineering Company introduced the world to a new class of acid gas absorbents known as Sterically Hindered Amines. (Kohl A., 1997)

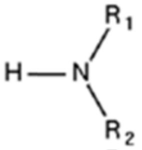
2.2 1,3-Diaminopropane, the chemistry

As mentioned previously, the alkanolamines have at least one amine group and one hydroxyl group, which could be categorized into three major groups.

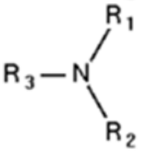
i. Primary amines: Amines having two hydrogen atoms directly attached to a nitrogen atom. Examples are Monoethanolamine(MEA) and 2-(2-aminoethoxy) ethanol (DGA).



ii. Secondary amines: It includes those amines having one hydrogen atom attached to the nitrogen atom. Diethanolamine (DEA) and Diisopropanolamine (DIPA) are worthy examples in this category.

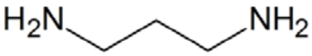


iii. Tertiary amines: Amine with no Hydrogen atom bonded with the nitrogen atom. Triethanolamine (TEA) and Methyldiethanolamine (MDEA) are a few examples for tertiary amines.



R1, R2 & R3 represents the groups in the molecular structure attached to the functional amines.

The subsequent thrust of this work is primarily subjected to 1,3-Diaminopropane (DAP), which is a primary diamine with structure as shown below.



2.2.1 Physical Data about DAP

DAP used for the lab experiment in this work is being brought from Sigma Aldrich Co. LLC with a purity level of ≥ 99%. Material safety data sheet is attached as Appendix:**S**, for the safety, relevant hazards, ecological concerns and emergency protocols involved with the chemical. The data has also been borrowed from Sigma Aldrich material safety data sheet.

IUPAC Name	Propane-1,3-diamine
CAS Number	109-76-2
Molecular Wt.	74.12 g/mol
Molecular Formula	$C_3H_{10}N_2$
Appearance	Form: Liquid Colour: light Yellow
Melting Point	12^0C
Boiling Point	140^0C
Flash Point	51^0C

Relative Density	0.888 g/cm^3 at 25^{0}C
Vapor Pressure	< 11 hPa at 20^{0}C

2.2.2 Reaction scheme of DAP in the loaded system.

The main reactions when DAP in aqueous from reacts with CO_2 would be represented in the following mechanism.

1) Ionization of water:

$$2H_2O \leftrightarrow H_3O^+ + OH- \qquad (i)$$

2) Bicarbonate formation :

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad (ii)$$

3) Carbonate formation:

$$HCO^-_3 + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \qquad (iii)$$

4) 1st Protonation of DAP :

$$H_3O^+ + DAP \leftrightarrow DAPH^+ + H_2O \qquad (iv)$$

5) 2nd Protonation of DAP:

$$H_3O^+ + DAPH^+ \leftrightarrow DAPH_2^+ + H_2O \qquad (v)$$

6) Carbamate formation:

$$CO_2 + DAP + H_2O \leftrightarrow H_3O^+ + DAPCOO^- \qquad (vi)$$

7) Zwitterion formation:

$$H_3O^+ + DAPCOO^- \leftrightarrow DAPH^+COO^- + H_2O \qquad (vii)$$

8) BiCarbamate formation:

$$H_2O + CO_2 + DAPCOO^- \leftrightarrow DAP(COO)_2^{-2} + H_3O^+ \qquad (viii)$$

From the structure of DAP it seems to be symmetrical so the formation of primary zwitterion and secondary zwitterion would not be possible instead it would form 1st zwitterion (reaction vii) followed by 2nd zwitterion, as both the amine group react with the same intent. The same is true for the carbamate production i.e. instead of primary and secondary carbamate formation the DAP would form carbamate (reaction vi) followed by bicarbamate formation (reaction viii). The remaining reactions starting from i, ii, iii, iv, v and vi would be similar to the way any other secondary amine reacts.

2.3 N_2O Solubility

CO_2 can be bound chemically by an absorbent or remain as free CO_2- physically soluble in an absorbent. Physical solubility of CO_2 into an absorbent at various concentrations and temperature is necessary in the development of kinetics and thermodynamic models for the system. The problem is that CO_2 reacts with the absorbent, thus direct measurement of physical solubility is not possible. This measurement is thus carried out indirectly by the use of N_2O, a corresponding nonreactive gas, by applying an analogy, the N_2O analogy. The N_2O analogy was originally proposed by Clark (1964) and verified by Laddha et al (1981) by:

$$\text{(solubility of } CO_2 \text{ in absorbent)} = C_1 \text{ (solubility of } N_2O \text{ in absorbent)} \quad (2.1)$$

with

$$C_1 = \text{(solubility of } CO_2 \text{ in absorbent)} / \text{(solubility of } N_2O \text{ in absorbent)} \quad (2.2)$$

This analogy has been applied to amine systems including blended systems (Versteeg and van Swaaij, 1988; Mandal et al 2005; Hartono et al, 2008; Haimour and Sandall, 1984; Park and Sandall, 2001; Tsai et al. 2000; Xu et al. 1992; Li and Lai, 1995; Li and Lee 1996; Al Ghawas et al, 1989.)

The Solubility of N_2O gas in an aqueous amine/amino acid solvent can be expressed by an apparent Henry`s law coefficient describing the equilibrium between the solute in the gas phase and the solute concentration in the liquid phase. At low concentrations and pressures, a solute concentration in proportional to its mole fraction while pressure is approximately equal to gas phase fugacity. Thus Henry`s law could be written as:

$$p_i = H_i x_i \quad (2.3)$$

Inconsistencies in solubility data may contribute to inconsistent results for reaction kinetics (Blauwhoff et al. 1984). The kinetic rate constant is proportional to the square of Henry`s law constant, thus 10% error in the CO_2 solubility could result in 20% error in a reaction rate constant (Hartono, 2009; Mahajani and Joshi, 1988).

2.4 pKa Determination

pKa of an amine is a direct measure of the rate at which CO_2 is being absorbed in the amines. According to Rochelle et al (2001) and da Silva & Svendsen (2007) related pKa with absorption rate, while Versteeg et al (1996) observed correlations between pKa and reaction rates of amine, increases with the reaction rate.

The relative strength of amines as bases (basicity) is usually expressed as either the pK_b or as the pKa of the conjugate acid.

$$BH^+ \rightleftharpoons B + H^+ \quad (2.4)$$

$$K_a = \frac{a_B a_{H^+}}{a_{BH^+}} \quad (2.5)$$

$$pK_a = -\log K_a \quad (2.6)$$

$$pK_a + pK_b = pK_w = 14 \quad (2.7)$$

A strong base thus has low pK_b and high pK_a for the corresponding conjugate acid (Lawrence, 2004; Perrin, 1965). Basicity of amine are governed by two parameters, namely the electronic effect and the steric effect. A combination of both plays significant role in amine basicity. [Aronu, 2011]

2.5 Thermodynamic Framework and Vapor Liquid Equilibrium

Alkanolamines are extensively used as solvents to remove the acid gases from gas streams in the absorbers and strippers. The absorption process is designed by the equilibrium stage methodology, which relates partial pressure of the acid gas and the equilibrium solubility of the gas in the alkanolamine solution. Figure 2 explains the balance between the phase and chemical equilibria.

Phase equilibria is applied to the molecular species within the vapor and the liquid phase while chemical equilibria is applicable to the distribution of the species in molecular and ionic form for the liquid and gas phase.

2.5.1 Importance of Reference state

There are two ”Limiting” laws that have strong applicability in the vapor liquid equilibrium determination and they are:

1) **Raoult`s law**: At low solute concentrations the vapor pressure of the solvent is simply the solvent mole fraction ratio times the vapor pressure of the pure solvent, i.e. $P_i = x_i P_i^*$ where x_i is the pure solvent mole fraction and P_i^* is the vapor pressure of the pure solvent.
2) **Henry`s Law**: The concentration of the solute, ”i” is directly proportional to the vapor pressure of a solute, i.e. $P_i = x_i H_i$ where $H_i$ is the Henry`s law constant.

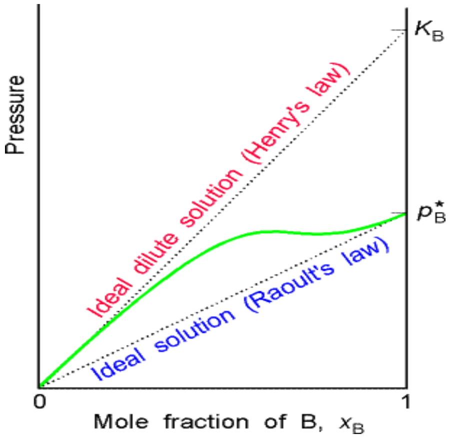


Figure 2: Ideal dilute solution vs ideal solutions [Svein, 2004]

Ideal solutions obeys Raoult`s law as well as the solute and the solvent is concerned, but if the real solutions are considered, then for low solute concentrations the solvent follows the above mentioned limiting law only. From here we can define as the ”*Ideal Solution*” which is one having the solvent molecules following the Raoult`s law while the solute follows the Henry`s law.

The difference in behavior is obvious as in very dilute solutions the solvent molecules act as pure because they are almost surrounded by solvent molecules while on the other hand solute act in a fashion as if they are in a highly modified state. So the Raoult`s law could be stated as $\frac{d\gamma_A}{dx_A}=1$ which converges to the thermodynamic equilibrium criteria for standard vapor liquid equilibrium problem [Erik, 2010] as $\mu_i^{vap}(T,P,n)=\mu_i^{liq}(T,P,n)$ where μ_i^{vap} and μ_i^{liq} are the chemical potentials of the species ”i” in the vapor and the liquid phase respectively. After that an equation of state and an activity model for the liquid phase is used to deduce the following equation.

$$\phi_i y_i p = \gamma_i x_i E_i \psi_i \tag{2.8a}$$

where, ϕ_i and ψ_i are the fugacity coefficient and pressue correction factor also known as Poynting factor, required in the high pressure G^E models.

2.5.2 Chemical and Phase equilibria

Vapor liquid equilibrium is referred to the dynamics between the vapor phase species to the liquid phase species, as illustrated in the figure 3. It governs on two equillbria, i.e., chemical and phase. Chemical equilibria is achieved by minimizing the Gibbs free energy at constant Temperature and Pressure, which can be defined by the following equation.

$$\sum_{i=1}^{N} v_{ij}\mu_i = 0 \tag{2.8b}$$

where i= 1,..., N species and j = 1,...., R reactions

Here, the chemical equilibrium constant can be defined by eq 2.9

$$\prod_i (\gamma_i x_i)^{v_i} = \exp\left[-\frac{\sum_{i=1}^{N} v_i \mu_i^0}{RT}\right] \tag{2.9}$$

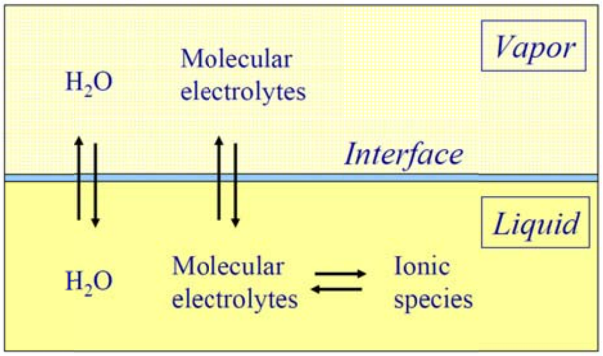


Figure 3: Phase and chemical equilibria in the system [Edwards et al. 1978]

Keeping the temperature, pressure and the chemical potential over the entire system uniform so the chemical potential can hence be expressed as:

$$\mu_i^{0V} + RT\ln\frac{f_i^V}{f_i^{0V}} = \mu_i^{0L} + RT\ln\frac{f_i^L}{f_i^{0L}} \qquad (2.10)$$

Eq 2.10 can be used to derive the basic Vapor Liquid Equilibrium condition.

$$f_i^V(T,p,y) = f_i^L(T,p,x) \qquad (2.11)$$

So, by using the fugacity coefficient, φ_i, the desired relation between vapor phase fugacity and accessible vapor phase state variable can be explained.

$$f_i^V = p_i\varphi_i = y_i p\varphi_i \qquad (2.12)$$

The fugacity coefficient $\varphi_i = {}^{f_i}\!/\!_{py_i}$ is 1 for ideal gas. Furthermore, at low pressure the real systems may be treated as ideal. In order to guess the fugacity coefficient as an initial guess, the following equation can be employed [Gmehling and Onkan, 1977].

$$\varphi_i = \exp\left(\frac{1}{RT}\int_0^P\left(V_i^G - \frac{RT}{P}\right)dP\right) \qquad (2.13)$$

where, V_i^G is the partial molar volume in the gas phase which could be calculated from equation of states.

2.5.3 Activity Coefficient

γ_i, the activity coefficient in the liquid phase, "i" may be related with liquid phase fugacity as, f_i^L:

$$f_i^L = x_i y_i f_i^{0L} \qquad (2.14)$$

$$\gamma_i = {f_i}/{x_i f_i^{0L}} \tag{2.15}$$

Hence, by using the basic definition and experimentally measureable parameters, eq 2.15 could be transformed to 2.16

$$\gamma_i = \frac{y_i P}{x_i P_i^0}\phi_i \tag{2.16}$$

where, ϕ_i is expressed as $\phi_i = \frac{\phi_i}{\phi_i^{0L}}\exp\left(\frac{-V_i^L(P-P_i^{sat})}{RT}\right)$ (2.17)

ϕ_i can be of negligible importance as at low pressure, gases tend to behave ideally. At high pressure, the Poynting factor is employed to determine the activity coefficient as expressed in eq 2.18 [Gmelhing and Onkan, 1977].

$$y_i\phi_i P = x_i\gamma_i p_i^0\phi_i \exp\left(\frac{1}{RT}\int_{P_i^0}^{P} V_i^L.dP\right) \tag{2.18}$$

2.5.4 Standard states

Standard state is defined as the state in which the pure component exists at the temperature and pressure at interest. Defining the standard states we can reach to the solution of the equation 2.14 & 2.15 as by taking x_i=1; $f_i^L = f_i^{0L}$ and γ_i =1.

The equation 2.19 expresses the relation of fugacity of pure component to its vapor pressure [Gmelhing and Onkan, 1977].

$$f_i^L = p_i^0\phi_i^0 \exp\left(\frac{1}{RT}\int_{P_i^0}^{P} V_i^L dP\right) \tag{2.19}$$

where, $\frac{1}{RT}\int_{P_i^0}^{P} V_i^L dP$ is expressed as the effect of change in pressure (p to p^0) as well as fugacity is concerned. It is also known as Poynting correlation.

2.5.5 Liquid phase coefficient correlations

Excess functions

Excess functions are defined quite well as " For the purpose of describing the non-ideal behavior of mixtures, the excess functions are defined as the difference between thermodynamic functions of a real mixture and those of ideal mixture at same conditions of temperature, pressure and composition" [Gmelhing and Onkan, 1977]

$$\Delta G^E = \Delta G - \Delta G^{ideal} \tag{2.20a}$$

where ΔG^E expresses the activity coefficient of all components within a mixture. Eq 2.20b relates the Gibbs free energy with the activity coefficients as:

$$\Delta G^E = RT \sum_i x_i \ln \gamma_i \tag{2.20b}$$

$$\left(\frac{\partial \left(G^E / T \right)}{\partial T} \right) = -\frac{H^E}{T^2} \tag{2.21}$$

H^E is being expressed in eq 2.21 with the Gibbs free energy and is an important perspect in modeling as it gives the temperature dependency of G^E resulting in Gibbs Helmholtz equation [Kim, 2009].

2.5.6 Thermodynamic Consistency

Thermodynamic consistency verification is applied on vapor liquid equilibrium data by employing Gibbs Duhem equation which relates the chemical potentials of the mixture components to one another. Some of the common consistency tests are given as [Jackson and Wilsak, 1995]:

- Infinite Dilution test
- Differential test
- Integral test
- Van Ness Byer-Gibbs test

2.6 NRTL Framework

Using assumption of non-randomness, as employed by Wilson and based upon Scott`s two liquid models, in 1968, Renon H and J.M. Parusnitz put forward a correlation named as "Non Random Two Liquid model" (NRTL). The basic assumption for the NRTL model is that in comparing to the heat of mixing, the non-ideal entropy of mixing is negligible. For binary systems the activity coefficient, modified expressions of Gibbs free energy and other parameter are given in eq 2.22, 2.23a, 2.23b, 2.24a and 2.24b.

$$\frac{G^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} \right) \tag{2.22}$$

where,

$$\tau_{12} = \frac{\left(g_{12} / g_{22} \right)}{RT} \tag{2.23a}$$

$$\tau_{21} = \frac{\left(g_{21} / g_{11} \right)}{RT} \tag{2.23b}$$

$$G_{12} = \exp\left(-\alpha_{12}\tau_{12}\right) \tag{2.24a}$$

$$G_{21} = \exp\left(-\alpha_{12}\tau_{21}\right) \tag{2.24b}$$

In the eq 2.24, α is independent of temperature and an empirical factor which accounts for the non-randomness in the solution.

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}{}^2}{\left(x_1 + x_2 G_{21}\right)^2} + \frac{\tau_{12} G_{12}{}^2}{\left(x_2 + x_1 G_{12}\right)^2} \right] \tag{2.26a}$$

$$\ln \gamma_2 = x_1^2 \left[\frac{\tau_{21} G_{12}{}^2}{\left(x_2 + x_1 G_{12}\right)^2} + \frac{\tau_{12} G_{21}{}^2}{\left(x_1 + x_2 G_{21}\right)^2} \right] \tag{2.26b}$$

2.7 e-NRTL Framework

The e-NTRL is basically an electrolyte-Non Random Two Liquid model based on the local composition model. Austgen and Rocelle (1989) took the NRTL model of Chen and coworkers [Chen et al (1982), Chen and Evans (1986)] employed it to the gas-alkanolamine-water system. There are actually two major contributions to the excess Gibbs energy of the mixed solvent which formulates the basic postulates of the model. One contributes is related to the long range interaction ion-ion interactions existing far from the closest neighbor of a central ionic species. Other contribution is that express the short range interactions between different ions and polar-nonploar neutral species. It is expressed as:

$$g^E = g^E_{Long} + g^E_{Short} \tag{2.27}$$

g^E_{Long} is the long range contribution while g^E_{Short} is the short range contribution. The activity coefficients can also be expressed as eq 2.28 as the partial molar excess Gibbs excess energy is directly related to the logarithm of the activity coefficient.

$$\ln\gamma_i = \ln\gamma_i^{long} + \ln\gamma_i^{short} \tag{2.28}$$

2.7.1 Long range interaction contribution

Long range interaction contribution includes the Pitzer Debye-Huckel part and the Born term, as mentioned in the eq 2.29.

$$g_{LR}^{E*} = g_{PDH}^{E*} + g_{BORN}^{E} \tag{2.29}$$

where g_{PDH}^{E*} is the Pitzer Debye Huckel contribution denoted by eq 2.30

$$g_{PDH}^{E*} = -RT\left(\sum_k x_k\right)\left(\frac{1000}{M_m}\right)^{1/2}\left(\frac{4A_\Phi I_x}{\rho}\right)\ln\left(1+\rho I_x{}^{1/2}\right) \tag{2.30}$$

while g_{BORN}^{E} is the Bron contribution, which is there as to include the excess Gibbs free energy of moving an ion at infinite dilution in the mixed solvent to infinite dilution in the aqueous phase [Scauflaire et al, 1989]as depicted in eq 2.31.

$$g_{BORN}^{E} = RT\left(\frac{e^2}{2kT}\right)\left(\sum_i \frac{x_i z_i^2}{r_i}\right)\left(\frac{1}{D_m}-\frac{1}{D_w}\right) \tag{2.31}$$

2.7.2 Short range interaction contribution

Short range interaction contribution includes two additional assumptions employed to the local composition model. First is depicting that the repulsive forces between the like charged ions are extremely large and hence the local concentration of cations around cations is zero, or vice versa. Secondly, the anions and cations are distributed in a manner that the net local ionic charge is zero. So, the total excess Gibbs energy of electrolyte solution is expressed as:

$$g_{NRTL}^{E} = x_m\left(g^{(m)} - g_{ref}^{(m)}\right) + x_c\left(g^{(c)} - g_{ref}^{(c)}\right) + x_a\left(g^{(a)} - g_{ref}^{(a)}\right) \tag{2.32}$$

which reduces to eq 2.33 when the relations of the residual and reference Gibbs energy are combined to the eq 2.32.

$$\frac{g_{NRTL}^{E}}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \frac{X_{a'}\sum_j G_{jc,a'c}\tau_{jc,a'c}}{\sum_{a''} X_{a''}\sum_k X_k G_{kc,a'c}} + \sum_a X_a \sum_{c'} \frac{X_{c'}\sum_j G_{ja,c'a}\tau_{jc,a'c}}{\sum_{c''} X_{c''}\sum_k X_k G_{ka,c'a}}$$

(2.33)

Applying the two body interaction assumption, followed by electroneutrality assumption, then the relations derived are listed on next page.

$$G_{cm} = \sum_{a} \frac{X_a G_{ca,m}}{\sum_{a'} X_{a'}} \qquad G_{am} = \sum_{c} \frac{X_c G_{ca,m}}{\sum_{c} X_{c'}}$$

$$\alpha_{cm} = \sum_{a} \frac{X_a G_{ca,m}}{\sum_{a'} X_{a'}} \qquad \alpha_{am} = \sum_{c} \frac{X_c \alpha_{ca,m}}{\sum_{c} X_{c'}}$$

$$G_{jc,a'c} = \exp(-\alpha_{jc,a'c}\tau_{jc,a'c}) \qquad G_{ja,c'a} = \exp(-\alpha_{ja,c'a}\tau_{ja,c'a})$$

$$G_{im} = \exp(-\alpha_{im}\tau_{im}) \qquad G_{ca,m} = \exp(-\alpha_{ca,m}\tau_{ca,m})$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca} \qquad \tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca}$$

These relations help to reduce the number of parameters involved. The adjustable parameters of the model are non-randomness parameters: $\alpha_{ca,c'a}$, $\alpha_{ca,ca'}$, $\alpha_{ca,m}$ and $\alpha_{m,m}$ while the binary interaction parameters are $\tau_{m,ca}$, $\tau_{ca,m}$, $\tau_{m',m}$, $\tau_{m,m'}$, $\tau_{ca,ca'}$, $\tau_{ca',ca}$, $\tau_{ca,c'a}$ and $\tau_{c'a,ca}$. A schematic diagram of the regression methodology is shown in figure 4. The activity coefficient expressions regarding e-NRTL modeling are shown in Appendix: **M2**.

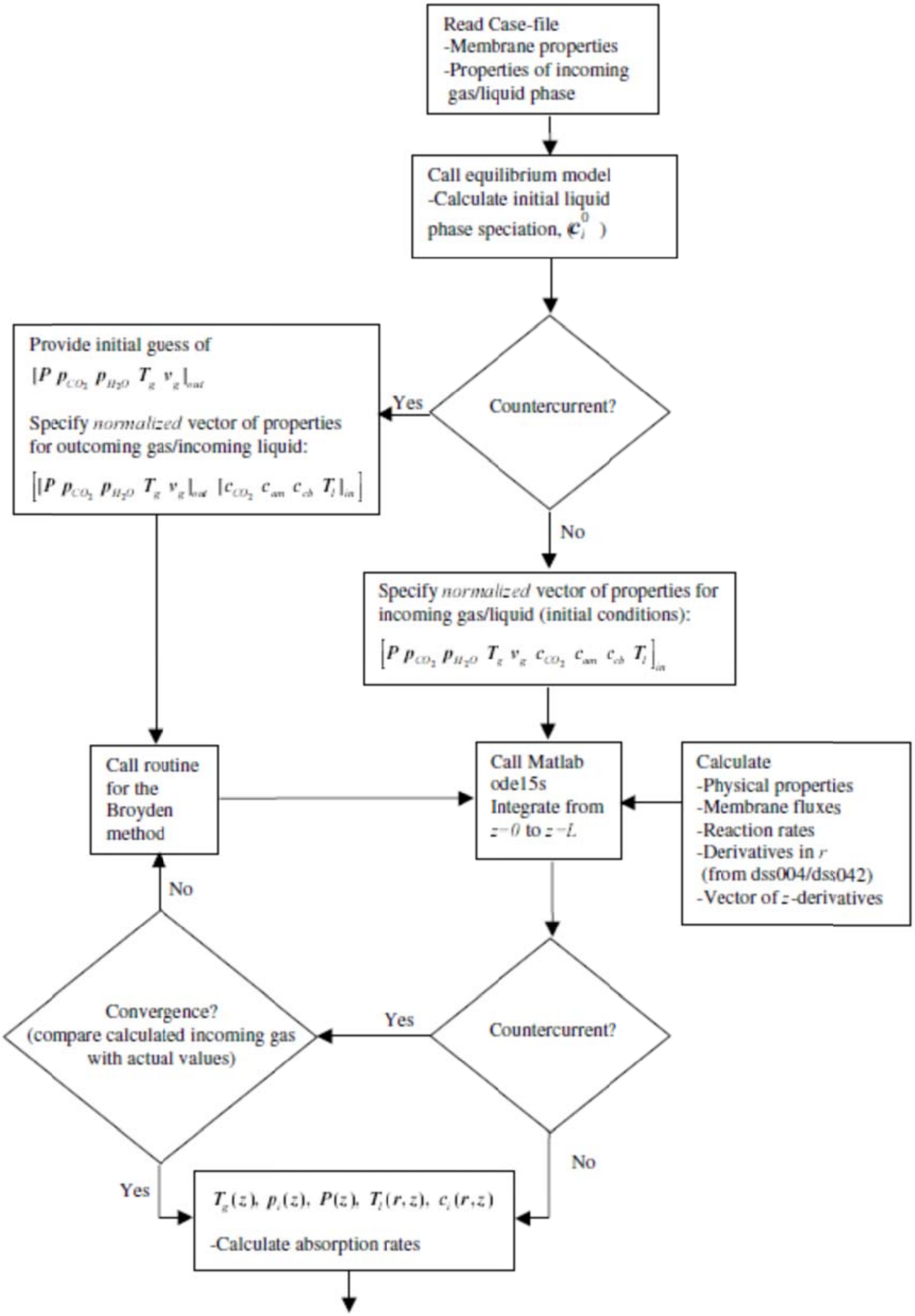


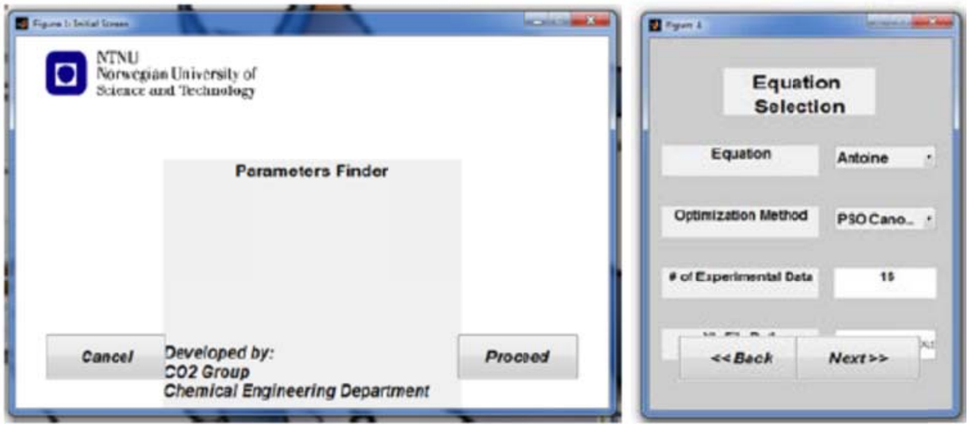
Figure 4: A schematic diagram of the regression methodology [Karl, A.H. 2003]

2.8 Modfit and Parafinder

Modfit is an in-house tool developed to regress a huge number of parameters. Basically three files are needed to run Modfit. First one defines the data, number of attritions, former guess about the initial parameters and the maximum-minimum limits. Second is the one that contains the experimental data and third on contains the model.

Optimal values are being calculated through Least Square Criteria, as well as the unknown parameters are concerned.

Parafinder is regression tool, based on Matlab with results generated on excel, which is still in the development phase. It was developed by Pinto, D.D.D., PhD student in CO_2 capture and storage research group. Parafinder is efficient enough to give a deviation less than Modfit and applicable to P-T data only. The user interface of Parafinder is in illustrated in figure 5.



