

FMH606 Master's Thesis 2021

Process Technology

Literature Review and Correlation of Density for Amines Relevant for CO₂ Capture Process

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Course: FMH606 Master's Thesis, 2021

Title: Literature Review and Correlation of Density for Amines Relevant for CO₂ Capture Process

Number of pages: 124

Keywords: Density, aqueous, AMP, PZ, MEA, MDEA, Correlation, CO₂

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Summary:

This work mainly deals with study of Carbon dioxide Capture Plants and solely focuses on density of different amines and their mixtures available limitedly in literature with reference to CO₂ capture plants. Different amines used in the plant for absorbing CO₂ are discussed in this thesis. Also, various correlation methods such as Jae-Hoon Song Method, Modified Tammann-Tait equation, Modified Rackett equation, Samanta et al. Method, Henni et al. Method, Modified Setschenow Method, Amundsen et al Method, Hartono et al. Method etc. are used as mathematical correlation methods using python code in this thesis with the AARD (%) found to be 0.0074, 0.04, 0.926, 0.018, 0.086, 0.120, 0.160 & 0.180 respectively.

Preface

The world is suffering from increasing greenhouse gas emission. Carbon dioxide (CO_2) is the most influential gas for increasing global warming in earth. Various alkanolamines are used till present and research are ongoing for choosing suitable amine for CO_2 capture for industries process. The basic thing to be considered is the physical properties of Alkanolamines for absorption process. This thesis deals with densities of different aqueous amines at different temperatures which are basically used for the acid gas absorption process. Different density data from several literatures at different temperatures and concentration are investigated and correlated with different methods in this work.

I would really like to thank & express my gratitude towards supervisor Dr. Zulkifli Bin Idris for giving the opportunity to know about the CO_2 capture plants and helped me to have a broad knowledge of the role of amines and their density in CO_2 capture systems. I am grateful and would like to thank my teachers and the University of South-Eastern Norway, Porsgrunn campus for providing support and effective guidelines during this thesis.

It is worth mentioning, this thesis has been completed in critical situation of Covid-19 pandemic. There were too many difficulties on our way due to insufficient experimental data of density of different amine blends, but I tried my best to be confident and give a satisfactory and reasonable output of the work.

Porsgrunn, May 24, 2021

Pradeep Baral

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Nomenclature

°C	Celsius
°F	Fahrenheit
AAD	Average absolute deviations
AARD	Absolute Average Relative Deviation
AMD	Absolute Maximum Deviation
AMP	2-Amino-2-methyl-1-propanol
Aq.	Aqueous
CAPX	Annualized Capital Expenditure
Cco ₂	Carbon dioxide Concentration
CCS	Carbon Capture and Storage
CH ₄	Methane
CO ₂	Carbon dioxide
Cpz	Piperazine
DEA	Diethanolamine
DEAE	Diethylaminoethanol\
EG	Ethylene glycol
FOLU	Forestry and Other Land Use
g/mol	gram per mole
GHG	Green House Gas
gm/cm ³	gram per cubic centimeter

Nomenclature

H ₂ O	Water
H ₂ S	Hydrogen sulfide
Hg	Mercury
K	Kelvin
kg/m	kilogram per meter
Kg/m ³	kilogram per cubic meter
kgm ⁻³ K ⁻¹	kilogram per cubic meter per Kelvin
LPG	Liquefied Petroleum Gases
m ³ mol ⁻¹	cubic meter per mole
MAX	maximum
MDEA	N-methyl diethanolamine
MEA	Monoethanolamine
mg/mL	milli-gram per milli liter
mm	millimeter
mm Hg	millimeter of mercury
Mol/kg	mole per kilogram
MPa	mega pascal
Mpa K ⁻¹	mega pascal per kelvin
MpaK ⁻²	mega pascal per square kelvin
N	number of data points
N ₂	Nitrogen
N ₂ O	Nitrous oxide

Nomenclature

NO ₂	Nitrogen dioxide
NO _x	Nitrogen Oxide
O ₂	Oxygen
OH	Hydro oxide
OPEX	Operating Expenditure
PH	Potential of hydrogen
ppm	parts per million
PZ	Piperazine
R	Molar gas constant, (atm cm ³)/(mol K)
R ₁ R ₂ NH	Secondary amine
R ₁ R ₂ R ₃ N	Tertiary amine
RNH ₂	Primary amine
SO ₂	Sulfur oxide
SO _x	Sulphur Oxide
Tr	Reduced temperature, T/T _c
WGS	Water-Gas Shift
wt	Weight
α/mol	CO ₂ Loading
ρ	Density
P _c	Critical pressure, atm
T _c	Critical temperature, K

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1 Introduction

1.1 Background

The change in climate due to global warming has become an important issue these days which is mostly caused by emission of greenhouse gas (GHG). GHG refers to the harmful gases that are emitted incessantly into the earth's atmosphere through the activities like burning fossil fuels, deforestation caused by human beings and through natural processes like volcanic eruptions. The gases causing greenhouse effects are carbon dioxide (CO₂), methane (CH₄), NO_x, SO_x, etc. In the list of GHG, carbon dioxide (CO₂) is considered to be the significant one in emission amount.

Carbon dioxide (CO₂) , nitrous oxide (N₂O), methane (CH₄) and fluorinated gases are the primary greenhouse gases emitted by human activities. According to the data of annual anthropogenic Greenhouse gas emissions recorded from 1970-2010, CO₂ is emitted in maximum quantity from fossil fuel combustion and industrial process i.e. 65% , from Forestry and Other Land Use (FOLU)-16%, Nitrous Oxide (N₂O) - 6.2%, Methane(CH₄)-11% and Fluorinated gases-2%. Mostly, Emission of CO₂ is increasing rapidly, and it has direct negative impact on us and our atmosphere. About 50 % of progressive anthropogenic CO₂ emissions between 1750 and 2010 have occurred only in last 4 decades. Recently, in 2018 at Hawaii's Mauna Loa Atmospheric Baseline Observatory, Carbon dioxide levels reached 411 parts per million(ppm) and it is the highest monthly average ever recorded [1].

Greenhouse Gas Emissions by Economic Sectors

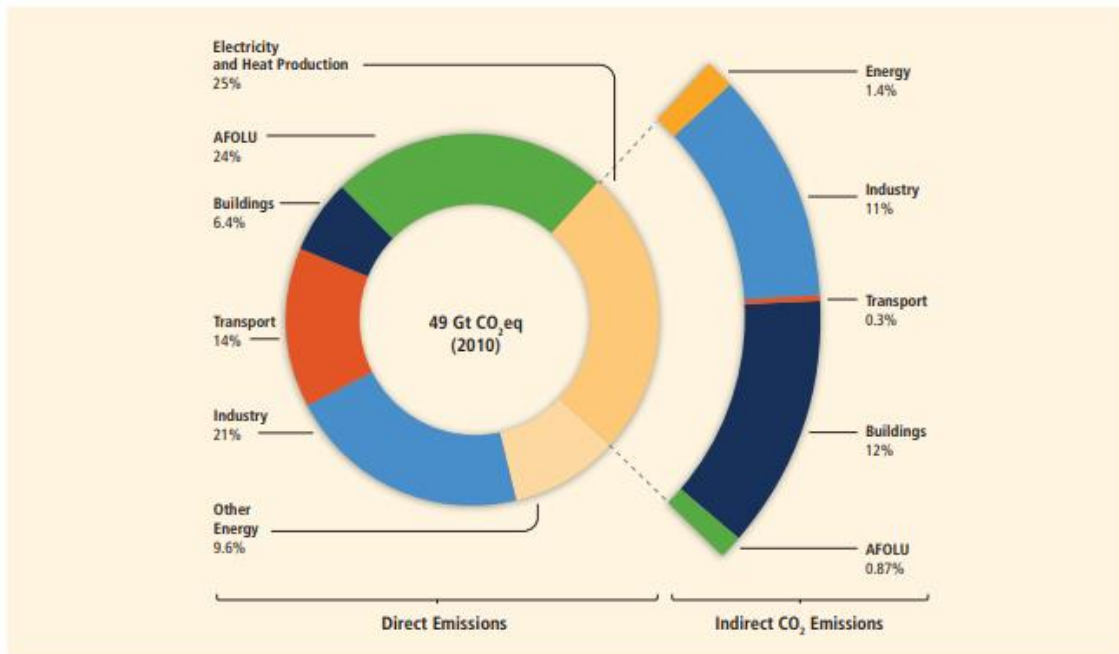


Figure 1.1: Economic sectors total anthropogenic GHG emissions (GtCO₂ eq/yr)[2]

Globally, economic and population growth has been playing major role for the rise of CO₂ emissions from fossil fuels combustion. The Earth's atmosphere contained 278 parts of CO₂ per million during the initial phase of industrial revolution. Nowadays (after more than 250 years), earth's atmosphere contains 414 parts of CO₂ per million. If the increment of CO₂ continues this way, then by 2060 it would pass 560 ppm which is more than double of the initial phase [2].

Greenhouse gases leads to several environmental and health threats. Carbon dioxide emissions is the core leading to global climate change. We must avoid the worst impacts of climate change by taking required steps urgently to reduce emissions.

Researchers have developed end pipe technologies i.e. Carbon-Capture and Storage which involves in capture, transport and storage of carbon

1.2 Aim of this work

This work mainly deals with density of different amines and their mixtures available limitedly in literature with reference to CO₂ capture plants. Different amines used in the plant for absorbing CO₂ in the plant are discussed in this thesis. Densities for unloaded and CO₂-loaded amine solutions found in literature are analyzed using suitable correlation methods. The literature data is correlated by fitting parameters to appropriate models such that these models can account for mixture densities at various temperatures, amine concentrations and CO₂ loadings. Also, various correlation methods such as Jae-Hoon Song Method, Modified Tammann-Tait equation, Modified Rackett equation, Samanta et al. Method, Modified Setschenow Method, etc are discussed in this thesis.

1.3 Complications due to COVID-19 Pandemic Situation

This thesis mainly deals about density of various binary, tertiary & quaternary mixtures density for CO₂ absorption process. As the university lab was closed due to COVID-19 situation & also being in home country Nepal, the experimental data of density couldn't be available at this moment. Due to lack of sufficient data points for calculating density at different temperature range, the data used in this thesis are interpolated in between as well.

2 Carbon Capture & Storage

2.1 CO₂ capture systems

CO₂ can be captured and separated using different processes like Chemical absorption, Physical absorption, Adsorption, Membranes, Cryogenics, Chemical Looping, Ionic Liquid, Biological etc. This system generates a concentrated stream of CO₂ at high pressure and is further moved to the storage site. There are three systems used to capture the CO₂ produced from fossil fuel and discussed in this thesis.

2.1.1 Post combustion capture system

In this system, CO₂ is captured from a flue gas which is generated after the combustion of carbon-based fuel. Normally these systems use liquid solvent to capture the small fraction of CO₂ typically (3-15)% by volume. For the separation of CO₂, flue gas is passed through the equipment. In conventional fossil fuel or power plants, the generated heat energy is converted into electricity. More than 60% of the electricity in the US is produced from fossil fuel power plants so, the deployment of post-combustion capture technologies is must to reduce CO₂ emissions. [3],[4].

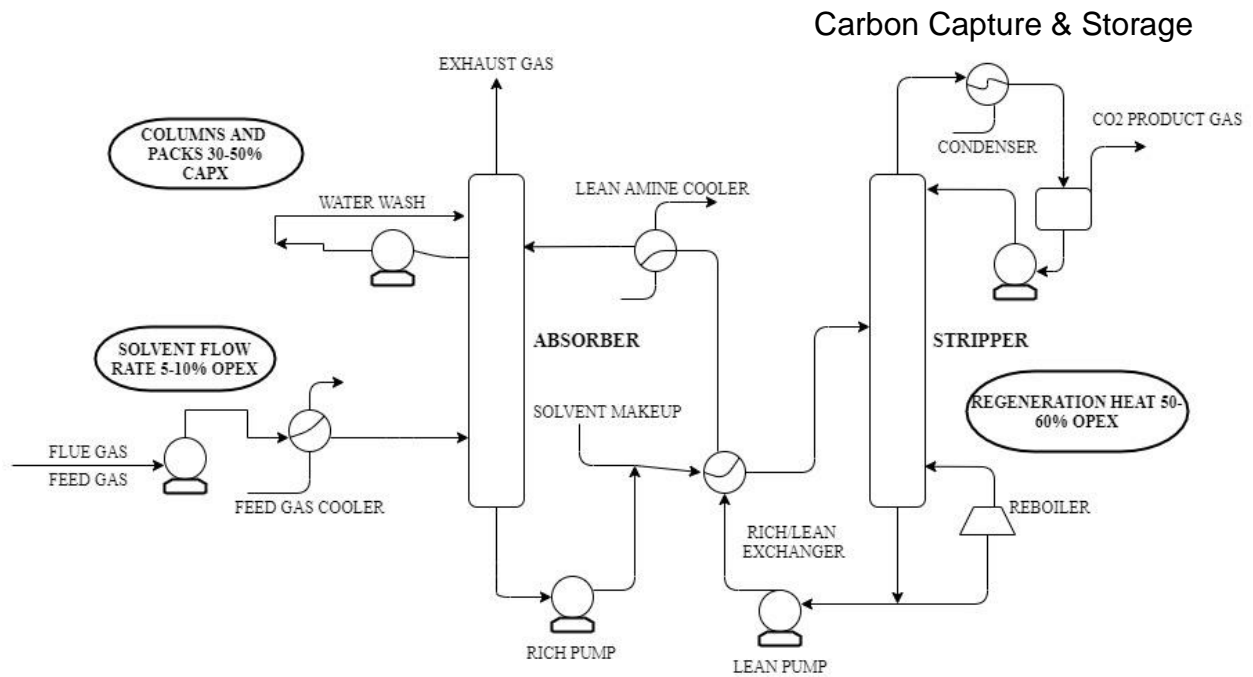


Figure 2.1: Post-Combustion Capture System

2.1.2 Pre-Combustion Capture System

In this system, CO₂ is captured from a flue gas which is generated before the combustion of carbon-based fuel. Using gasification and reforming process carbon dioxide gets separated and Synthesis gas (Syngas) is formed. The Synthesis gas is basically the combination of Hydrogen, Carbon Monoxide, and CO₂ gas & have water-gas shift reaction to convert CO & water to H₂ and CO₂ rich gas mixture i.e. 15-50% by Volume. In an integrated gasification combined cycle (IGCC), syngas produces electricity by fueling a gas-turbine generator. The recovered heat produce steam which also leads turbine generator to produce electricity. Carbon initially captured before syngas is combusted in the gas turbine. To ease carbon capture and increase hydrogen production, the syngas is passed in water-gas shift to produce extra hydrogen and convert carbon monoxide into CO₂ which can be captured, transported & stored & H₂ rich fuel shall be combusted. Post combustion capture is normally less effective than pre- combustion capture [5].

Carbon Capture & Storage

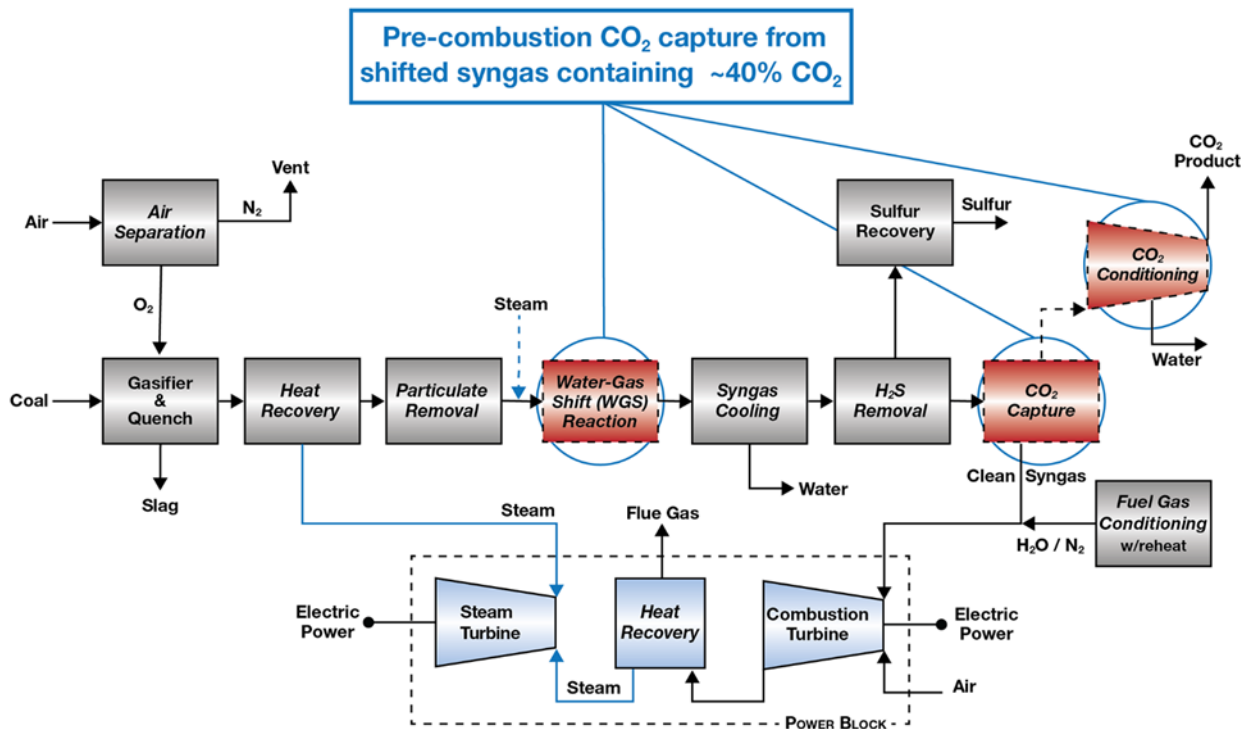


Figure 2.2: Pre-Combustion Capture System [5]

2.1.3 Oxy-fuel Combustion

Oxy fuel combustion is the process of burning fuel using pure oxygen instead of air. It removes nitrogen from the oxidizer. It recycles flue gas to achieve a lower flame temperature. This system is the most efficient energy saving technology.

Due to the use pure oxygen instead of air for fuel combustion, high concentrations of CO₂ is obtained. It requires a part of flue gas to be recirculated to control the furnace flame and balance the property of heat transfer.

The oxygen is diluted with flue gas instead of nitrogen to control the temperature. This system is used to produce flue gas with very high concentrations of CO₂ and water vapor and then capture or separate the carbon dioxide (CO₂) using low temperature dehydration and

Carbon Capture & Storage

desulfurization process. The oxy-fuel combustion process results to reduced nitrogen oxide emissions, highly pure carbon dioxide and lower gas volumes [6].

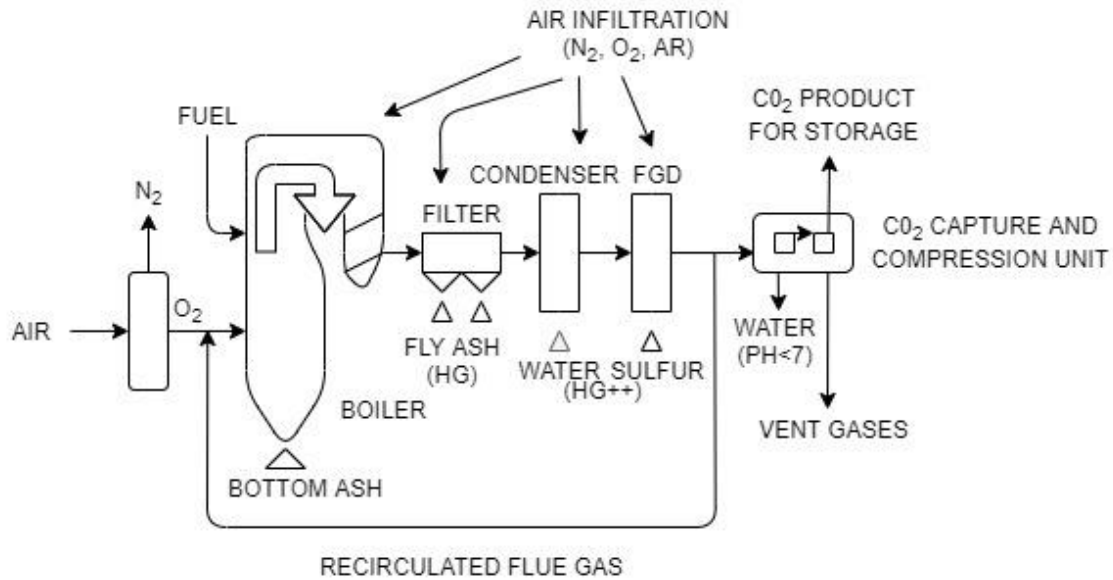


Figure 2.3: Oxy-Fuel Combustion

This system is more competitive compared to other CO_2 control technology.

Table 2.1 Comparison of different types of CO_2 capture systems

CO_2 Capture Systems	Advantages	Disadvantages
Post-combustion Capture	<ul style="list-style-type: none"> • Applicable to existing coal-fired power plants • Added option by retrofitting technology 	<ul style="list-style-type: none"> • Diminution of flue gas in CO_2 • Low CO_2 partial pressure
Pre-combustion Capture	<ul style="list-style-type: none"> • Concentrated Synthesis gas in CO_2 • High CO_2 partial pressure 	<ul style="list-style-type: none"> • Equipment cost is high • Only Applicable to new plants
Oxyfuel Combustion	<ul style="list-style-type: none"> • reduced NO_x emissions • minimize excess air coefficient 	<ul style="list-style-type: none"> • expensive for cryogenic oxygen production • low efficiency and higher auxiliary load

2.2 CO₂ Transport

The CO₂ captured should be moved from the point of capture to a storage site for avoiding fugitive emissions, maintaining healthy environment aspect and managing economic aspect. CO₂ is mostly found in liquified and gaseous form for transport and storage. CO₂ pipelines operate as the most prevalent means of bulk CO₂ transport technology in operation today. Through the pipeline, CO₂ is transported through 'dense phase' mode. Then, CO₂ is compressed to a pressure above 8 MPa which avoids two phase flow regimes. It increases the density leading to easier and economic way to transport [7].

Also, CO₂ is transported as a liquid in ships, road, or rail in insulated tank at a temperature below ambient, and much lower pressure than pipeline transport but on a relatively minor scale due to its insignificance. In the case when CO₂ must be transported over large distances or overseas, transport by ship similar to LPG transport may be economical and materialistic as the properties of liquified CO₂ are similar to those of LPG [8]. Other possible way of transport is through road and rail tankers where CO₂ is transported at a temperature of -20 °C and 2 MPa pressure. However, this technique of transport is uneconomical relatively, except on a very small scale CCS [9].

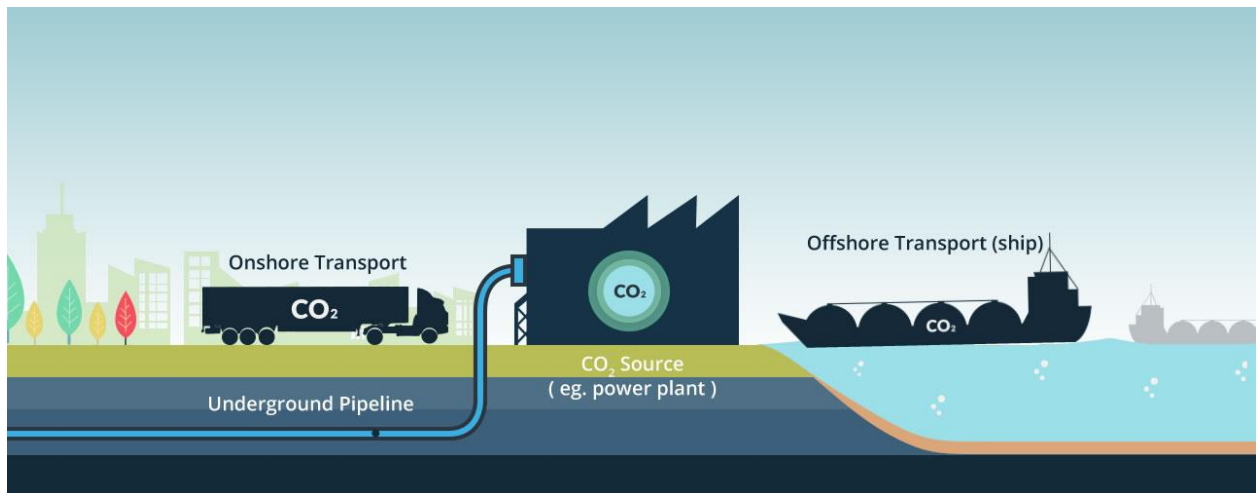


Figure 2.4: CO₂ Transport [10]

2.2.1 Risk aspects

Though major obstacles are not seen during the transportation of CO₂ but some of the protective major should be taken to avoid risks. Route selection, leakage detection, over pressure protection and other factors (e.g., pipeline should be made from corrosion resistant alloy or polymer coated) must be considered. These precautions could help to mitigate corrosion and avoid leakage in transportation and storage [8].

2.3 CO₂ Storage

After the CO₂ is captured, it is either injected in underground geological formation or stored through another non-geological storage technique. Several factors should be considered before storing CO₂ for a sustainability to project like identification of site enough to store maximum amount of CO₂, temperature, pressure and chemical properties of CO₂, source, mode of transportation and duration of operation etc. Geological Carbon Sequestration Process stores CO₂ in underground geologic formation and then liquified to inject into porous rock formations. This method is also referred as tertiary recovery because of its use producing oil well. Also the liquid CO₂ is used in oil bearing formation to reduce the viscosity of oil and allow it's flow easily to the oil well [11].

2.3.1 Effects of high CO₂ Inhalation

When CO₂ level reaches to 50% in the air ,people dies either by oxygen depletion or due to harmful effects of Carbon dioxide inhalation. There is various incident around the globe caused due to high level of CO₂ inhalation and CO₂ storage and transport.

Nearly 15 tons of CO₂ was accidentally spread from a fire extinguishing installation in Monchengladbach, Germany (2008) which leads to 107 number of intoxicated people where 19 of them were hospitalized [12].

Carbon Capture & Storage

In 1986 approximately 1700 people & 3500 livestock died, due to unexpectedly release of an estimated 1.6 million tons of CO₂ in Lake Nyos ,Cameron which is naturally saturated by CO₂ due to magma chamber underneath the lake [12].

In 2019, Nineteen people needed hospital treatment after leak from fire extinguishing system & 10 peoples died on a Chinese cargo ship during repair work at dock in Shandong province[13].

Various incidents were caused due to leakage of CO₂ while storing as well as transporting. Also, inhaling more CO₂ by humans lead to serious diseases or demise. So, harmful gases like CO₂ needs to be stored and transported carefully.

2.4 Utilization of Captured Carbon with Enhanced Technologies

Despite the negative impact of CO₂ directly or indirectly in environment and other different sectors, it has been utilized in proper manner for beneficial purpose too. At present, CO₂ is being used directly by sequestration as EOR (i.e. Enhanced Oil Recovery), coolant, as well as in making fizzy drinks. Also, indirectly CO₂ is being converted into wide variety of commercial products such as chemicals or intermedium synthetic fused construction materials and the polymers, etc. This production process is being explored all over the world to overcome economically unfavorable conversion processes. The technologies involving catalytic conversion, electrochemical, mineralization, biological using microbes/enzymes, photocatalytic and photosynthetic processes have been reached a semi-commercial stage of development with possibility of being commercialized on a large scale[14]. Some of the recent technologies practiced out in different countries are discussed in this section.

A German company "Sunfire" has designed a process using high temperature called electrolysis of steam and CO₂ to produce syngas which is afterwards converted into synthetic fuels like gasoline, diesel etc.[15]. Similarly, "Pellet plant" successfully produce high quality diesel fuel by similar process. Another German company "EtoGas" developed processes that reacts CO₂ with hydrogen generated by water electrolysis to form methane which has been producing EtoGas using wind power and CO₂ from bio-gas plant.

Carbon Capture & Storage

Also, the Japanese company "Hitachi Zosen Inova" acquired EtoGas gas technology where plant takes fossil fuel CO₂ emissions and the combined CO₂ with hydrogen produce methane which is fed into existing gas grid besides the company's EtoGas gas catalytic reactor for the methylation process[16].

Likewise CRI (Carbon Recycling International) technology has been implemented in the 3-D steel plant to demonstrate residue plaster furnish gas converted into liquid fuel [17].The Canadian company "Carbon engineering" develops air-to-fuel process to produce liquid hydrocarbon fluid. It combines direct air capture technology with water electrolysis and fuel synthesis [18].

"Lanzatech's fermentation" which is process for ethanol production using microbes through CO rich fuel gas from steel mill [19].The technologies have also been developed by ACT(Accelerated Carbonization Technology) in order to produce construction and other materials through CO₂ mineralization. The Carbon Cure company also implements various process to converge industrial waste to cement materials, light weight aggregates etc.[20].

Similarly, the SkyMine carbon mineralization process by US company is designed to remove CO₂ from gaseous waste stream and transform into marketable products such as baking soda, caustic soda, bleach etc. [21].

The "Covestro plant" in Germany uses carbon dioxide as a basic material for the formation of chemical building blocks for high-quality plastics through copolymerization [22].

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3 Literature Review

3.1 Amine-based technology

Amine scrubbing system is used to capture and separate CO₂ from flue gas stream. Initially, for the separation of CO₂ from flue gas stream, a continuous scrubbing system is used. The system consists of two main components i.e. an Absorber and a Regenerator. In an absorber, CO₂ is removed in concentrated form whereas in regenerator (or stripper), CO₂ is released (in concentrated form) and original solvent is recovered [23].

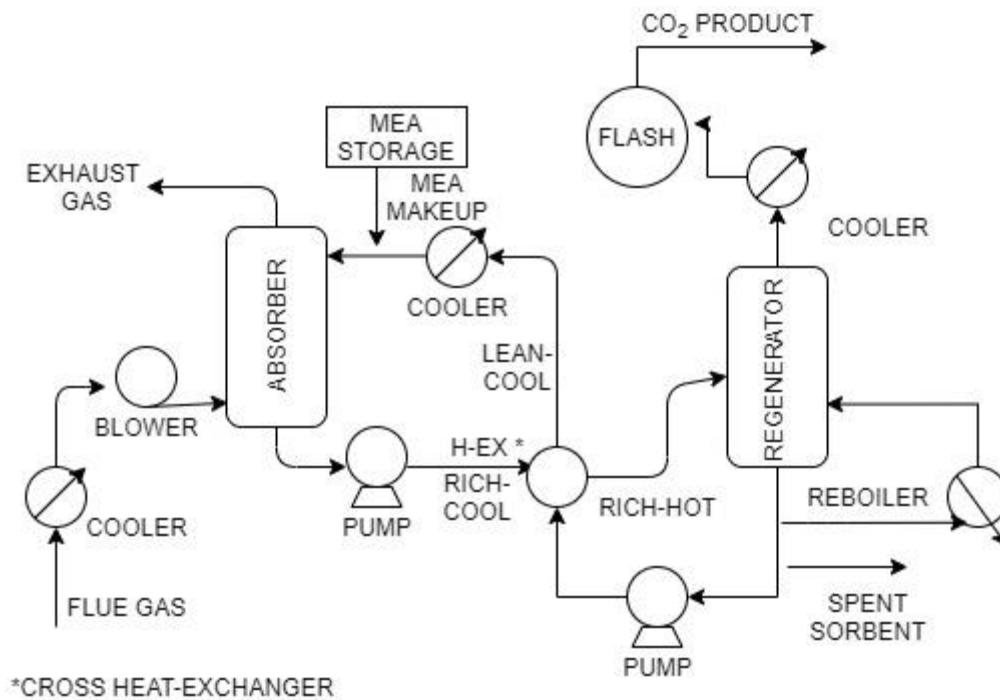


Figure 3.1: Flowsheet of CO₂ Gas Capture from flue gases applying Amine-Based System

Amine based technology is considered the most materialistic organized method in capture and separation of CO₂ from flue gas. It processes by passing CO₂ through the continuous amine scrubbing system that consists of an absorber and a stripper. The flue gas is sent off to the absorber unit from the bottom and exposed with the alkaline solvent, (mostly an amine-rich CO₂ solution) introduced from the top. After the exposure of CO₂ with amine solution, weak salts are formed that isolate CO₂ from the flue gas. The lean CO₂ solution is passed through the

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rich solution heat exchanger and then eventually to the stripper. In the stripper, the chemical reaction takes place at high temperature which restore solvent. By cooling the gas passing through the top of the stripper, vapor is separated from CO₂. Thus, the obtained CO₂ product is compressed and stored by sending the regenerated amine solution back to the absorber.

In this system, huge quantity of heat is necessary for regeneration of the solvent. This heat is drawn from the steam cycle which significantly reduces the net efficiency of power plant. Considerable amount of electrical energy is also required to pressurize the captured CO₂ for pipeline transport to the storage site. The overall energy of this process has serious impact on system performance as well as the overall cost of the system. Acid gases like SO₂ and NO₂ reacts with MEA to generate heat-stable salts which decreases the CO₂ absorption capacity of the solvent. Thus, very low concentrations of these gases (in the order of 10 ppm) are responsible to avoid excessive loss of costly solvents.

This system is based on Gas-Liquid Mass Transfer Process. The chemical reactions allowing diffusion of CO₂ intensifies the rate of mass transfer. Thus, the removal of carbon dioxide in absorber is affected by various parameter (e.g. Flue Gas Composition, CO₂ Concentration, MEA Concentration, Temperature, Flow Rates, Absorber Design and Pressure). Correspondingly, the conditions and detailed design of the regenerator also affects the energy requirements and overall performance of the system[24].

3.2 Significance of using amines

Most of the CO₂ capture plants are usually based on chemical absorption process using Monoethanolamine (MEA) based solvents. MEA is an organic chemical compound also known as ethanolamine. It belongs to amines family. It was developed 60 years ago as a non-selective solvent to clear acidic gas impurities (e.g. CO₂, H₂S) from the natural gas streams. Monoethanolamine (MEA) is most used amine for CO₂ capture in amine scrubbing technology, resulting the recovery rate of 8% for CO₂. However, by using improved solvents (amines) compared to MEA, 40% of energy requirements can be reduced. So many new solvents are on the way which are professed to have superior absorption and desorption characteristics.

Literature Review

Inorganic solvents such as Arsenic, Potassium Carbonate, Sodium Carbonate can be used for CO₂ absorption process but each of them has drawbacks like Arsenic is potent chemical which may harm to animal/plant life. Similarly, Carbonates may release Sodium and Potassium in product gas that leads to corrosion, erosion and can promote deposition in gas turbines. Generally, about 75% to 90% of CO₂ is captured using this technology developing a nearly pure (>99%) CO₂ product stream [23].

Physical properties of amines play an important role in CO₂ capture plant. The overall impact of different physical properties of amines with respect to temperature and cost of the overall project also rely on the type of amines used as an absorbent. Density, Viscosity, Solubility, Thermal Coefficient, Corrosiveness plays an important role in design of the absorption tower. Similarly, the Carbon capture technology needs more research in the field of absorbent used. An amine-based CO₂ capture system consists materials such as absorption column, desorption column, pumps and heat exchangers which are designed considering their density. Density of solvents are very important in process modelling, simulations, design of commercial plant as well. Other physical properties like density and viscosity of solvents are also very essential in calculations of molar volume, free energy of activation, entropy etc. which helps in better understanding of intermolecular interactions, theory of rate process for further designing and enhancement. Also, these properties are important in performing mathematical modelling and simulations for the sizing of process equipment. Further properties are functional in calculation to select material transfer equipment like pumps and valves [25]. Complete study of physical properties of amines and their mixture used as a solvent is important as large concentration of CO₂ is present in the absorber, stripper and other unit in large scale CO₂ capture system. Concentration of PZ studied below 14 mass % at 20 ° C are not useful for CO₂ capture applications as they cannot compete MEA solvent in CO₂ capture process [26].

Amines with various physical properties play different roles in making the work beneficial and effective. The lower aliphatic amines are gases with fishy odor whereas the primary amines with three or more carbon atoms are liquid and still higher ones are solid. Similarly, Aniline and other Aryl amines are also colorless but during storage due to atmospheric oxidation[27].

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Lower aliphatic amines form hydrogen bond with water molecules as they are easily soluble in water. Consequently, the boiling point of these compounds are higher than those of the corresponding phosphines with higher intermolecular association. The solubility of these amines decreases with an increase in carbon atoms, due to increase in hydrophobicity of the compound along which the chain length increases. Aromatic amines are those amines which participate in conjugate ring and donate their lone pair of electrons to the benzene ring, due to it the potential to engross in hydrogen bonding decreases. This ultimately consequences in a decrease in their solubility in water and high boiling point[28].