Developed by:
CO2 Group
Chemical Engineering Department

Equation: Antoine
Optimization Method: PSO Cano...
# of Experimental Data: 15

Figure 5: User interface of Parafinder

3

EXPERIMENTAL PROCEDURE

3.1 Materials

Density Meter

The Anton Paar density module was calibrated by using the DI water as shown by the figure 12.

pKa Determination

The calibration of the module was done by using the Mettler Toledo buffer solutions of pH 2.00, 7.00, 9.21 and 11.00 at 20^{o}C

N_2O Solubility

N_2 used during the experiment was 99.999% pure under the brand name of Yara Praxair while the N_2O used was Yara with purity level of 99.998%.

Low Temperature Vapor Liquid Apparatus

The calibration of all four CO_2 analyzers was done on daily basis. The CO_2 analyzers with a maximum range of 20% and 5% were calibrated using Yara Praxair CO_2 with purity level of 5.0 while for lower channels with a range of 1% and 2000 ppm were calibrated by Yara Praxair CO_2 100ppm in N_2. The Yara Praxair Nitrogen was used during the experiment with a purity level of 2.6 i.e. 99.6%

High Temperature Vapor Liquid Apparatus

The Yara Praxair CO_2 was used during the experiment with purity of 99.999%.

3.1.2 Solutions

For this research work, one amine system (2M and 5M) was used to determine Henry`s constant in N_2O solubility, density, pKa-Dissociation constant and the vapor liquid equilibrium using HTA and LTA. Aqueous 1,3-Diaminopropane (DAP) was prepared for molarity of 2M and 5M weighing in volumetric basis at room temperature. .

The loaded solution of each amine systems were pre-loaded with CO_2. The solution preparation sheet is attached as Appendix **E6**.

Unloaded

2M-5M solutions of DAP were prepared by weight from the received chemicals: 1,3-Diaminopropane (purity ≥ 99%) in mixtures with deionized water, at room temperature. It is assumed that the impurity did not contain any active amines, so, the makeup solution was added to adjust the purity of the amine, which means the required amount of amine is being calculated by:

$$amount\ of\ amine\ required = \frac{Molecular\ Wt\ of\ Amine}{purity\ (\%)} \qquad (3.1)$$

Loaded

In order to load the amine systems, CO_2 was preloaded in each of the solutions that were prepared on the electric balance by adding the CO_2 sparger carrying the CO_2 to the solution and increasing the weight to the required level. Afterwards, a sample was also withdrawn for CO_2 and amine analysis to calculate to the precise level the amount of CO_2 that was being loaded within the solution.

3.1.3 CO_2 and Amine Analysis

The standard solutions used for the CO_2 and Amine Analysis for the samples collected during the experiments were 0.1 N $BaCl_2$, 0.1 N HCl, 0.1 N NaOH and 0.2 N H_2SO_4.

3.2 N2O Solubility

The Physical Solubility of N_2O into DAP 2M was measured using the solubility apparatus shown in figure 6. It consists of a stirred jacketed glass vessel of volume 7.76 $x10^{-4}m^3$. A known mass of solvent is weighed into the reactor (about half the reactor volume). This was then degassed under vacuum at ambient temperature and left until vapor-liquid equilibrium is established; this occurred at about 25mBar. Solvent loss during degassing is minimized by having a condenser at the reactor outlet cooling to about 3.5°C. The reactor was heated to the desired temperature after degassing and the initial temperature and pressure in the reactor and in the N_2O gas holding vessel were recorded. N_2O gas was then added by shortly opening the valve between the N_2O steel gas holding vessel and the reactor. During the experiment the reactor temperature was controlled by circulating water through the jacketed glass reactor. Equilibrium was established after about 4-5 hours and final values were recorded. Pressures were recorded by two pressure transducers Druck PTX 610 and PTX 7517-1 with uncertainty +/- 0.08% (8 bar) and +/-0.1% (2 bar) of full scale, respectively. Temperatures were recorded with K-type thermocouples with accuracy +/- 0.1 °C. All data was acquired using a FieldPoint and LabVIEW data acquisition system.

At equilibrium the partial pressure of N_2O, p_{N2O}, is taken as the difference between the total pressure in the reactor, p_R, and the solvent vapor pressure, p_s^o, wherer the solvent pressure is the measured total pressure in the reactor before adding N_2O. The assumption made is thus that the added N_2O does not change the original solution vapor pressure.

$$p_{N2O} = p_R - p_s^o \tag{3.1}$$

The total amount of N_2O added is calculated from the difference between the initial and final pressure of the N_2O gas vessel after each feeding of N_2O as given in the equation below:

$$n_{N2O}^{added} = \frac{V_v}{RT_v}\left[\frac{p_{v1}}{z_1} - \frac{p_{v2}}{z_2}\right] \tag{3.2}$$

where $p_v$is pressure, $T_v$is temperature, V_v is volume of the stainless steel N_2O gas holding vessel, z is the compressibility factor of the gas and R is the universal gas constant, subscript 1 and 2 denotes the initial and final conditions respectively.

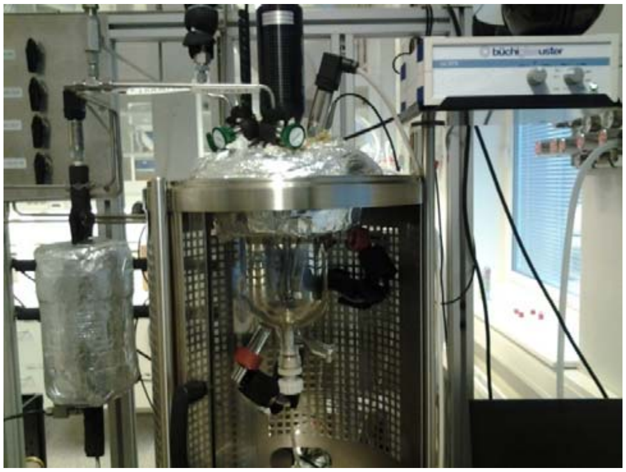


Figure 6:The schematic diagram of the N2O solubility apparatus

The amount of N_2O remaining in the gas phase at equilibrium, n_{N2O}^g , is calculated using eq below.

$$n_{N2O}^{g} = \frac{p_{N2O}\,(V_R - V_S)}{z_{N2O} R T_R} \tag{3.3}$$

Here V_R, V_S, T_R and z_{N2O} are the total reactor volume, volume of solvent, reactor temperature and compressibility factor for N_2O respectively. The density of the solvent is needed to calculate the solvent volume, V_S, and the compressibility factor is calculated using the Peng-Robinson equation of state. The amount of N_2O absorbed into the liquid phase is then the difference between N_2O added, n_{N2O}^{added}, and N_2O remaining in the gas phase, n_{N2O}^{g}. Thus, the concentration of N_2O in the liquid phase C_{N2O}^{l} is calculated by:

$$C_{N2O}^{l} = \frac{n_{N2O}^{added} - n_{N2O}^{g}}{V_S} \tag{3.4}$$

The solubility is thus expressed by Henry`s law constant as

$$p_{N2O} = H_{N2O} C_{N2O}^{l} \tag{3.5}$$

The correlations for density, viscosity and N_2O solubility calculation are derived from experimental data and can be expressed both in terms of molar concentration (mol/l) of the amino acid solvent prepared and in mole fractions (mol/l) of the components used to prepare the solutions. [Aronu, 2011]

3.3 Vapor Liquid Equilibrium

VLE for amine can be measured by two apparatus i.e. Low Temperature Apparatus (LTA) and High Temperature Apparatus (HTA). The gas phase CO_2 concentration or the total pressure (in case of HTA) is measured as a function of temperature and loading. For LTA, the equilibrium was measured at 40°C, 60°C and 80°C at atmospheric pressure while in case of HTA, the equilibrium temperatures were 80°C, 100°C and 120°C at a pressure range of 2 Bar- 10Bar. For lower loading amine solutions the low temperature apparatus was used and for higher loadings of amine solutions the high temperature apparatus was employed.

DAP 2M and DAP 5M amine solutions used to determine the vapour liquid equilibrium, later on the sample solutions collected were tested for amine and CO_2 contents.

3.3.1 Low Temperature Apparatus

The detailed diagram is shown in the figure 7. The solutions of amine were preloaded when being placed in the cell 2-4. The reason lie in the fact that there is no way CO_2 could be added within the apparatus. Preloading was done by adding CO_2 in to the solution until the weighing machine shows no gain. The CO_2 analyser could measure CO_2 in gas phase up to 20%. So the solution was preloaded to maximum then put within the cells labelled 2-4, with each containing up to 150ml of the solution. If the analyser shows more than 20% gas phase CO_2 then the solution is diluted until it lies within the range. Then after setting the desired temperature the circulation pump was turned on. The moment CO_2 analyser reading stabilized, the solution was extracted. A small amount of the collected sample is placed in sample bottle as a sample for the CO_2 and amine content analysis. The remaining solution was diluted carefully again to get a data point that could have a lower gas phase CO_2 %. It should be noted that the calibration should be done on daily basis to avoid uncertainty.

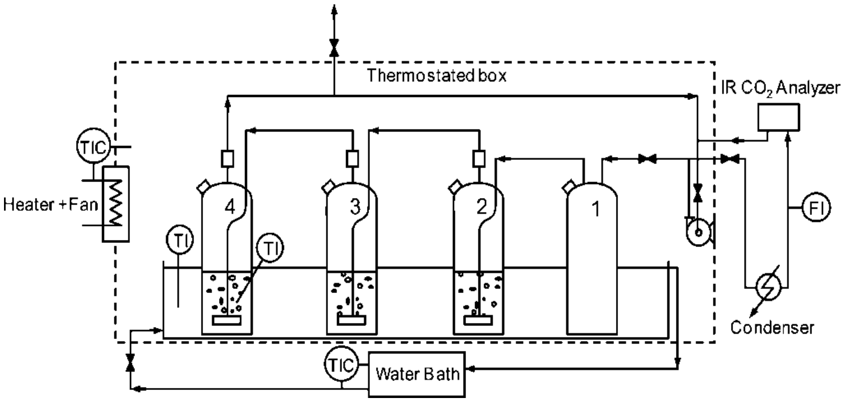


Figure 7: Flowsheet of Low Temperature Apparatus (Ma`mun, 2007)

Calibration curves for DAP 2M

Figure 8 below shows the calibration analysis for channel 1, 2, 3 and 4 as done along the experiment on Low Temperature Apparatus.

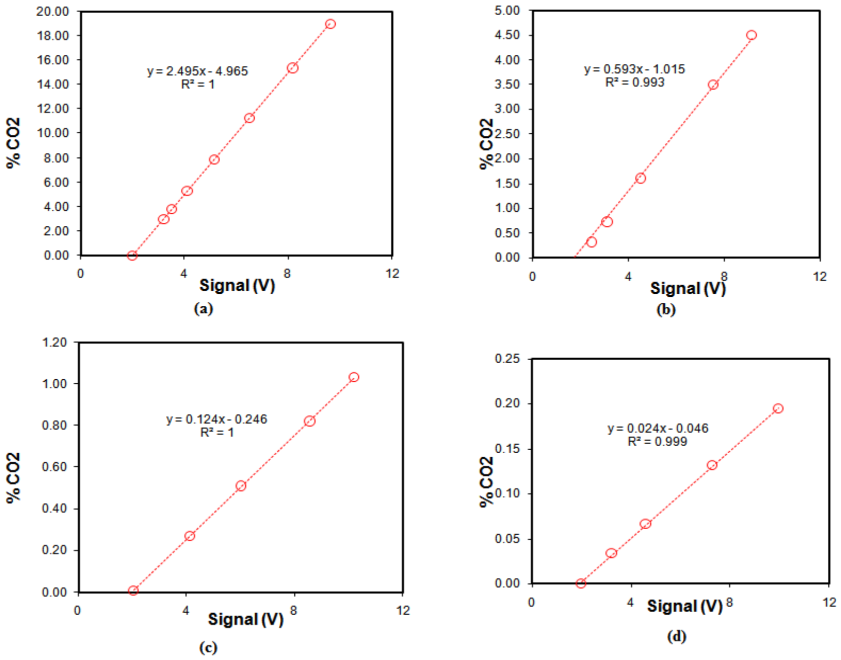
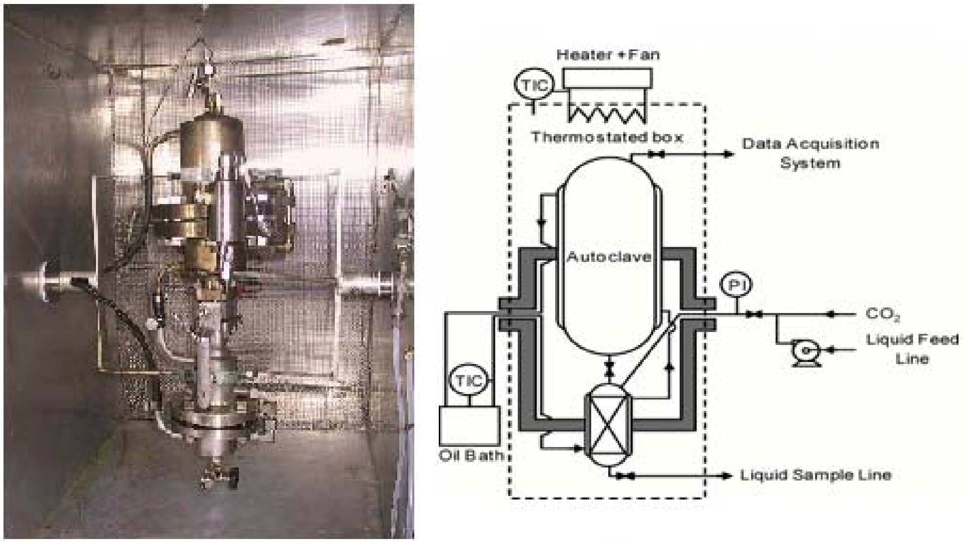


Figure 8: Calibration analysis for DAP 2M at 40°C as shown in the figure (a) channel 4, (b) channel 3, (c) channel 2 and (d) channel 1.

3.3.2 High Temperature Apparatus

Figure 9 depicts the details of the High Temperature Apparatus. The autoclave rotates at 180^o to ensure a mixing is there. The temperature ranges from 80-150^{o}C while the pressure ranges from 1-10 Bar. This apparatus operates at higher pressure so higher loading can be achieved within the solution.



(a) (b)

Figure 9: High Temperature Apparatus for vapor-liquid equilibrium. (a) shows the pictorial representation and (b) shows the schematic depiction [Ma`mun, 2007]

The temperature of the autoclave was maintained by oil bath. 200 ml of the unloaded solution was added by piston pump and the total pressure-temperature was displayed on the computer attached to HTA. The inside of the autoclave was filled with packing material in manner, to ensure good contact between the liquid and the gas phase. The equilibrium was established after 4-6 hr ensuring that the temperature remained constant to ±0.2 °C and pressure ±5 kPa. The sample was taken out from the smaller autoclave using a sampling cylinder of volume. A 75 cm^3 of fresh solution was already been injected into the sampling cylinder, which was then cooled to ambient temperature to test for the CO_2 and amine content.

3.4 CO_2 and Amine Analysis

CO_2 Analysis

CO_2 analysis was being done by the Precipitation method. The liquid sample was added to 250cm^3 Erlenmeyer flask having 50cm^3 of 0.1N NaOH along with 25cm^3 of 0.1N $BaCl_2$. The liquid sample to be added depends upon the amount of CO_2 content in the sample. The flask was heated to an extent such that it boiled for 3-5 min and by doing this Barium Carbonate precipitates were produced. Then the suspension was cooled to room temperature. After this, the content in the flask was filtered with 0.45 µm Millipore paper and washed with deionized water. The remains of the filter paper were collected carefully, and placed in a beaker with 100cm^3 DI water and 0.1N HCl to dissolve the Barium carbonate precipitates. After doing the dissolution, the unused HCl was then titrated with 0.1 N NaOH in an automatic titrator (Metrohm 702 SM Titrino) with an end point of pH 5.3.

Amine Analysis

Due to heat of dissolution and high temperature evaporation resulted in some losses of the amine, so in order to determine the exact concentrations of amine used during the experiments, the amine analysis were run for each experimental reading. This was done by taking the small amount of the liquid sample and blended with 60cm^3 of DI water and after that it was titrated with 0.2N H_2SO_4, using the Metrohm 702 SM Titrator. The end point was attained when the pH lies in a range of 4-5.

3.5 pKa Determination

Mettler Toledo G20 Compact Titrator with a DGi115-SC pH glass electrode (uncertainty +/-0.02) was used for the parallel measurements to dispense approximately 40 cm^3 of amine solution with 0.1M HCl. The readings were taken at a range of 20^{o}C-90 ^{o}C with 10 ^{o}C apart.

Figure 10: pKa Determining module

pKa was defined in the experiment as the point when the pH reaches the half of the neutralization point as shown by the figure 10.

3.6 Density determination

The density data is essential in calculating the Henry`s law constant as far as the solubility calculations are concerned. During this work, the density profiles for DAP unloaded and loaded (0.1, 0.3 & 0.5) were measured using Anton Paar density meter as shown in the figure 11.

Figure 11: Anton Paar Density module

4

RESULTS & DISCUSSION

4.1 Density determination for DAP 2M

The density measurement experiment was performed for the DAP 2M solution, which was first run for unloaded density experiments then for the loading of 0.1, followed by 0.3 loading and lastly for 0.5. To validate the results the DI water was also measured for the density. The results are shown in figure 12.

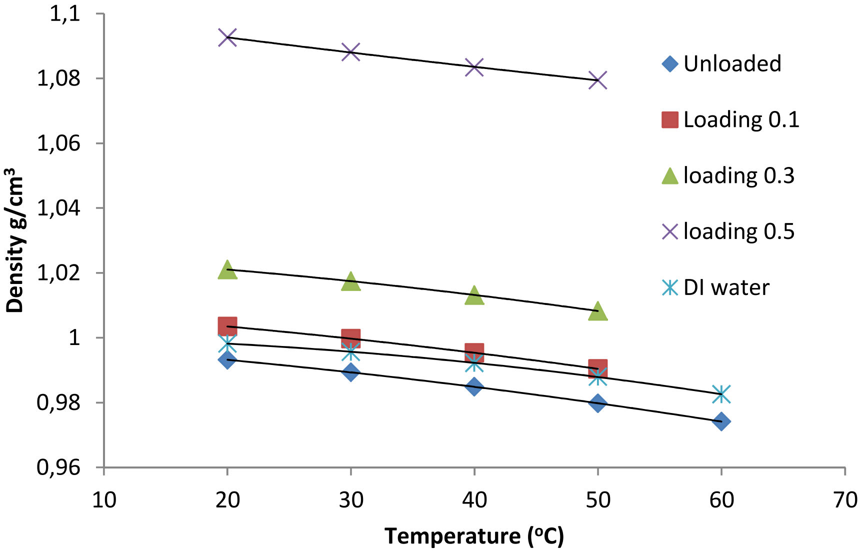


Figure 12: Density results from the experiment done on the DAP 2M unloaded and loaded (0.1, 0.3 and 0.5). DI water density was also determined in order to compare the results

Exception to unloaded DAP 2M and DI water, 0.1, 0.3 and 0.5 loaded solutions were measured for the temperature of 20°C, 30°C, 40°C and 50°C while the former were measured uptil 60°C. All the measured values were in density. The trends shown in the figure 12 shows that the density is minimum for the unloaded solution of DAP 2M then increasing with the increase in the amount of loading. This could be reasoned as the amount of CO_2 per unit volume of solution increases so is the density but with the increase in temperature it observed that the tendency of density is towards the decreasing side. This could be attributed to the fact that if the mass is kept constant then with increase in temperature would enforce higher intermolecular energy to the solution particles causing a slight increase in the volume and hence decreasing the density as a whole.

The density experiment was done in order to provide the Henry`s Constant calculation with the required parameter in terms of DAP 2M density. The data is provided in Appendix **E2**.

4.2 Dissociation Constant-pKa

The dissociation constant is measure of the electron donating capability of an amine i.e. higher the pKa value higher would be the electron donating capability and higher would be the reactivity. As well as this work is concerned, 1,3-Diaminopropane is a primary diamine, hence, it must have two (2) dissociation constants.

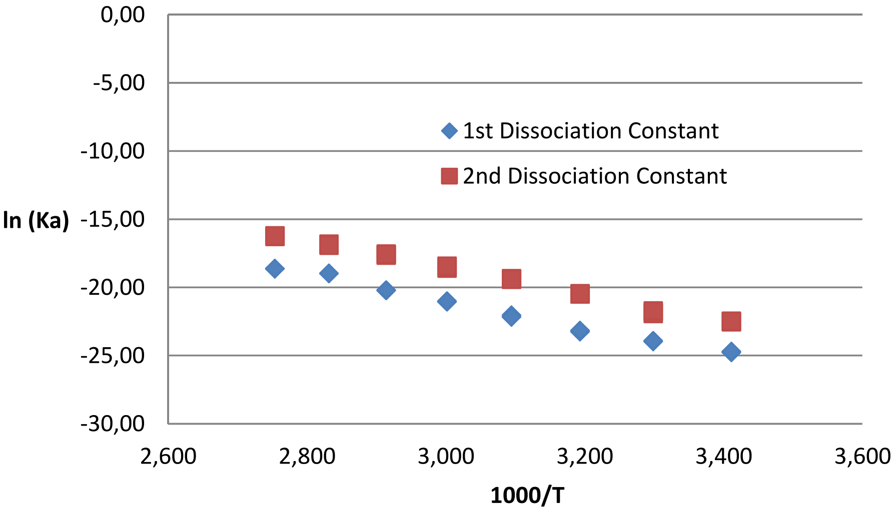


Figure 13: Dissociation Constants for DAP starting form 20^{o}C to 90^{o}C.

The experimental data as shown in the figure 13 shows that the amine is good in reactivity. The data was generated for 20^{o}C, 30^{o}C, 40^{o}C, 50^{o}C, 60^{o}C, 70^{o}C, 80^{o}C and 90^{o}C regarding both the dissociation constant. The increase in temperature tends to decrease both the dissociation constants. It could be further noted that the two dissociation constants are having values quite close to each other which could be justified by looking at the structure of DAP, as shown in section 2.2. The amine is quite symmetrical in structure which makes both the amine group to react with almost the same reactivity, as if comparing with the other amine group of the structure.

The data is provided in Appendix: **E1.** The dissociation constant data for 1,3-Diaminopropane is essentially needed for the modeling of the amine system.

4.3 Henry`s Constant determination for DAP 2M

The Henry's law constant is actually the proportionality of CO_2 pressure in gaseous phase with the CO_2 concentration in the liquid phase. Higher the value means lower the concentration or in other terms higher would be the CO_2 partial pressure in the gas phase which would result in a situation that would describe the CO_2 as if having lower solubility in the liquid phase, see figure 14.

During the experiment, all the data points were retraced except of DAP 2M-B.

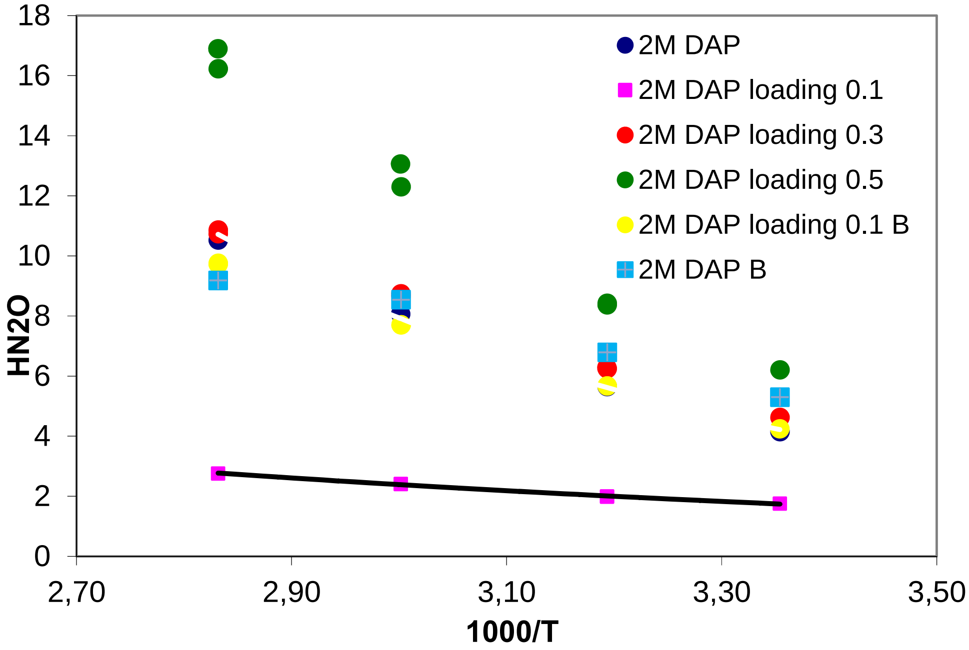


Figure 14: Experimental results of Henry`s law constant of DAP 2M

For the experimental calculations involving Henry`s law constant, the density is direly required, for which the density experiments are performed but for temperatures upto 60°C for unloaded DAP 2M and loaded upto 50°C. Then for the densities of 60°C and 80°C the trend was extrapolated.

Higher loaded solution tends to produce higher CO_2 partial pressure in the gaseous phase which could be observed in the figure 14 showing the results from the experiment. With a rise in temperature, the loaded solution heats up and tends to dissociate CO_2 to the vapor phase and as the loading rises, it literally means that more CO_2 is available to be sent in to the vapor phase, hence, increasing the value of the Henry`s law constant. The trends for 0.1, 0.3 and 0.5 loaded solutions show good agreement with the theoretical justification but as far as the unloaded trend (**blue**) is concerned then it could be observed that value of Henry`s law constant is a bit more than it should have to be. This could say that more CO_2 is present in the vapor as it would have to be. Here, an experimental error could be given the benefit as during the performance of unloaded solubility experiment on DAP 2M, initially the N_2O injected was way more less than it should be. So in order to secure the experiment the N_2O was injected again but noting down the exact moles of the initially present N_2O. This was later on compensated to the end calculations when finally added N_2O moles were subtracted from the initially present gas moles, this time adding to the term the initially injected N_2O. But the results were weird. Experimental error in calculating the initially injected N_2O could be erroneous. Else the unloaded trend would have to be in the most bottom part of the graph.

The trend line at the most bottom (i.e. having a trend line and data points drawn in (pink) is the initial 0.1 loaded experiment which was way too low then with the rest experimental trends. It was later found to have leakage which had compensated for the vapor phase partial pressure. Later on repetition, the 0.1 loaded solution was having quite higher value data points (**yellow**).

The results in detail calculations are shown in the Appendix:**E3.**

4.4 Vapor Liquid Equilibrium

For the vapor liquid equilibrium the 1,3-Diaminoporpane was run in 5M and 2M solutions against low and high temperatures. The calculations are shown in the Appendix:**E4** and **E5**

4.4.1 DAP 5M

The data points shown on the figure 15 represents DAP 5M which shows the CO_2 partial pressure along with the loading on abscissa. The graph is showing the LTA and HTA results plotted for the case of DA 5M on a semi-log plot. For atmospheric pressure the VLE data was collected for 40^oC, 60^oC and 80^oC while for higher pressures, the VLE data was collected for 80^oC, 100^oC and 120^oC.