3.3 Examples of Amines used in CO₂ capture

Amines are organic compounds derived from ammonia by replacement of one or more hydrogen atoms by organic groups. Amines are classified into three different types which are primary ($R-NH_2$), secondary (R_1R_2-NH) and tertiary ($R_1R_2R_3-N$) depending on one, two, or three hydrogen atoms over nitrogen replaced by the organic functional group. An amine with an organic group OH is called alkanolamine. The most used primary amine solvent for CO₂ capture in chemical absorption process is the aqueous solution of Monoethanolamine (MEA). MEA has its own advantages over other alkanolamine like high reactivity, low molecular weight, high absorption capacity on weight basis, low solubility of hydrocarbons and good thermal stability, so it's the most reasonable amine used [29]. Figure 3.2 shows the structure of amines depending upon number of H replaced from NH₃.

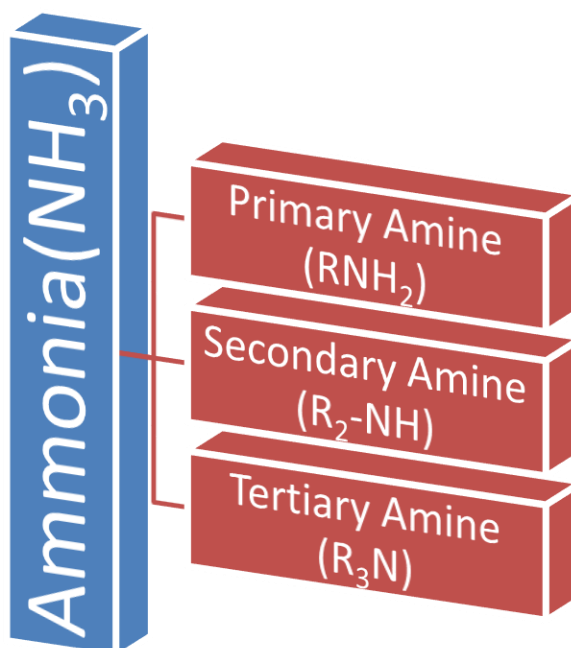
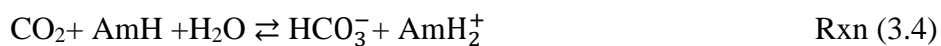


Figure 3.2: Structure of Amines [30]

General reaction scheme of CO₂ - Primary or Secondary amine system



General reaction scheme of CO₂ - Sterically Hindered Amine System



where,

AmH Amine molecule

AmCOO⁻ is stable carbamate ion

AmCOO⁻ is sterically hindered amine

HCO₃⁻ is Bicarbonate ion

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There are some amines too whose reaction is different from primary, secondary, and tertiary amines which is called sterically hindered amines which are basically primary or secondary amines whose amino group is attached to a tertiary carbon atom[31]. The sterically hindered amines are proposed as efficient absorbents which has been an eager regard in post combustion process. This is because of its advantages like high absorption rates at high CO₂ loadings, resistance to degradation. Also, due to lower enthalpy of reactions between carbonate and bicarbonate ions the amine can be regenerated by heating while lowering the cost of solvent as well[32]. Table 3.1 shows examples for alkanolamines and sterically hindered amines.

Table 3.1: Examples of Alkanolamines and Sterically Hindered Amines [33]

Primary alkanolamine	Secondary alkanolamine
Monoethanolamine(MEA)	Diethanolamine(DEA)
$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{N} - \text{C}_2\text{H}_4\text{OH} \end{array}$	$\begin{array}{c} \text{C}_2\text{H}_4\text{OH} \\ \\ \text{H} - \text{N} - \text{C}_2\text{H}_4\text{OH} \end{array}$
Tertiary alkanolamine	Sterically hindered amines
N-methyldiethanolamine (MDEA)	2-amino-2methyl-1-propanol (AMP)
$\begin{array}{c} \text{C}_2\text{H}_4\text{OH} \\ \\ \text{CH}_3 - \text{N} - \text{C}_2\text{H}_4\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{OH} - \text{CH}_2 - \text{C} - \text{NH}_2 \\ \\ \text{CH}_3 \end{array}$

Hence, significance of different physical properties like Density, Viscosity, Solubility, Thermal Coefficient, Corrosiveness, etc. and importance of different amines used in CO₂ capture system are discussed in this thesis. Frequently used amines as a solvent in CO₂ capture system with their pure values of densities are discussed in the following section:

3.3.1 MEA

Monoethanolamine (MEA) with the molecular formula of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ and molecular weight of 61.08 g/mol, is widely used as a solvent to chemically absorb carbon dioxide (CO_2) for the industrial process. MEA has a similar odor of ammonia. It is also a colorless liquid[34].

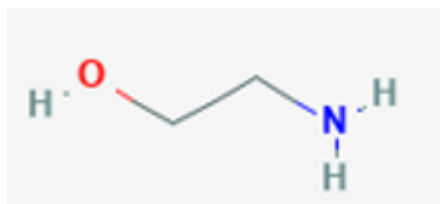


Figure 3.3: Chemical Structure of Monoethanolamine (MEA) [34]

MEA is primary and strongest amine among other amines. MEA's chemical structure is shown in Figure 3.3. MEA can remove both CO_2 and H_2S . Overall reaction of MEA with CO_2 are as in Reaction (3.5).



This mechanism comprises two steps, namely CO_2 amine zwitter ions formation in Reaction (3.6), followed by base catalyzed deprotonation of this zwitterions as in Reaction (3.7) where B is a base.



The above-mentioned reaction is reversible and can be obtained by changing the temperature. The chemical reaction involving carbamate dimerization is shown in Figure 3.4. Different physical and chemical properties of MEA are mentioned in Table 3.2.

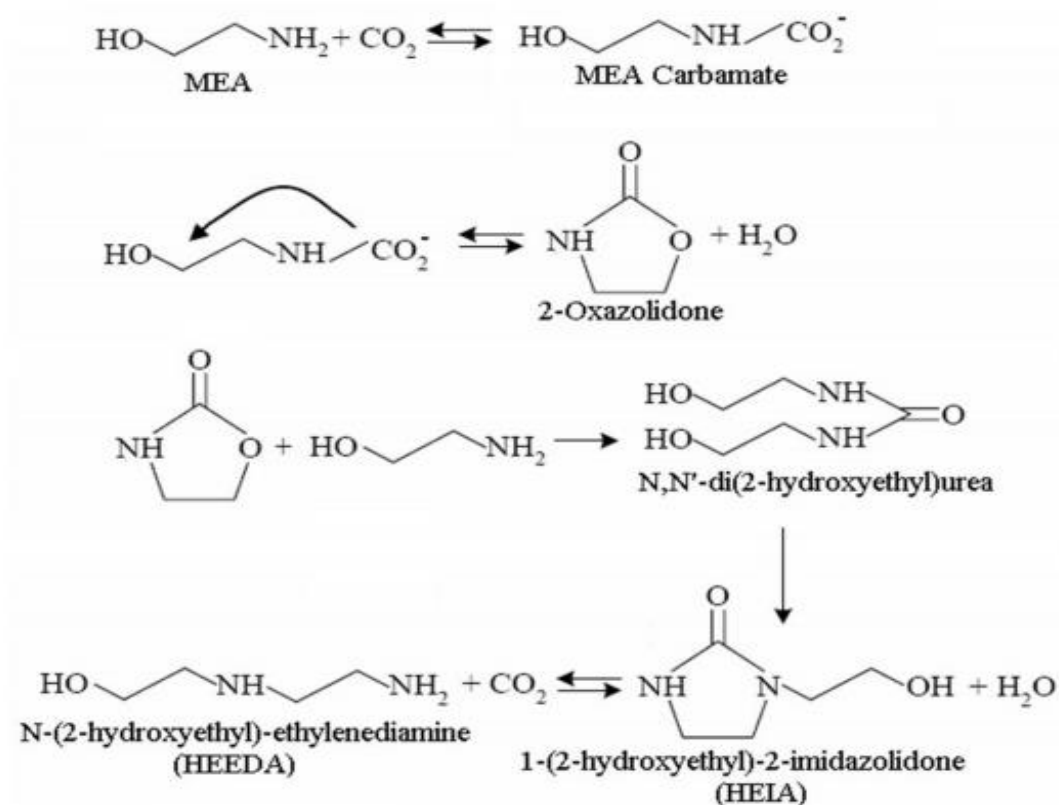


Figure 3.4: Possible thermal degradation of MEA (also called carbamate dimerization) in the CO₂ capture process [35]

Table 3.2: Different parameters of MEA [30], [31], [34]

Description	Remarks
Molecular Formula	C ₂ H ₇ NO
IUPAC NAME	Aminoethanol
Molecular weight	61.08 gmol ⁻¹
Appearance	Clear colorless liquid
Odor	Ammonia Like smell
Boiling Point	338° F at 760mm Hg
Melting Point	50.5° F
Flash Point	200° F
Density	1.016 gm/cm ³ at 68 °F
Solubility	greater than or equal to 100 mg/mL at 68° F Used as absorbent in carbon dioxide (CO ₂)
Chemical stability	capture . Stable under recommended storage conditions.

Literature Review

Previous researchers did various experiments and used various correlation methods for finding values of density of pure MEA at different temperature & concentration . This thesis summarizes the results of previous literatures available for MEA in Table 3.3. MEA is quite widely studied in preference to other amines. Similarly ,when temperature of pure MEA increases, density goes on decreasing as shown in Figure 3.5.

Table 3.3: Density of Pure MEA from previous literatures (g.cm⁻³)

Temperature/K	Density of Pure MEA from previous literatures				
	Density (g.cm ⁻³)				
	Song et al.[36]	DiGuillo et al. [37]	Wang et al.[38]	Murrleta-Guevara et al.[39]	Lee & Lin et al.[40]
293.15		1.0147	1.016234		
298.15				1.0127	
303.15	1.0091		1.008323	1.0089	1.009
308.15				1.0033	
313.15	1.0013	0.9998	1.00037	1.0002	0.9999
318.15				0.9967	
323.15	0.9934		0.992364	0.9918	0.9918
328.15				0.9876	
333.15	0.9854	0.9843	0.984301	0.9833	
338.15					
343.15	0.9774		0.976153		

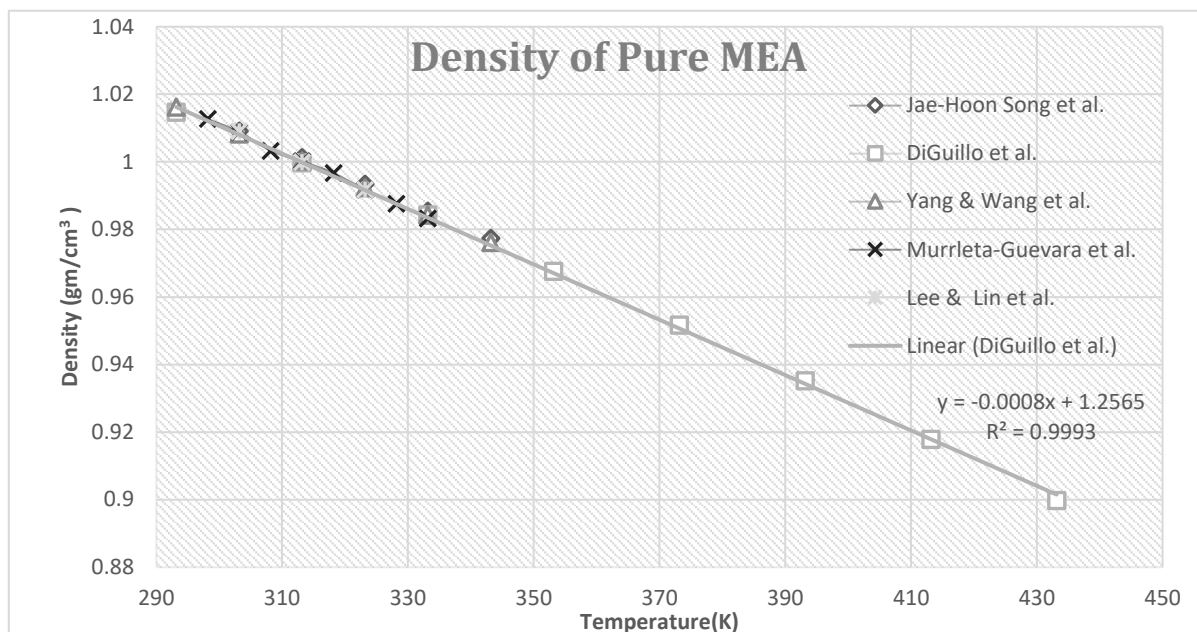


Figure 3.5: Density of Pure MEA at various temperature according to previous literatures with the trend line followed by DiGuillo et al.

3.3.2 PIPERAZINE

Piperazine (PZ) is another novel amine solvent with appearance of white crystalline solid presently used in for carbon dioxide (CO₂) absorption process [26]. It consists of a six-membered ring where two nitrogen atoms are at opposite position of ring. Piperazine is commonly available industrially as the hexahydrate with the form C₄H₁₀N₂·6H₂O, that melts at 44° C and boils at 125-130° C [41].

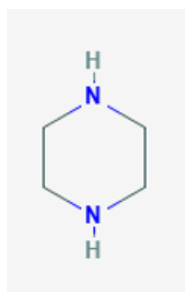


Figure 3.6: Chemical structure of PZ[42]

Literature Review

Due to its superiority performance to the previous industry standard i.e. 7 m MEA(30 mass % MEA) to 8 m piperazine(40 mass % PZ), piperazine comes in alternate to MEA. At process set-up, 8 m PZ has double the absorption rate and CO₂ capacity with more stability at high temperature and less prone to oxidation compared to MEA. These conveniency of 8 m PZ render into an expected energy cost with improved process design as new standard for amine scrubbing[23].Different physical and chemical aspects of piperazine are mentioned in Table 3.4.

Table 3.4: Different parameters of Piperazine [41], [42]

Description	Remarks
Molecular Formula	C ₄ H ₁₀ N ₂
IUPAC NAME	Piperazine
Molecular weight	86.14 g/mol
Appearance	White or colorless Crystals
Odor	Ammonia Like smell
Boiling Point	295° F at 760 mm Hg
Melting Point	223° F
Flash Point	190° F
Density	1.1 g.cm ⁻³ at 68 °F
Solubility	Very Soluble
Chemical stability	Used as absorbent in carbon dioxide (CO ₂) capture. Stable at temperatures to 270 °C and in neutral or acid media /Piperazine hydrochloride

Table 3.5: Experimental densities of Piperazine+ Water mixture at various conditions of temperature and pressure [32]

Density (Kgm ⁻³)						
Pressure (Mpa)	Temperature (K)					
	293.15	313.15	333.15	353.15	373.15	393.15
0.1	1004.70	998.00	988.20	977.80	963.90	948.30
0.5	1004.80	998.20	988.40	977.90	964.10	948.70
1	1005.00	998.40	988.60	978.10	964.40	948.90
2	1005.50	998.80	989.10	978.60	965.00	949.50
5	1006.70	1000.00	990.30	979.90	966.40	951.00
10	1008.80	1002.00	992.40	982.20	968.70	953.60
15	1010.80	1004.00	994.40	984.30	971.00	956.00
20	1012.80	1005.90	996.40	986.50	973.40	958.50
30	1016.90	1009.90	1000.40	990.80	977.90	963.20
40	1020.80	1013.80	1004.40	994.80	982.20	967.80
50	1024.50	1017.50	1008.10	998.90	986.20	972.20
60	1028.30	1021.30	1011.90	1002.90	990.30	976.60
70	1032.10	1024.90	1015.70	1006.70	994.40	981.00
80	1035.50	1028.40	1019.20	1010.50	998.30	984.80
90	1039.20	1031.80	1022.70	1014.00	1002.20	988.90
100	1042.70	1035.40	1026.30	1017.70	1005.90	992.90
110	1045.90	1038.70	1029.70	1021.30	1009.50	996.70
120	1049.40	1042.00	1033.30	1024.70	1013.10	1000.40
130	1052.80	1045.30	1036.50	1028.20	1016.60	1004.00
140	1055.90	1048.50	1039.90	1031.50	1020.00	1007.80

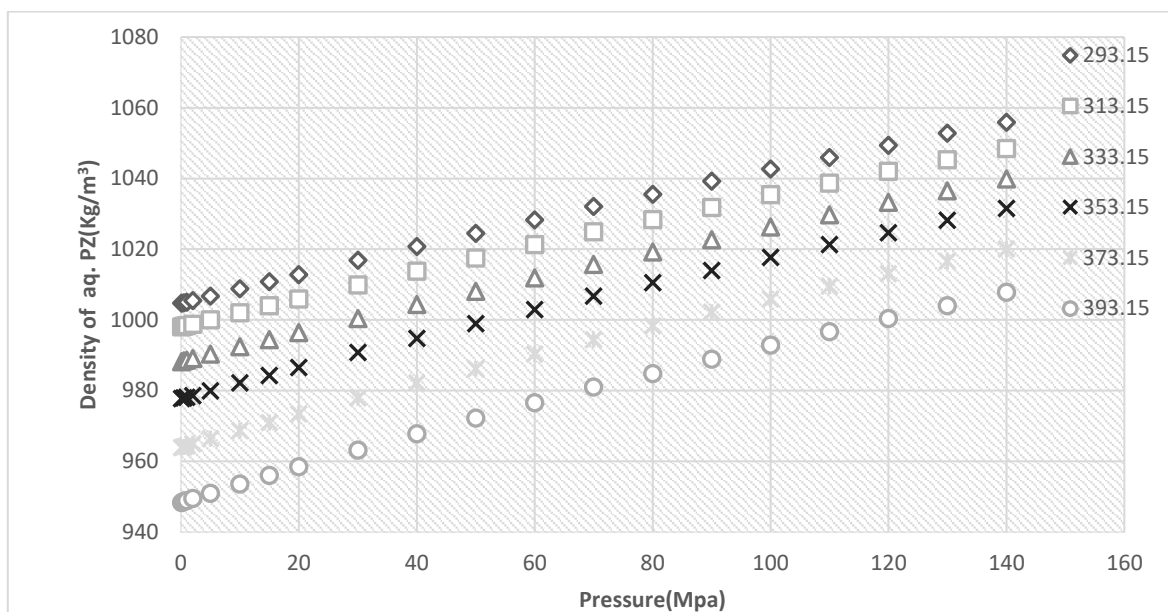


Figure 3.7: Experimental values of densities of PZ + H₂O mixture at different conditions of temperature and pressure [43]

According to Eduardo[43], experimental values taken for density of binary mixture of Piperazine & Water as a function of temperature & pressure was measured using a vibrating tube densimeter (Anton Paar DMA HPM) with an expanded uncertainty ($k = 2$) less than 0.7 kg/m³ & is tabulated in Table 3.5. The graph of experimental densities of PZ + H₂O mixture at different conditions of temperature, T, and pressure are shown in Figure 3.7.