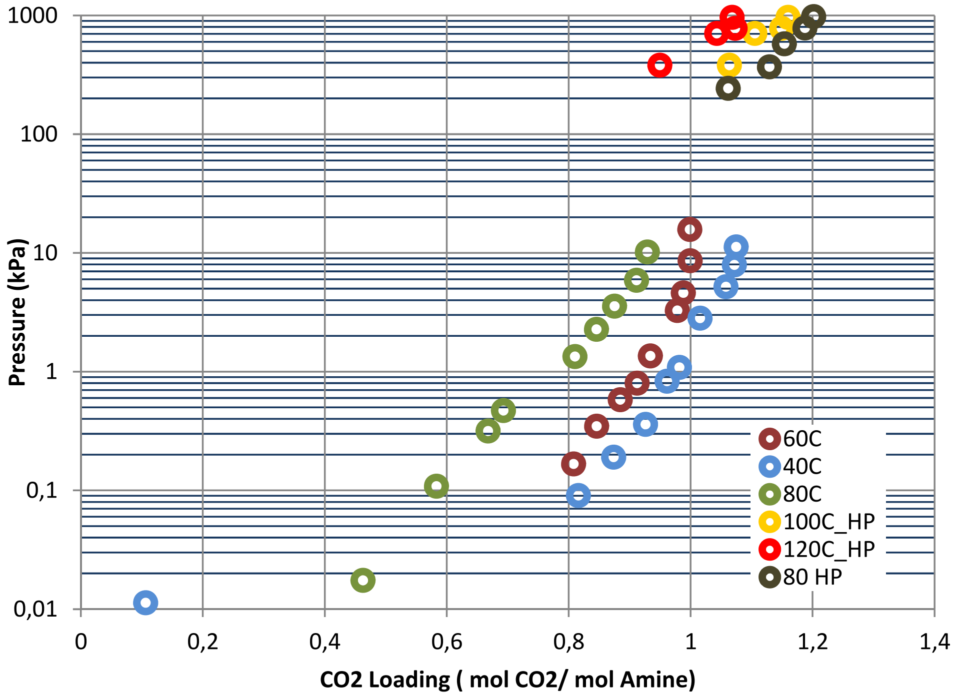


Figure 15:Vapor Liquid Equilibrium data for DAP 5M on the semi-log plot

Lower temperature has lower energy which would not be enough to release that much amount of CO_2 as it would be in the case of the amount of CO_2 release in case of higher temperatures. The trend justifies the theoretical study for low temperature data points as well as the higher temperature data points, as predicted by eq 2.18 and 2.19. As low as 0.10 loading is attained with CO_2 partial pressure of 0.011kPa for 40^{o}C and the maximum loading goes upto 1.20 with a partial pressure of 980kPa for 80^{o}C.

4.4.2 DAP 2M

Figure 16 is attributed to VLE data points for DAP 2M as shown on a semi-log plot with CO_2 partial pressure on vertical axis and loading on the horizontal axis. The trend are quite clear in the entire spectrum of high temperature and low temperature experimental runs.

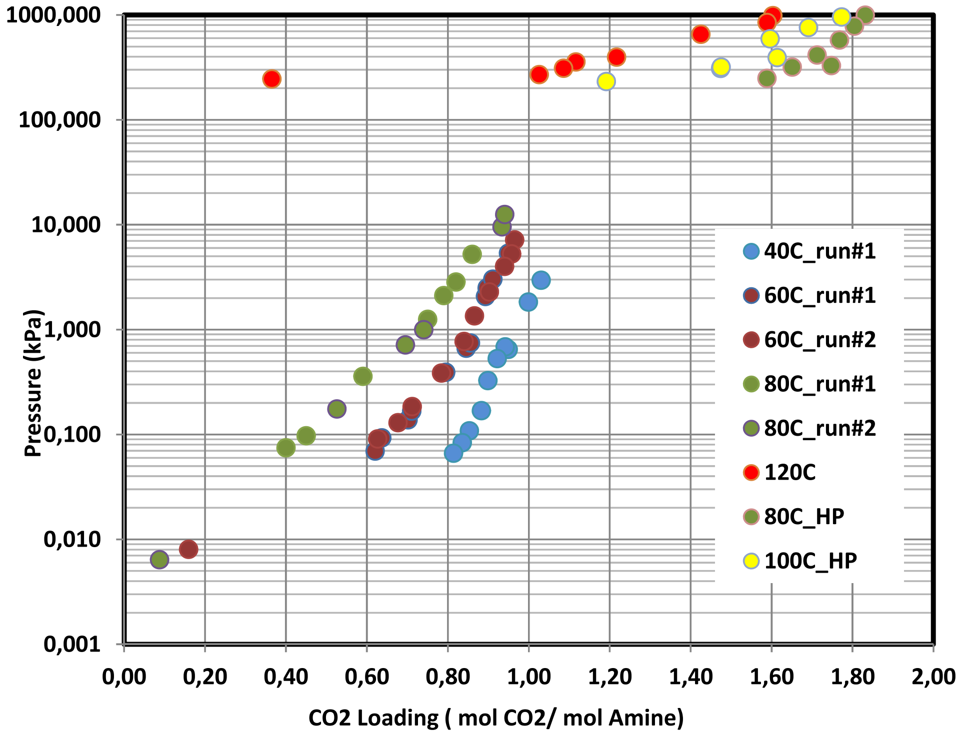


Figure 16:Vapor Liquid Equilibrium data for DAP 2M on the semi-log plot

While performing low temperature VLE DAP 2M experiment, the data points were retraced as well which showed good consistency and reproducibility as well as the initial points was concerned. These points are shown on the figure 16 as run#2. High temperature data points show exceptional high loading which is weird. The CO_2 and amine analysis were performed with precision between the two parallel at max to 3.00%. The calculations were rechecked with out any dispute. The only attribution that could be made in the case is the pressure transducer was not calibrated which has produced erroneous result.

4.4.3 Comparing DAP 5M and DAP 2M

Figure 17 below shows the comparison of DAP 5M with DAP 2M as well as the VLE data is concerned. Although the individual trends seems fine but the overall representation showed some absurd behaviour especially when low temperature data points are considered.

The DAP 5M are considered to be the data points which could be trusted as far as the DAP 2M is concerned then, the latter was a part of training as well and during the performance of the experiment N_2 was not flushed through the 3 cells (shown in the figure 7) to create an inert environment in fact the experiment was started as such. These data points were meant to be improved in the latter session but the only constraint that was prevailing over the project was”time”.

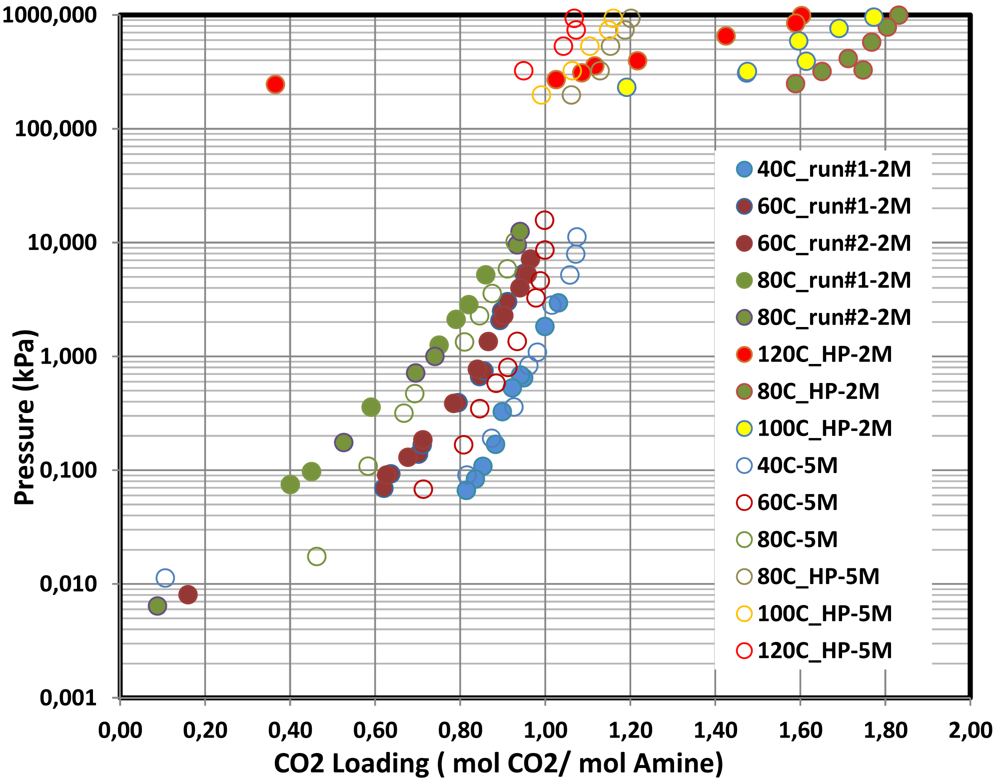


Figure 17: Data point for DAP 5M (with circles) and DAP 2M (with filled points) for low and high temperatures

The condensate collected during the experimental run was also tested for amine content but with negligible traces which can attribute to the scenario that DAP does not evaporate to a significant level.

4.5 Modeling

The figure 18, 19, 20 and 21 shows the model by using e-NRTL model and depicted on in-house tool Modfit to compare with the experimental results. 265 attritions were done to produce the following results and the rest were shown in Appendix: **M1** . The P_{CO2} and P_{Total} were plotted as a function the loading of DAP 2M and 5M at the temperatures of 40^{o}C, 60^{o}C, 80^{o}C, 100^{o}C, and 120^{o}C. The critical properties were being taken from DIADEM 2004 V4.1.0: Information and data evaluation manager for the design institute for physical properties.

4.5.1 P_{CO2} and Loading

For the modeling results for P_{CO2} and loading the AARD (Average Absolute Relative Deviation percent) = 37.4289 % could have been lesser. The isotherm in the figure 18 shows that the model at very low loading was underpredicting the experimental points but by proceeding with the loading the model synchronized well with the experimental results, although deviating a bit but was good in modeling the highest loading points.

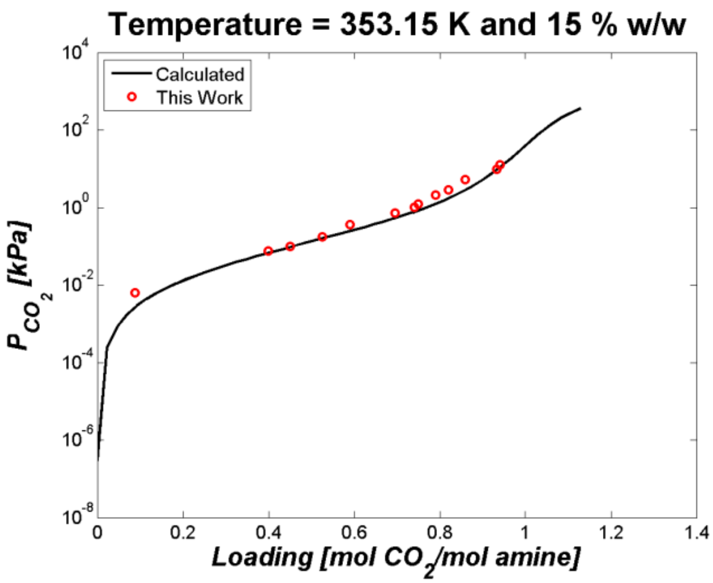


Figure 18: P_{CO2} plotted against loading for 80°C and DAP 2M

At low loading, the concentration of carbamate formation was very high as the DAP has the structure, as shown in the figure 24 and 26, is fast in accepting CO_2. Later on the dicarbamate formation triggers a constant increase until the DAP deplete out at the loading of 1. So at this stage either the amine is protonated or reacted to form carbamate/bicarbamate. After loading of 1, the P_{CO2} tends to increase further but on account of depletion of carbamate/bicarbamate. The carbon dioxide released at this point is used to convert the carbamate/bicarbamate to bicarbonate which further adds CO_2 to the vapor phase.

While looking at the figure 19, the model does not seem to converge to a convincing solution. It is obvious from the figure that the model is converging to two solutions for the experimental results which is inconclusive. At low loading, it can be inferred that the model is predicting a solution but then suddenly move to another solution. Then, at moderate loading the model and the experimental data fits well with each other of some loading and partial pressure range but then at loading of 1 the model is highly underpredicting the experimental results.

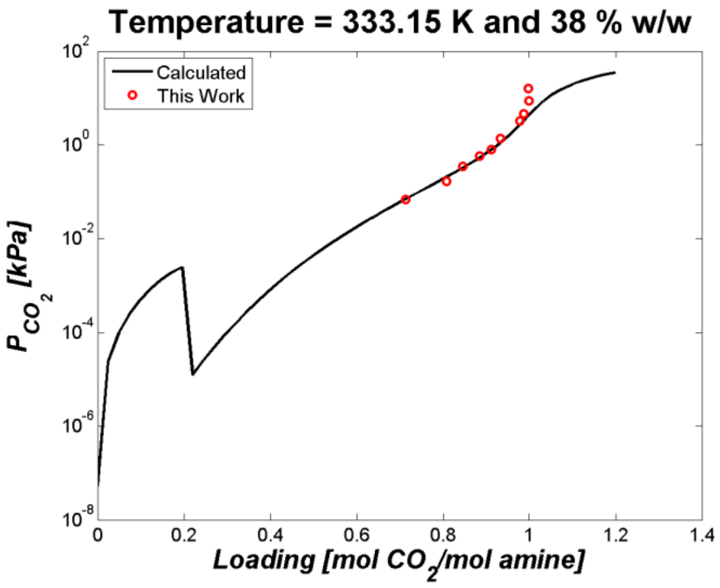


Figure 19: P_{CO2} plotted against loading for 60°C and DAP 5M

This makes it deducible that more experimental data points are needed to model accurately specially for lower loadings where the model is non-convergent, although, for an industrially applicable amine systems, it is preferred that the amine should have to be loaded to the maximum capacity. The list of parameter and their respective values are shown in the Appendix:**M3.**

4.5.2 P_{Total} and Loading

The figure 20 relates the P_{Total} as a function of loading. The P_{Total} model is overpredicting slightly but it has AARD = 26.0773% which seems fine. With the increase in the loading, the P_{Total} increases. P_{Total} is almost a straight line, this is due to the fact that at low loading P_{CO2} approaches to 0, see figure 19. For the loading up to 1, the slope is not that much if compared to the slope for the loading higher than 1, see figure 18.

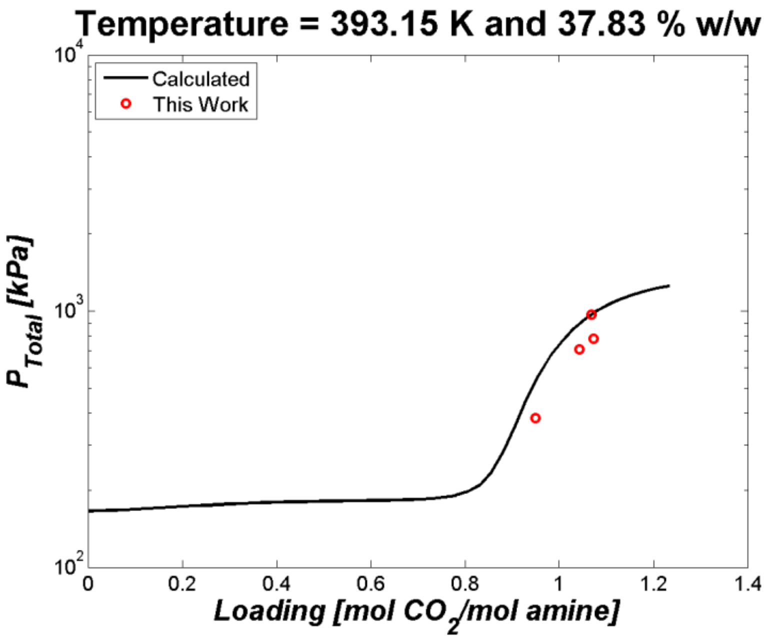


Figure 20: PTotal plotted against loading for 120°C and DAP 5M

Although the model is slightly over predicting P_{Total} but can be good in a sense that the equipment designed using this model would be able to meet the disturbances.

4.5.3 Consistency Test

For the validation of the models, a consistency test was performed to verify the authenticity of the method. Figure 21 shows the consistency test of P_{CO2}model and P_{CO2} experimental. The model agrees well with the experimental data.

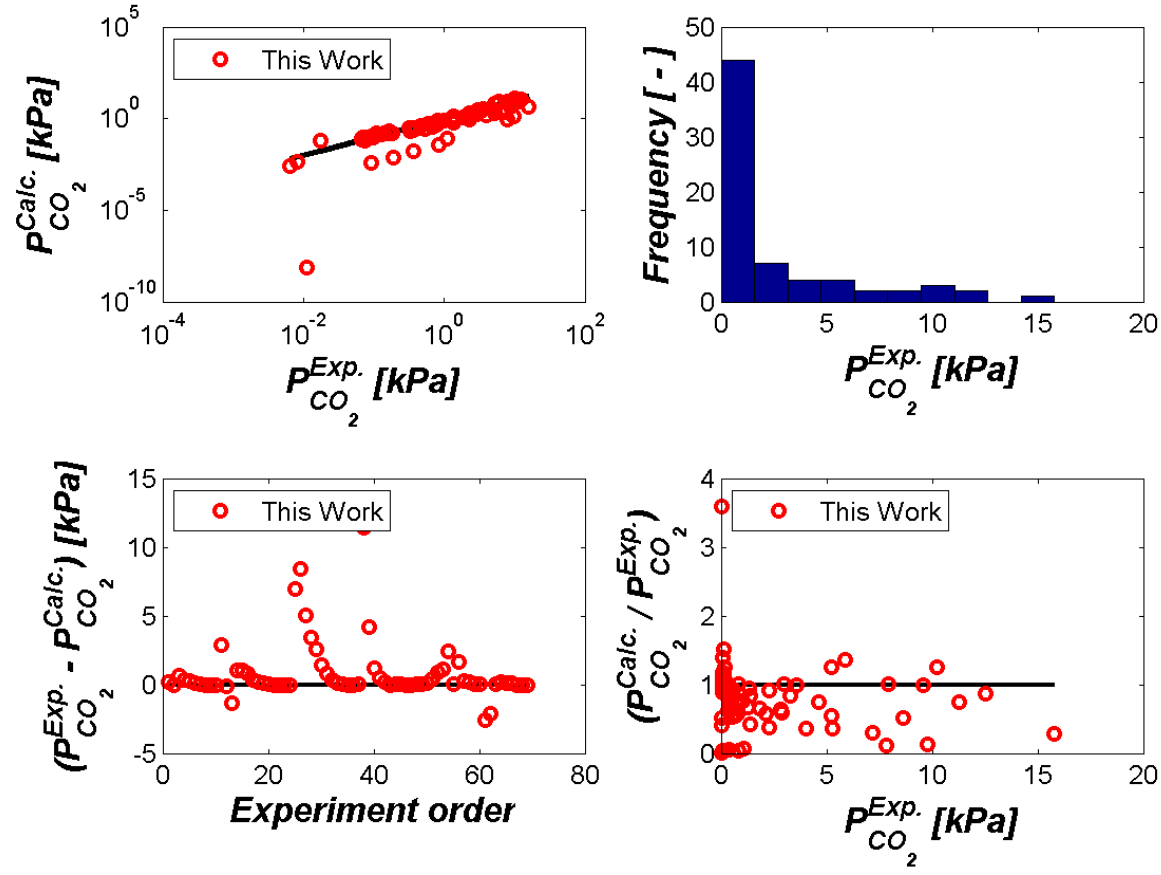


Figure 21: Consistency test for modeled and experimental PCO_2

5

COMPARISON WITH OTHER LITERATURE

5.1 Dissociation constant (pKa)

Dissociation constant shows the potential of generating an ion in a solution.

5.1.1 Comparison with MEA

The experimental results for dissociation constant determination of DAP are compared with MEA uptil 50°C [Bates, R.G. & Pinching G.D. 1954], as shown in the figure below.

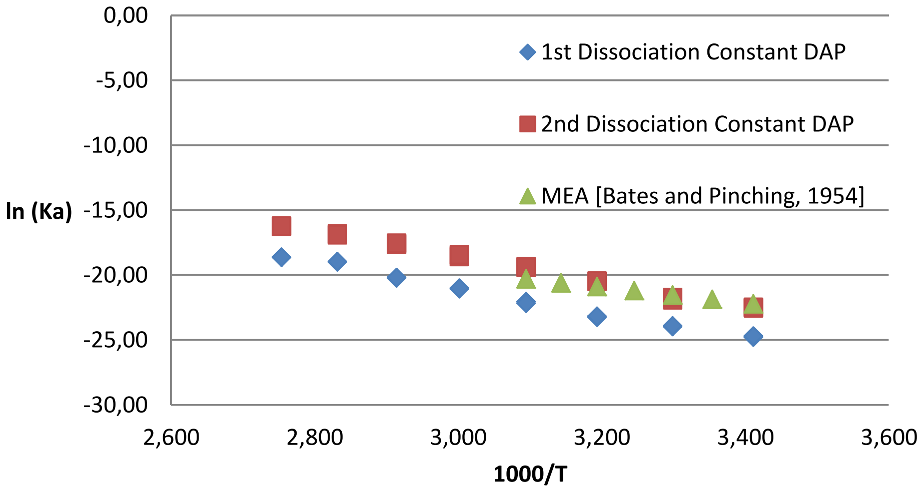


Figure 22: Dissociation constant data comparison of present work with MEA [Bates and Pinching, 1954]

It could be treated as higher the Ka (dissociation constant) higher would be the reaction rate [Versteeg, et al, 1996]. If MEA is showing a trend which could be extrapolated then, it is crossing the DAP-Ka_2 profile uptil DAP-Ka_1 profile. Hence, it could be stated that at lower temperatures MEA reaction rates would be a bit slower if comparing with DAP. But at higher temperature, if MEA follows the same trend, then the MEA would be faster even than the 1st dissociation constant. If only dissociation constants are considered then, DAP would be faster at lower temperatures while MEA would be a better choice at higher temperatures.

5.1.2 Comparison with Piperazine

After comparing with the base case of MEA, it would be a lot better to compare DAP with a diamine i.e. Piperazine as shown in the figure 23 [Hetzer, H.B, 1968].

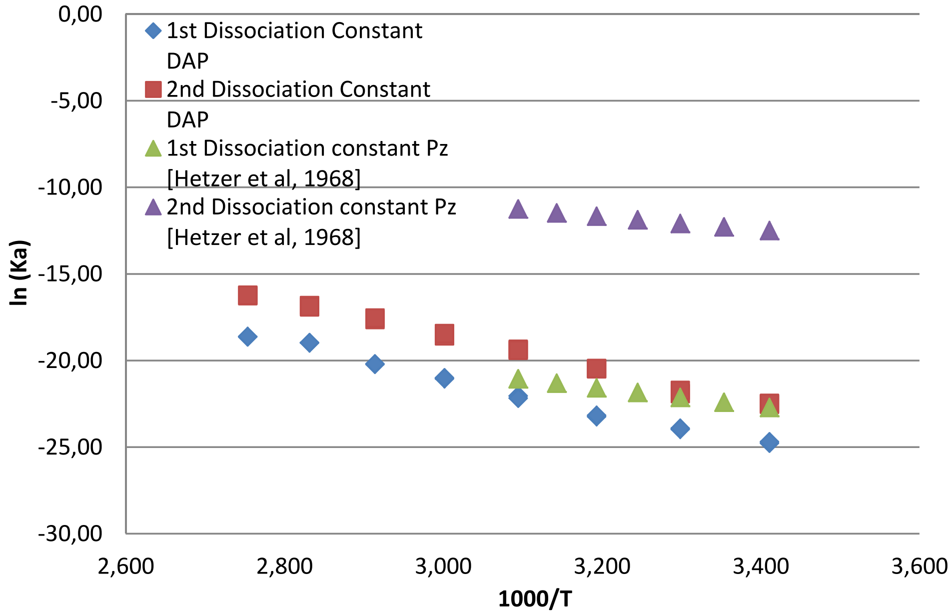


Figure 23: Dissociation constant data comparison of present work with Piperazine [Hetzer, et al, 1968]

In figure 23, the Ka_1 for Piperazine is somewhat similar to MEA but Ka_2 is quite smaller. It can be said in a way that at lower temperatures, DAP reaction rates are faster if Ka_1 is considered from Piperazine, only and as higher temperature are considered then Piperazine would yield a faster reaction rate. As far as the Ka_2-Piperazine is evaluated then its reactivity is way less than the Ka_2-DAP. The reason lie in the structure of the two; DAP is a straight chain with both amines attached to the far end as shown in the figure below, while Piperazine is cyclic which makes the 2nd dissociation of amine a lot more difficult.

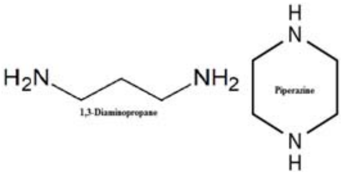


Figure 24: Structure comparison of DAP and Piperazine

5.2 Solubility

Henry`s law constant is a relation of the $CO_2$ in vapor phase with the $CO_2$ in liquid phase. By referring to the figure 25, it could be stated that the Piperazine (1.5M & 0.5M) is having a higher value of Henry`s law constant for the same temperature of DAP 2M.

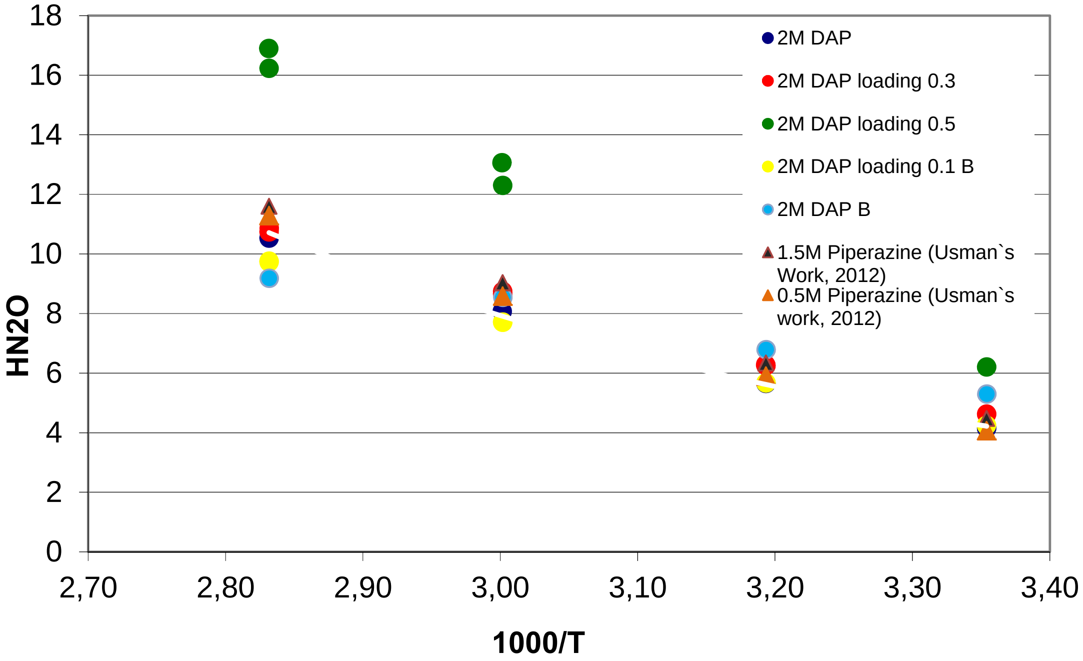


Figure 25: Solubility data comparison of DAP with Piperazine [Usman`s Thesis, 2012]

The gaseous phase in not only having water vapors + N_2O (an analogy used instead of CO_2) but Piperazine is also having some fraction in the gaseous phase which is true for the higher value of the Henry`s law constant. Piperazine being volatile tends to show the property in the compared results with DAP 2M.

5.3 Vapor Liquid Equilibrium

VLE data of DAP is compared with MEA, the most investigated amine and Piperazine, another diamine.

5.3.1 Comparison with MEA 15 wt% and 30 wt%

Figure 27 and 28 illustrates that MEA 15wt% has the equilibrium profile higher for the same loading of DAP 15.18 wt% (2M). The structure of MEA plays an important role for higher partial pressure; figure 26 depicts the structural difference between the two. MEA has the maximum loading of 0.5 while DAP, being diamine, is having 1. This fact contributes to the P_{CO2} of MEA to be higher for the same loading.

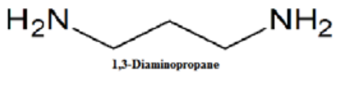


Figure 26: Structure comparison of DAP and MEA

By looking at the structure of MEA, the –OH group present in MEA tends to form Hydrogen bonding with water in the liquid phase while on the other hand, DAP does not seem to have this influential interaction. This factor makes DAP more susceptible to react with amine, CO_2 and any other species being formed in the process.