3.3.3 MDEA

Methyl diethanolamine (MDEA) is the organic compound with an ammonia odor widely used as sweetening agent. The unique property of MDEA compared to other amines is that it removes hydrogen sulfide and strip carbon dioxide from sour gas streams [44].

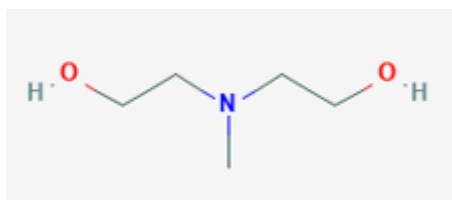


Figure 3.8: Chemical Structure of MDEA [45]

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MDEA is also considered the pertinent amine for chemical absorption method because of its advantages like low vapor pressure which allows for high amine consumption without appreciable loss, resistant to thermal and chemical degradation. Similarly, MDEA has a comparatively low heat of reaction with hydrogen sulphide and carbon dioxide, which permits for lower reboiler duties reducing the operating costs [37].

Table 3.6: General parameters of MDEA [45]

Description	Remarks
Molecular Formula	$C_5H_{13}NO_2$ or $C_5H_{13}O_2N$ or $CH_3N(C_2H_4OH)_2$
IUPAC NAME	2-[2-hydroxyethyl(methyl)amino]ethanol
Molecular weight	119.16 gmol^{-1}
Appearance	colorless liquid
Odor	Ammonia like odor
Boiling Point	477°F at 760 mm Hg
Melting Point	-6°F
Flash Point	260°F
Density	1.0377 gm/cm^3 at 68°F
Solubility	Very soluble
Chemical stability	Stable under recommended storage conditions

Table 3.7: Density of Pure MDEA from various literatures

Temperature/K	Density of Pure MDEA				
	(g.cm ⁻³)				
	Karunarathne et al.[25]	Diguillo et al. [37]	Hawrylak et al.[46]	Pinto et al. [47]	Maham et al.[48]
293.15	1.0406	1.0371		1.04012	
298.15	1.0368		1.03688		1.0359
303.15	1.0332				1.032
308.15	1.0294		1.02901		
313.15	1.0256			1.02474	1.02445
318.15	1.0218		1.02264		
323.15	1.018			1.01727	1.0166
328.15	1.0141	1.0143			
333.15	1.0103			1.00956	1.009
338.15	1.0064				
343.15	1.0025				1.00124

Previous researcher did various experiments and used various correlation methods for finding values of density of pure MDEA at different temperature. This thesis summarizes the results of previous literatures in Table 3.7. MDEA is quite widely studied in preference to other amines. Similarly ,when temperature of pure MDEA increases, density goes on decreasing as shown in Figure 3.9 and the linear trend is followed as per Karunarathne et al [25].

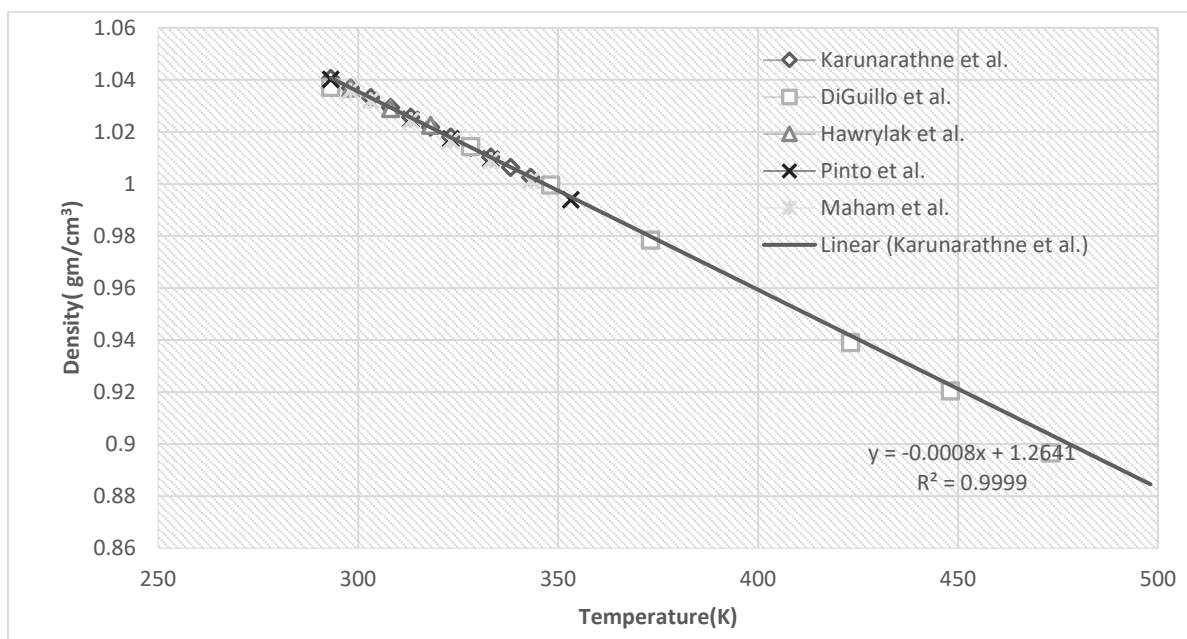


Figure 3.9: Density of Pure MDEA from various literatures

3.3.4 DEAE

Diethylaminoethanol (DEAE) is the solvent used in chemical absorption process that has good potential for the removal of CO₂ from gaseous streams and can be prepared from renewable resources [49].

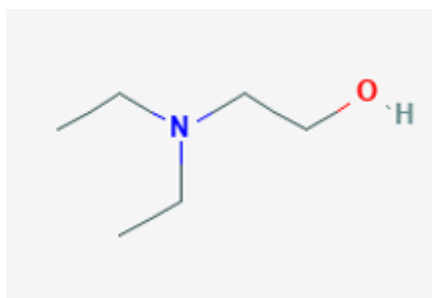


Figure 3.10: Chemical Structure of DEAE [33]

The result from various researches showed that DEAE provides better performance for CO₂ absorption than MEA [39].

Table 3.8: General properties of DEAE [50], [51]

Description	Remarks
Molecular Formula	$C_6H_{15}NO$ or $(C_2H_5)_2NC_2H_4OH$
IUPAC NAME	2-(diethylamino)ethanol
Molecular weight	117.19 g/mol
Appearance	colorless liquid
Odor	Nauseating Odor
Boiling Point	325 °F at 760 mm Hg
Melting Point	-94 °F
Flash Point	140 °F (NTP, 1992)
Density	0.8921gm/cm ³ at 77 °F (USCG, 1999)
Solubility	Very soluble (NTP, 1992)
Chemical stability	Stability During Transport: Stable [29], [30]

Table 3.9: Density of Pure DEAE from various literatures

Temperature	Density			
	g.cm ⁻³			
K	Karunaratne et al. [25]	Hawrylak et al. [35]	Pinto et al. [36]	Zhang et al. [52]
293.15	0.8843			0.8842
298.15	0.8797	0.87952	0.87947	0.87954
303.15	0.8751			0.87482
308.15	0.8704	0.8714		
313.15	0.8658		0.86554	0.86556
318.15	0.8611	0.86182		
323.15	0.8563		0.85612	
328.15	0.8515			
333.15	0.8467		0.84661	
338.15	0.8419			
343.15	0.8371		0.83703	

Previous researcher did various experiments and used various correlation methods for finding values of density of pure DEAE at different temperature. This thesis summarizes the results of

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previous literatures in Table 3.9. DEAE/DEEA is quite widely studied in preference to other amines. Similarly, when temperature of pure MDEA increases, density goes on decreasing as shown in Figure 3.11 and the linear trend is followed as per Karunaratne et al [25].

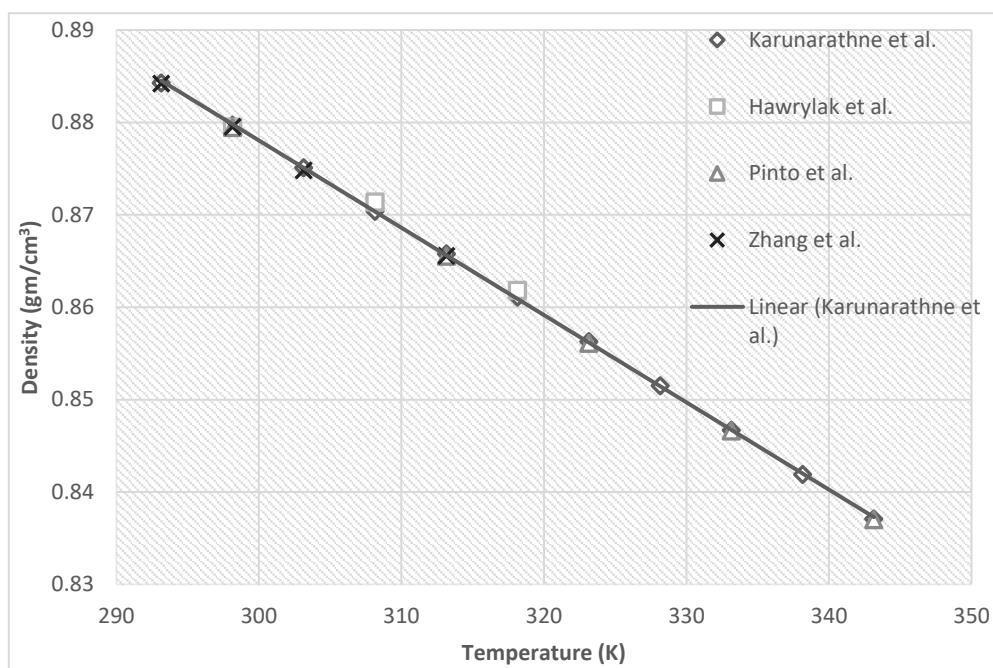


Figure 3.11: Density of Pure DEAE from various literatures

3.3.5 AMP

2-Amino-2-Methylpropanol (AMP) is an organic compound with the formula $C_4H_{11}NO$. It is insoluble in water and also colorless.

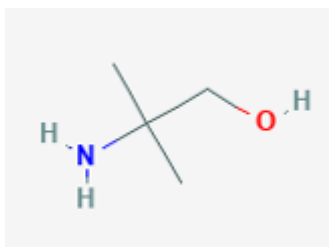


Figure 3.12: Chemical Structure of AMP [53]

Table 3.10: General properties of AMP [54], [55]

Description	Remarks
Molecular Formula	$C_4H_{11}NO$ or $(CH_3)_2C(NH_2)CH_2OH$
IUPAC NAME	2-amino-2-methylpropan-1-ol
Molecular weight	89.14 g/mol
Appearance	clear light-colored liquid, insoluble in water as well
Form	crystals or colorless liquid
Boiling Point	165 °C @ 760 MM HG
Melting Point	31 °C
Flash Point	67 °C
Density	0.934 g.cm ⁻³ @ 20 °C
Solubility	miscible with water; sol in alcohols
Used	Viscous liquid /commercial

Table 3.11: Density (g.cm⁻³) of pure AMP from previous literatures

Temperature (K)	Density of Pure AMP				
	Literature				
	g.cm ⁻³				
	Karunarathne et al.[43]	Aguila et al.[44]	Henni et al. [45]	Xu et al.[46]	Zhang et al.[47]
303.15				0.9254	0.92572
308.15	0.9214				0.92148
313.15	0.9173	0.9172	0.91965		0.9173
318.15	0.9133			0.916	0.91309
323.15	0.9091	0.9092	0.91124		0.90886
328.15	0.905			0.9062	0.90459
333.15	0.9004	0.9007	0.90287		0.90029
338.15	0.896			0.897	0.89595
343.15	0.8916		0.89428		0.89157
348.15	0.8872				0.88718
353.15	0.8827			0.8864	0.88275
363.15	0.8737				
368.15				0.8748	

Literature Review

Previous researcher did various experiments and used various correlation methods for finding values of density of pure AMP at different temperature. This paper explains the results of previous literatures in Table 3.11. AMP is quite widely studied in preference to other amines. Similarly, when temperature of pure AMP increases, density goes on decreasing as shown in Figure 3.13.

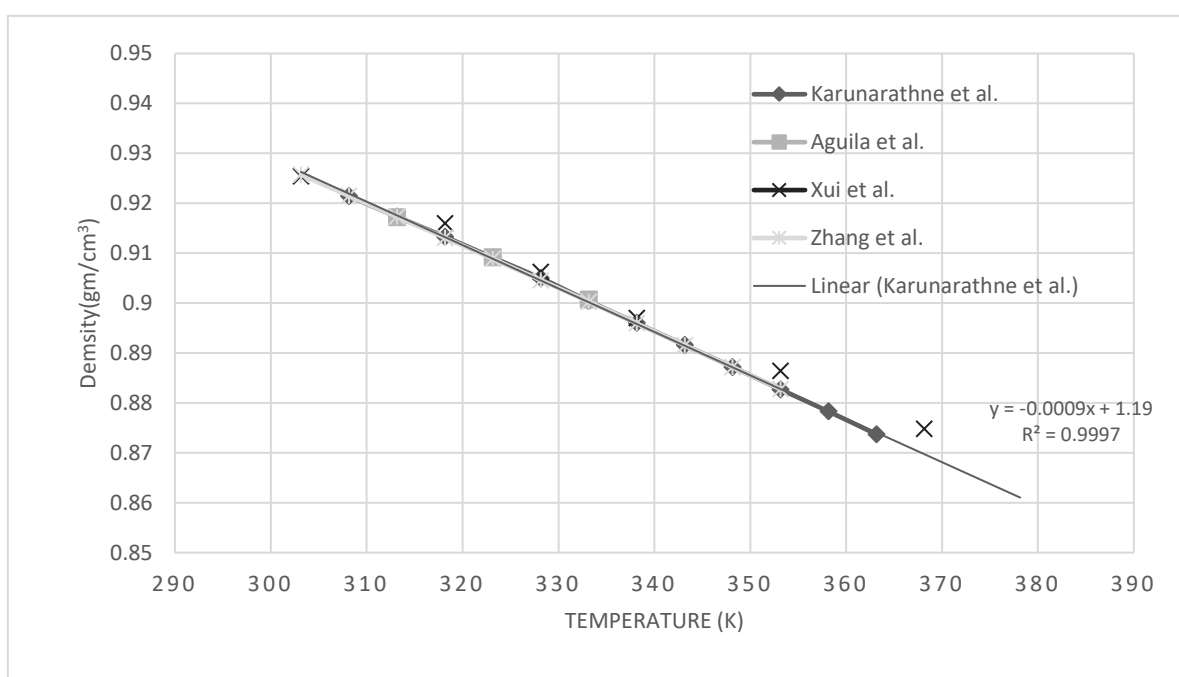


Figure 3.13: Density ($\text{g}\cdot\text{cm}^{-3}$) of pure AMP from previous literatures

3.4 Literature details on common Amines

Different amines have been studied by different researchers whose experimental values are available in different Literature. This section includes density of various unloaded binary, tertiary amine mixtures & CO_2 loaded mixtures as a function of Temperature. Some of the mixtures are discussed in this thesis.

3.4.1 Binary Mixture: Monoethanolamine (MEA)+ Water (H₂O)

The binary mixture of MEA & water was studied with a temperature range of 25 to 80 °C [56]. Due of high affinity for CO₂ absorption process, MEA has really been an attention for many researchers. Densities and other physical properties like Viscosity, Solubility, etc. of the absorbent are must for analyzing different engineering constraints such as dimensioning the column diameter, velocities and pressure drop in a columned [56]. The limited studies had been made in the field of amines. The following data has been experimental taken in lab which was at different mass fraction of MEA and which were later correlated using Wieland et al method [57].

Table 3.12: Density of MEA+Water at various mass fraction & Temperature[34]

Density					
Temperature	20%MEA+Water	30%MEA+Water	40%MEA+Water	50%MEA+Water	70%MEA+Water
K	g.cm ⁻³				
298	1.0041	1.0100	1.0173	1.0252	1.0364
313	1.0017	1.0069	1.0130	1.0196	1.0279
323	0.9996	1.0041	1.0095	1.0152	1.0220
340	0.9961	0.9992	1.0031	1.0070	1.0101
350	0.9934	0.9961	0.9992	1.0022	1.0034

3.4.2 Binary Mixture: Piperazine (PZ)+Water (H₂O)

The binary mixture of Piperazine & water was studied with a temperature range of (288-333)K. Recently, Piperazine has been proven as an effective promoter in MEA, MDEA & potassium carbonate and highly demanded component commercially as an absorbent to capture CO₂. The following table shows the experimental values of density of piperazine at different mass fraction & temperature performed at Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati by Mandal et al.[58], [59].

Literature Review

The densities of the amine solutions were measured using a 26.76 mL Gay-Lussac pycnometer [59]. The pycnometer which contained the amine solution was dipped in a constant temperature bath. The experimental densities from Mandal et al. is mentioned in Table 3.13.

Table 3.13: Density of PZ + Water at different mass fraction & Temperature [58]

Temperature K	Density		
	1.74% PZ +water	3.45% PZ +water	5.16% PZ +water
	gm/cm ³		
298	0.9978	0.9987	0.9995
303	0.9964	0.9973	0.9981
308	0.9949	0.9957	0.9965
313	0.9931	0.9939	0.9948
318	0.9912	0.992	0.9928
323	0.989	0.9899	0.9907
328	0.9867	0.9876	0.9884
333	0.9843	0.9851	0.9859

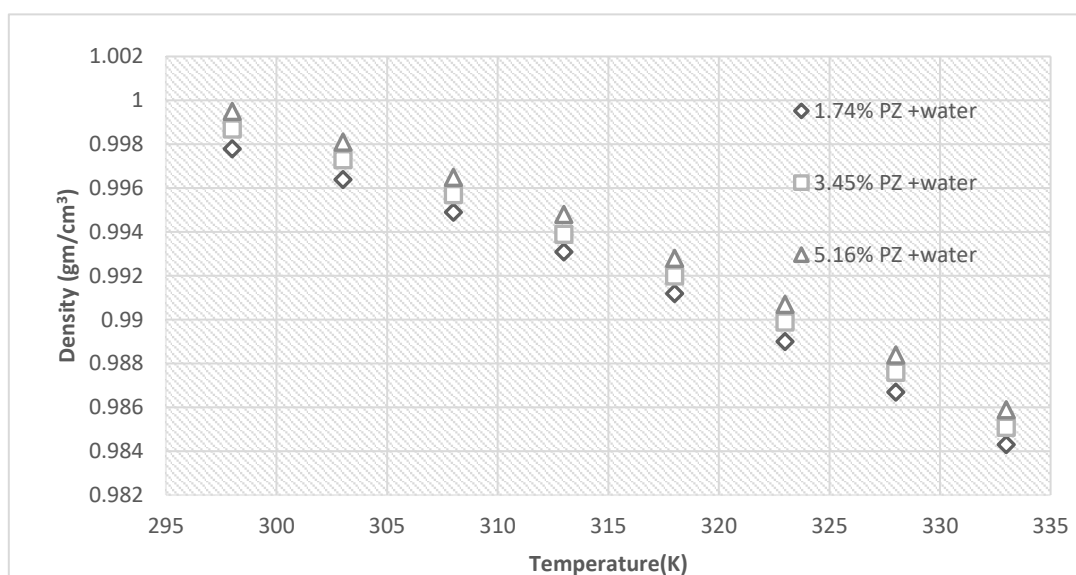


Figure 3.14: Density of PZ at different mass fractions & at various temperature[58]

This density data was later correlated as function of temperature and concentration of amine[51]. This data is also discussed more in this paper and reproduced using python codes and compared as well.

3.4.3 Binary Mixture: Methyl diethanolamine (MDEA)+ Water (H₂O)

The binary mixture of MDEA & water was studied with a temperature range of 15 to 60 °C [58]. The tertiary amine MDEA requires lower energy requirement for regeneration in CO₂ capture plant due to high equilibrium loading capacity and low heat of reaction with CO₂. Moreover, over comparison with AMP & MDEA in equal CO₂ loading value, reaction rate is higher with MDEA. AMP doesn't form a stable carbamate ,thus reduce energy cost in regeneration by aqueous MDEA solutions [58].

Table 3.14: Density of MDEA+ H₂O (g.cm⁻³) [47]

Temperature (K)	Density of MDEA+ H ₂ O (g.cm ⁻³)		
	10% MDEA	20% MDEA	30% MDEA
	gm/cm ³		
288	1.703	2.624	4.399
313	0.899	1.305	1.929
333	0.63	0.86	1.218

The density of binary mixture of MDEA+ H₂O was measured by Paul & Mandal et al. using a 26.76 mL Gay-Lussac pycnometer [58]. The experimental values are tabulated in Table 3.14 and the graph is shown in Figure 3.15.

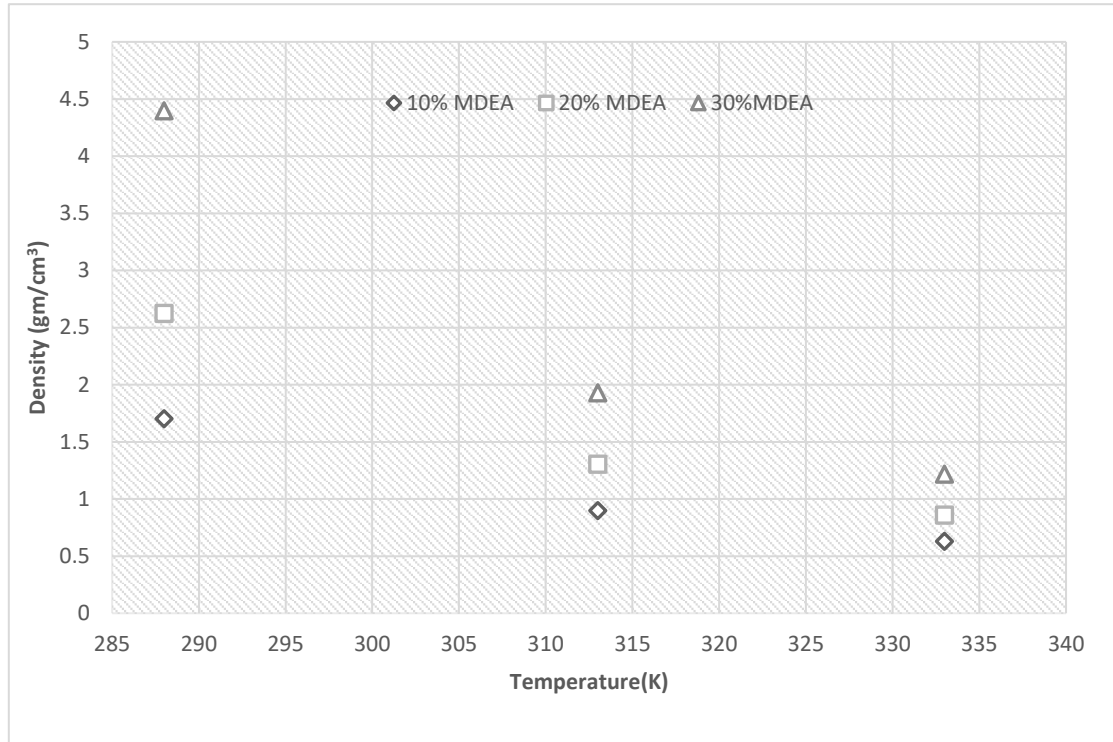


Figure 3.15: Density of MDEA+ Water (g.cm⁻³)[50]

3.4.4 Ternary Mixture: MDEA + MEA + H₂O

The ternary mixture of MDEA, MEA & water was studied with a temperature range of 20 to 70 ° Celsius[25]. This mixture's density was measured using a density meter of DMA 4500 from Anton Paar (Graz, Austria) under atmospheric conditions. It has a temperature controller with an precision of ± 0.03 K and the precision of the density measurement is ± 0.05 kg.m⁻³ CO₂ [25]. The following table shows the experimental values of density of ternary mixture of MDEA + MEA+ H₂O at different mass fraction & temperature performed at University of South-Eastern Norway, Kjølnes by Karunaratne et al.[25].

Table 3.15: Densities and excess molar volume V_E of MDEA + MEA + Water mixtures [11].

Mixtures		MDEA/MEA						
mass %/%	15/15		20/10		25/5		30/0	
*X ₁ /X ₂	0.0296/0.0577		0.0398/0.0388		0.0502/0.0196		0.0609/0.0000	
Temperature	ρ	V _E	ρ	V _E	ρ	V _E	ρ	V _E
(K)	(kgm ⁻³)	(×10 ⁶)	(kgm ⁻³)	(×10 ⁶)	(kgm ⁻³)	(×10 ⁶)	(kgm ⁻³)	(×10 ⁶)
293.15	1019.70	−0.292	1022.10	−0.321	1024.50	−0.351	1026.90	−0.382
298.15	1017.60	−0.288	1019.90	−0.317	1022.30	−0.347	1024.70	−0.377
303.15	1015.30	−0.284	1017.60	−0.313	1020.05	−0.342	1022.40	−0.371
308.15	1012.80	−0.282	1015.20	−0.310	1017.60	−0.339	1019.90	−0.367
313.15	1010.30	−0.281	1012.60	−0.308	1015.00	−0.336	1017.30	−0.364
318.15	1007.60	−0.280	1009.90	−0.306	1012.20	−0.332	1014.60	−0.361
323.15	1004.80	−0.278	1007.10	−0.304	1009.30	−0.329	1011.70	−0.357
328.15	1001.90	−0.277	1004.10	−0.302	1006.30	−0.324	1008.70	−0.354
333.15	998.80	−0.276	1000.90	−0.297	1003.20	−0.323	1005.60	−0.350
338.15	995.60	−0.273	997.50	−0.288	999.70	−0.312	1002.30	−0.346
343.15	991.70	−0.257	993.10	−0.261	995.40	−0.287	998.70	−0.336

3.4.5 Ternary Mixture : PZ + AMP+ Water

The density of ternary mixture of aqueous solutions of Piperazine, AMP & water was studied with a temperature range of 25 to 60 ° C [59]. Pure Piperazine(> 99 % pure) & Pure AMP were used from E. Merck, FRG . The density of these ternary mixture was measured using a 25.78 mL Gay-Lussac pycnometer at 298 K. During each run the pycnometer with the amine solution was immersed in a constant-temperature bath.[59].The experiments is taken at different temperatures and at different mass fractions and is listed in the Table 3.16.

Table 3.16: Density of ternary mixture of aqueous solutions of Piperazine, AMP & water[59]

Density of PZ+AMP+Water (g.cm ⁻³)								
w ₂ /w ₁	T=298K	T=303K	T=308K	T=318K	T=323K	T=328K	T=333K	T=338K
30/0	0.9970	0.9942	0.9914	0.9884	0.9854	0.9821	0.9788	0.9755
28/2	0.9987	0.9959	0.9931	0.9903	0.9871	0.9838	0.9807	0.9770
25/5	1.0010	0.9984	0.9956	0.9926	0.9895	0.9865	0.9831	0.9799
22/8	1.0037	1.0010	0.9982	0.9950	0.9922	0.9889	0.9858	0.9824

These calculated values of density at different temperature and mass fraction are compared with the data available in the literature. The experimental density data were correlated as a function of temperature and concentration of amine and the correlation is used in this thesis as well.

3.4.6 Ternary Mixture : AMP+MEA+Water

The density of ternary mixture of MEA, AMP & water was studied with a temperature range of 25 to 60 ° Celsius[52].The density of these ternary mixture was measured an Anton Paar DMA 4500 density meter [60]. The experiments were taken at different temperatures and at different mass fractions and is listed in the table below:

Table 3.17: Density of Aqueous AMP+ MEA at different mass fraction & Temperature [60]

Temperature (K)	Density g.cm ⁻³		
	21% AMP+9%MEA	24% AMP+6%MEA	27% AMP+3%MEA
293.15	1.0035	1.0022	1.0008
298.15	1.0011	0.9997	0.9982
303.15	0.9985	0.9971	0.9956
308.15	0.9958	0.9943	0.9927
313.15	0.9930	0.9914	0.9897
318.15	0.9900	0.9883	0.9867

			Literature Review
323.15	0.9869	0.9853	0.9835
328.15	0.9837	0.9820	0.9802
333.15	0.9804	0.9786	0.9768
338.15	0.9769	0.9751	0.9733
343.15	0.9734	0.9716	0.9697

These data of density at various temperature and mass fraction are contrasted with the available data in the literature. The experimental density data were correlated as a function of temperature and concentration of amine using Weiland et al., Setschenow-type correlation and the correlation is also used in this thesis as well [61].

3.4.7 CO₂ Loaded Mixture: PZ + CO₂

Freeman et al.[62] in his papers has discussed about the importance of physical properties of CO₂ absorbent like density & Viscosity of different mixtures. Solubility data plays a crucial role in operating large scale PZ systems where insolubility anywhere within the system can results in inefficient system. Concentrated piperazine has been widely used in coal fired power plant to capture flue gas. Also, Piperazine is used as a CO₂ rate promoter in solvents of MDEA, AMP, MEA ,etc. [63]. The experiments were taken at different temperatures and at different concentrations and is listed in the Table 3.18.

Table 3.18: Experimental values of density of Piperazine+ Carbon dioxide at different concentration and at different temperature [55]

		Density (g.cm ⁻³)		
PZ Concentration	CO ₂ Concentration	T=20°C	40°C	60°C
C _{pz} (mol/kg)	C _{co} (mol/kg)			
1.67	0	1.0067	0.9994	0.9891
1.64	0.186	1.0146	1.0072	0.9974
1.64	0.366	1.0222	1.0148	1.0049
1.63	0.545	1.0299	1.0224	1.0129
1.61	0.728	1.0373	1.0299	1.0202

			Literature Review	
1.61	0.894	1.0441	1.0365	1.027
1.59	1.08	1.0515	1.0438	1.0344
1.58	1.246	1.0581	1.0505	1.0407
1.57	1.416	1.0644	1.0567	
1.55	1.516	1.0688	1.0607	
3.25	1.433	1.0749	1.0655	1.0548
3.21	1.78	1.0874	1.0782	1.0676
3.03	3.023	1.1278	1.1188	1.1081
4.01	1.726	1.0923	1.0821	1.0707
3.72	3.023	1.1473	1.1379	1.1277
4.28	1.722	1.1007	1.09	1.0785
3.98	3.297	1.1601	1.1504	1.1402
4.59	1.879	1.107	1.0961	1.0843
4.24	3.471	1.1687	1.1589	1.1487
4.73	2.875	1.149	1.1387	1.1278
4.41	3.726	1.1807	1.1708	1.1605
5.23	2.65	1.1219	1.1101	1.0978
4.73	3.985	1.1895	1.1793	1.169
6.7	2.123	1.1256	1.1108	1.096.2

The experimental values of density of the CO₂ loaded piperazine as a function of PZ concentration (C_{pz}), CO₂ Concentration (C_{co2}) and temperature (T) are listed in Table 3.18.

3.4.8 CO₂ Loaded Mixture: MEA + Water + Carbon Dioxide

Amundsen et al.[56] in his paper, measured and correlated the density of Monoethanolamine (MEA), water, and carbon dioxide (CO₂) at 20-40% mass fraction with CO₂ loading of 0- 0.5 mol CO₂ per MEA within temperature range of 25-80° C. With increase in CO₂ loading, densities increase significantly at all temperatures. Pure MEA(99.5%) was purchased from Merck and MEA + H₂O + CO₂ density was measured using an Anton Paar density meter (DMA 4500) [56]. The experimental values from Amundsen et al. at different mass fraction of MEA is tableted in Table 3.19,3.20 & 3.21.

Table 3.19: Density for MEA + Water + Carbon dioxide from T=(25-80) °C & CO₂ Loading from α =(0.1-0.5) at mass fraction MEA= 20% [56]

Temperature	Density (g.cm ⁻³)				
°C	A				
	0.1	0.2	0.3	0.4	0.5
25	1.0188	1.0327	1.0476	1.064	1.08
40	1.0125	1.0264	1.0413	1.0579	1.0735
50	1.0076	1.0215	1.0364	1.053	1.068
70	0.9965	1.0105	1.0254	1.0419	1.057
80	0.9902	1.0043	1.0192	1.036	

Table 3.20: Density for MEA + Water + Carbon dioxide from T=(25-80) °C & CO₂ Loading from α =(0.1-0.5) at mass fraction MEA=30% [56]

Temperature	Density (g.cm ⁻³)				
°C	A				
	0.1	0.2	0.3	0.4	0.5
25	1.038	1.063	1.093	1.1285	1.1597
40	1.03	1.055	1.085	1.121	
50	1.024	1.049	1.0797	1.115	
70	1.012	1.037	1.068	1.104	
80	1.005	1.031	1.062	1.0977	

Table 3.21: Density for MEA + Water+ Carbon dioxide from T=(25-80) °C & CO₂ Loading from α =(0.1-0.5) at mass fraction MEA=40% [56]

Temperature °C	Density (g.cm ⁻³)				
	A				
	0.1	0.2	0.3	0.4	0.5
25	1.028	1.048	1.07	1.0957	1.1211
40	1.021	1.041	1.0629	1.0885	1.114
50	1.016	1.0355	1.058	1.083	1.108
70	1.004	1.024	1.0464	1.0719	
80	0.997	1.0176	1.0402	1.066	

3.4.9 CO₂ Loaded Mixture: AMP + MEA + CO₂

Karunaratne et al.[64] in his paper showed various correlation method for finding density of mixture of AMP, MEA & CO₂. Density measurement was done within temperature range of 293.15 K to 343.15 K. Table 21 shows different amine mass ratios, CO₂ loading and temperature at a pressure of 4 bar(N₂)gas. Density increases with the increase of CO₂ loading and decrease with increase of temperature.

Table 3.22: Density of CO₂ loaded AMP + MEA+ H₂O at different Carbon dioxide loadings & Temperature [64]

α / (mol CO ₂ ·mol/ amine)	0.107	0.21	0.308	0.4	0.518
9 % MEA+21% AMP					
	X ₄ =0.0095	X ₄ =0.0125	X ₄ =0.0200	X ₄ =0.0349	X ₄ =0.0407
Temperature (K)	Density (gm/cm ³)				
293.15	1019.8	1036.4	1053.6	1071.3	1087.2
298.15	1017.4	1034	1051.1	1068.7	1084.5
303.15	1014.9	1031.5	1048.6	1066	1081.7
308.15	1012.2	1028.9	1045.9	1063.2	1078.9
313.15	1009.4	1026.1	1043.2	1060.3	1075.9
318.15	1006.6	1023.3	1040.3	1057.3	1072.9

					Literature Review
323.15	1003.6	1020.3	1037.4	1054.4	1070
328.15	1000.5	1017.3	1034.3	1051.3	1066.7
333.15	997.2	1014.2	1031.2	1048	1063.4
338.15	993.8	1011	1027.9	1044.7	1059.4
343.15	990.4	1007.5	1024.6	1041.3	1054.9

Table 3.23: Correlated Density of CO₂ loaded AMP + MEA+ Water at different CO₂ loadings & Temperature using python coding [64]

$\alpha/(\text{mol CO}_2 \cdot \text{mol/ amine})$	0.107	0.21	0.308	0.4	0.518
21% AMP +9 % MEA					
	X4=0.0095	X4=0.0125	X4=0.0200	X4=0.0349	X4=0.0407
Temperature (K)	Density (g.cm⁻³)				
293.15	1014.283	1028.292	1042.77	1066.723	1074.235
298.15	1011.639	1025.585	1039.973	1063.686	1071.083
303.15	1008.995	1022.878	1037.177	1060.651	1067.933
308.15	1006.047	1019.863	1034.068	1057.298	1064.463
313.15	1002.998	1016.746	1030.856	1053.84	1060.889
318.15	999.949	1013.629	1027.644	1050.383	1057.316
323.15	996.698	1010.307	1024.225	1046.715	1053.532
328.15	993.345	1006.882	1020.702	1042.943	1049.643
333.15	989.891	1003.355	1017.075	1039.066	1045.65
338.15	986.335	999.726	1013.345	1035.085	1041.552
343.15	982.679	995.994	1009.512	1030.999	1037.35

In this way, with reference to previous study by different researchers, the density of different amine solvents used as a CO₂ absorbent in CO₂ capture plant has been studied with respect to temperature and their concentration and some of the correlation method have been elaborated detailly in this thesis.