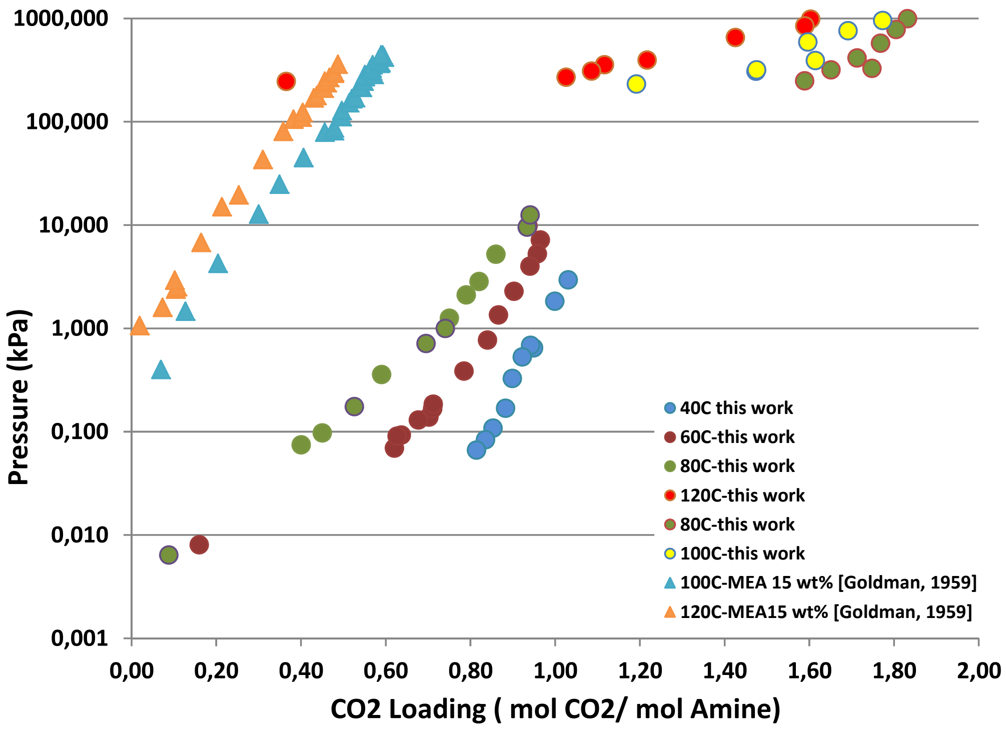


Figure 27: Comparison of DAP 2M with MEA 15 wt% [Goldman, 1959]

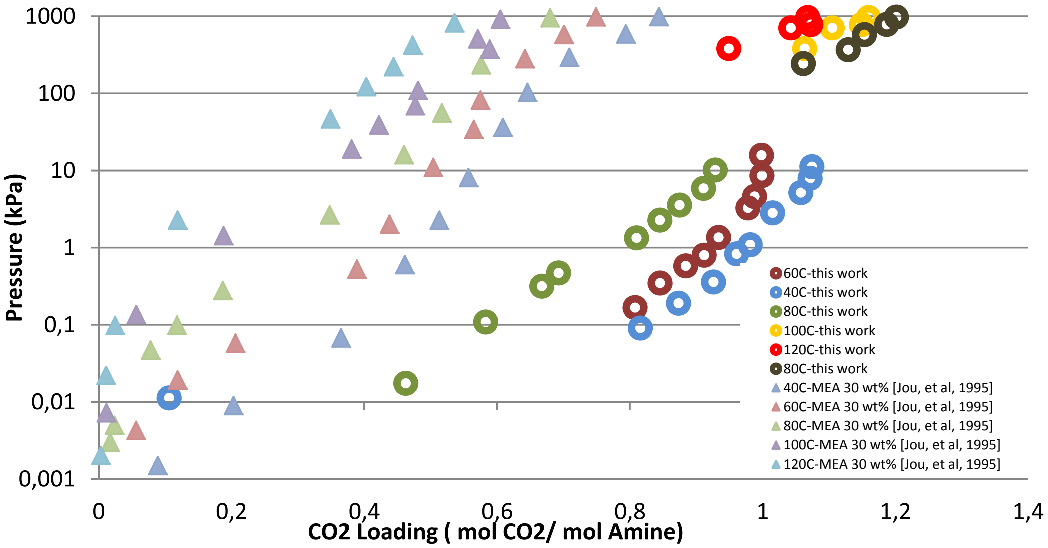


Figure 28: Comparison of DAP 5M with MEA 30wt% [Jou, et al, 1995]

MEA is being compared with DAP as it is the most investigated amine as far as any other amine is concerned. MEA tends to be the most applicable amine in the industry, as well. Else DAP and MEA are different in reaction mechanisms (DAP forms dicarbamate), structure (MEA is monoamine), physicochemical properties and different cyclic capacity (MEA=0.5 and DAP=1)

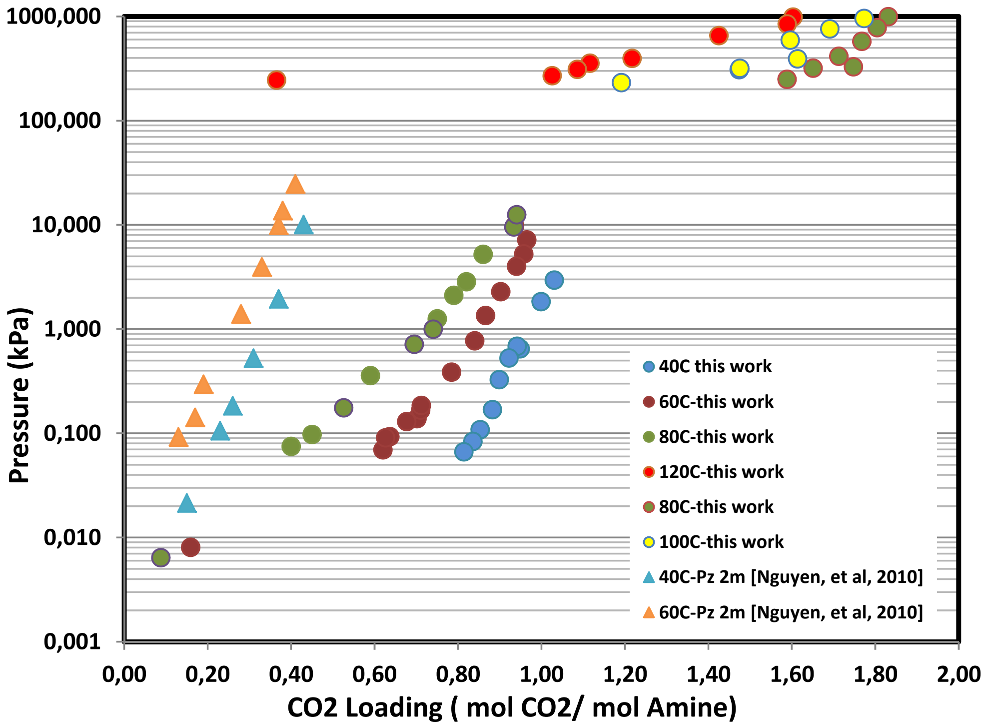


Figure 29: Comparison of DAP 2M with Piperazine 2m [Nguyen, et al, 2010]

5.3.2 Comparison with Piperazine 2m and 5m

Piperazine is a diamine with a cyclic structure. By looking at the figure 29 and 30 it shows that Piperazine is having higher P_{CO2} for the same loading of DAP. It can be concluded that at all concentrations partial pressure of CO_2 is higher for Piperazine compared to DAP. This shows that DAP has higher tendency to absorb CO_2 even at low partial pressures.

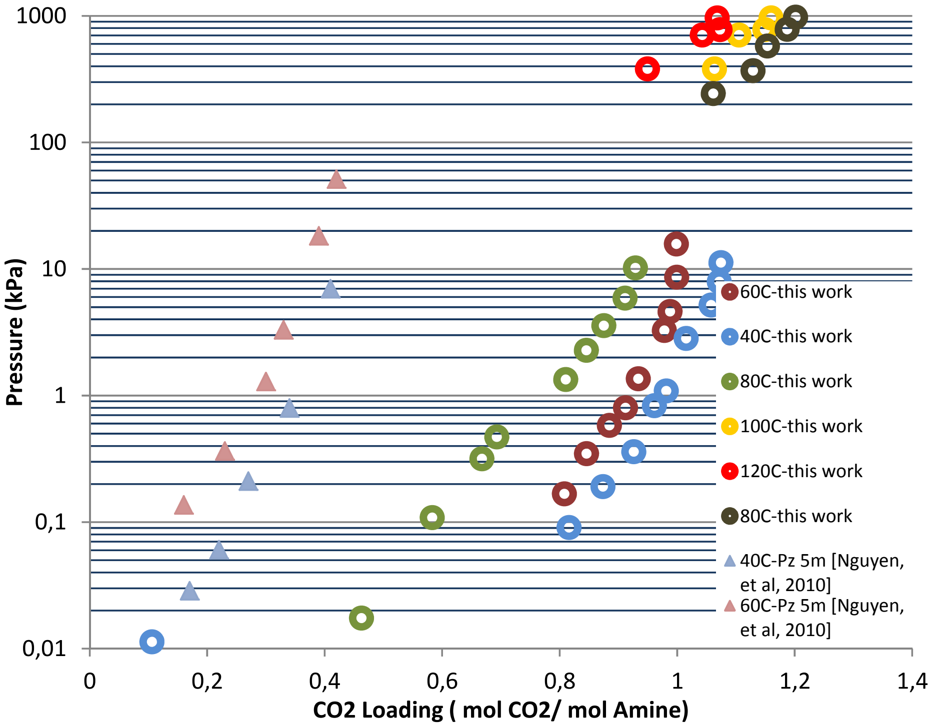


Figure 30: Comparison of DAP 5M with Piperazine 5m [Nguyen, et al, 2010]

6

ERRORS & RISK ANALYSIS

6.1 Errors

1,3-Diaminopropane used during the thesis work including density, dissociation constant, Henry`s constant and Vapor-liquid equilibrium was of 99.0% purity. The entire post-experimental calculations and modeling were done by treating the amine as 100.0% purity, which means that the remaining 1.00% amine actually did not contain any active amine which could affect the results significantly, at any stage. The titration results of the DAP solution of different concentrations showed the percentage difference to be less than 1% if compared to the gravimetric analysis, hence it could be assumed that the assumption stood fine within the scope of this work.

6.2 Risk Analysis

The amine used during this work was flammable, corrosive, toxic and produce fumes when placed in the pure form. This induced extreme cautions on the use and the handling of the chemical when preparing the solutions for different experimental analysis, running the experiments, collecting the samples and disposing off the remains of the experiments and samples. Lab coat, safety goggles and safety gloves were supposed to be compulsory articles of the lab work dress code. DAP was seen to leave the ***white residue*** even in solution form when left to dry in open air, which could be an environmental concern as well.

A complete detail of the Material Safety Data Sheet of 1,3-Diaminopropane is also attached as Appendix: **S** at the end of the report from Sigma Aldrich, the provider of the amine during the work.

7

CONCLUSIONS

7.1 Experimental part

- From the solubility experiment, it can be deduced that the amount of CO_2 getting dissolved in 1,3-Diaminopropane is more than Piperazine.
- Dissociation constant (Ka_1) for 1,3-Diaminopropane is higher than Monoethanol amine for lower temperatures but as the temperature increases, then at higher temperatures, Monoethanol amine has higher Ka_1 value instead of 1,3-Diaminopropane.
- Higher the dissociation constant, higher would be the reaction rates [Versteeg, 1996] and in the same manner, it can be concluded that at higher temperatures Monoethanol amine is having high reactivity than 1,3-Diaminopropane. While at lower temperatures, 1,3-Diaminopropane shows high reaction constant if compared with Monoethanol amine.
- 1st amine group of Piperazine is having high reactivity at high temperatures and low reactivity at low temperatures by comparing with 1,3-Diaminopropane. But for the case of 2nd amine group it is very slow in reactivity.
- From the dissociation constant results, it can be stated that 1st and 2nd amine groups of 1,3-Diaminopropane exhibit almost the same reactivity, as depicted by the structure of the amine as well.
- At all studied conditions, it was found that 1,3-Diaminopropane produced lesser equilibrium partial pressure of CO_2.
- At low loadings, the experimental data is susceptible to errors when the lower channel is under consideration (i.e. 2000 ppm channel).
- 1,3-Diaminopropane produces white residue when left to dry which increases the chances of experimental errors.
- There is not much literature available for 1,3-Diaminopropane, hence, the present work can be used as a guideline for the future work.

7.2 Modeling part

- e-NRTL is semi-empirical model for which a lot of data, efficient regression tool and sufficient time is required. But due to shortage of time, the regression period was compromised and hence, modeling lacks in some accurate convergence of the experimental results.
- More experimental data points are needed to support the model at low loadings, although industrially, the amine is supposed to be loaded to the maximum limit.
- -OH ions are an important species at low loadings and affect the vapor liquid equilibrium in the range. So accurate pH and conductivity data is significant for the better fitting of VLE data.
- e-NRTL is efficient enough for extrapolating and interpolating the experimental data, adequately.

8

RECOMMENDATIONS FOR FUTURE WORK

Based on this work, 1,3-Diaminopropane shows high solubility compared to Piperazine, appreciable reaction rate with regards to Monoethanol amine and lower equilibrium partial pressure with both above mentioned amines.Hnece, it should be further investigated as a promoter for blended amine systems.

8.1 Experimental part

- It is suggested that the data points for vapor liquid equilibrium of 1,3-Diaminopropane 2M at higher temperature and the data from N_2O solubility experiment for unloaded 1,3-Diaminopropane should be repeated to verify the experimental trends.
- The sampling method for Low temperature apparatus should be improved. It employs the technique of sucking the sampling solution through the syringe which in case of viscous liquids is very tedious and risking towards liquid spillage.

8.2 Modeling part

- More experimental data is required for low loadings in order for better convergence of the model and ensuring the validity of the trend, at low loadings.
- The time given to model the experimental data points was scarce so, it is suggested that more time should be given to regression.
- e-NRTL and NRTL are both available in the Aspen Tech Hysys. By using the generated parameters during the modeling of this work, it is possible to simulate the CO_2 capture plant.

9

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APPENDICES

A: List of figures

B: List of symbols

C: Solution Preparation Sheet for DAP

M1: Modeling results

M2: Activity Coefficient expressions

M3: Modeling parameter of e-NRTL and nonrandomness

S: Material Safety Data Sheet of DAP

Experimental results

E1: Dissociation Constant (DAP)

E2: Density determination of DAP 2M Unloaded and loaded (0.1, 0.3, 0.5)

E3: N_2O Solubility Experiment of DAP 2M Unloaded and loaded (0.1, 0.3 & 0.5)

E4: Sample calculations of Low Temperature Experiment for DAP 2M at 40^0C.

E5: Sample calculations of High Temperature Experiment for DAP 5M at 80^0C.

E6: CO_2 & Amine analysis sheet

Risk analysis sheet

R1: VLE

R2: N_20 solubility apparatus

Appendix A:Table of Figures

Appendix B: List of Symbols

α	Activity
A_ϕ	Debye-Hückel parameter
b	Parameter of Soave-Redlich-Kwong equation of state
C	Parameter of electrolyte-NRTL equation
d	Density
D	Dielectric constant
e	Electron charge
f	fugacity
g	Molar Gibbs free energy, energy of interaction in electrolyte-NRTL equation
G	Parameter of electrolyte-NRTL equation
H	Henry's law constant
I	Ionic strength
K	Equilibrium constant of chemical reaction
k	Boltzmann's constant
M	Molar mass
m	Molality
N_0	Avogadro's number
P	Pressure
p	Partial pressure
R	Gas constant
r	Ionic radius
T	Temperature
v	Molar volume
x	Mole fraction in liquid phase
X	Effective mole fraction
y	Mole fraction in gas phase
Z	Absolute value of ionic charge
z	Ionic charge

GREEK LETTERS

ν	Stoichiometric coefficient
μ	Chemical potential
γ	Activity coefficient
φ	Fugacity coefficient
Θ	Poynting factor
ρ	Closest approach parameter of the Pitzer-Debye-Hückelequation, Denity
α	Non-randomness factor of electrolyte-NRTL equation, Parameter of Soave-Redlich-Kwong equation of state
τ	Interaction energy parameter of electrolyte-NRTL

	equation
ω	Accentric factor

SUBSCRIPTS

a, a’	Anion
c, c’	Cation
i, j, k	Any species
m	Molecular species
ref	Reference state
s	Solvent
w	Water

SUPERSCRIPTS

∞	Infinite dilution
0	Property evaluated at standard state
E	Excess property
L	Liquid phase
s	Saturation
V	Vapor phase

Appendix C: Solution preparation sheet for DAP 2M and 5M

Chemical	Molecular Weight (g/mol)	Purity	Dated	Molarity	Mass of Chemical added (g)	Mass of Water added (g)	Mass fr. of Chemical	Mass fr. of Water	Comments
DAP	74.12	99%	12.02.2012	2M	299.5	1673.0	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	13.02.2012	2M	299.5	1672.9	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	16.02.2012	2M	299.5	1673.0	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	27.02.2012	2M	299.5	1673.0	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	12.03.2012	2M	299.5	1672.9	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	27.02.2012	2M	299.5	1673.0	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	02.04.2012	2M	299.5	1672.9	0.1518	0.8482	2 L of solution (room temp)
DAP	74.12	99%	09.04.2012	5M	748.7	1230.3	0.3783	0.6217	2 L of solution (room temp)
DAP	74.12	99%	09.04.2012	5M	748.7	1230.3	0.3783	0.6217	2 L of solution (room temp)
DAP	74.12	99%	18.04.2012	5M	748.7	1230.3	0.3783	0.6217	2 L of solution (room temp)
DAP	74.12	99%	19.05.2012	5M	748.7	1230.3	0.3783	0.6217	2 L of solution (room temp)

Appendix E: Experimental Results

E1: Dissocaition Constant (DAP)

	EDA				DAP			
	pKa1	pKa2	rel dev		pKa1	pKa2	rel dev	
20	10.111	8.531	0.018	0.011	10.759	9.781	0.036	0.023
20	10.129	8.542			10.723	9.758		
30	9.826	8.312	0.018	0.074	10.409	9.512	0.026	0.08
30	9.844	8.238			10.383	9.432		
40	9.602	7.879	0.016	0.022	10.094	8.892	0.035	0.011
40	9.618	7.901			10.059	8.881		
50	9.386	7.235	0.005	0.014	9.571	8.401	0.057	0.024
50	9.391	7.249			9.628	8.425		
60	8.708	6.731	0.006	0.039	9.142	8.065	0.021	0.061
60	8.714	6.692			9.121	8.004		
70	8.341	6.138	0.024	0.017	8.781	7.654	0.012	0.036
70	8.365	6.121			8.769	7.618		
80	8.129	5.548	0.008	0.023	8.245	7.302	0.01	0.037
80	8.137	5.571			8.235	7.339		
90	7.859	5.184	0.011	0.012	8.092	7.058	0.011	0.017
90	7.87	5.172			8.081	7.041		

	EDA				DAP			
	ln(Ka1)	ln(Ka2)	rel dev		ln(Ka1)	ln(Ka2)	rel dev	
20	-23.28	-19.64	-0.18	-0.13	-24.77	-22.52	-0.34	-0.24
20	-23.32	-19.67			-24.69	-22.47		
30	-22.63	-19.14	-0.18	-0.89	-23.97	-21.90	-0.25	-0.84
30	-22.67	-18.97			-23.91	-21.72		
40	-22.11	-18.14	-0.17	-0.28	-23.24	-20.47	-0.35	-0.12
40	-22.15	-18.19			-23.16	-20.45		
50	-21.61	-16.66	-0.05	-0.19	-22.04	-19.34	-0.59	-0.29
50	-21.62	-16.69			-22.17	-19.40		
60	-20.05	-15.50	-0.07	-0.58	-21.05	-18.57	0.048354	0.140458
60	-20.06	-15.41			-21.00	-18.43		
70	-19.21	-14.13	-0.29	-0.28	-20.22	-17.62	0.027631	0.082893
70	-19.26	-14.09			-20.19	-17.54		
80	-18.72	-12.77	-0.10	-0.41	-18.98	-16.81	0.023026	0.085196
80	-18.74	-12.83			-18.96	-16.90		
90	-18.10	-11.94	-0.14	-0.23	-18.63	-16.25	0.025328	0.039144
90	-18.12	-11.91			-18.61	-16.21		

E2: Density determination of DAP 2M Unloaded and Loaded (0.1, 0.3 & 0.5)

T emp	DAP unloaded			DI water after unloaded			DAP alfa=0.1		
	1st run	2nd run	averaged	1st run	2nd run	averaged	1st run	2nd run	averaged
20	0.99318	0.99318	0.99318	0.99822	0.99822	0.99822	1.00348	1.00347	1.003475
29.99	0.98935	0.98935	0.98935	0.99563	0.99562	0.995625	0.99974	0.99974	0.99974
39.99	0.98486	0.98486	0.98486	0.99222	0.99222	0.99222	0.99535	0.99535	0.99535
49.99	0.97977	0.97977	0.97977	0.98799	0.98796	0.987975	0.99041	0.99041	0.99041
59.99	0.97416	0.97415	0.974155	0.98254	0.98214	0.98234	x	x	x

T emp	DAP alfa=0.3			DAP alfa=0.5		
	1st run	2nd run	averaged	1st run	2nd run	averaged
20	1.02103	1.02103	1.02103	1.09257	1.0926	1.092585
29.99	1.01749	1.01748	1.017485	1.08816	1.08813	1.088145
39.99	1.01318	1.01317	1.013175	1.08345	1.08335	1.0834
49.99	1.00825	1.00827	1.00826	1.07945	1.07945	1.07945
59.99	x	x	x	x	x	x

E3: N_2O Solubility experiment of DAP 2M Unloaded and Loaded (0.1, 0.3 & 0.5))

Volume of vessel	1035.05	cm^3
Volume of reactor	1051.01	cm^3

3,7599E+08e-4,8085E+00x

y = 8,6662E+07e-4,2266E+00x

Run No.	Atmosphere			Solvent Added		Gas Vessel						$n_{N2O\ added}$, kmol	Reactor						
						INITIAL			FINAL				INITIAL			FINAL			
	T_{atm}, °C	P_{atm}, mmHg	P_{atm}, mbar	W_1, g	W_2, g	T_{v1}, °C	P_{v1abs}, mbar	z_1	T_{v2}, °C	P_{v2abs}, mbar	z_2		P_{R1abs}, mbar	T_{R1}, °C	P_{Rmax}, mbar	P_{R2abs}, mbar	T_{R2}, °C	P_{N2O}	z
2M DAP																			
1	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	1907.30	120.00	0.00	3001.45	120.00	1094.15	0.997270
2	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	965.35	100.02	0.00	1959.99	100.00	994.64	0.997026
3	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	447.67	80.00	0.00	1375.54	80.00	927.87	0.996780
4	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	189.13	60.03	0.00	1034.97	60.03	845.84	0.996506
5	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	79.06	40.00	0.00	823.05	40.00	743.99	0.996252
6	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	39.61	25.00	0.00	700.55	25.00	660.94	0.996138
7	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	79.06	40.00	0.00	823.14	40.00	744.08	0.996252
8	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	189.13	60.00	0.00	1030.65	59.58	841.52	0.996510
9	18.0	753.0	1003.92	535.03	117.37	23.79	3821.10	0.977267	23.79	3282.72	0.980503	2.356E-05	447.67	80.00	0.00	1372.25	80.00	924.58	0.996792
2M DAP loading 0.1																			
1	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	1965.32	120.00	0.00	3375.16	120.00	1409.84	0.996219
2	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	1029.00	100.00	0.00	2354.56	100.00	1325.56	0.996130
3	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	516.69	80.00	0.00	1737.75	79.99	1221.06	0.995825
4	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	252.76	60.00	0.00	1366.40	60.00	1113.64	0.995386
5	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	132.23	40.00	0.00	1116.43	40.00	984.20	0.994962
6	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	58.87	25.00	0.00	960.96	25.00	902.09	0.994753
7	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	132.23	40.00	0.00	1114.53	40.00	982.30	0.994969
8	18.0	753.0	1003.92	532.32	85.95	23.00	4410.76	0.973503	23.00	3389.28	0.979706	4.503E-05	252.76	60.00	0.00	1363.08	60.00	1110.32	0.994774
2M DAP loading 0.3																			
1	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	1935.26	120.00	0.00	3338.29	120.00	1403.03	0.996505
2	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	979.78	100.00	0.00	2309.52	100.00	1329.74	0.996073
3	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	460.02	80.00	0.00	1694.70	79.99	1234.68	0.995661
4	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	197.47	60.00	0.00	1325.55	60.00	1128.08	0.995261
5	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	79.45	40.00	0.00	1082.35	40.02	1002.90	0.994935
6	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	40.12	25.00	0.00	932.65	25.00	892.53	0.994800
7	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	79.45	40.00	0.00	1081.17	40.00	1001.72	0.994940
8	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	197.47	60.00	0.00	1323.47	60.00	1126.00	0.995270
9	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	460.02	80.00	0.00	1692.38	80.00	1232.36	0.995670
10	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	979.78	100.00	0.00	2307.52	100.00	1327.74	0.996079
11	18.0	753.0	1003.92	534.24	83.23	23.25	4386.32	0.973717	23.25	3693.70	0.977917	3.056E-05	1935.26	120.00	0.00	3334.73	120.01	1399.47	0.996514

n_{N2O} gas, kmol	Volume of solvent		n_{N2O} liquid, kmol	C_{N2O} liquid, kmol m^{-3}	H, kPa m^3 $kmol^{-1}$	Reprodc, %	1/T	H, kPa m^3 mol^{-1}	Versteeg's Equation
	$\rho_{Solvent}$, g cm^{-3}	$V_{Solvent}$, cm^3					K^{-1}		
1.956E-05	0.8918	468.33	4.004E-06	8.5494E-03	12798		2.5435584	12.798	
1.904E-05	0.9104	458.77	4.518E-06	9.8474E-03	10101		2.6798874	10.101	
1.981E-05	0.9798	426.27	3.755E-06	8.8090E-03	10533		2.8316579	10.533	
1.907E-05	0.9742	428.74	4.494E-06	1.0482E-02	8069		3.0013806	8.069	
1.798E-05	0.9849	424.08	5.579E-06	1.3156E-02	5655		3.1933578	5.655	
1.685E-05	0.9913	421.34	6.707E-06	1.5919E-02	4152		3.3540164	4.152	
1.798E-05	0.9849	424.08	5.577E-06	1.3151E-02	5658		3.1933578	5.658	
1.899E-05	0.9742	428.74	4.566E-06	1.0650E-02	7902		3.0054398	7.902	
1.974E-05	0.9798	426.27	3.825E-06	8.9743E-03	10303		2.8316579	10.303	
2.383E-05	0.8918	500.53	2.120E-05	4.2359E-02	3328		2.5435584	3.328	
2.405E-05	0.9104	490.30	2.098E-05	4.2800E-02	3097		2.6798874	3.097	
2.506E-05	0.9898	450.97	1.998E-05	4.4295E-02	2757		2.8317381	2.757	
2.439E-05	0.9982	447.17	2.064E-05	4.6167E-02	2412		3.0016509	2.412	
2.289E-05	0.9954	448.46	2.214E-05	4.9373E-02	1993		3.1933578	1.993	
2.214E-05	1.0016	445.65	2.289E-05	5.1360E-02	1756		3.3540164	1.756	
2.285E-05	0.9954	448.46	2.219E-05	4.9472E-02	1986		3.1933578	1.986	
2.433E-05	0.9982	447.17	2.070E-05	4.6296E-02	2398		3.0016509	2.398	
2.349E-05	0.8918	505.73	7.074E-06	1.3987E-02	10031		2.5435584	10.031	
2.391E-05	0.9104	495.39	6.652E-06	1.3429E-02	9902		2.6798874	9.902	
2.547E-05	1.0068	447.96	5.091E-06	1.1365E-02	10864		2.8317381	10.864	
2.483E-05	1.0152	444.26	5.732E-06	1.2902E-02	8743		3.0016509	8.743	
2.345E-05	1.0132	445.15	7.105E-06	1.5962E-02	6283		3.1931539	6.283	
2.202E-05	1.0193	442.49	8.536E-06	1.9291E-02	4627		3.3540164	4.627	
2.343E-05	1.0132	445.15	7.132E-06	1.6021E-02	6253		3.1933578	6.253	
2.478E-05	1.0152	444.26	5.778E-06	1.3006E-02	8658		3.0016509	8.658	
2.542E-05	1.0068	447.96	5.140E-06	1.1473E-02	10741		2.8316579	10.741	
2.387E-05	0.9104	495.39	6.689E-06	1.3502E-02	9834		2.6798874	9.834	
2.343E-05	0.8918	505.73	7.134E-06	1.4106E-02	9921		2.5434937	9.921	

2M DAP loading 0.5

1	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	3307.78	80.00	0.00	4486.89	80.03	1179.11	0.992596
2	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	1752.69	60.00	0.00	2836.19	60.05	1083.50	0.987240
3	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	817.94	40.00	0.00	1795.49	40.00	977.55	0.995062
4	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	425.06	25.00	0.00	1307.82	25.00	882.76	0.994857
5	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	817.94	40.00	0.00	1794.32	40.00	976.38	0.995062
6	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	1752.69	60.00	0.00	2835.48	59.99	1082.79	0.995451
7	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	3307.78	80.00	0.00	4485.23	80.00	1177.45	0.995863
8	18.0	753.0	1003.92	525.20	54.84	22.50	5414.13	0.967204	22.50	4782.95	0.971088	2.831E-05	1752.69	60.00	0.00	2831.38	59.99	1078.69	0.995469

2M DAP loading 0.1 B

1	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	1903.52	120.00	0.00	3973.45	119.98	2069.93	0.994842
2	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	969.46	100.00	0.00	2917.71	100.00	1948.25	0.994245
3	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	448.77	80.00	0.00	2263.82	80.00	1815.05	0.993619
4	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	196.79	60.00	0.00	1850.36	59.99	1653.57	0.993048
5	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	78.43	40.00	0.00	1556.36	40.00	1477.93	0.992526
6	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	40.01	25.00	0.00	1362.48	25.01	1322.47	0.992285
7	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	78.43	40.00	0.00	1556.30	40.00	1477.87	0.992527
8	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	196.79	60.00	0.00	1850.56	59.99	1653.77	0.993047
9	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	448.77	80.00	0.00	2263.00	80.00	1814.23	0.993622
10	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	969.46	100.00	0.00	2910.75	99.97	1941.29	0.994265
11	18.0	753.0	1003.92	575.84	162.47	22.88	5424.22	0.967267	22.88	4368.20	0.973731	4.717E-05	1903.52	120.00	0.00	3965.43	120.01	2061.91	0.994864

2M DAP b

1	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	1899.56	120.00	0.00	3956.40	120.00	2362.25	0.994115
2	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	967.36	100.02	0.00	2892.22	100.00	2230.28	0.993412
3	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	449.49	80.00	0.00	2238.27	79.99	2094.19	0.992635
4	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	197.18	60.03	0.00	1820.95	59.98	1929.19	0.991885
5	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	79.20	40.00	0.00	1517.75	39.99	1743.96	0.991175
6	18.0	753.0	1003.92	545.39	109.19	20.92	5467.34	0.966347	20.92	4455.90	0.972668	4.558E-05	38.42	25.00	0.00	1314.48	24.99	1581.48	0.990766

2.535E-05	1.1084	424.36	2.961E-06	6.9778E-03	16898		2.8314174	16.898	
2.478E-05	1.1056	425.43	3.528E-06	8.2937E-03	13064		3.0012005	13.064	
2.327E-05	1.0834	434.15	5.036E-06	1.1600E-02	8427		3.1933578	8.427	
2.218E-05	1.0904	431.38	6.132E-06	1.4214E-02	6210		3.3540164	6.210	
2.325E-05	1.0834	434.15	5.064E-06	1.1664E-02	8371		3.1933578	8.371	
2.457E-05	1.1056	425.43	3.744E-06	8.8015E-03	12302		3.001741	12.302	
2.523E-05	1.1084	424.36	3.078E-06	7.2524E-03	16235		2.8316579	16.235	
2.447E-05	1.1056	425.43	3.838E-06	9.0212E-03	11957		3.001741	11.957	
3.740E-05	0.8918	463.52	9.776E-06	2.1090E-02	9815		2.5436878	9.815	
3.770E-05	0.9104	454.05	9.469E-06	2.0854E-02	9342		2.6798874	9.342	
3.940E-05	0.9898	417.63	7.768E-06	1.8601E-02	9758		2.8316579	9.758	
3.829E-05	0.9982	414.12	8.884E-06	2.1454E-02	7707		3.001741	7.707	
3.636E-05	0.9954	415.30	1.082E-05	2.6043E-02	5675		3.1933578	5.675	
3.432E-05	1.0016	412.71	1.286E-05	3.1152E-02	4245		3.3539039	4.245	
3.635E-05	0.9954	415.30	1.082E-05	2.6046E-02	5674		3.1933578	5.674	
3.829E-05	0.9982	414.12	8.880E-06	2.1443E-02	7712		3.001741	7.712	
3.939E-05	0.9898	417.63	7.786E-06	1.8644E-02	9731		2.8316579	9.731	
3.757E-05	0.9104	454.05	9.601E-06	2.1146E-02	9180		2.6801029	9.180	
3.725E-05	0.8918	463.52	9.924E-06	2.1411E-02	9630		2.5434937	9.630	
4.085E-05	0.8918	489.12	1.163E-05	2.3771E-02	9937		2.5435584	9.937	
4.138E-05	0.9104	479.14	1.109E-05	2.3147E-02	9635		2.6798874	9.635	
4.176E-05	0.9284	469.84	1.071E-05	2.2803E-02	9184		2.8317381	9.184	
4.236E-05	0.9742	447.77	1.011E-05	2.2585E-02	8542		3.0018311	8.542	
4.109E-05	0.9849	442.91	1.138E-05	2.5688E-02	6789		3.1934598	6.789	
3.934E-05	0.9913	440.04	1.313E-05	2.9840E-02	5300		3.3541289	5.300	

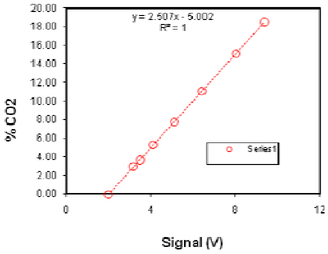
E4: Sample calculations for Low Temperaure Experiment of DAP 2M against 40⁰C

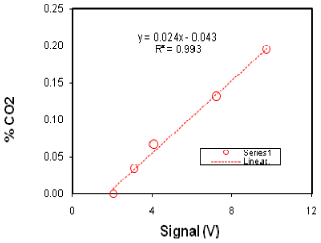
W_{amine}	299.45	g
W_{H2O}	1672.95	g
M_{Amine1}	74.12	g/mol
M_{H2O}	18.02	g/mol
$\rho_{fresh\ sol}$	0.9862	g/ml
C_{Amine}	2.048	mol/kg
	2.020	mol/l

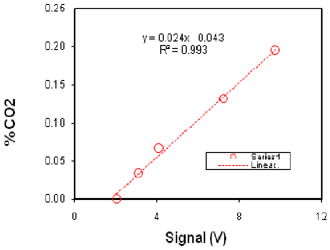
						Raoult's Law					
No	T_{bath} °C	T_{cooler} °C	T_{cell} °C	x_{H2O}	x_{Amine}	Pwater Cell Temperature	PAmine (kpa)	Pwater Cooler Temperature	PAmine (kpa)	Psol @ Tcell (kPa)	Psol @ Tcoole (kPa)
3k4	40.1	12.2	40.1	0.9583	0.0417	7.4518	1.5174	1.4295	0.2280	7.2043	1.3794
2k4	40.1	10.9	40	0.9583	0.0417	7.4123	1.5083	1.3117	0.2062	7.1661	1.2656
1k4	40.1	10.9	39.9	0.9583	0.0417	7.3729	1.4992	1.3117	0.2062	7.1280	1.2656
3k3	40.1	11.7	40	0.9583	0.0417	7.4123	1.5083	1.3831	0.2194	7.1661	1.3346
2k3	40.1	11.5	40	0.9583	0.0417	7.4123	1.5083	1.3649	0.2161	7.1661	1.3170
3k2	40.1	12.9	40	0.9583	0.0417	7.4123	1.5083	1.4967	0.2406	7.1661	1.4443
2k2	40.1	13	40	0.9583	0.0417	7.4123	1.5083	1.5065	0.2424	7.1661	1.4538
1k2	40.1	13.1	40	0.9583	0.0417	7.4123	1.5083	1.5164	0.2443	7.1661	1.4633
1k2	40	13.6	39.9	0.9583	0.0417	7.3729	1.4992	1.5666	0.2538	7.1280	1.5119
3k1	40	10.9	39.9	0.9583	0.0417	7.3729	1.4992	1.3117	0.2062	7.1280	1.2656
2k1	40.1	10.7	39.9	0.9583	0.0417	7.3729	1.4992	1.2944	0.2031	7.1280	1.2488
1k1	40.1	10.9	40	0.9583	0.0417	7.4123	1.5083	1.3117	0.2062	7.1661	1.2656
0k1	40.2	11	40	0.9583	0.0417	7.4123	1.5083	1.3204	0.2079	7.1661	1.2740

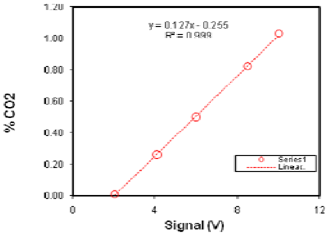
Antoine eq (Ebulliometer)								
Psol @ Tcell (kPa)	Psol @ Tcooler (kPa)	P ambient (mmHg)	P ambient (kPa)	CO2 analyser (Volts)	%CO2 analyser (%)	%CO2 real (%)	PCO2 (kPa)	Loading
		761.1	101.471	4.3385	5.90	5.87288	5.6172	
		745.6	99.405	2.2830	2.43	0.72207	0.6752	
		745.5	99.392	2.2720	0.44	0.69449	0.6496	0.9489
		760.8	101.431	6.9485	3.10	3.09740	2.9611	1.0307
		760.4	101.378	5.0705	1.93	1.92474	1.8387	0.9989
		760	101.325	7.9240	0.74	0.71829	0.6867	0.9417
		759.7	101.285	6.5495	0.57	0.55463	0.5301	0.9220
		759.5	101.258	4.7745	0.35	0.34330	0.3280	0.8987
		745.4	99.378	3.1700	0.15	0.14746	0.1383	
		745.3	99.365	9.1150	1780.00	0.18099	0.1692	0.8827
		745	99.325	6.4775	1119.00	0.11617	0.1086	0.8530
		744.8	99.298	5.4005	851.00	0.08970	0.0838	0.8355
		744.6	99.272	4.6520	664.00	0.07130	0.0666	0.8141

Calibration of channels









E5: Sample calculations for High Temperaure Experiment of DAP 5M against 80^0C

Sample nr:		**VIPPE 01**	**VIPPE 02**	**VIPPE 03**	**VIPPE 04**	**VIPPE 05**
Type amin:		**DAP5M**	**DAP5M**	**DAP5M**	**DAP5M**	**DAP5M**
Date:	ddmmåå					
W(DAP 5M)	g	748.7	748.7	748.7	748.7	748.7
W(H2O)	g	1230.3	1230.3	1230.3	1230.3	1230.3
Concentration:	wt %	37.8	37.8	37.8	37.8	37.8
n(H20)	mol	68.27	68.27	68.27	68.27	68.27
n(DAP2M)	mol	10.10	10.10	10.10	10.10	10.10
XH2O	molfraction	0.87	0.87	0.87	0.87	0.87
X(DAP2M)	molfraction	0.13	0.13	0.13	0.13	0.13
C(DAP2M)	mol/kg	5.10	5.10	5.10	5.10	5.10
den		0.9895	0.9895	0.9895	0.9895	0.9895
Gas Phase						
Totalpressure	bara	9.8	7.853	5.782	3.696	2.439
Totalpressure	kPa	980	785.3	578.2	369.6	243.9
Temperature	oC	80.02	80.05	79.99	79.94	80.04
Temperature	K	353.17	353.2	353.14	353.09	353.19
P (H2O)	bar	17.95	17.97	17.92	17.89	17.96
P (amin)	bar	**0.4507**	**0.4513**	**0.4502**	**0.4493**	**0.4511**
P (CO2)	bar	9.35	7.40	5.33	3.25	1.99
P (CO2)	kPa	934.93	740.17	533.18	324.67	198.79
Liquid sample						
Weight empty	g	1638.9	1639	1638.9	1639	1639
Weight empty + unloaded	g	1701.9	1706	1701.4	1702.9	1704.6
weight empty + unloaded + loaded	g	1807.7	1807	1807.6	1806.5	1804.6
Amine Analysis						
Total weight sample	g	168.8	168	168.7	167.5	165.6
Weight unloaded sample	g	63	67	62.5	63.9	65.6
Weight loaded sample	g	105.8	101	106.2	103.6	100
Dato:	ddmmåå					
Parallell 1:						
Sample weight	g	0.298	0.295	0.296	0.294	0.296
HCl	g	35.399	35.386	35.36	35.444	35.392
NaOH	ml	16.956	17.975	17.496	18.306	19.259
pH:		5.25	5.25	5.25	5.25	5.25
CO2 conc (unloaded + loaded)	mol/kg	3.0168	2.8725	2.9394	2.8359	2.6470
CO2 conc (loaded sample)	mol/kg	4.8132	4.7781	4.6692	4.5850	4.3834
Parallell 2:						
Sample weight	g	0.297	0.296	0.298	0.294	0.295
HCl	g=ml	35.355	35.386	35.337	35.406	35.41
NaOH	g=ml	16.852	17.877	17.305	18.184	19.394
pH:		5.25	5.25	5.25	5.25	5.25
CO2 conc (unloaded + loaded)	mol/kg	3.0370	2.8794	2.9478	2.8502	2.6361
CO2 conc (loaded sample)	mol/kg	4.8455	4.7895	4.6826	4.6081	4.3654
		6.1585	**6.0683**	**5.8978**	**5.7801**	**5.4032**
Blind Sample						
HCl	g=ml	10.357	10.357	10.357	10.357	10.357
NaOH	g=ml	9.894	9.894	9.894	9.894	9.894
pH:		5.25	5.25	5.25	5.25	5.25
Blindverdi:	g=ml	0.463	0.463	0.463	0.463	0.463
Avg CO2 conc (loaded sample)	mol/kg	4.8293	4.7838	4.6759	4.5966	4.3744
% difference	%	-0.67	-0.24	-0.29	-0.50	0.41
Beregnet aminkons(approx amine conc):	mol/kg ladet lø	4.0196	4.0298	4.0540	4.0719	4.1218
Loading basert på ber. Amin	mol CO2/mol a	1.2014	1.1871	1.1534	1.1289	1.0613

Amine Analysis (A)	mol/kg	8.5088	8.9177	8.9677	9.1034	9.1253
Amine Analysis (B)	mol/kg	8.5021	8.9193	8.9701	9.1096	9.1284
Avg [Amine]	mol/kg	4.252725	4.45925	4.48445	4.55325	4.563425
Amine		2.1264	2.2296	2.2422	2.2766	2.2817
Loading	mol/mol	**1.1356**	**1.0728**	**1.0427**	**1.0095**	**0.9586**
[amine] mol/ kg loaded solutio		3.7457	4.0314	4.1197	4.2134	4.2087
Loading (molCO2/kg loaded solution)		1.2936	1.1880	1.1366	1.0937	1.0372

E6: CO_2 and Amine analysis sheet

DAP 2M for Low Temperature Apparatus

40C

	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH (ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
0k1	1.058	40.614	6.689	10.666	10.187	1.581	3.899		**0.41**	**0.8141**
	1.030	40.828	7.583	10.666	10.187	1.591	3.891	-0.6		
						1.586	3.895	0.2		
1K1	0.986	40.978	8.355	10.666	10.187	1.630	3.898		**0.42**	**0.8355**
	0.893	41.053	11.751	10.666	10.187	1.614	3.867	1.0		
						1.622	3.883	0.8		
2K1	0.849	41.043	12.237	10.666	10.187	1.668	3.914		**0.43**	**0.8530**
	0.984	40.654	7.280	10.666	10.187	1.672	3.916	-0.2		
						1.670	3.915	0.0		
3K1	0.951	41.032	8.020	10.666	10.187	1.710	3.878		**0.44**	**0.8827**
	0.963	41.153	7.689	10.666	10.187	1.713	3.878	-0.1		
						1.712	3.878	0.0		
1K2	1.059	40.038	2.691	9.763	9.226	1.738	3.869		**0.45**	**0.8987**
	1.060	40.035	2.695	9.763	9.226	1.736	3.861	0.1		
						1.737	3.865	0.2		
2K2	0.965	40.463	5.286	9.763	9.226	1.795	3.837		**0.46**	**0.9220**
	1.040	40.531	3.516	9.763	9.226	1.754	3.861	2.3		
						1.774	3.849	-0.6		
3K2	1.012	40.529	3.371	9.763	9.226	1.809	3.851		**0.47**	**0.9417**
	0.948	40.403	5.457	9.763	9.226	1.815	3.846	-0.3		
						1.812	3.849	0.1		
2K3	1.053	40.451		9.763	9.226	1.895	3.831		**0.50**	**0.9989**
	0.963	40.580	2.849	9.763	9.226	1.931	3.830	-1.9		
						1.913	3.830	0.0		
3K3	0.968	40.631	2.227	9.763	9.226	1.956	3.796		**0.52**	**1.0307**
	0.973	40.696	2.131	9.763	9.226	1.954	3.792	0.1		
						1.955	3.794	0.1		
1K4	0.971	40.684	3.975	9.763	9.226	1.863	3.872		**0.47**	**0.9489**
	1.013	40.495	3.248	9.763	9.226	1.812	3.873	2.8		
						1.837	3.873	0.0		
2K4	0.986	40.645	3.222	9.763	9.226	1.871	3.846		**0.48**	**0.9657**

	0.992	40.660	3.250	9.763	9.226	1.859	3.876	0.6		
						1.865	3.861	-0.8		
3K4	1.060	40.590	1.189	9.763	9.226	1.833	3.803		**0.49**	**0.9735**
	0.968	40.573	3.805	9.763	9.226	1.871	3.807	-2.0		
						1.852	3.805	-0.1		

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No	Sample weight (g)	HCL(g)	NaoH(ml)	Blank HCL(g)	NaoH(ml)	Total CO2 (mol/kg)	[Amine] (mol/kg)	diff	loading (mol alkalinity)	loading (mol amine)
1k1	0.416	40.368	28.750	10.299	9.658	1.319	4.257		**0.31**	**0.6202**
	0.415	40.426	28.717	10.299	9.658	1.333	4.298	-1.1		
						1.326	4.278	-0.9		
2k1	0.415	40.432	28.754	10.299	9.658	1.330	4.194		**0.32**	**0.6366**
	0.416	40.469	28.712	10.299	9.658	1.336	4.181	-0.5		
						1.333	4.188	0.3		
3k1	0.418	40.478	27.586	10.299	9.658	1.465	4.173		**0.35**	**0.7016**
	0.415	40.453	27.903	10.299	9.658	1.435	4.095	2.1		
						1.450	4.134	1.9		
4k1	0.417	40.314	27.564	10.299	9.658	1.452	4.097		**0.36**	**0.7104**
	0.413	40.407	27.688	10.299	9.658	1.462	4.106	-0.7		
						1.457	4.102	-0.2		
2k2	0.422	40.345	26.210	10.299	9.658	1.599	4.009		**0.40**	**0.7947**
	0.421	40.521	26.483	10.299	9.658	1.591	4.020	0.5		
						1.595	4.014	-0.3		
3k2	0.422	40.540	25.286	10.299	9.658	1.731	4.077		**0.42**	**0.8454**
	0.418	40.447	25.519	10.299	9.658	1.709	4.062	1.3		
						1.720	4.069	0.4		
4k2	0.420	40.449	25.188	10.299	9.658	1.740	4.038		**0.43**	**0.8555**
	0.422	40.495	25.344	10.299	9.658	1.719	4.049	1.2		
						1.730	4.044	-0.3		
1k3	0.532	40.269	20.227	10.756	9.890	1.802	4.021		**0.45**	**0.8929**
	0.399	40.396	25.240	10.756	9.890	1.791	4.026	0.6		
						1.796	4.024	-0.1		
2k3	0.427	40.373	24.360	10.756	9.890	1.774	3.925		**0.45**	**0.8970**
	0.427	40.352	24.599	10.756	9.890	1.743	3.917	1.7		
						1.758	3.921	0.2		
3k3	0.427	40.515	24.301	10.756	9.890	1.797	3.948		**0.46**	**0.9111**
	0.427	40.502	24.238	10.756	9.890	1.803	3.956	-		

								0.3		
						1.800	3.952	-0.2		
1k4	0.428	40.411	23.852	10.756	9.890	1.833	3.885		**0.47**	**0.9498**
	0.428	40.489	23.809	10.756	9.890	1.847	3.865	-0.8		
						1.840	3.875	0.5		
2k4	0.426	40.399	24.876	10.756	9.890	1.720	3.821		**0.45**	**0.9037**
	0.427	40.450	24.851	10.756	9.890	1.725	3.805	-0.3		
						1.723	3.813	0.4		
3k4	0.429	40.618	24.168	10.756	9.890	1.816	3.906		**0.47**	**0.9354**
	0.428	40.795	24.200	10.756	9.890	1.838	3.906	-1.2		
						1.827	3.906	0.0		

80C

	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH(ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
2k1	0.408	39.833	31.904	10.095	9.534	0.903	4.572		**0.20**	**0.4028**
	0.407	39.672	31.728	10.164	9.771	0.928	4.517	-2.7		
						0.915	4.544	1.2		
3k1	0.405	39.896	31.358	10.164	9.771	1.006	4.417		**0.23**	**0.4507**
	0.402	39.828	31.398	10.164	9.771	1.000	4.481	0.6		
						1.003	4.449	-1.4		
1k2	0.509	39.713	25.710	10.095	9.534	1.320	4.533		**0.29**	**0.5893**
	0.511	39.711	25.620	10.095	9.534	1.324	4.441	-0.3		
						1.322	4.487	2.1		
2k2	0.405	39.721	28.750	10.095	9.534	1.285	4.463		**0.29**	**0.5755**
	0.412	39.762	28.717	10.095	9.534	1.272	4.425	1.0		
						1.279	4.444	0.9		
1k3	0.416	39.747	25.886	10.095	9.534	1.599	4.265		**0.38**	**0.7549**
	0.417	39.762	25.840	10.095	9.534	1.602	4.214	-0.2		
						1.600	4.240	1.2		
3k3	0.418	39.763	25.109	10.095	9.534	1.686	4.195		**0.40**	**0.7943**
	0.419	39.712	25.345	10.095	9.534	1.647	4.198	2.3		
						1.667	4.196	-0.1		
4k3	0.418	39.772	25.133	10.095	9.534	1.684	4.120		**0.41**	**0.8202**
	0.418	39.724	25.044	10.095	9.534	1.689	4.105	-0.3		
						1.686	4.112	0.4		
1k4	0.422	40.853	25.627	10.756	9.890	1.701	3.909		**0.43**	**0.8555**

	0.423	40.960	25.753	10.756	9.890	1.695	4.031	0.4		
						1.698	3.970	-3.0		
2k4	0.423	41.103	25.483	10.756	9.890	1.744	3.918		**0.45**	**0.8918**
	0.424	41.163	25.557	10.756	9.890	1.738	3.891	0.3		
						1.741	3.905	0.7		
3k4	0.418	39.883	24.229	10.164	9.771	1.825	3.869		**0.48**	**0.9565**
	0.422	39.875	23.709	10.164	9.771	1.869	3.856	-2.3		
						1.847	3.862	0.3		

60C (2nd run)

	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH(ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
1k1	0.408	39.833	36.024	10.341	9.525	0.367	4.572		**0.08**	**0.1593**
	0.407	39.672	35.949	10.341	9.525	0.357	4.517	2.7		
						0.362	4.544	1.2		
2k1	0.415	40.432	28.754	10.341	9.525	1.309	4.194		**0.31**	**0.6265**
	0.416	40.469	28.712	10.341	9.525	1.315	4.181	-0.5		
						1.312	4.188	0.3		
3k1	0.418	40.278	27.786	10.341	9.525	1.397	4.173		**0.34**	**0.6769**
	0.415	40.353	27.903	10.341	9.525	1.402	4.095	-0.4		
						1.399	4.134	1.9		
1k2	0.417	40.314	27.364	10.341	9.525	1.455	4.097		**0.36**	**0.7119**
	0.413	40.407	27.488	10.341	9.525	1.465	4.106	-0.7		
						1.460	4.102	-0.2		
2k2	0.422	40.345	26.210	10.341	9.525	1.578	4.009		**0.39**	**0.7843**
	0.421	40.521	26.483	10.341	9.525	1.570	4.020	0.5		
						1.574	4.014	-0.3		
3k2	0.420	40.449	25.188	10.341	9.525	1.720	4.077		**0.42**	**0.8400**
	0.422	40.495	25.344	10.341	9.525	1.698	4.062	1.2		
						1.709	4.069	0.4		
1k3	0.420	41.449	26.088	10.341	9.525	1.732	4.038		**0.43**	**0.8658**
	0.422	41.495	25.744	10.341	9.525	1.770	4.049	-2.1		
						1.751	4.044	-0.3		
2k3	0.532	40.269	20.327	10.341	9.525	1.798	4.021		**0.45**	**0.9024**
	0.399	40.396	24.949	10.341	9.525	1.833	4.026	-2.0		
						1.816	4.024	-0.1		

3k3	0.427	40.373	23.850	10.341	9.525	1.839	3.925		**0.47**	**0.9403**
	0.427	40.352	23.759	10.341	9.525	1.847	3.917	-0.4		
						1.843	3.921	0.2		
0k4	0.427	40.515	23.585	10.341	9.525	1.887	3.948		**0.48**	**0.9575**
	0.427	40.502	23.486	10.341	9.525	1.897	3.956	-0.5		
						1.892	3.952	-0.2		
1k4	0.428	40.411	23.452	10.341	9.525	1.886	3.885		**0.48**	**0.9649**
	0.428	40.489	23.809	10.341	9.525	1.853	3.865	1.8		
						1.870	3.875	0.5		
2k4	0.426	40.399	23.776	10.341	9.525	1.855	3.821		**0.49**	**0.9711**
	0.427	40.450	23.858	10.341	9.525	1.847	3.805	0.4		
						1.851	3.813	0.4		

80C (2nd run)

	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH(ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
1k1	0.246	40.188	38.654	10.164	9.582	0.193	4.479		**0.04**	**0.0876**
	0.243	39.963	38.423	10.164	9.582	0.197	4.430	-1.8		
						0.195	4.454	1.1		
1k2	0.255	39.882	33.393	10.164	9.582	1.158	4.462		**0.26**	**0.5258**
	0.255	39.908	33.329	10.164	9.582	1.176	4.416	-1.5		
						1.167	4.439	1.0		
1k3	0.260	40.014	31.542	10.164	9.582	1.517	4.390		**0.35**	**0.6950**
	0.259	39.930	31.486	10.164	9.582	1.518	4.344	0.0		
						1.517	4.367	1.0		
2k3	0.258	39.960	31.112	10.164	9.582	1.602	4.352		**0.37**	**0.7403**
	0.261	40.077	31.055	10.164	9.582	1.617	4.344	-0.9		
						1.609	4.348	0.2		
3k4	0.265	39.930	28.720	10.164	9.582	2.005	4.165		**0.47**	**0.9406**
	0.264	39.967	28.844	10.164	9.582	1.996	4.344	0.4		
						2.001	4.254	-4.1		
4k4	0.264	39.994	28.651	10.164	9.582	2.038	4.418		**0.47**	**0.9338**
	0.264	40.094	28.558	10.164	9.582	2.075	4.390	-1.8		
						2.056	4.404	0.6		

DAP 5M for Low Temperature Apparatus

40C

No	**Sample weight (g)**	**HCL (g)**	**NaoH (ml)**	**Blank HCL(g)**	**NaoH (ml)**	**Total CO2 (mol/kg)**	**[Amine] (mol/kg)**	**diff**	**loading** (mol alkalinity)	**loading** (mol amine)
2K4	0.308	35.080	6.118	9.872	9.360	4.619	8.519		**0.54**	**1.0744**
	0.306	35.061	6.154	9.872	9.360	4.640	8.715	-0.5		
						4.629	8.617	-2.2		
1K4	0.302	35.113	6.918	9.872	9.360	4.583	8.522		**0.54**	**1.0715**
	0.305	35.115	6.901	9.872	9.360	4.541	8.510	0.9		
						4.562	8.516	0.1		
3K3	0.307	35.027	6.915	9.872	9.360	4.495	8.602		**0.53**	**1.0577**
	0.279	35.099	8.873	9.872	9.360	4.608	8.612	-2.5		
						4.552	8.607	-0.1		
2K3	0.303	35.013	8.256	9.872	9.360	4.331	8.580		**0.51**	**1.0150**
	0.302	34.983	8.271	9.872	9.360	4.338	8.500	-0.2		
						4.334	8.540	0.9		
1K3	0.305	35.013	9.402	9.872	9.360	4.115	8.459		**0.49**	**0.9813**
	0.305	34.998	9.046	9.872	9.360	4.170	8.427	-1.3		
						4.143	8.443	0.4		
3K2	0.303	35.068	9.210	9.872	9.360	4.183	8.648		**0.48**	**0.9610**
	0.304	35.056	9.473	9.872	9.360	4.124	8.638	1.4		
						4.153	8.643	0.1		
2K2	0.303	35.069	10.849	9.872	9.360	3.912	8.539		**0.46**	**0.9259**
	0.297	34.994	10.803	9.872	9.360	3.986	8.523	-1.9		
						3.949	8.531	0.2		
1K2	0.306	35.201	11.884	10.041	9.543	3.729	8.668		**0.44**	**0.8735**
	0.302	35.262	11.664	10.041	9.543	3.824	8.626	-2.5		
						3.776	8.647	0.5		
2K1	0.302	35.221	13.209	10.041	9.543	3.562	8.748		**0.41**	**0.8157**
	0.301	35.129	13.245	10.041	9.543	3.552	8.696	0.3		
						3.557	8.722	0.6		
1K1	0.271	35.331	8.281	10.041	9.543	4.899	10.124		**0.48**	**0.1059**
	0.273	35.139	7.951	10.041	9.543	4.888	10.158	0.2		
						4.893	10.141	-0.3		