4 Correlation methods

4.1 Jae-Hoon Song Method

Song et al.[65] in his paper had measured densities of MEA (15% mass) + Ethylene glycol (EG)+ water at the temperature range of 30-70° Celsius using a calibrated pycnometer having a bulb volume of 25 cm³ with constant temperature of water bath and is mentioned in Table 3.24. The experimental density data at different temperature and concentration is calculated using density as a function of temperature.

$$\rho \left(\frac{gm}{cm^3} \right) = a_1 + a_2 T(K) + a_3 (T(K))^2 \quad (4.1)$$

Where

ρ = density in gm/cm³

T= Temperature in Kelvin

To calculate values of density using Equation (3.1), the values of parameters are mentioned in Table 3.25 at different temperatures and is used in python code mentioned in Appendix B to get the density of the mixture at different temperature and concentrations.

Table 4.1: Experimental Densities (g cm-3) of Monoethanolamine +Ethylene Glycol + Water Systems (w₁ = 15.3%)[65]

Temperature (K)	0/84.7	15/69.7	30/54.7	45/49.7	60/24.7
303.15	1.0013	1.0208	1.0402	1.0584	1.0737
313.15	0.9974	1.0160	1.0345	1.0520	1.0670
323.15	0.9928	1.0107	1.0286	1.0454	1.0601
333.15	0.9875	1.0047	1.0220	1.0386	1.0529
343.15	0.9820	0.9990	1.0156	1.0315	1.0456

Correlation methods

Table 4.2: Different parameters(a_1, a_2, a_3) required for correlation and AAD using correlated values[42]

Parameter	w_2/w_3				
	0/84.7	15/69.7	30/54.7	45/49.7	60/24.7
a_1	0.8586	1.0015	1.0712	1.1432	1.1754
$10^4 a_2$	13.152	6.05	3.5236	0.6656	-0.106
$10^6 a_3$	-2.7857	-1.7857	-1.5	-1.1429	-1.0714
AAD/%	0.008	0.013	0.009	0.004	0.002

Average absolute deviations (AAD) between the measured and calculated values & also different parameters(a_1, a_2, a_3) required for correlation are presented in Table 3.25. Using the values from Jae-Hoon Song et al., reproducing the values of density at 15% mass MEA in solution of 70% mass Ethylene Glycol & water, the following values of densities are correlated using python code in this thesis.

Table 4.3: Correlated Densities (gcm^{-3}) of Monoethanolamine + Ethylene Glycol + Water Systems ($w_{\text{MEA}} = 15.3\%$) using Jae-Hoon Song

Temperature (K)	0/84.7	15/69.7	30/54.7	45/49.7	60/24.7
303.15	1.001	1.021	1.040	1.058	1.074
313.15	0.997	1.016	1.034	1.052	1.067
323.15	0.993	1.011	1.028	1.045	1.060
333.15	0.988	1.005	1.022	1.039	1.053
343.15	0.982	0.999	1.015	1.031	1.046

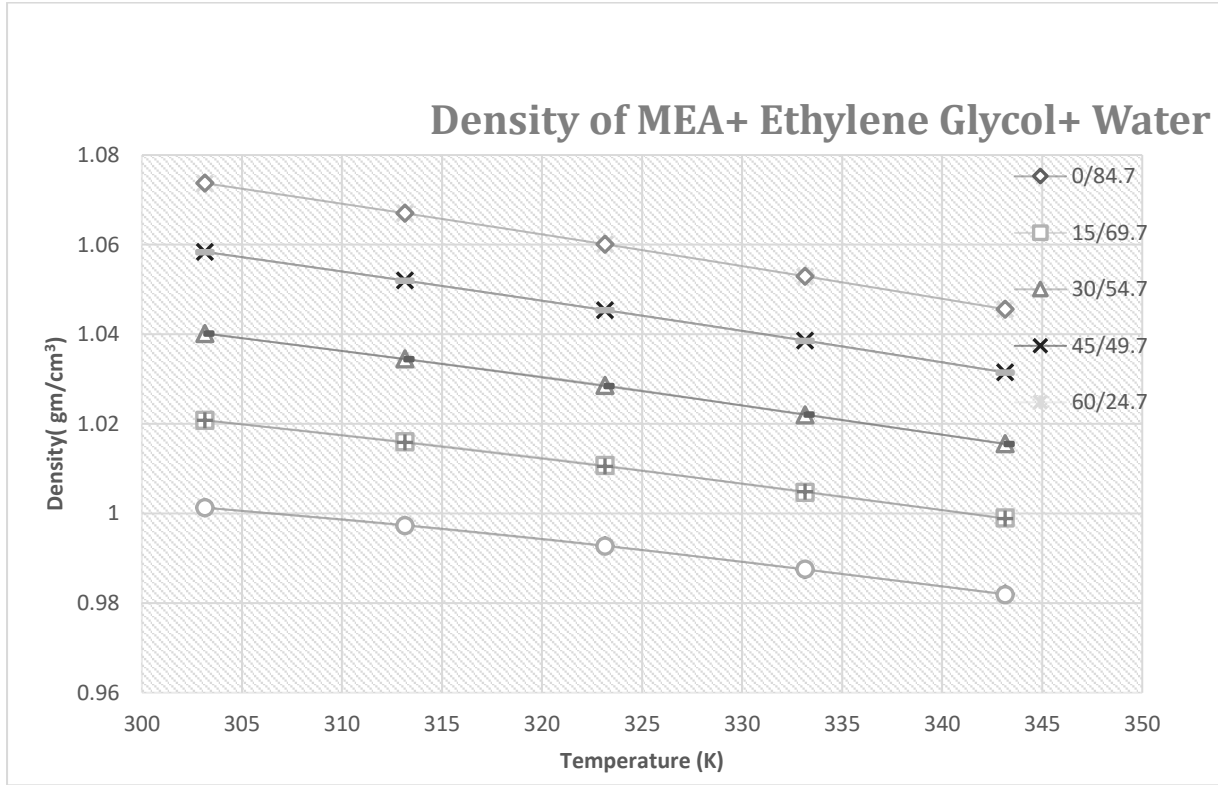


Figure 4.1: Correlated Density of MEA+ Ethylene glycol+ H₂O

In Figure 4.1, Lines represent correlated values for different mass fraction of MEA + Ethylene glycol + Water using Jae-Hoon Song Method. The values of density according to Song et al. are presented and the lines refers to the correlation trend using Equation (3.1) and the python codes are mentioned in Appendice B. The maximum deviation AAD was found to be 0.174 kg/m³ and AARD to be 0.0074%. Hence, the correlation shows good agreement with experimental data measured by Jae-Hoon Song et al.[65].

4.2 Modified Tammann-Tait equation

This correlation for finding density of the mixture is a function of Pressure & Temperature. The experimental data are correlated for each composition using a modified Tammann-Tait equation i.e.

$$\rho(T, p) = \frac{A_0 + A_1 T + A_2 T^2}{1 - C \ln \left(\frac{B_0 + B_1 T + B_2 T^2 + p}{B_0 + B_1 T + B_2 T^2 + 0.1 \text{ MPa}} \right)} \quad (4.2)$$

Where,

Table 4.4: Parameters of a modified Tammann-Tait equation for Piperazine + Water

Parameters	PZ +H ₂ O (w ₁ =0.1001)
A_0/kgm^{-3}	867.144
$A_1/\text{kgm}^{-3}\text{K}^{-1}$	1.2366
$A_2/\text{kgm}^{-3}\text{K}^{-2}$	-0.00262
B_0/Mpa	-161.649
B_1/MpaK^{-1}	3.2407
B_2/MpaK^{-2}	-0.00568
C	0.12572
σ/kgm^{-3}	0.381

The values of density of PZ & Water mixture at different pressure and temperature was taken and listed in Table 4.5 [43].

Generally, density decreases when temperature is increased from 293.15 K to 393.15 K.

Similarly, density also decreases for aqueous solution of PZ. Here, the reduction in density ranges from 5.6% to 4.6 % at 0.1 MPa and 140 MPa respectively for the above-mentioned range.

Table 4.5: Experimental densities of (PZ + H₂O) mixture at various conditions of temperature (T) and pressure (P)

Pressure(Mpa)	Temperature(K)					
	293.15	313.15	333.15	353.15	373.15	393.15
0.1	1004.7	998	988.2	977.8	963.9	948.3
0.5	1004.8	998.2	988.4	977.9	964.1	948.7
1	1005	998.4	988.6	978.1	964.4	948.9
2	1005.5	998.8	989.1	978.6	965	949.5
5	1006.7	1000	990.3	979.9	966.4	951
10	1008.8	1002	992.4	982.2	968.7	953.6
15	1010.8	1004	994.4	984.3	971	956
20	1012.8	1005.9	996.4	986.5	973.4	958.5
30	1016.9	1009.9	1000.4	990.8	977.9	963.2
40	1020.8	1013.8	1004.4	994.8	982.2	967.8
50	1024.5	1017.5	1008.1	998.9	986.2	972.2
60	1028.3	1021.3	1011.9	1002.9	990.3	976.6
70	1032.1	1024.9	1015.7	1006.7	994.4	981
80	1035.5	1028.4	1019.2	1010.5	998.3	984.8
90	1039.2	1031.8	1022.7	1014	1002.2	988.9
100	1042.7	1035.4	1026.3	1017.7	1005.9	992.9
110	1045.9	1038.7	1029.7	1021.3	1009.5	996.7
120	1049.4	1042	1033.3	1024.7	1013.1	1000.4
130	1052.8	1045.3	1036.5	1028.2	1016.6	1004
140	1055.9	1048.5	1039.9	1031.5	1020	1007.8

The above parameters from Table 4.4 in Equation (4.2) using the python code and hence obtained the following table.

Correlation methods

Table 4.6: Correlated densities ρ for PZ + Water mixture ($w_{PZ} = 0.1001$)a at different conditions of temperature T and pressure p using Modified Tammann-Tait equation

Density						
$\rho(\text{kg/m}^3)$						
p(Mpa)	Temperature(K)					
	293.15	313.15	333.15	353.15	373.15	393.15
0.1	1004.499	997.460	988.326	977.096	963.770	948.348
0.5	1004.667	997.630	988.499	977.275	963.959	948.551
1	1004.877	997.841	988.715	977.498	964.194	948.805
2	1005.296	998.263	989.145	977.944	964.664	949.311
5	1006.546	999.522	990.429	979.274	966.065	950.819
10	1008.611	1001.599	992.548	981.468	968.375	953.302
15	1010.651	1003.652	994.641	983.632	970.652	955.747
20	1012.666	1005.680	996.708	985.769	972.898	958.156
30	1016.628	1009.665	1000.768	989.963	977.301	962.870
40	1020.502	1013.560	1004.733	994.056	981.591	967.453
50	1024.292	1017.369	1008.609	998.052	985.775	971.913
60	1028.002	1021.098	1012.401	1001.958	989.858	976.258
70	1031.636	1024.750	1016.113	1005.779	993.847	980.496
80	1035.198	1028.328	1019.749	1009.518	997.747	984.632
90	1038.692	1031.837	1023.312	1013.180	1001.562	988.671
100	1042.119	1035.279	1026.805	1016.768	1005.296	992.620
110	1045.485	1038.658	1030.233	1020.286	1008.954	996.483
120	1048.790	1041.975	1033.598	1023.737	1012.539	1000.264
130	1052.037	1045.235	1036.903	1027.125	1016.055	1003.967
140	1055.230	1048.438	1040.150	1030.451	1019.505	1007.597

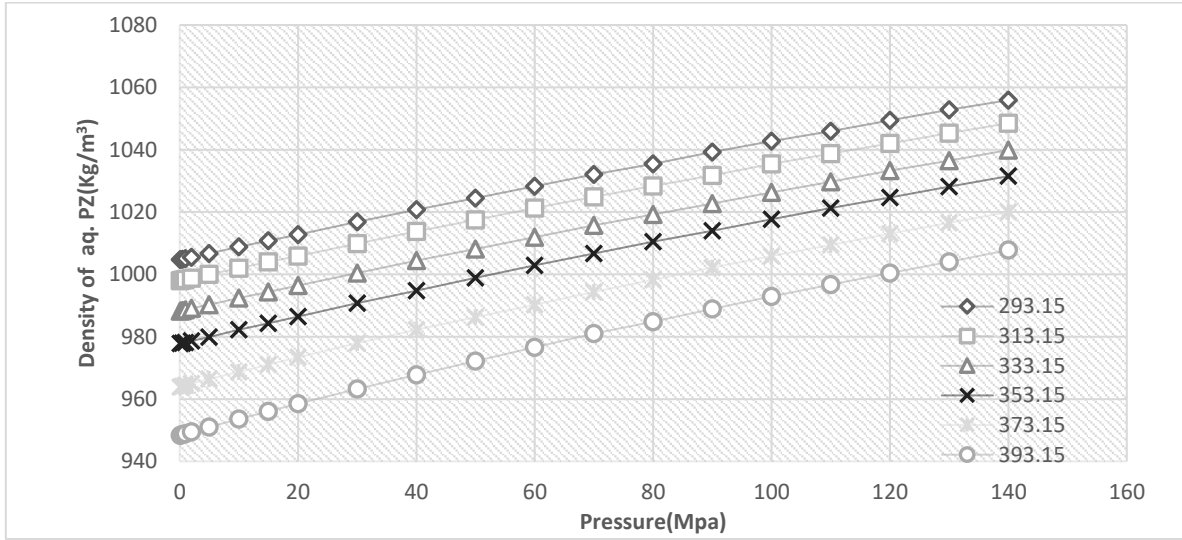


Figure 4.2: Densities of Piperazine + Water mixture ($w_{PZ} = 0.1001$) at various temperature T and Pressure p .

In Figure 4.2, Lines represents correlated value of density of PZ + H₂O using Modified Tammann-Tait equation. The Absolute Average Relative Deviation (AARD) was found to be less than 0.04% and Absolute Maximum Deviation (AMD) to be 1.075 kg/m³ and the python code are mentioned in Appendix C. The correlation shows good agreement with experimental data measured by Eduardo et al.[43].

4.3 Modified Rackett equation

According to Murrleta-Guevara et al. [39], a modified form of the Rackett equation is suitable for predicting liquid solvent density as a function of temperature. Z_{RA} is a constant determined from experimental data for each of the solvents which depends on the critical temperature & pressure through Lydersen's method [66],[67].

$$\frac{1}{d} = (RT^C/P^C)Z_{RA}[1 + (1 - T_r)^{2/7}] \quad (4.3)$$

Where,

d = Density, g cm⁻³

T = temperature, °C

T^C =critical temperature, K

Correlation methods

P^C =critical pressure, atm

R= molar gas constant,

T_r =reduced temperature, T/T_c

N= number of data points[39]

This correlation method is used for pure solvents used in CO₂ capture plant. From Equation (4.3) ,the values of density of pure MEA is tabulated in Table 4.7 and the parameters required are calculated to be as in Table 4.8.

According to Murrleta-Guevara et al. , a modified form of the Rackett equation is suitable for predicting liquid solvent density as a function of temperature.

Table 4.7: Experimental Data of density of Pure MEA at Various Temperatures

Temperature K	DENSITY of Pure MEA					
	(gm/cm ³)					
	Song et al.[28]	DiGuillo et al. [29]	Wang et al.[30]	Murrleta- Guevara et al.[31]	Lee & Lin et al.[32]	Correlated using modified Rackett
293.15		1.015	1.0162			
298.15				1.013		1.029
303.15	1.009		1.0083	1.009	1.009	1.020
308.15				1.003		1.011
313.15	1.001	1.000	1.0004	1.000	0.9999	1.003
318.15				0.997		0.994
323.15	0.993		0.9924	0.992	0.9918	0.985
328.15				0.988		0.976
th333.15	0.985	0.984	0.9843	0.983		0.968
338.15						
343.15	0.977		0.9762			
AARD %	0.926					

Correlation methods

Table 4.8: Different parameters value required for modified Rackett equation

Critical Temperature	Critical Pressure	Molar gas constant	Reduced Temperature
T^c	P^c	R	T_r
K	am	(atm cm ³)/(mol K)	
636.73	67.84	82.134	0.468-0.523

These values mentioned in Table (4.8) is used in Equation (4.3) using a python code in Appendix D.

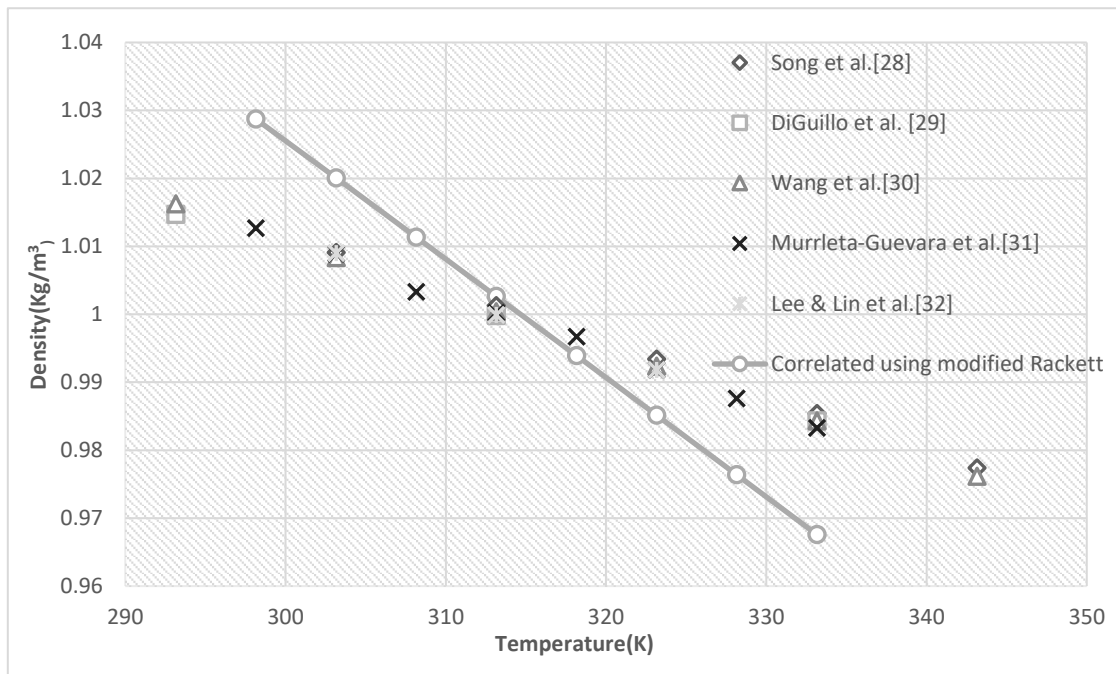


Figure 4.3: Density vs Temperature graph for pure MEA from literatures.