60C

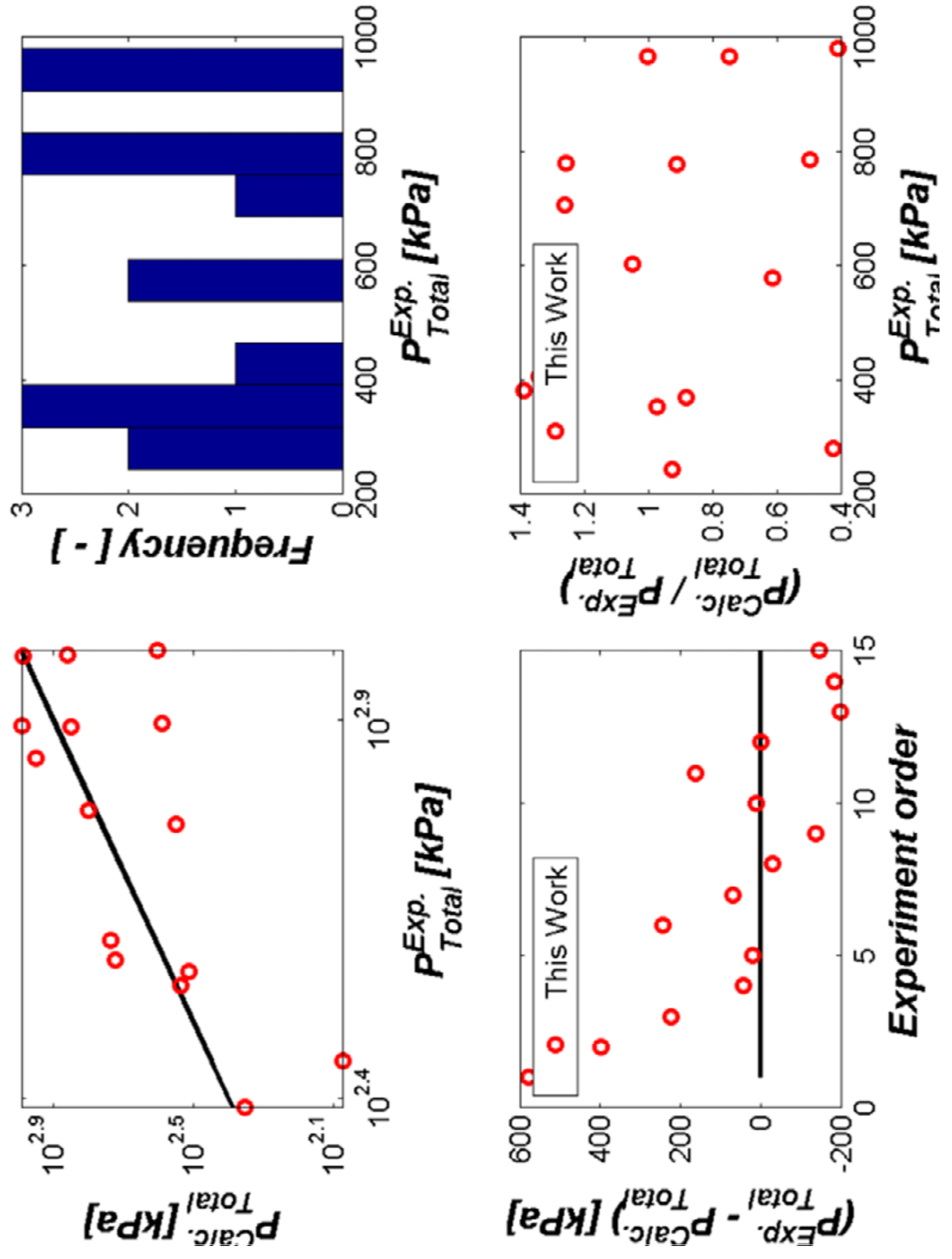
	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH(ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
3K4	0.308	35.069	8.593	9.872	9.360	4.215	8.503		**0.50**	**0.9984**
	0.304	34.994	8.307	9.872	9.360	4.305	8.565	-2.1		
						4.260	8.534	-0.7		
2K4	0.307	35.126	7.982	9.872	9.360	4.337	8.742		**0.50**	**0.9990**
	0.303	35.011	8.006	9.872	9.360	4.372	8.695	-0.8		
						4.355	8.718	0.5		
1K4	0.304	35.041	8.371	9.872	9.360	4.302	8.730		**0.49**	**0.9878**
	0.309	35.130	7.951	9.872	9.360	4.315	8.718	-0.3		
						4.309	8.724	0.1		
2K3	0.302	35.256	9.391	10.015	9.609	4.215	8.597		**0.49**	**0.9779**
	0.302	35.398	9.680	10.015	9.609	4.191	8.594	0.6		
						4.203	8.596	0.0		
1K3	0.298	35.370	10.564	10.015	9.609	4.094	8.752		**0.47**	**0.9337**
	0.309	35.347	9.851	10.015	9.609	4.060	8.714	0.8		
						4.077	8.733	0.4		
0K3	0.297	35.362	11.251	10.015	9.609	3.991	8.820		**0.46**	**0.9120**
	0.194	35.419	19.314	10.015	9.609	4.046	8.806	-1.4		
						4.018	8.813	0.2		
3K2	0.302	35.344	11.153	10.015	9.609	3.938	8.889		**0.44**	**0.8843**
	0.302	35.413	11.607	10.015	9.609	3.874	8.778	1.6		
						3.906	8.834	1.3		
2K2	0.300	35.509	12.627	10.015	9.609	3.746	8.893		**0.42**	**0.8455**
	0.295	35.400	12.870	10.015	9.609	3.750	8.838	-0.1		
						3.748	8.865	0.6		
3K1	0.295	35.469	13.969	10.015	9.609	3.575	8.852		**0.40**	**0.8078**
	0.299	35.352	13.647	10.015	9.609	3.562	8.819	0.4		
						3.568	8.836	0.4		
2K1	0.297	35.463	15.922	10.015	9.609	3.221	9.118		**0.36**	**0.7128**
	0.297	35.339	15.524	10.015	9.609	3.268	9.088	-1.4		
						3.244	9.103	0.3		

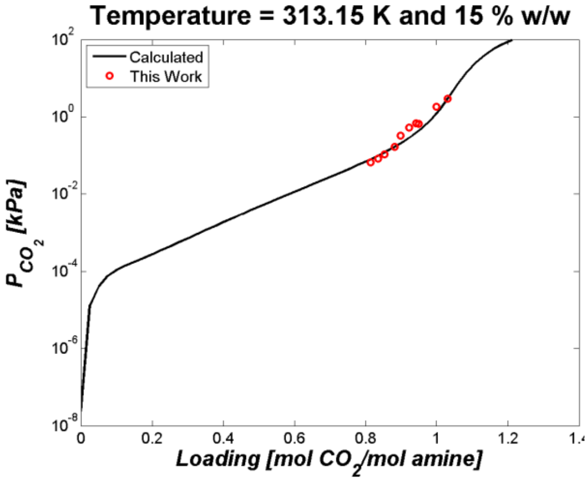
80C

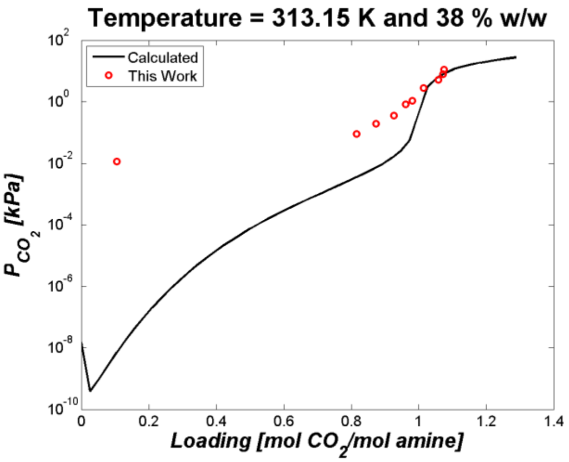
	Sample			**Blank**		**Total CO2**	**[Amine]**		**loading**	**loading**
No	**weight (g)**	**HCL(g)**	**NaoH(ml)**	**HCL(g)**	**NaoH(ml)**	**(mol/kg)**	**(mol/kg)**	**diff**	(mol alkalinity)	(mol amine)
3k4	0.308	39.977	13.643	10.253	9.233	4.109	8.854		**0.46**	**0.9288**
	0.304	40.010	13.848	10.253	9.233	4.135	8.900	-0.6		
						4.122	8.877			
2k4	0.305	39.929	14.064	10.253	9.233	4.073	8.950		**0.46**	**0.9110**
	0.300	39.901	14.227	10.253	9.233	4.109	9.014	-0.9		
						4.091	8.982			
1k4	0.305	39.971	14.897	10.253	9.233	3.943	8.982		**0.44**	**0.8749**
	0.305	39.941	15.021	10.253	9.233	3.918	8.988	0.6		
						3.931	8.985			
3k3	0.301	39.985	14.606	10.253	9.233	4.046	9.430		**0.42**	**0.8452**
	0.299	39.914	15.645	10.253	9.233	3.888	9.345	4.1		
						3.967	9.387			
1k3	0.302	39.938	15.735	10.253	9.233	3.838	9.385		**0.41**	**0.8100**
	0.300	39.986	16.220	10.253	9.233	3.791	9.452	1.2		
						3.815	9.419			
3k2	0.298	39.939	19.387	10.253	9.233	3.277	9.606		**0.35**	**0.6927**
	0.285	39.830	19.687	10.253	9.233	3.355	9.542	-2.3		
						3.316	9.574			
2k2	0.301	39.940	19.614	10.253	9.233	3.207	9.750		**0.33**	**0.6675**
	0.296	39.919	19.463	10.253	9.233	3.283	9.698	-2.3		
						3.245	9.724			
1k2	0.300	39.942	21.614	10.253	9.233	2.885	9.938		**0.29**	**0.5829**
	0.298	39.958	21.645	10.253	9.233	2.902	9.914	-0.6		
						2.893	9.926			
1k1	0.293	39.833	25.686	10.246	9.738	2.327	10.002		**0.23**	**0.4624**
	0.292	39.672	25.738	10.246	9.738	2.299	10.007	1.2		
						2.313	10.004			

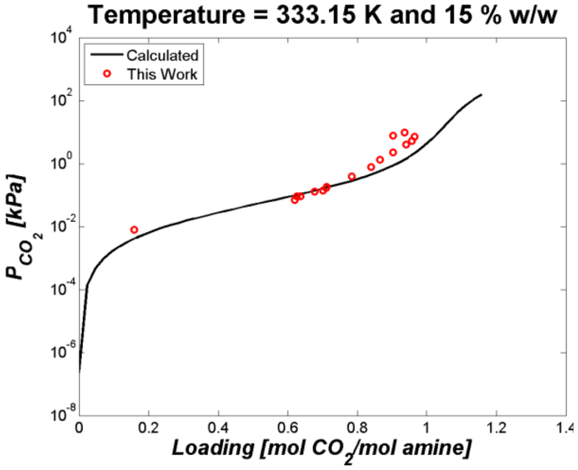
Appendix M1: Modeling results

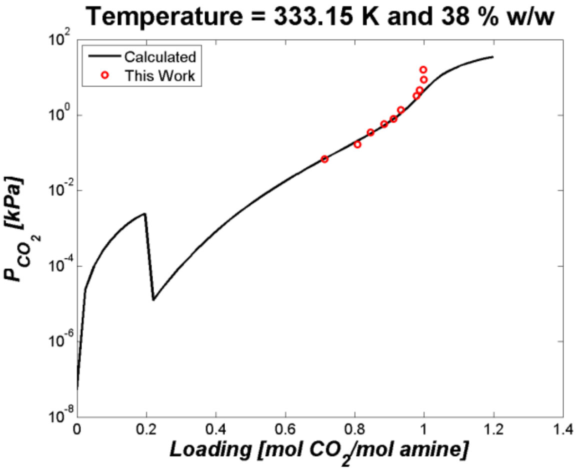
Consistency test for P_{Total}

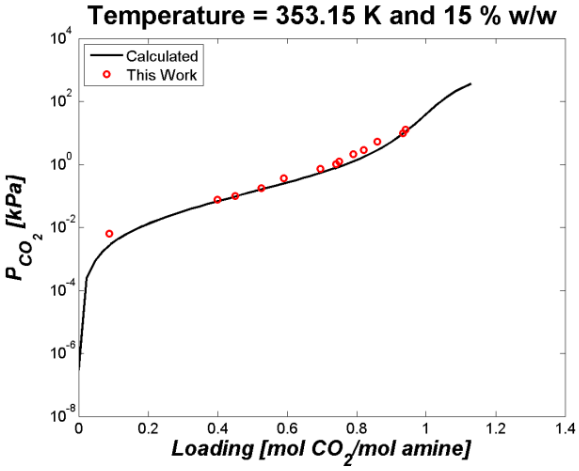


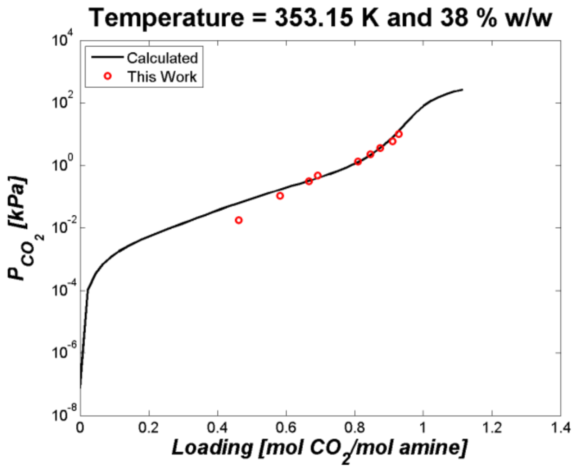

Temperature = 313.15 K and 15 % w/w

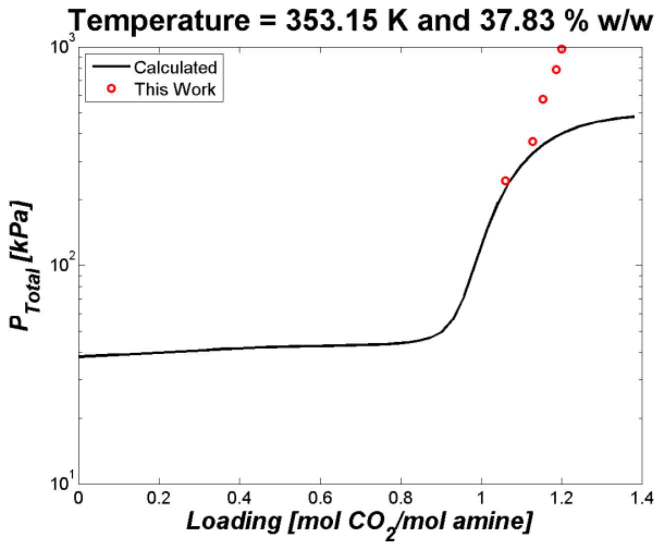

Temperature = 313.15 K and 38 % w/w

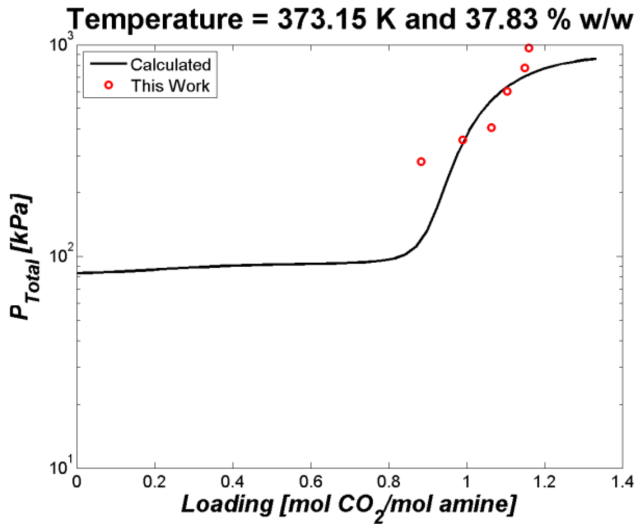

Temperature = 333.15 K and 15 % w/w

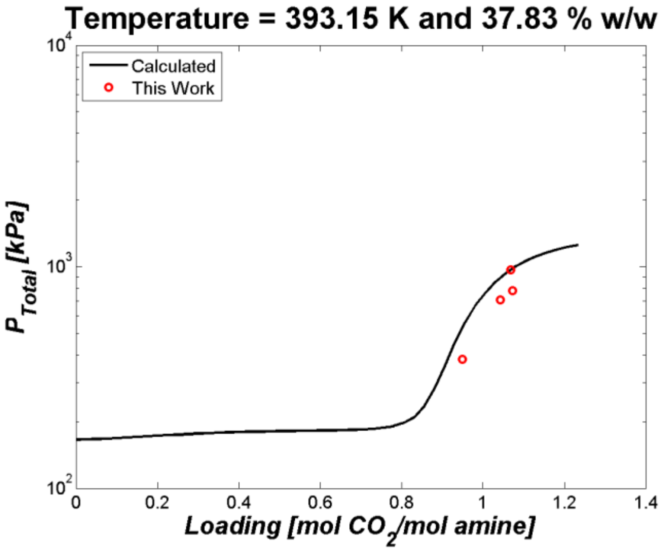

Temperature = 333.15 K and 38 % w/w


Temperature = 353.15 K and 15 % w/w


Temperature = 353.15 K and 38 % w/w


Temperature = 353.15 K and 37.83 % w/w
Calculated
This Work
P_{Total} [kPa]
Loading [mol CO_2/mol amine]
10^3
10^2
10^1
0
0.2
0.4
0.6
0.8
1
1.2
1.4


Temperature = 373.15 K and 37.83 % w/w
Calculated
This Work
P_{Total} [kPa]
Loading [mol CO_2/mol amine]
10^3
10^2
10^1
0
0.2
0.4
0.6
0.8
1
1.2
1.4


Temperature = 393.15 K and 37.83 % w/w
Calculated
This Work
P_{Total} [kPa]
Loading [mol CO_2/mol amine]
10^4
10^3
10^2
0
0.2
0.4
0.6
0.8
1
1.2
1.4

Appendix M2: Activity Coefficient Expressions regarding e-NRTL modeling

Table M2.1: ACTIVITY COEFFICIENT FOR MOLECULAR SPECIES

PDH contribution (MEA, H_2O)	$\ln\gamma_s^{PDH}=2\left(\frac{1000}{M_m}\right)^{1/2}A_\Phi\frac{I_x^{3/2}}{\left(1+\rho I_x^{1/2}\right)}$
NRTL contribution	$\ln\gamma_m^{NRTL}=\frac{\sum_j X_jG_{jm}\tau_{jm}}{\sum_k X_kG_{km}}+\sum_{m'}\frac{X_{m'}G_{mm'}}{\sum_k X_kG_{km}}\left(\tau_{mm'}-\frac{\sum_k X_kG_{km'}\tau_{km'}}{\sum_k X_kG_{km'}}\right)$ $+\sum_c\sum_{a'}\frac{X_{a'}}{\sum_{a''}X_{a''}}\frac{X_cG_{mc,a'c}}{\sum_k X_kG_{kc,a'c}}\left(\tau_{mc,a'c}-\frac{\sum_k X_kG_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_kG_{kc,a'c}}\right)$ $+\sum_a\sum_{c'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{X_aG_{ma,c'a}}{\sum_k X_kG_{ma,c'a}}\left(\tau_{ma,c'a}-\frac{\sum_k X_kG_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_kG_{kc,c'a}}\right)-\left(\tau_{wm}+G_{mw}\tau_{mw}\right)$

Table M2.2: ACTIVITY COEFFICIENT FOR CATIONS

PDH contribution	$\ln\gamma_c^{PDH}=-\left(\frac{1000}{M_m}\right)^{1/2}A_\Phi\left\{\left(\frac{2z_c^2}{\rho}\ln\left(1+\rho I_x^{1/2}\right)\right)+\frac{\left(z_c^2I_x^{1/2}-2I_x^{3/2}\right)}{\left(1+\rho I_x^{1/2}\right)}\right\}$
BORN contribution	$\ln\gamma_c^{Born}=-\left(\frac{e^2}{2kT}\right)\left(\frac{z_c^2}{r}\right)\left(\frac{1}{D_m}-\frac{1}{D_{H_2O}}\right)$
NRTL contribution	$\frac{1}{Z_c}\ln\gamma_c^{NRTL}=\sum_{a'}\frac{X_{a'}}{\sum_{a''}X_{a''}}\frac{\sum_k X_kG_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_kG_{kc,a'c}}+\sum_m\frac{X_mG_{km}}{\sum_k X_kG_{km}}\left(\tau_{cm}-\frac{\sum_k X_kG_{km}\tau_{km}}{\sum_k X_kG_{km}}\right)$ $+\sum_a\sum_{c'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{X_aG_{ca,c'a}}{\sum_k X_kG_{ca,c'a}}\left(\tau_{ca,c'a}-\frac{\sum_k X_kG_{ka,c'a}\tau_{ka,c'a}}{\sum_k X_kG_{ka,c'a}}\right)-\left(G_{cw}\tau_{cw}+\frac{\sum_{a'}x_{a'}\tau_{wc,a'c}}{\sum_{a''}x_{a''}}\right)$

Table M2.3: ACTIVITY COEFFICIENT FOR ANIONS

PDH contribution	$\ln\gamma_a^{PDH}=-\left(\frac{1000}{M_m}\right)^{1/2}A_\Phi\left\{\left(\frac{2z_a^2}{\rho}\ln\left(1+\rho I_x^{1/2}\right)\right)+\frac{\left(z_a^2I_x^{1/2}-2I_x^{3/2}\right)}{\left(1+\rho I_x^{1/2}\right)}\right\}$

BORN contribution	$\ln\gamma_a^{Born}=-\left(\frac{e^2}{2kT}\right)\left(\frac{z_a^2}{r}\right)\left(\frac{1}{D_m}-\frac{1}{D_{H_2O}}\right)$
NRTL contribution	$\frac{1}{Z_a}\ln\gamma_a^{NRTL}=\sum_{c'}\frac{X_{c'}}{\sum_{c''}X_{c''}}\frac{\sum_k X_k G_{kc,c'a}\tau_{ka,c'a}}{\sum_k X_k G_{ka,c'a}}+\sum_m\frac{X_m G_{km}}{\sum_k X_k G_{km}}\left(\tau_{cm}-\frac{\sum_k X_k G_{km}\tau_{km}}{\sum_k X_k G_{km}}\right)$ $+\sum_c\sum_{a'}\frac{X_{a'}}{\sum_{a''}X_{a''}}\frac{X_c G_{ac,a'c}}{\sum_k X_k G_{ac,a'c}}\left(\tau_{ac,a'c}-\frac{\sum_k X_k G_{kc,a'c}\tau_{kc,a'c}}{\sum_k X_k G_{kc,a'c}}\right)-\left(G_{aw}\tau_{aw}+\frac{\sum_{c'}x_{c'}\tau_{wa,c'a}}{\sum_{c''}x_{c''}}\right)$

Appendix M3: List of eNRTL and Nonrandomness parameters

eNRTL			
Molecular Parameters			
$a_{1,2}$	4.76375	**$b_{1,2}$**	482.9316
$a_{1,3}$	5.382685	**$b_{1,3}$**	-1195.45
$a_{2,1}$	5.688853	**$b_{2,1}$**	136.9581
$a_{2,3}$	-0.91275	**$b_{2,3}$**	-147.473
$a_{3,1}$	-0.11039	**$b_{3,1}$**	-985.53
$a_{3,2}$	2.072139	**$b_{3,2}$**	-631.048
Molecule-Salt Parameters			
$a_{1,4-7}$	8	**$b_{1,4-7}$**	0
$a_{1,4-8}$	8	**$b_{1,4-8}$**	0
$a_{1,4-9}$	8	**$b_{1,4-9}$**	0
$a_{1,4-10}$	-3.40605	**$b_{1,4-10}$**	-74.1476
$a_{1,4-11}$	-0.69847	**$b_{1,4-11}$**	332.467
$a_{1,4-12}$	-4.31472	**$b_{1,4-12}$**	65.61079
$a_{1,5-7}$	-1.89959	**$b_{1,5-7}$**	-269.766
$a_{1,5-8}$	1.93944	**$b_{1,5-8}$**	-255.881
$a_{1,5-9}$	2.181721	**$b_{1,5-9}$**	36.4721
$a_{1,5-10}$	-3.47914	**$b_{1,5-10}$**	-406.381
$a_{1,5-11}$	-0.96727	**$b_{1,5-11}$**	24.58873
$a_{1,5-12}$	-0.46771	**$b_{1,5-12}$**	177.1001
$a_{1,6-7}$	-3.72696	**$b_{1,6-7}$**	243.0918
$a_{1,6-8}$	-1.6239	**$b_{1,6-8}$**	396.0471
$a_{1,6-9}$	2.317076	**$b_{1,6-9}$**	100.5087
$a_{1,6-10}$	2.396636	**$b_{1,6-10}$**	-479.457
$a_{1,6-11}$	4.633285	**$b_{1,6-11}$**	-66.2745
$a_{1,6-12}$	0.880797	**$b_{1,6-12}$**	-40.343
$a_{2,4-7}$	15	**$b_{2,4-7}$**	0
$a_{2,4-8}$	15	**$b_{2,4-8}$**	0
$a_{2,4-9}$	15	**$b_{2,4-9}$**	0
$a_{2,4-10}$	-2.844	**$b_{2,4-10}$**	-118.77
$a_{2,4-11}$	-1.78584	**$b_{2,4-11}$**	301.2501
$a_{2,4-12}$	-1.41215	**$b_{2,4-12}$**	154.3013
$a_{2,5-7}$	4.795462	**$b_{2,5-7}$**	174.4725
$a_{2,5-8}$	7.171947	**$b_{2,5-8}$**	120.0857
$a_{2,5-9}$	5.571434	**$b_{2,5-9}$**	27.84474
$a_{2,5-10}$	2.294398	**$b_{2,5-10}$**	-29.6356

Non-randomness Parameters	
Molecular Parameters	
$\alpha_{1,2}$	0.2
$\alpha_{1,3}$	0.2
$\alpha_{2,1}$	0.2
$\alpha_{2,3}$	0.2
$\alpha_{3,1}$	0.2
$\alpha_{3,2}$	0.2
Salt-Molecules Parameters	
$\alpha_{4,7-1}$	0.2
$\alpha_{4,7-2}$	0.1
$\alpha_{4,7-3}$	0.1
$\alpha_{4,8-1}$	0.2
$\alpha_{4,8-2}$	0.1
$\alpha_{4,8-3}$	0.2
$\alpha_{4,9-1}$	0.1
$\alpha_{4,9-2}$	0.2
$\alpha_{4,9-3}$	0.1
$\alpha_{4,10-1}$	0.2
$\alpha_{4,10-2}$	0.1
$\alpha_{4,10-3}$	0.2
$\alpha_{4,11-1}$	0.1
$\alpha_{4,11-2}$	0.2
$\alpha_{4,11-3}$	0.1
$\alpha_{4,12-1}$	0.2
$\alpha_{4,12-2}$	0.1
$\alpha_{4,12-3}$	0.2
$\alpha_{5,7-1}$	0.1
$\alpha_{5,7-2}$	0.2
$\alpha_{5,7-3}$	0.1
$\alpha_{5,8-1}$	0.2
$\alpha_{5,8-2}$	0.1
$\alpha_{5,8-3}$	0.2
$\alpha_{5,9-1}$	0.1
$\alpha_{5,9-2}$	0.2
$\alpha_{5,9-3}$	0.1
$\alpha_{5,10-1}$	0.2