In Figure 4.3 ,Lines represents correlated value of density MEA using Modified Rackett equation. The Absolute Average Relative Deviation (AARD %) is found to be 0.926% while taking modified Rackett equation as a correlation method. As increase in temperature ,density of MEA goes on decreasing as shown in Figure 3.18 and the python code for the correlation is mentioned in Appendix D.

4.4 Samanta et al. Method

Samanta & Bandyopadhyay et al. had measured densities of PZ (mass fraction 1.74%-6.88%) & water at the temperature range of 25-60 degree Celsius and using a 25.78 mL (at 298 K) Gay-Lussac pycnometer with constant temperature of water bath at Separation Science Laboratory, Indian Institute of Technology, Kharagpur and [59]. The experimental data measured by them is listed in the Table 4.9.

Table 4.9: Experimental Densities for Piperazine + Water from 298 K to 333 K [59]

Temperature (K)	PZ MASS FRACTION			
	1.74	3.45	5.16	6.88
298	0.9978	0.9985	0.9994	1.0006
303	0.9965	0.9972	0.9981	0.999
308	0.9951	0.9957	0.9965	0.9976
313	0.9932	0.9941	0.9947	0.9956
318	0.9914	0.9922	0.9925	0.9938
323	0.9893	0.9902	0.9904	0.9914
328	0.9867	0.9874	0.988	0.9891
333	0.9842	0.9845	0.9857	0.9874

The experimental density data of Piperazine+ water mixtures were correlated as function of temperature and concentration of amine, i.e.

$$\rho = \sum_{i=0}^2 [A_i W^i + B_i W^i (T/K) + C_i W^i (T/K)^2] \dots \dots \dots (4.4)$$

Where,

ρ = Density of the mixture

T = Temperature of the mixture

A_i , B_i & C_i are correlation parameter whose values are given in the table below.

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These values mentioned in Table (4.10) is used in Equation (4.4) using a python code in Appendix E.

Table 4.10: Parameters used in the correlation

i	Parameters		
	Ai	Bi	Ci
i=0	7.55E-01	1.89E-03	-3.61E-06
i=1	3.17E-04	7.00E-07	-6.13E-10
i=2	3.54E-05	-1.75E-07	2.21E-10

Table 4.11 Correlated Densities for PZ + Water from 298 K to 333 K using Samanta & Bandyopadhyay et al

Temperature (K)	Piperazine Mass Fraction			
	1.74	3.45	5.16	6.88
298	0.9978	0.9987	0.9995	1.0004
303	0.9964	0.9973	0.9981	0.999
308	0.9949	0.9957	0.9965	0.9974
313	0.9931	0.9939	0.9948	0.9956
318	0.9912	0.992	0.9928	0.9937
323	0.989	0.9899	0.9907	0.9916
328	0.9867	0.9876	0.9884	0.9893
333	0.9843	0.9851	0.9859	0.9868
AMD	0.6			
AARD	0.018			

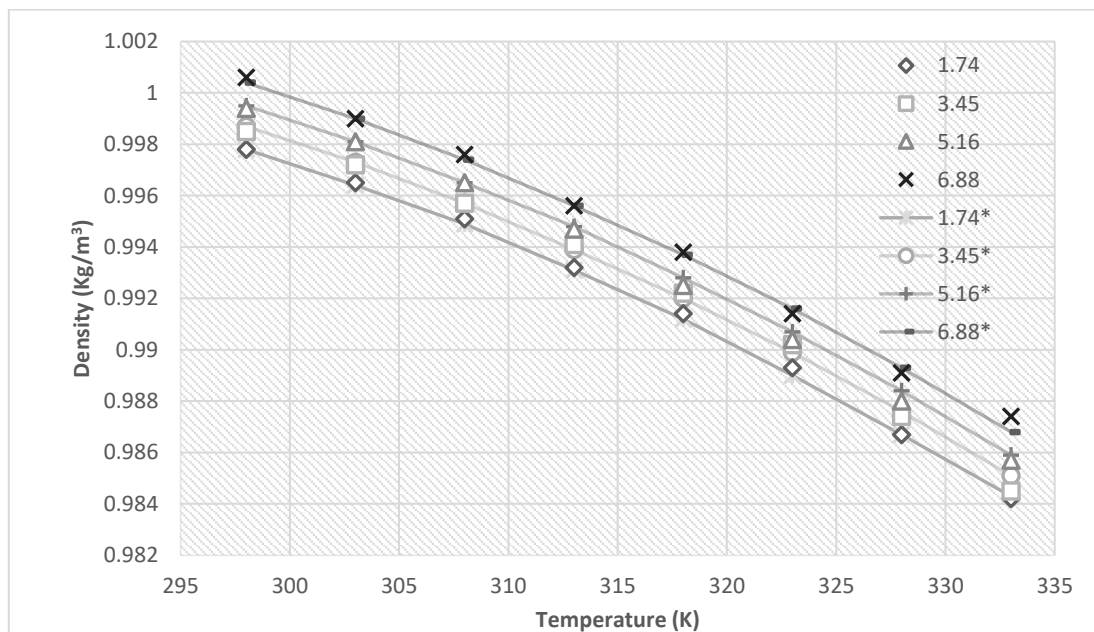


Figure 4.4: Densities for Piperazine + Water from 298 K to 333 K at different mass fraction of PZ.

In Figure 4.4, Lines represents density of PZ + H₂O data of correlated Samanta et al. Method. The comparison between experimental values of Density of PZ+ H₂O mixture and the correlated values using Samanta & Bandyopadhyay et al. is shown in Figure 4.5. The parameters used in this correlation method contribute to the accuracy of the values in this process. The AARD value has been found to be 0.018 % & AMD to be 0.6 kg/m³, when compared with the experimental data of Samanta & Bandyopadhyay et al. using python codes mentioned in Appendix E.

4.5 Henni et al. Method

Amr Henni, Jonathan J. Hromek, Paatoon Tontiwachwuthikul, and Amit Chakma had in their research measured density and viscosity of aqueous 2-amino-2-methyl-1-propanol (AMP) solutions at five temperatures with the range of 25-60 °Celsius over the whole concentration range and using an Anton Paar DMA-4500 density meter at Process Systems Laboratory, Faculty of Engineering, University of Regina, Regina [68]. The experimental data measured

Correlation methods

by them is listed in the Table 4.13 and the correlation method proposed by them is mentioned in Equation (4.5). The required values of parameters are tabulated in Table 4.12.

$$\rho/\text{g.cm}^{-3} = \sum_{k=0}^n a_k x_2^k \quad (4.5)$$

Where

ρ = density in gm/cm³

x_2 = mole fraction of amine

T = Temperature in Kelvin

Table 4.12: Different Parameters at five different temperatures required for Correlation by Henni et al.

Temperature	Parameters					
C	a ₀	a ₁	a ₂	a ₃	a ₄	a ₅
25	0.99664	0.05597	-0.71889	1.442	-1.26103	0.41692
30	0.99578	0.00862	-0.4275	0.64412	-0.29992	
40	0.9923	-0.01389	-0.46712	0.99755	-0.87903	0.29021
50	0.98794	-0.05063	-0.35228	0.83676	-0.77954	0.26908
60	0.98311	-0.08256	-0.24621	0.6674	-0.65025	0.23148

These values mentioned in Table (4.12) is used in Equation (4.5) using a python code in Appendix F.

Average absolute deviations (AAD) between the measured and calculated values to be are presented in Table 4.12 & Table 4.13 respectively .Using the parameters values & reproducing the values of density at AMP & water, the values of densities are correlated using python code in this thesis are shown in Figure 4.6.

Table 4.13: Experimental Densities (gm cm⁻³) of Water + AMP Mixtures at Various Temperatures

Experimental Densities (gm/cm ³) of Water + AMP Mixtures at Various Temperatures					
Temperature °C					
x ₂	25	30	40	50	60
0.000	0.997	0.995	0.992	0.988	0.983
0.0503	0.996	0.994	0.989	0.984	0.978
0.0704	0.997	0.994	0.988	0.982	0.976
0.1005	0.997	0.993	0.987	0.980	0.973
0.2006	0.989	0.985	0.977	0.969	0.961
0.2939	0.978	0.974	0.966	0.958	0.949
0.4982	0.959	0.955	0.947	0.939	0.930

Table 4.14: Correlated Densities (gm/cm³) of Water + AMP Mixtures at Various Temperatures

Temperature °C					
x ₂	25	30	40	50	60
0*	0.9966	0.9958	0.9920	0.9879	0.9831
0.0503*	0.9978	0.9952	0.9903	0.9846	0.9784
0.0704*	0.9975	0.9945	0.9891	0.9829	0.9763
0.1005*	0.9963	0.9930	0.9868	0.9801	0.9729
0.2006*	0.9887	0.9851	0.9772	0.9692	0.9611
0.2939*	0.9791	0.9762	0.9670	0.9586	0.9502
0.4982*	0.9595	0.9560	0.9473	0.9390	0.9304
AARD %	0.0761	0.0861	0.0579	0.0364	0.0393
AMD(kg/m ³)	1.8120	1.0726	1.2709	0.9598	1.1775

In Figure 4.5, the values of density according to Henni et al. ,are presented and the dotted lines refers to the correlation trend using Equation (4.5) and the python codes are mentioned in Appendix F. The Average maximum deviation AMD was found to be 0.0761 kgm⁻³ at 25 °C 0.0861 kgm⁻³ at 30 °C kg/m³, 0.0579 kgm⁻³ at 40°C kg/m³,0.0364 kgm⁻³ at 50°C & 0.0393 kgm⁻³ at 60 °C and AARD to 1.8120% at 25 °C, 1.0726% at 30°C , 1.2709% at 40 °C, 0.9598%

Correlation methods

at 50 °C & 1.1775 at 60 °C Hence, the correlation shows good agreement with experimental data measured by Henni et al.[68]

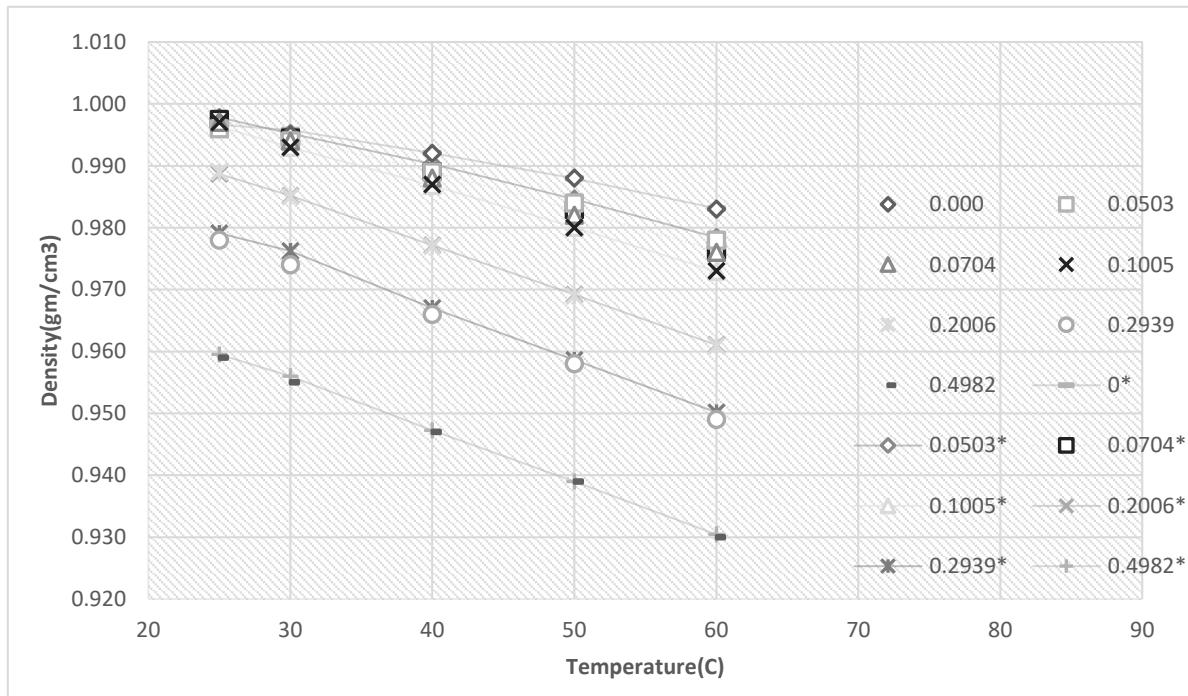


Figure 4.5: Correlated Densities of the water + AMP at various temperatures using Henni et al. Method

4.6 Modified Setschenow Method

Karunaratne et al. [60] in his paper had measured and correlated using various method of mathematical correlation. The modified Weiland's correlation represents experimental densities of assured densities within the temperature range from 293.15 K to 343.15 K. Shokouhi et al.[69] used Setschenow method to corelated density of the amine mixture. Karunaratne et al. in his thesis used this correlation method as a modified Setschenow method [60].

$$\ln\left(\frac{\rho}{\rho_0}\right) = (a_{0,0} + a_{0,1}T)x_4 + (a_{1,0} + a_{1,1}T)x_4^2 \quad (4.6)$$

Where,

$\frac{\rho}{\rho_0}$ = ratio between density of CO₂ loaded and unloaded mixtures at different temperatures.

$a_{i,j}$ = temperature dependent parameters

x_4 = CO₂ mole fraction

T = Temperature in kelvin

These values mentioned in Table (4.15) is used in Equation (4.6) using a python code in Appendix G.

Table 4.15: Parameters of the Setschenow-type correlation Equation (4.6) for the density of MEA + H₂O + AMP + CO₂ mixtures with relevant AMD and AARD (%)

CO ₂ Loaded -27%AMP 3%MEA 70% Water		AARD(%)	AMD(kgm ⁻³)
$a_{0,0}(-) = 2.376$	$a_{1,0}(-) = -3.7$	0.096025341	2.059457812
$a_{0,1}/(K^{-1}) = -6.204$	$a_{1,1}/(K^{-1}) = -0.03917$		

Correlation methods

Table 4.16: Experimental Density of CO₂ loaded 24 % AMP+ 6 % MEA+ 70 % Water using Setschenow method

$\alpha/(\text{molCO}_2 \cdot \text{mol/amine})$	0.083	0.165	0.314	0.418	0.508
x_4	0.0071	0.0141	0.0264	0.0349	0.042
T/K	$\rho/\text{kg} \cdot \text{m}^{-3}$				
293.15	1014.800	1029.400	1049.400	1066.400	1081.600
298.15	1012.300	1026.900	1046.800	1063.500	1078.600
303.15	1009.700	1024.300	1044.100	1060.500	1075.500
308.15	1006.900	1021.600	1041.200	1057.400	1072.300
313.15	1004.100	1018.800	1038.200	1054.300	1069.000
318.15	1001.100	1015.800	1035.200	1051.000	1065.700
323.15	998.000	1012.800	1032.000	1047.700	1062.300
328.15	994.800	1009.600	1028.800	1044.300	1058.900
333.15	991.500	1006.400	1025.500	1040.900	1055.400
338.15	988.100	1003.000	1022.100	1037.400	1051.700
343.15	984.100	999.600	1018.600	1033.700	1047.400

Table 4.17: Correlated Density of CO₂ loaded 24 % AMP+ 6 % MEA+ 70 % Water using Setschenow method

α	0.072	0.152	0.246	0.461	0.511
(molCO ₂ ·mol/amine)					
x_4	0.0059	0.0125	0.02	0.0369	0.0407
T/K	$\rho(\text{kg} \cdot \text{m}^{-3})$				
293.15	1014.283	1028.292	1042.770	1066.723	1074.235
298.15	1011.639	1025.585	1039.973	1063.686	1071.083
303.15	1008.995	1022.878	1037.177	1060.651	1067.933
308.15	1006.047	1019.863	1034.068	1057.298	1064.463
313.15	1002.998	1016.746	1030.856	1053.840	1060.889
318.15	999.949	1013.629	1027.644	1050.383	1057.316
323.15	996.698	1010.307	1024.225	1046.715	1053.532
328.15	993.345	1006.882	1020.702	1042.943	1049.643
333.15	989.891	1003.355	1017.075	1039.066	1045.650
338.15	986.335	999.726	1013.345	1035.085	1041.552
343.15	982.679	995.994	1009.512	1030.999	1037.350
AARD%	0.180				
AMD	0.004 kg·m⁻³				

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In Figure 4.6, lines represent the correlated density of the mixture at different mass fraction (0.083*,0.165*,0.418*,0.508*). * represents the mass fraction used using Setschenow method. The graph shows as increase in CO₂ loading ;density increases with the decreases with temperature. The measured density data as per Karunarathne et al.[61] were fit into a Setschenow-type correlation .AARD % for 27% AMP+ 3% MEA+ 70% H₂O was found to be with 0.180 % & AMD to be 0.004 kg·m⁻³ using python codes mentioned in Appendices G. Thus, the accuracy of density using modified Setschenow-type correlation can be regarded as satisfactory for correlations in engineering calculations.