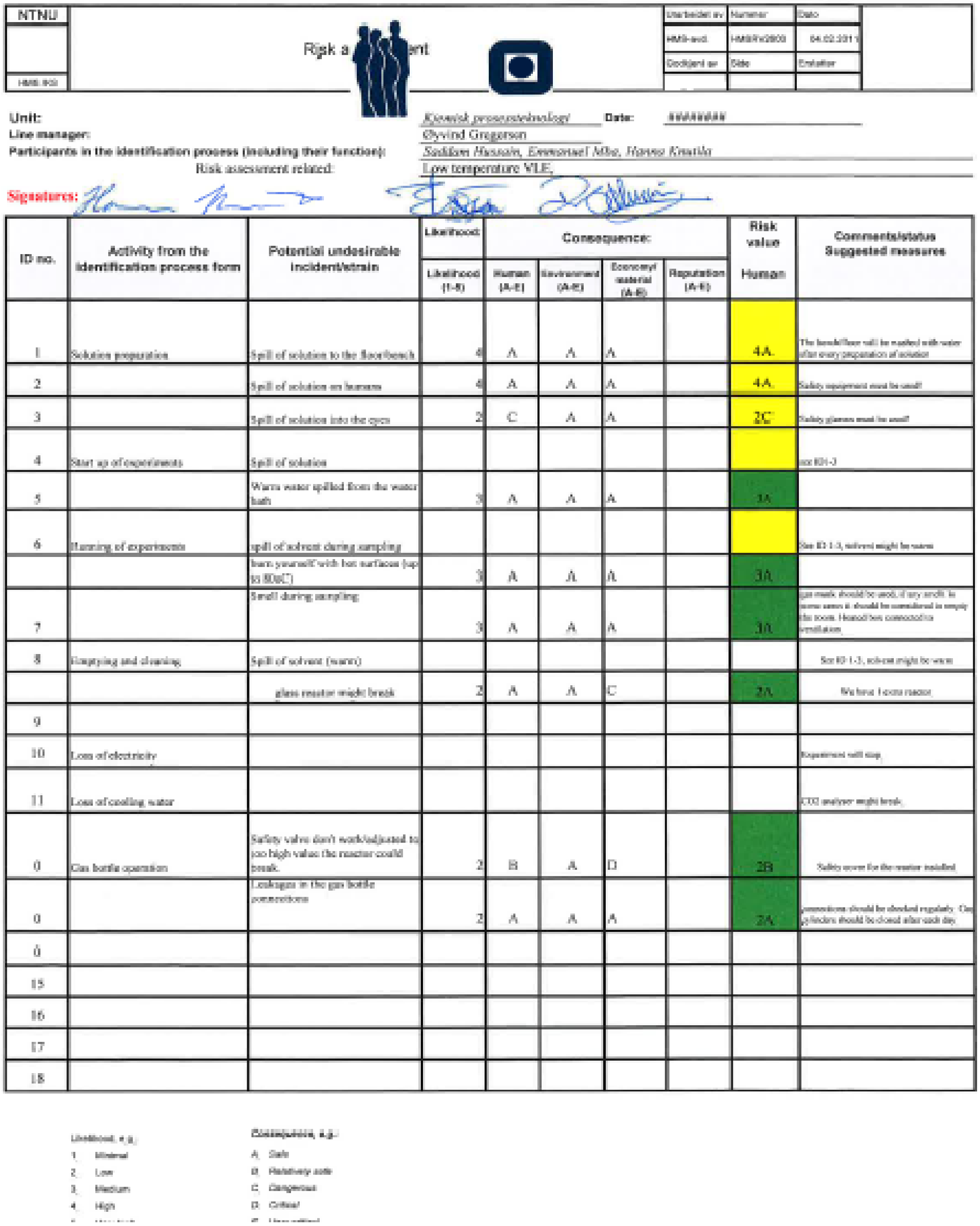
$a_{2,5-11}$	5.635159	$b_{2,5-11}$	-177.573
$a_{2,5-12}$	-4.01315	$b_{2,5-12}$	-137.758
$a_{2,6-7}$	3.423827	$b_{2,6-7}$	212.6511
$a_{2,6-8}$	-3.46461	$b_{2,6-8}$	-157.944
$a_{2,6-9}$	0.25895	$b_{2,6-9}$	-433.525
$a_{2,6-10}$	4.874992	$b_{2,6-10}$	-130.4
$a_{2,6-11}$	-8.63787	$b_{2,6-11}$	288.0943
$a_{2,6-12}$	-4.49573	$b_{2,6-12}$	410.6673
$a_{3,4-7}$	8.408979	$b_{3,4-7}$	95.0447
$a_{3,4-8}$	-0.67386	$b_{3,4-8}$	-152.938
$a_{3,4-9}$	3.885884	$b_{3,4-9}$	117.079
$a_{3,4-10}$	-5.03275	$b_{3,4-10}$	222.6538
$a_{3,4-11}$	-0.01556	$b_{3,4-11}$	240.181
$a_{3,4-12}$	6.021469	$b_{3,4-12}$	-21.7494
$a_{3,5-7}$	2.40642	$b_{3,5-7}$	-94.7668
$a_{3,5-8}$	-0.07062	$b_{3,5-8}$	-202.646
$a_{3,5-9}$	1.688239	$b_{3,5-9}$	-110.403
$a_{3,5-10}$	-2.9375	$b_{3,5-10}$	148.3806
$a_{3,5-11}$	1.96057	$b_{3,5-11}$	244.4299
$a_{3,5-12}$	4.799599	$b_{3,5-12}$	56.93798
$a_{3,6-7}$	-7.19014	$b_{3,6-7}$	569.7613
$a_{3,6-8}$	-0.64189	$b_{3,6-8}$	66.11678
$a_{3,6-9}$	-3.60977	$b_{3,6-9}$	234.5947
$a_{3,6-10}$	-4.28879	$b_{3,6-10}$	112.1197
$a_{3,6-11}$	-1.93345	$b_{3,6-11}$	139.8237
$a_{3,6-12}$	6.372091	$b_{3,6-12}$	478.6
Salt-Molecules Parameters			
$a_{4-7,1}$	-4	$b_{4-7,1}$	0
$a_{4-7,2}$	-8	$b_{4-7,2}$	0
$a_{4-7,3}$	1.623619	$b_{4-7,3}$	537.9987
$a_{4-8,1}$	-4	$b_{4-8,1}$	0
$a_{4-8,2}$	-8	$b_{4-8,2}$	0
$a_{4-8,3}$	6.479648	$b_{4-8,3}$	6.494592
$a_{4-9,1}$	-4	$b_{4-9,1}$	0
$a_{4-9,2}$	-8	$b_{4-9,2}$	0
$a_{4-9,3}$	5.81618	$b_{4-9,3}$	-0.3131
$a_{4-10,1}$	4.263747	$b_{4-10,1}$	-190.479
$a_{4-10,2}$	-1.17852	$b_{4-10,2}$	-261.192
$a_{4-10,3}$	8.057429	$b_{4-10,3}$	43.028
$a_{4-11,1}$	0.863048	$b_{4-11,1}$	171.0036
$a_{4-11,2}$	-1.08114	$b_{4-11,2}$	265.3981

$\alpha_{5,10-2}$	0.1
$\alpha_{5,10-3}$	0.2
$\alpha_{5,11-1}$	0.1
$\alpha_{5,11-2}$	0.2
$\alpha_{5,11-3}$	0.1
$\alpha_{5,12-1}$	0.2
$\alpha_{5,12-2}$	0.1
$\alpha_{5,12-3}$	0.2
$\alpha_{6,7-1}$	0.1
$\alpha_{6,7-2}$	0.2
$\alpha_{6,7-3}$	0.1
$\alpha_{6,8-1}$	0.2
$\alpha_{6,8-2}$	0.1
$\alpha_{6,8-3}$	0.2
$\alpha_{6,9-1}$	0.1
$\alpha_{6,9-2}$	0.2
$\alpha_{6,9-3}$	0.1
$\alpha_{6,10-1}$	0.2
$\alpha_{6,10-2}$	0.1
$\alpha_{6,10-3}$	0.2
$\alpha_{6,11-1}$	0.1
$\alpha_{6,11-2}$	0.2
$\alpha_{6,11-3}$	0.1
$\alpha_{6,12-1}$	0.2
$\alpha_{6,12-2}$	0.1
$\alpha_{6,12-3}$	0.2

$a_{4-11,3}$	2.124255	$b_{4-11,3}$	-190.241
$a_{4-12,1}$	1.895039	$b_{4-12,1}$	-203.106
$a_{4-12,2}$	-0.46075	$b_{4-12,2}$	246.8492
$a_{4-12,3}$	5.565089	$b_{4-12,3}$	-283.946
$a_{5-7,1}$	-1.34388	$b_{5-7,1}$	-221.499
$a_{5-7,2}$	-5.05843	$b_{5-7,2}$	-116.252
$a_{5-7,3}$	6.569463	$b_{5-7,3}$	336.3343
$a_{5-8,1}$	6.630514	$b_{5-8,1}$	-266.949
$a_{5-8,2}$	-4.54486	$b_{5-8,2}$	74.035
$a_{5-8,3}$	-5.697	$b_{5-8,3}$	63.66884
$a_{5-9,1}$	1.981797	$b_{5-9,1}$	25.10514
$a_{5-9,2}$	0.048477	$b_{5-9,2}$	-12.9232
$a_{5-9,3}$	5.018173	$b_{5-9,3}$	-315.811
$a_{5-10,1}$	0.31418	$b_{5-10,1}$	287.6418
$a_{5-10,2}$	-1.32571	$b_{5-10,2}$	-158.088
$a_{5-10,3}$	2.626224	$b_{5-10,3}$	-115.072
$a_{5-11,1}$	-5.37797	$b_{5-11,1}$	103.6127
$a_{5-11,2}$	-3.43874	$b_{5-11,2}$	356.6459
$a_{5-11,3}$	-7.26456	$b_{5-11,3}$	-281.113
$a_{5-12,1}$	-2.73704	$b_{5-12,1}$	157.808
$a_{5-12,2}$	-2.33041	$b_{5-12,2}$	125.5598
$a_{5-12,3}$	0.18762	$b_{5-12,3}$	-50.9212
$a_{6-7,1}$	-3.40361	$b_{6-7,1}$	-499.733
$a_{6-7,2}$	-1.21646	$b_{6-7,2}$	-73.7033
$a_{6-7,3}$	5.18302	$b_{6-7,3}$	-466.821
$a_{6-8,1}$	-4.17008	$b_{6-8,1}$	-303.575
$a_{6-8,2}$	-0.88792	$b_{6-8,2}$	321.9439
$a_{6-8,3}$	1.877338	$b_{6-8,3}$	159.2628
$a_{6-9,1}$	2.550846	$b_{6-9,1}$	422.2095
$a_{6-9,2}$	1.353734	$b_{6-9,2}$	243.0251
$a_{6-9,3}$	-8.4693	$b_{6-9,3}$	251.9437
$a_{6-10,1}$	-1.12156	$b_{6-10,1}$	93.46567
$a_{6-10,2}$	3.994883	$b_{6-10,2}$	173.4728
$a_{6-10,3}$	4.68605	$b_{6-10,3}$	-91.5541
$a_{6-11,1}$	7.098667	$b_{6-11,1}$	150.5579
$a_{6-11,2}$	7.108437	$b_{6-11,2}$	96.84122
$a_{6-11,3}$	3.961345	$b_{6-11,3}$	282.2752
$a_{6-12,1}$	2.564837	$b_{6-12,1}$	-226.105
$a_{6-12,2}$	2.770212	$b_{6-12,2}$	-423.661
$a_{6-12,3}$	3.947262	$b_{6-12,3}$	126.8479

Appendix R: Risk assessment and Hazardous activity identification process sheets

R1: VLE



NTNU	Risk a ent	Utarbeidet av	Nummer
		HMS-avd.	HMSRV2603
HMS /KS		Godkjent av	Side

Dato: 04.02.2011
Erstatter

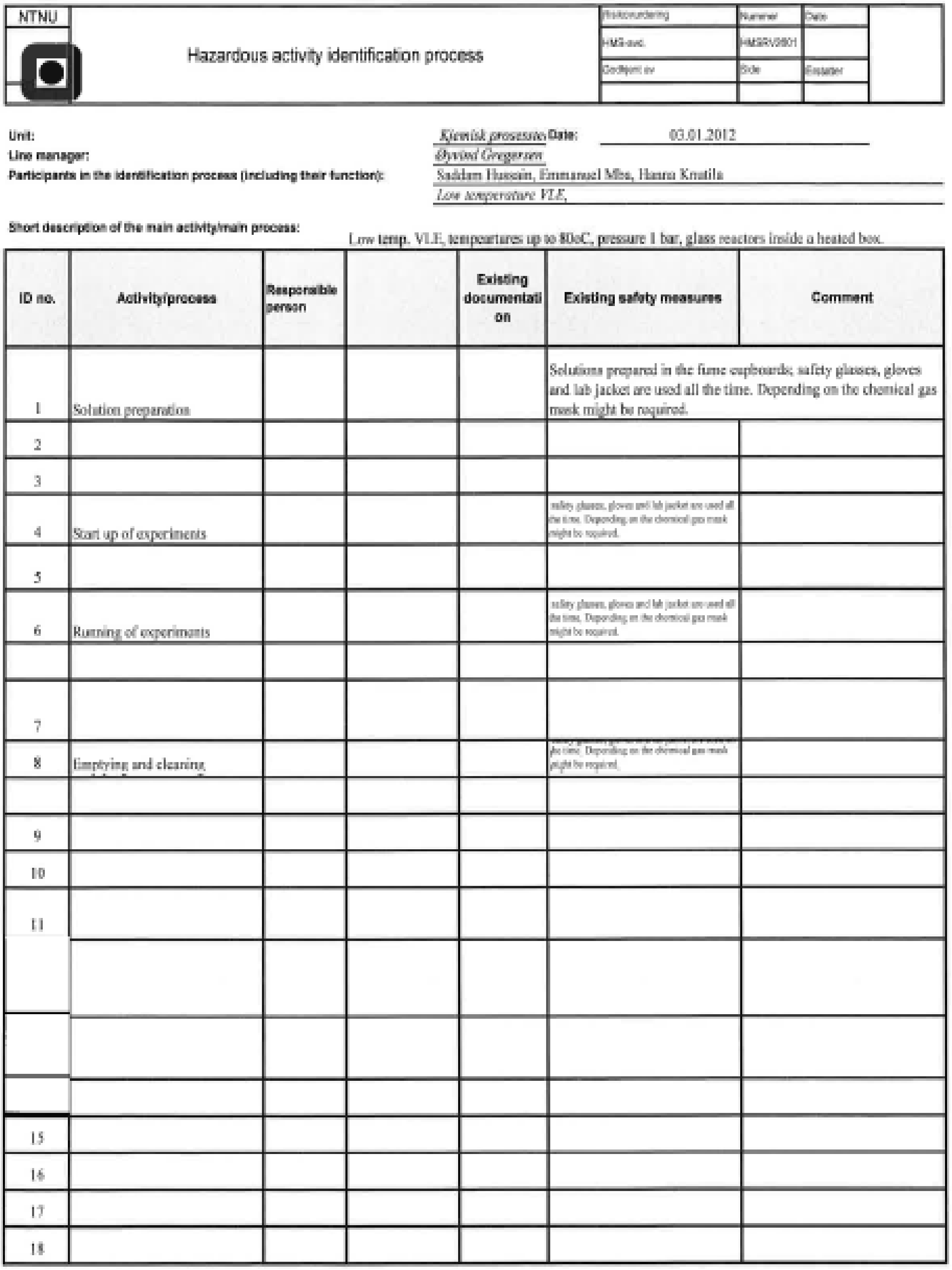
Unit: Kjemisk prosessteknologi Date: ########
Line manager: Øyvind Gregersen
Participants in the identification process (including their function): Saddam Hussain, Emmanuel Mba, Hanna Knuutila
Risk assessment related: Low temperature VLE

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	Solution preparation	Spill of solution to the floor/bench	4	A	A	A		4A	The bench/floor will be washed with water after every preparation of solution
2		Spill of solution on humans	4	A	A	A		4A	Safety equipment must be used!
3		Spill of solution into the eyes	2	C	A	A		2C	Safety glasses must be used!
4	Start up of experiments	Spill of solution						🟨	see ID1-3
5		Warm water spilled from the water bath	3	A	A	A		3A	
6	Running of experiments	spill of solvent during sampling						🟨	See ID 1-3, solvent might be warm
		burn yourself with hot surfaces (up to 80oC)	3	A	A	A		3A	
7		Smell during sampling	3	A	A	A		3A	gas mask should be used, if any smell. In worse cases it should be considered to empty the room. Heated box connected to ventilation
8	Emptying and cleaning	Spill of solvent (warm)							See ID 1-3, solvent might be warm
		glass reactor might break	2	A	A	C		2A	We have 1 extra reactor
9									
10	Loss of electricity								Experiment will stop
11	Loss of cooling water								CO2 analyser might break
0	Gas bottle operation	Safety valve don't work/adjusted to too high value the reactor could break.	2	B	A	D		2B	Safety cover for the reactor installed
0		Leakages in the gas bottle connections	2	A	A	A		2A	connections should be checked regularly. Gas cylinders should be closed after each day
0									
15									
16									
17									
18									

Likelihood, e.g.:
1. Minimal
2. Low
3. Medium
4. High

Consequence, e.g.:
A. Safe
B. Relatively safe
C. Dangerous
D. Critical



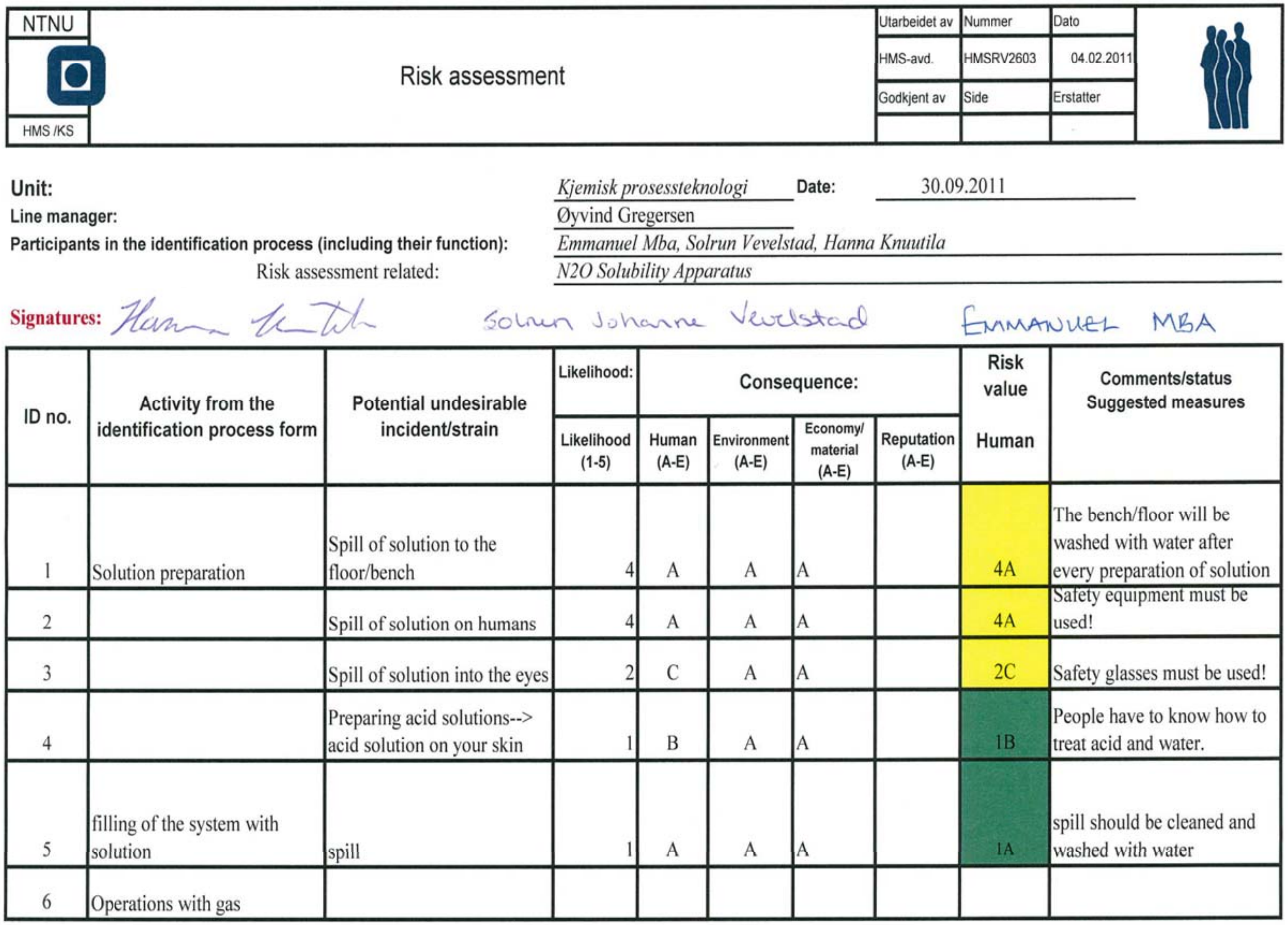
NTNU	**Hazardous activity identification process**	Risikovurdering	Nummer	Dato
		HMS-avd.	HMSRV2601	
		Godkjent av	Side	Erstatter

Unit: *Kjemisk prosessteo* **Date:** 03.01.2012
Line manager: *Øyvind Gregersen*
Participants in the identification process (including their function): Saddam Hussain, Emmanuel Mba, Hanna Knuutila
Low temperature VLE,

Short description of the main activity/main process: Low temp. VLE, temperatures up to 80oC, pressure 1 bar, glass reactors inside a heated box.

ID no.	Activity/process	Responsible person		Existing documentation	Existing safety measures	Comment
1	Solution preparation				Solutions prepared in the fume cupboards; safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	
2						
3						
4	Start up of experiments				safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	
5						
6	Running of experiments				safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	
7						
8	Emptying and cleaning				the time. Depending on the chemical gas mask might be required.	
9						
10						
11						
15						
16						
17						
18						

R2: N_20 solubility apparatus



NTNU	Risk assessment	Utarbeidet av	Nummer	Dato
		HMS-avd.	HMSRV2603	04.02.2011
HMS /KS		Godkjent av	Side	Erstatter

Unit: *Kjemisk prosessteknologi* **Date:** 30.09.2011

Line manager: Øyvind Gregersen

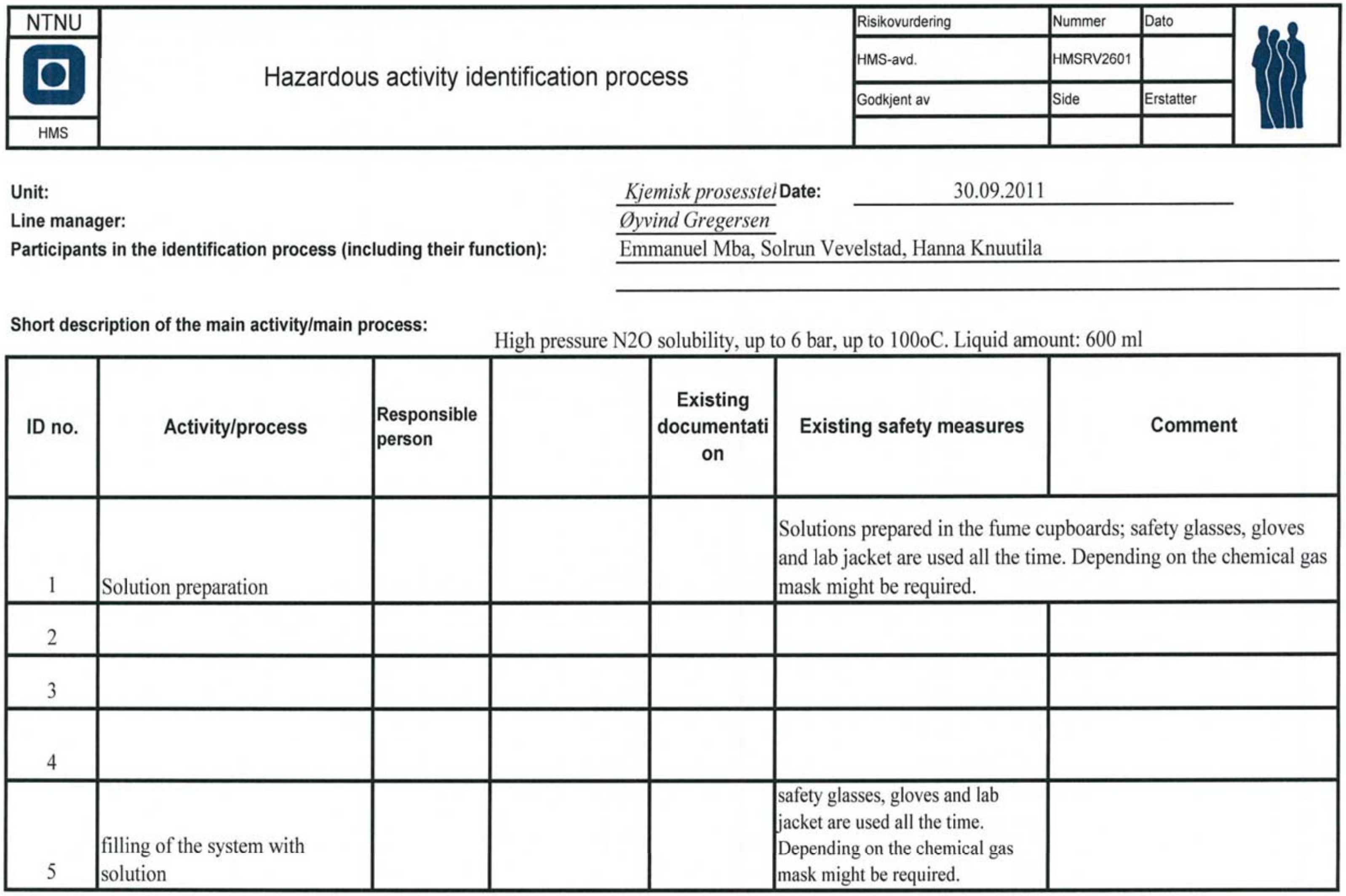
Participants in the identification process (including their function): *Emmanuel Mba, Solrun Vevelstad, Hanna Knuutila*

Risk assessment related: *N2O Solubility Apparatus*

Signatures: Solrun Johanne Vevelstad EMMANUEL MBA

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	Solution preparation	Spill of solution to the floor/bench	4	A	A	A		4A	The bench/floor will be washed with water after every preparation of solution
2		Spill of solution on humans	4	A	A	A		4A	Safety equipment must be used!
3		Spill of solution into the eyes	2	C	A	A		2C	Safety glasses must be used!
4		Preparing acid solutions--> acid solution on your skin	1	B	A	A		1B	People have to know how to treat acid and water.
5	filling of the system with solution	spill	1	A	A	A		1A	spill should be cleaned and washed with water
6	Operations with gas								

	0	Safety valve don't work/adjusted too high value the reactor could break.	2	B	A	D		2B	Safety cover for the reactor installed.
7		Leakages in the gas bottle connections	2	A	A	A		2A	connections should be checked regularly. Gas cylinders should be closed after each day.
8	During running of experiments	Loss of electricity	2	A	A	A		2A	Electricity has no harmful effects.
	0	Loss of cooling water	2	A	A	A		2A	Julabo will shut down.
9		Non functioning oil bath--> overheating	1	B	A	C		1B	
10		The stirrer drops to the bottom of the reactor	2	A	A	A		2A	
11		Leakage in the cooling water system	2	A	A	C		2A	Connections should be checked regularly.
12		Leakage from the reactor	2	A	A	C		2A	
13	Emptying and cleaning of the reactor	Spill							See ID 1-3
14		Too high temp. difference between the julabo+ reactor	2	A	A	D		2A	
15		spill of solution							see ID 1-3
16									
17									
18									



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

Unit: *Kjemisk prosesstel* **Date:** 30.09.2011

Line manager: *Øyvind Gregersen*

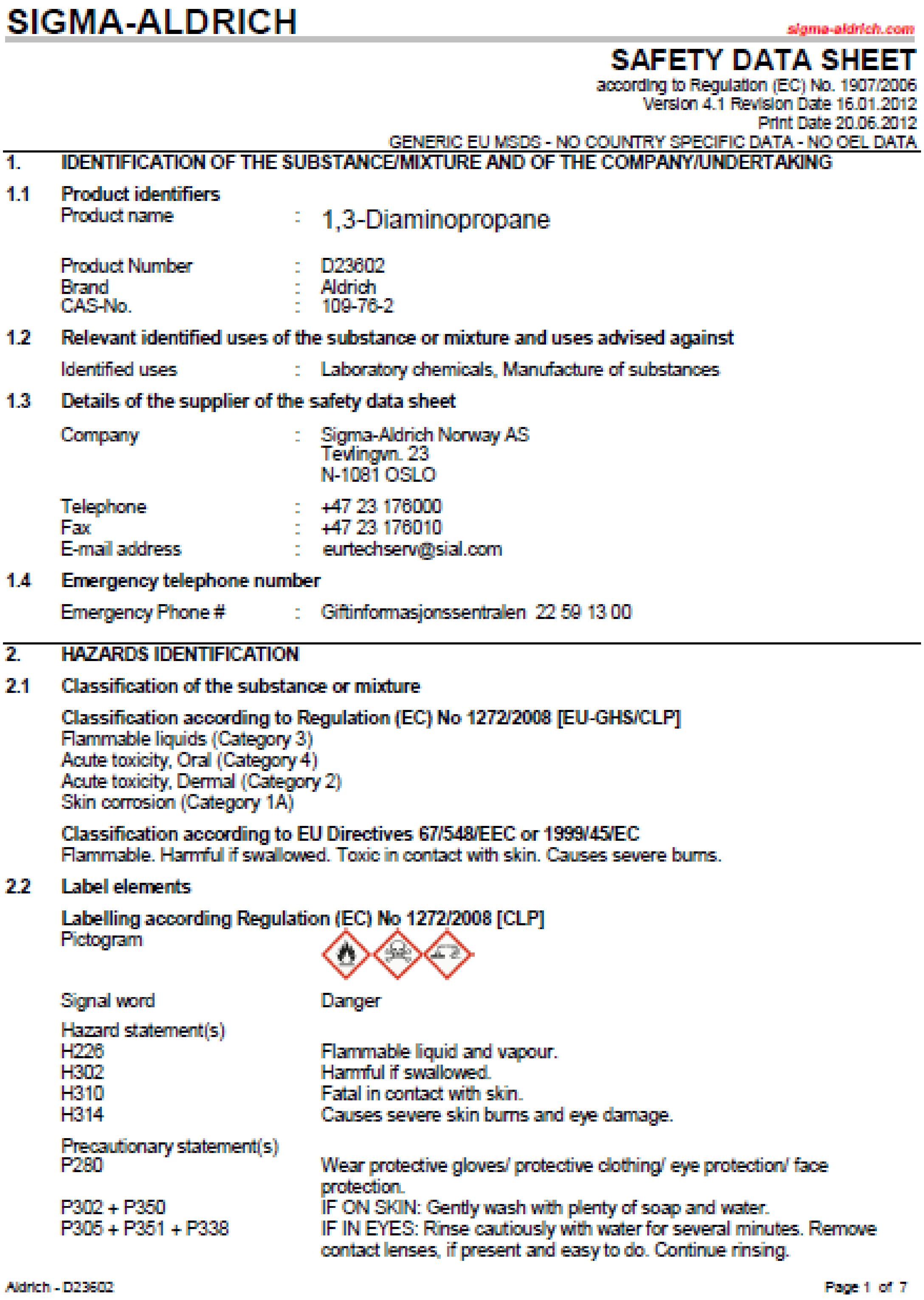
Participants in the identification process (including their function): Emmanuel Mba, Solrun Vevelstad, Hanna Knuutila

Short description of the main activity/main process: High pressure N2O solubility, up to 6 bar, up to 100oC. Liquid amount: 600 ml

ID no.	Activity/process	Responsible person		Existing documentation	Existing safety measures	Comment
1	Solution preparation				Solutions prepared in the fume cupboards; safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	
2						
3						
4						
5	filling of the system with solution				safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	

6	Operations with gas				Correct use of gas bottles needed. Correct use of reduction	N2O, N2 and CO2 is used
					Safety valve connected to the reactor.	
7						
8	During running of experiments					
9						
10						
11						
12						
13	Emptying and cleaning of the reactor				safety glasses, gloves and lab jacket are used all the time. Depending on the chemical gas mask might be required.	The temp d/ff b/w the reactor and julabo must not be more than 20C while emptying the reactor. Ammonia smell possible.
14						
15						
16						

Appendix S: Material Safety Data Sheet of 1,3-Diaminopropane (DAP)



SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET
according to Regulation (EC) No. 1907/2006
Version 4.1 Revision Date 16.01.2012
Print Date 20.06.2012
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 : 1,3-Diaminopropane

Product Number : D23602
Brand : Aldrich
CAS-No. : 109-76-2

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 Norway AS
Tevlingvn. 23
N-1081 OSLO

Telephone : +47 23 176000
Fax : +47 23 176010
E-mail address : eurtechserv@sial.com

1.4 Emergency telephone number

Emergency Phone # : Giftinformasjonssentralen 22 59 13 00

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

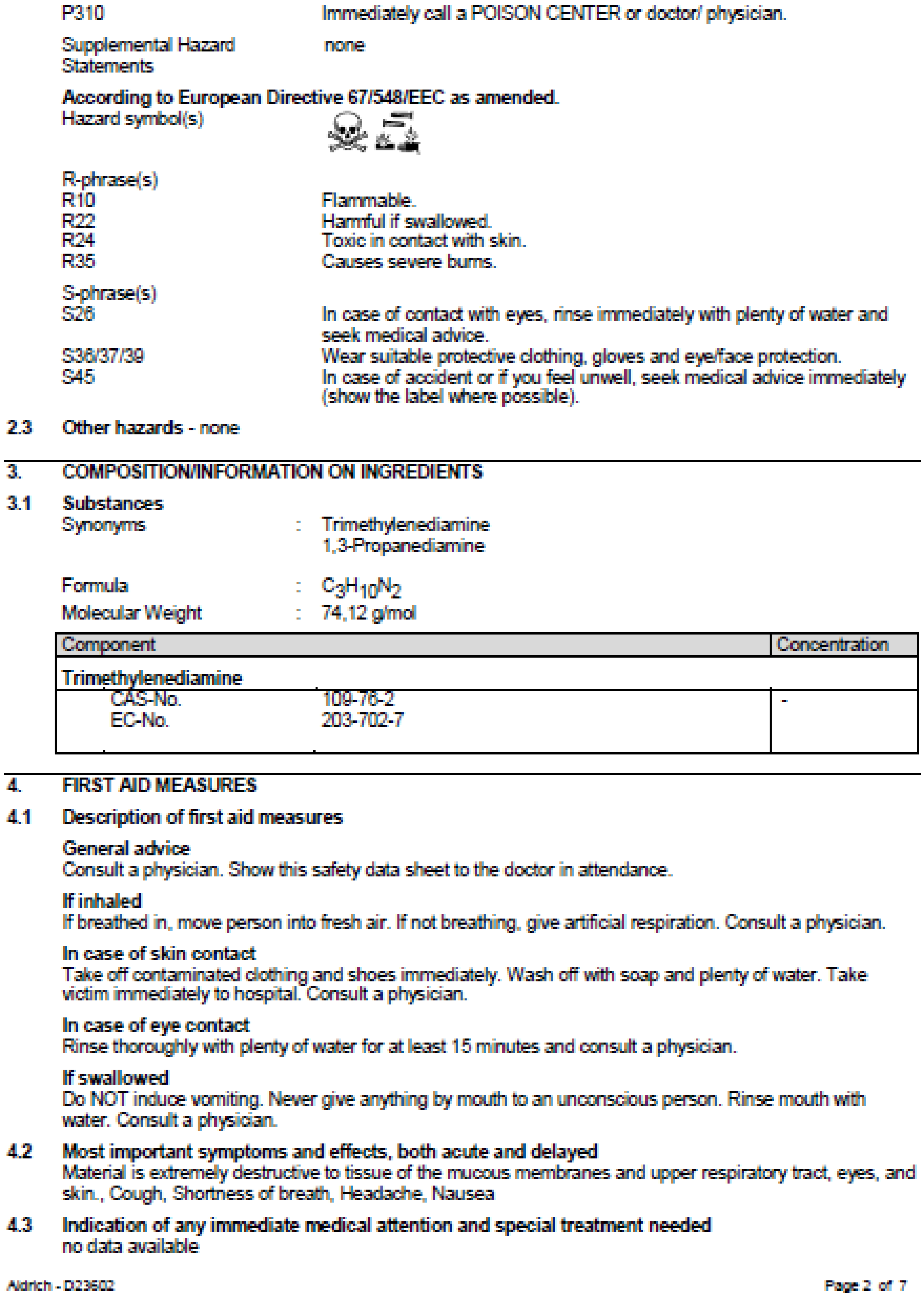
Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Flammable liquids (Category 3)
Acute toxicity, Oral (Category 4)
Acute toxicity, Dermal (Category 2)
Skin corrosion (Category 1A)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Flammable. Harmful if swallowed. Toxic in contact with skin. Causes severe burns.

2.2 Label elements

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

Pictogram	
Signal word	Danger
Hazard statement(s)	
H226	Flammable liquid and vapour.
H302	Harmful if swallowed.
H310	Fatal in contact with skin.
H314	Causes severe skin burns and eye damage.
Precautionary statement(s)	
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P302 + P350	IF ON SKIN: Gently wash with plenty of soap and water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.



P310	Immediately call a POISON CENTER or doctor/ physician.
Supplemental Hazard Statements	none

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

Hazard symbol(s)

R-phrase(s)	
R10	Flammable.
R22	Harmful if swallowed.
R24	Toxic in contact with skin.
R35	Causes severe burns.

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.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

2.3 Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Synonyms : Trimethylenediamine
1,3-Propanediamine

Formula : $C_3H_{10}N_2$

Molecular Weight : 74,12 g/mol

Component		Concentration
Trimethylenediamine		
CAS-No.	109-76-2	-
EC-No.	203-702-7	

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
Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Take victim immediately to hospital. 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
Do NOT induce vomiting. 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

Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin., Cough, Shortness of breath, Headache, Nausea

4.3 Indication of any immediate medical attention and special treatment needed

no data available

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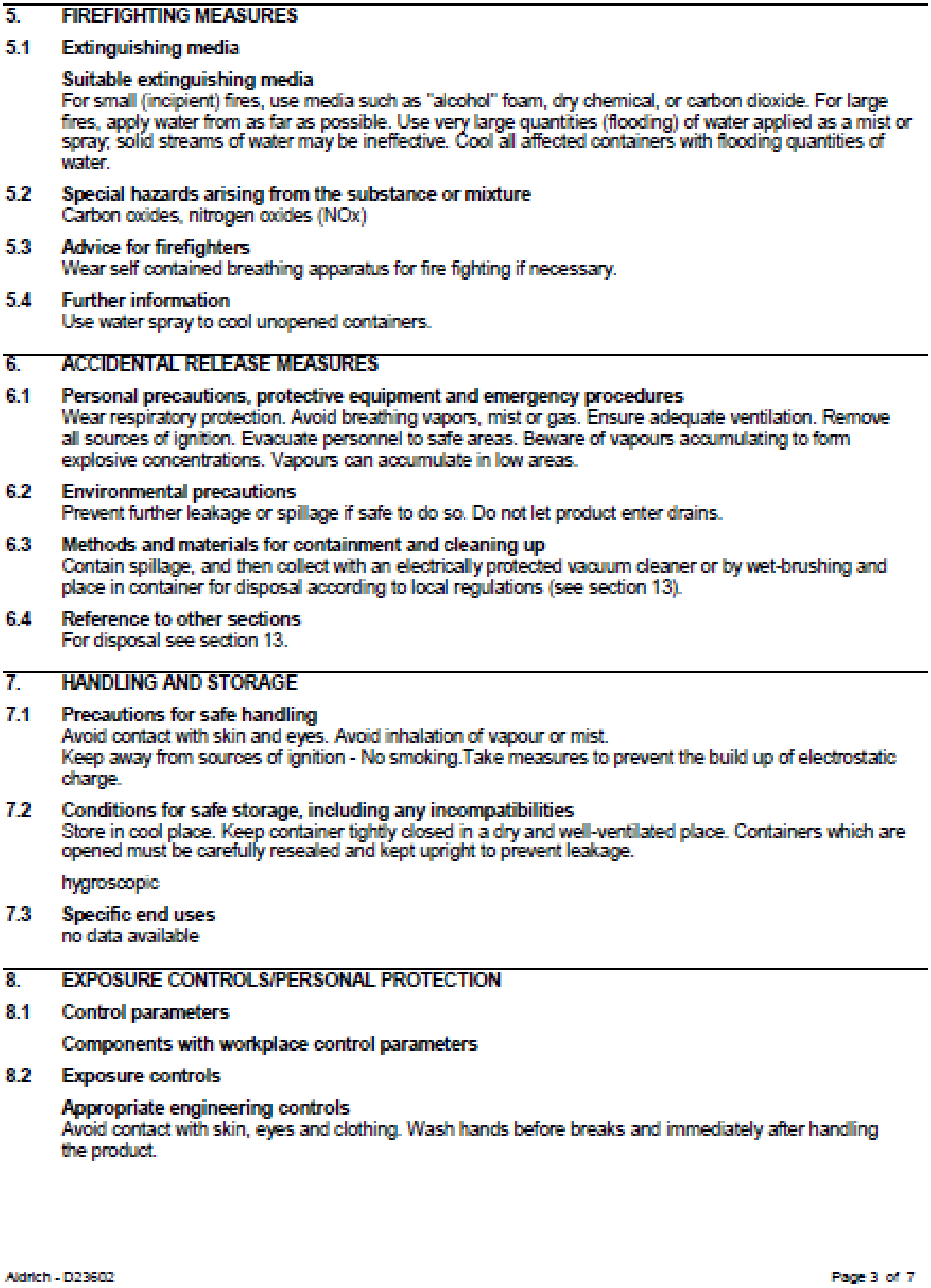


5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media
For small (incipient) fires, use media such as "alcohol" foam, dry chemical, or carbon dioxide. For large fires, apply water from as far as possible. Use very large quantities (flooding) of water applied as a mist or spray; solid streams of water may be ineffective. Cool all affected containers with flooding quantities of water.

5.2 Special hazards arising from the substance or mixture

Carbon oxides, nitrogen oxides (NOx)

5.3 Advice for firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information

Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures

Wear respiratory protection. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.

6.2 Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations (see section 13).

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.
Keep away from sources of ignition - No smoking.Take measures to prevent the build up of electrostatic charge.

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.

hygroscopic

7.3 Specific end uses

no data available

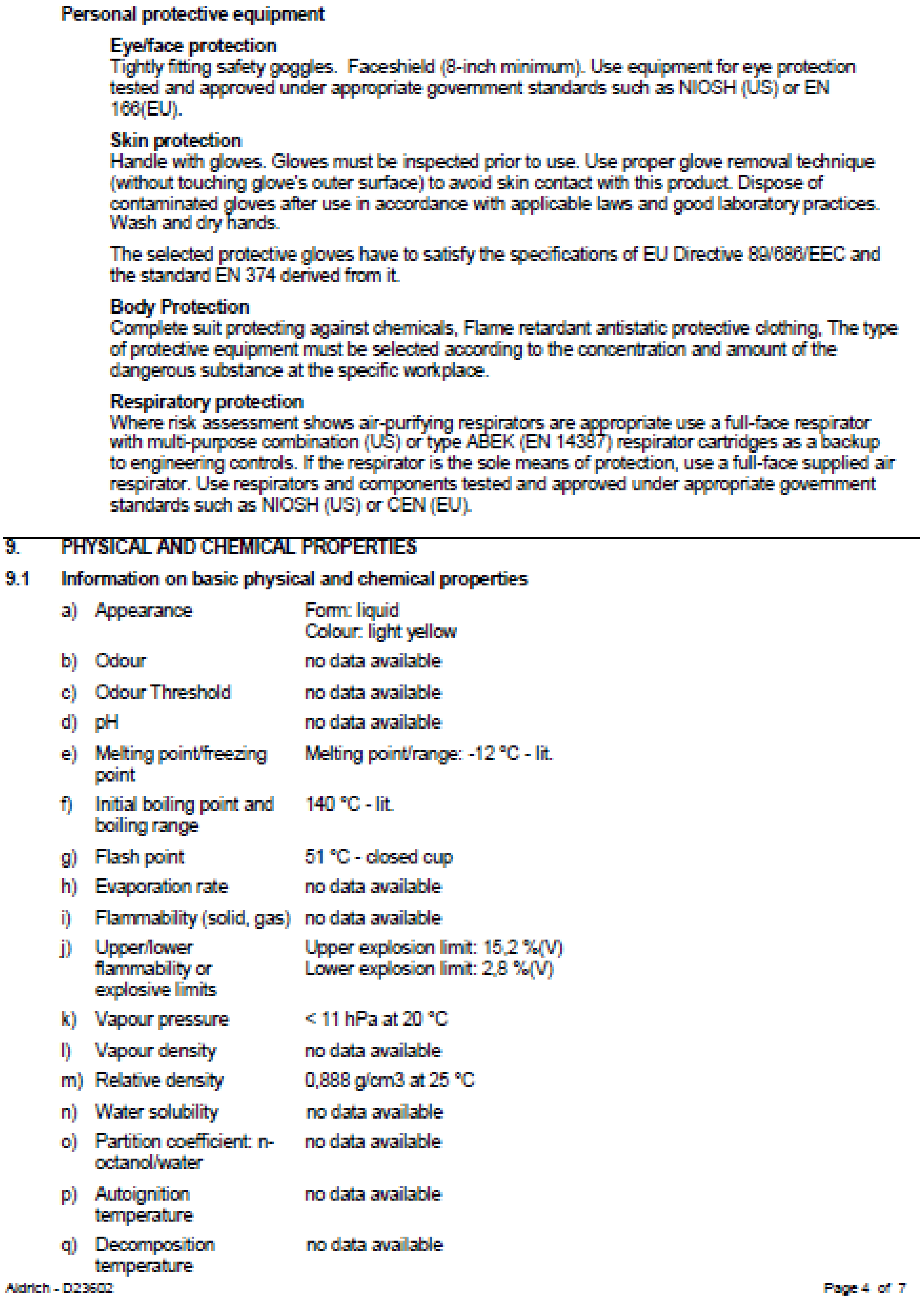
8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

8.2 Exposure controls

Appropriate engineering controls
Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.



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.

Body Protection
Complete suit protecting against chemicals, Flame retardant antistatic protective clothing, 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: liquid Colour: light yellow
b)	Odour	no data available
c)	Odour Threshold	no data available
d)	pH	no data available
e)	Melting point/freezing point	Melting point/range: -12 °C - lit.
f)	Initial boiling point and boiling range	140 °C - lit.
g)	Flash point	51 °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: 15,2 %(V) Lower explosion limit: 2,8 %(V)
k)	Vapour pressure	< 11 hPa at 20 °C
l)	Vapour density	no data available
m)	Relative density	0,888 g/cm3 at 25 °C
n)	Water solubility	no data available
o)	Partition coefficient: n-octanol/water	no data available
p)	Autoignition temperature	no data available
q)	Decomposition temperature	no data available

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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

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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
Avoid moisture.
Heat, flames and sparks.

10.5 Incompatible materials
acids, Acid chlorides, Acid anhydrides, Strong oxidizing agents, Carbon dioxide (CO2)

10.6 Hazardous decomposition products
Other decomposition products - no data available

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11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity
LD50 Oral - rat - 700 mg/kg

LD50 Dermal - rabbit - 177 mg/kg

Skin corrosion/irritation
Skin - rabbit - Corrosive

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Reproductive toxicity

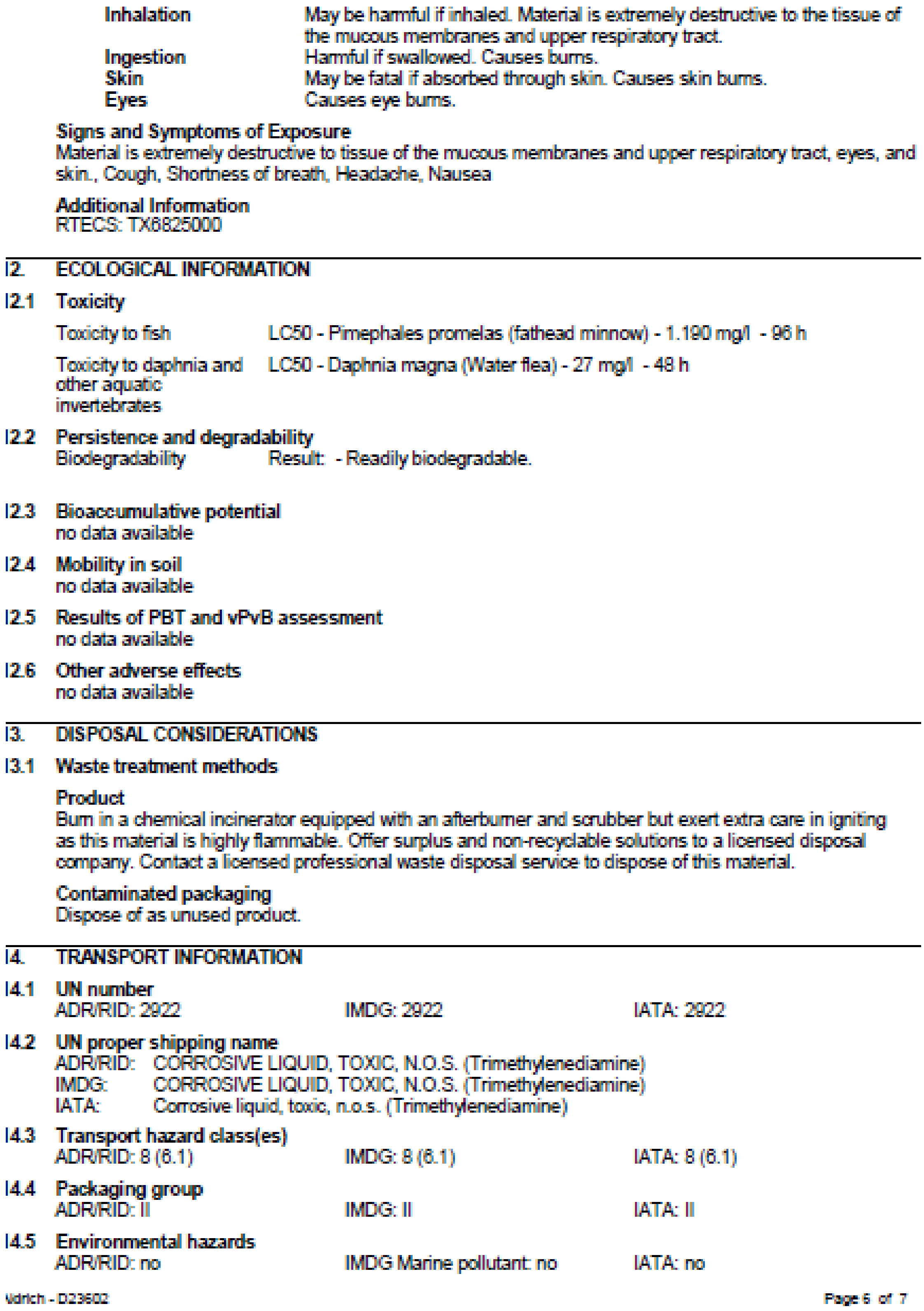
Developmental Toxicity - mouse - Intraperitoneal
Effects on Embryo or Fetus: Fetotoxicity (except death, e.g., stunted fetus). Effects on Embryo or Fetus: Other effects to embryo. Specific Developmental Abnormalities: Musculoskeletal system.

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. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract.
Ingestion	Harmful if swallowed. Causes burns.
Skin	May be fatal if absorbed through skin. Causes skin burns.
Eyes	Causes eye burns.

Signs and Symptoms of Exposure
Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin., Cough, Shortness of breath, Headache, Nausea

Additional Information
RTECS: TX6825000

12. ECOLOGICAL INFORMATION

12.1 Toxicity

Toxicity to fish	LC50 - Pimephales promelas (fathead minnow) - 1.190 mg/l - 96 h
Toxicity to daphnia and other aquatic invertebrates	LC50 - Daphnia magna (Water flea) - 27 mg/l - 48 h

12.2 Persistence and degradability

Biodegradability	Result: - 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
no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product
Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

14.1 UN number

ADR/RID: 2922	IMDG: 2922	IATA: 2922

14.2 UN proper shipping name

ADR/RID:	CORROSIVE LIQUID, TOXIC, N.O.S. (Trimethylenediamine)
IMDG:	CORROSIVE LIQUID, TOXIC, N.O.S. (Trimethylenediamine)
IATA:	Corrosive liquid, toxic, n.o.s. (Trimethylenediamine)

14.3 Transport hazard class(es)

ADR/RID: 8 (6.1)	IMDG: 8 (6.1)	IATA: 8 (6.1)

14.4 Packaging group

ADR/RID: II	IMDG: II	IATA: II

14.5 Environmental hazards

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

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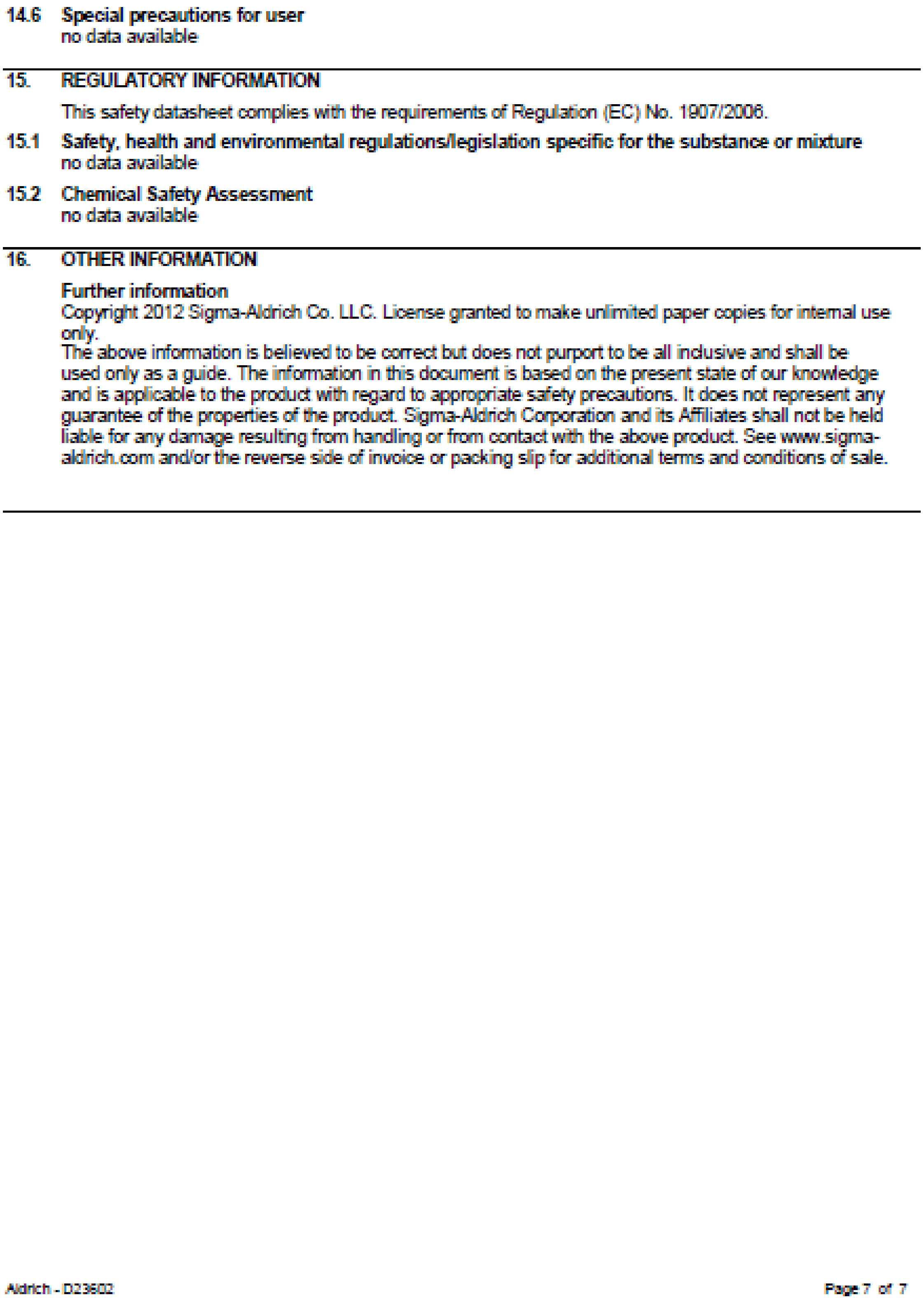

14.6 Special precautions for user
no data available

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

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.