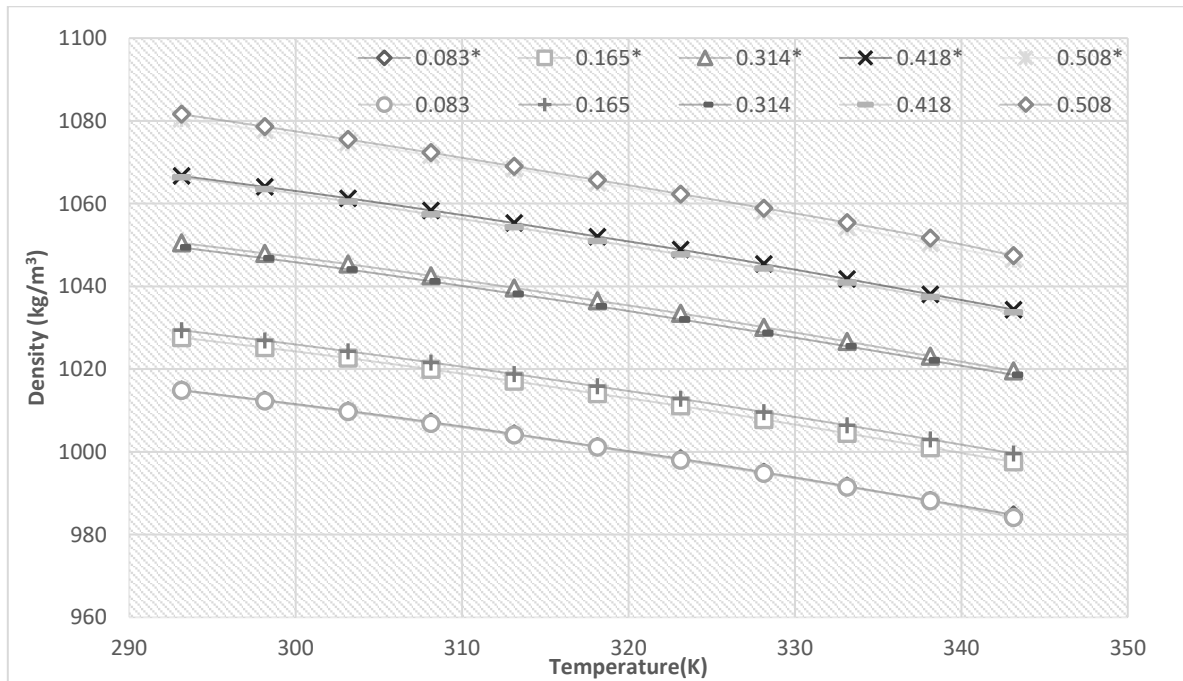


Figure 4.6: Comparison of Density of CO₂ loaded 24 % AMP+6 %MEA+ 70 % H₂O using Setschenow method

4.7 Amundsen et al Method

Trine G. Amundsen, Lars E. Øi, and Dag A. Eimer in their research measured density and viscosity of aqueous MEA at different mass fractions and temperatures with the range of 25-80 °Celsius and using an Anton Paar DMA-4500 density meter at then, Telemark University College, Porsgrunn, Norway[56]. The experimental data measured by authors is listed in the Table 4.19 and the correlation method proposed by them is mentioned in Equation (4.7-4.10)

Correlation methods

and is applied in this thesis using python codes in Appendices H. The required values of parameters are tabulated in Table 4.18 [56] .

$$V^E/(cm^3 \cdot mol^{-1}) = x_1 x_2 \sum_{k=0}^3 A_k (x_1 - x_2)^k \quad (4.7)$$

$$V = V^E + (x_1 V_1 + x_2 V_2) \quad (4.8)$$

$$V_1 = \frac{M_1}{D \cdot (T/K)^2 + E \cdot (T/K) + F} \quad (4.9)$$

$$\rho/g \cdot cm^3 = \frac{\sum_{i=1}^3 (x_i \cdot M_i)}{V} \quad (4.10)$$

Where

ρ = density in gm/cm³

x_i = mole fraction

T= Temperature in Kelvin

M_i = Molecular weight

These values mentioned in Table (4.18) is used in Equation (4.7-4.10) using a python code in Appendix H.

Table 4.18: Regressed Parameters of Redlich-Kister Excess Volume

Temperature(T)	Parameters			
K	A ₀	A ₁	A ₂	A ₃
25	-2.5263	0.7404	0.5698	-1.6062
40	-2.4787	0.6135	0.6018	-1.2561
50	-2.463	0.5338	0.642	-0.987
70	-2.4541	0.4324	0.703	-0.6392
80	-2.407	0.4664	0.539	-0.7186
D	5.35162 *10 ⁻⁷			
E	-0.000451417			
F	1.19451			

Correlation methods

Table 4.19: Experimental Density of MEA+ Water at different mass fraction of MEA(w_1)

Temperature	Experimental Density of MEA+ Water at different mass fraction of MEA(w_1)						
°C	20%	30.0%	40.0%	50.0%	70%	90%	100%
25	1.005	1.011	1.016	1.021	1.026	1.020	1.012
40	0.999	1.003	1.008	1.012	1.016	1.008	1.000
50	0.994	0.998	1.002	1.005	1.008	1.001	0.992
70	0.983	0.986	0.989	0.992	0.993	0.985	0.976
80	0.977	0.979	0.982	0.984	0.985	0.976	0.968

Table 4.20: Correlated Density of MEA+ Water at different mass fraction of MEA(w_1)

Temperature	Correlated Density of MEA+Water at different mass fraction of MEA(w_1)							AMD (kgm^{-3})
°C	20%	30.0%	40.0%	50.0%	70%	90%	100%	
25	1.018	1.021	1.025	1.029	1.031	1.022	1.012	12.420
40	1.006	1.010	1.013	1.016	1.018	1.010	1.001	6.953
50	0.998	1.002	1.005	1.008	1.010	1.001	0.993	3.926
70	0.982	0.985	0.988	0.991	0.993	0.985	0.977	0.871
80	0.974	0.977	0.980	0.983	0.984	0.977	0.968	2.651
AARD								2.959148428

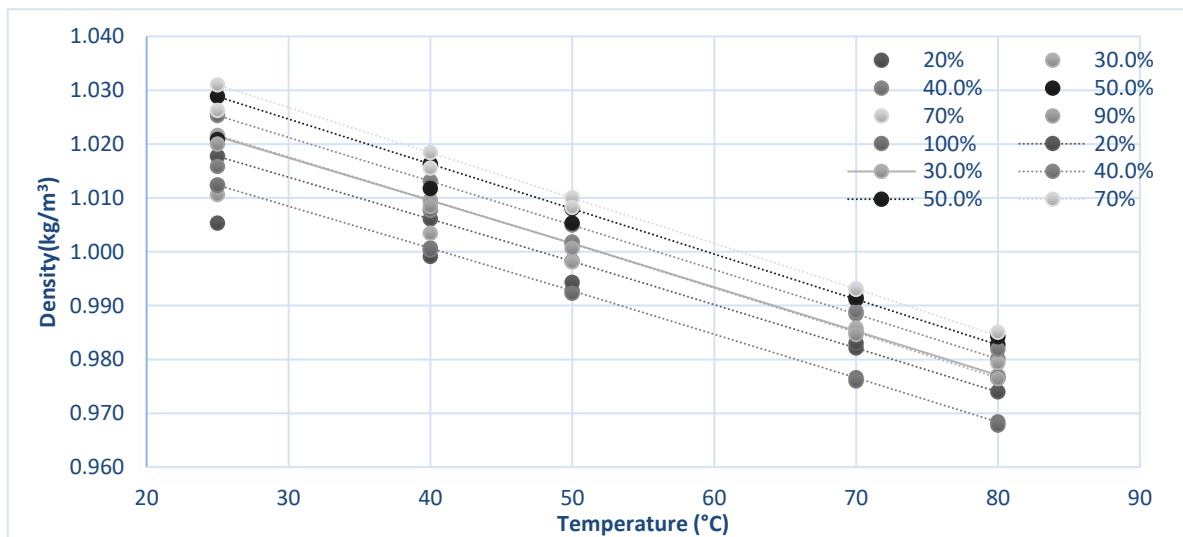


Figure 4.7: Correlated Densities of the Water + MEA at different temperatures using Amundsen et al Method

Correlation methods

In Figure 4.7, the values of density of aqueous MEA at different mass fractions according to Amundsen et al. ,are presented and the dotted lines refers to the correlation trend using Equation (4.7) - (4.10) and the python codes are mentioned in Appendix H .The Average maximum deviation AMD was found to be 12.420 kgm⁻³ at 25 °C ,6.9523 kgm⁻³ at 40 °C , 3.926 kgm⁻³ at 50 °C, 0.871 kg/m³ at 70 °C & 2.651 kgm⁻³ at 80 °C and AARD(%) to be 2.96. Hence, the correlation shows good agreement with experimental data measured by Amundsen et al.[56].

4.8 Hartono et al. Method

Aronu, Hartono and Svendsen [70], proposed the mathematical correlation method for density data of the mixture which is mentioned in Equation (4.11). Parameters required for the correlation are presented in Table 3.42 [71] and the pyhton code used for calculation are mentioned in Appendix I & Appendix J.

4.8.1 Correlation for the density of CO₂ Unloaded Mixture

$$\rho = k_1 + \left(\frac{k_2 x_2}{T}\right) \exp\left(\frac{k_3}{T^2} + \frac{k_4 x_1}{T^2} + k_5 \left(\frac{x_1}{T}\right)^2\right) \dots\dots\dots (4.11)$$

where T, ρ , x_1 , x_2 and k_i are density, temperature, mole fractions of MEA, H₂O of aqueous mixture.

According to Karunarathne et al. [70],the experimental measured densities of aqueous MEA solutions are listed in Table 4.21 and compared with values obtained from Equation (4.11).

These values mentioned in Table (4.22) is used in Equation (4.11) using a python code in Appendices H.

Table 4.21: Measured densities of MEA + Water solutions [70]

Measured Density									
w ₁	x ₁	Kgm ⁻³							
		293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K
0.3	0.1122	1012.6	1008.2	1003.3	997.9	991.6	986	979.4	972.3
0.4	0.1643	1018.4	1013.3	1007.8	1001.8	995.5	988.9	981.9	974.6
0.5	0.2278	1023.6	1017.8	1011.6	1005.2	998.4	991.4	984.1	976.4
0.6	0.3067	1027.7	1021.2	1014.5	1007.6	1000.4	993	985.4	977.4
0.7	0.4077	1029.3	1022.4	1015.2	1007.9	1000.4	992.7	984.8	976.4
0.8	0.5412	1028.1	1020.8	1013.3	1005.7	997.9	990	981.9	973.6
0.9	0.7264	1023.5	1015.8	1008.1	1000.3	992.4	984.3	976.1	967.8

Table 4.22: Correlation parameters for density of aqueous MEA[71]

MEA	Temperature	Parameters
w ₁	K	
0.3-0.9	293.15-363.15	k ₁ =683.5 k ₂ =1.344*10 ⁵ k ₃ =-1.089*10 ⁴ k ₄ =145.2 k ₅ =567.69

The comparison between experimental values of Density of MEA+ H₂O mixture and the correlated values using Hartono et al. Method et al.[71] is shown in Figure 4.8. The parameters used in this correlation method contribute to the accuracy of the values in this process. The AARD value has been found to be 0.1197 % & AMD to be 3.4409 kgm⁻³, when compared with the experimental data of Karunarathne et al. and using python codes mentioned in Appendix I.

Correlation methods

Table 4.23: Correlated densities of aqueous MEA solutions

w_1	x_1	Correlated density $\rho(\text{kgm}^{-3})$							
		293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	353.15 K	363.15 K
0.3	0.1122	1015.721	1009.640	1003.588	997.599	991.696	985.898	980.217	974.664
0.4	0.1643	1019.541	1013.043	1006.616	1000.286	994.076	987.999	982.065	976.281
0.5	0.2278	1023.569	1016.590	1009.730	1003.011	996.448	990.053	983.831	977.786
0.6	0.3067	1027.540	1020.010	1012.656	1005.494	998.534	991.781	985.237	978.901
0.7	0.4077	1030.789	1022.643	1014.743	1007.094	999.699	992.558	985.666	979.018
0.8	0.5412	1031.541	1022.770	1014.322	1006.192	998.374	990.861	983.642	976.707
0.9	0.7264	1024.828	1015.645	1006.855	998.443	990.395	982.694	975.325	968.270
AMD		3.4409 kg/m³							
AARD %		0.1197							

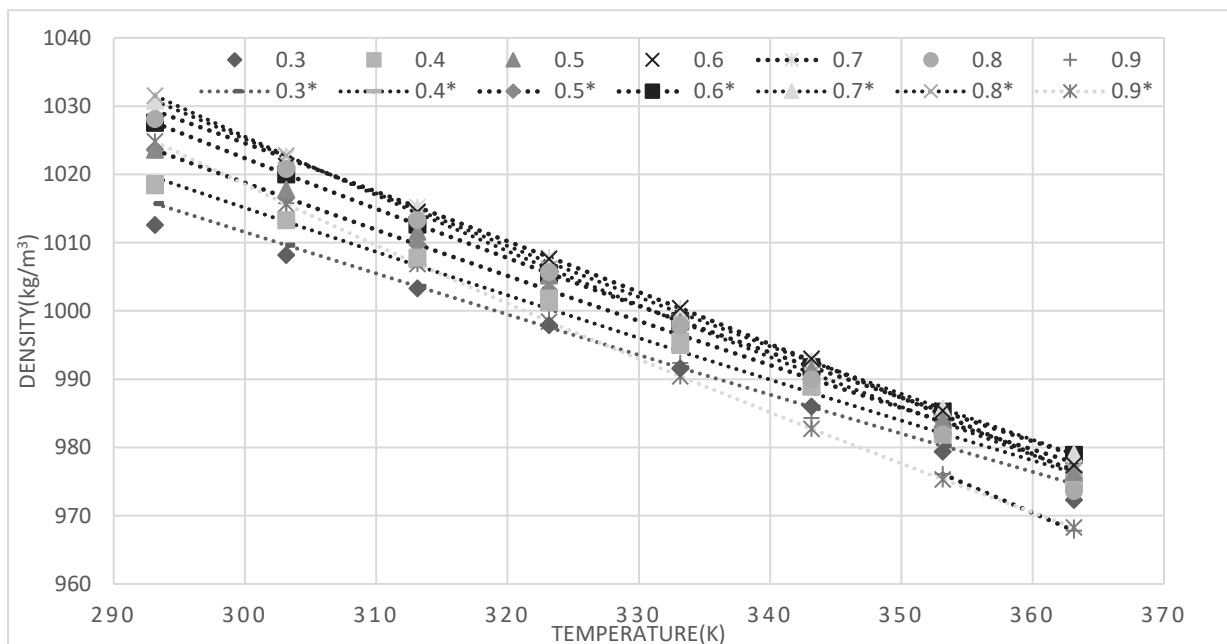


Figure 4.8: Comparison of Density of aqueous MEA at different mass fractions using Hartono et al. Method.

4.8.2 Correlation for the density of CO₂ loaded Mixture

Correlation for the density of CO₂ loaded MEA+H₂O:

$$\rho = (a_1 + a_2(T) + a_3(T)^2 + a_4x_3) \left(k_1 + \frac{k_2x_2}{T}\right) \exp\left(\frac{k_3}{T^2} + \frac{k_4x_1}{T} + k_5\left(\frac{x_1}{T}\right)^2\right) \dots\dots\dots (4.12)$$

where

T, ρ are temperature and density.

x₁, x₂, x₃ are mole fractions of MEA, H₂O, & CO₂ mixture.

These values mentioned in Table (4.22) is used in Equation (4.12) using a python code in Appendices J. According to Karunaratne et al. [70], the experimental measured densities of Carbon dioxide loaded MEA + Water solutions are shown below in Table (4.24) and compared with values obtained from Equation (4.12).

Table 4.24: Measured densities of Carbon dioxide loaded (α (mol CO₂·mol MEA⁻¹)⁻¹) aqueous MEA [59]

Experimental Densities (kgm ⁻³)								
x ₂	α	Temperature (K)						
		293.15	303.15	313.15	323.15	333.15	343.15	353.15
w ₁ =0.3								
0	0	1012.6	1008.2	1003.3	997.9	991.6	986	979.4
0.0105	0.095	1032	1027.6	1022.8	1017.4	1011.6	1005.1	995.5
0.0193	0.175	1052.5	1048.1	1043.3	1038.1	1032.4	1026.4	1020.1
0.0355	0.328	1077.8	1073.4	1068.6	1063.4	1057.9	1052	1044.1
0.0476	0.445	1103.3	1097.7	1092.8	1087.6	1082.1	1075.7	1069.3
0.0574	0.543	1123.1	1118.4	1113.4	1107.9			
w ₁ =0.4								
0	0	1018.4	1013.3	1007.8	1001.9	995.5	988.9	981.9
0.017	0.105	1045.6	1040.7	1035.3	1029.6	1023.6	1017.3	1010.6
0.0341	0.215	1073.4	1068.5	1063.3	1057.8	1051.9	1045.8	1039.4
0.0507	0.325	1102	1097.2	1092	1086.5	1080.8	1074.9	1068.6
0.0669	0.436	1130.3	1125.4	1120.2	1114.7	1109.2	1103.2	1097
0.0826	0.548	1155.5	1150.4	1145.1	1139.5			
w ₁ =0.5								
0	0	1023.6	1017.8	1011.6	1005.2	998.4	991.4	984.1
0.0205	0.092	1052.3	1046.7	1040.9	1034.7	1028.3	1021.7	1014.8
0.0406	0.186	1082.4	1077	1071.4	1065.5	1059.4	1053	1046.4
0.062	0.29	1112.7	1107.4	1101.9	1096.2	1090.3	1084.2	1077.9
0.0825	0.395	1144.5	1139.2	1133.8	1128.3	1122.5	1116.6	
0.1013	0.495	1175.7	1170.4	1165	1159.4	1153.6	1147.5	

Correlation methods

The comparison between experimental values of Density CO₂ loaded MEA + H₂O mixture and the correlated values using Hartono et al. Method et al.[71] is shown in Figure 4.9- 4.11. The parameters used in this correlation method contribute to the accuracy of the values in this process. The AARD value has been found to be 0.13% , 0.09%,0.13 % & AMD to be 4.045 kg/m³,2.177 kg/m³ ,4.044 kg/m³ respectively for w₁=0.3,0.4 & 0.5 when compared with the experimental data of Karunaratne et al. and using python codes mentioned in Appendix J.

Table 4.25: Correlated densities of CO₂-loaded (α /mol CO₂·mol MEA⁻¹) aqueous MEA

		Correlated Densities (kg/m ³)						
		Temperature (K)						
x ₂	α	293.15	303.15	313.15	323.15	333.15	343.15	353.15
w ₁ =0.3								
0	0	1012.57	1008.33	1003.50	998.12	992.23	985.86	979.03
0.0105	0.095	1033.01	1028.74	1023.87	1018.45	1012.52	1006.12	999.25
0.0193	0.175	1049.98	1045.67	1040.78	1035.33	1029.38	1022.95	1016.06
0.0355	0.328	1080.79	1076.45	1071.52	1066.04	1060.04	1053.57	1046.64
0.0476	0.445	1103.47	1099.11	1094.16	1088.65	1082.64	1076.14	1069.19
0.0574	0.543	1122.92	1118.52	1113.53	1107.98	1101.92	1095.38	1088.39
AMD		4.045 kg/m ³	AARD	0.13%				
w ₁ =0.4								
0	0	1016.34	1011.41	1006.12	1000.51	994.62	988.45	982.03
0.017	0.105	1046.15	1041.18	1035.85	1030.20	1024.26	1018.04	1011.58
0.0341	0.215	1075.58	1070.58	1065.23	1059.55	1053.58	1047.33	1040.84
0.0507	0.325	1103.61	1098.62	1093.25	1087.55	1081.56	1075.30	1068.78
0.0669	0.436	1130.27	1125.29	1119.93	1114.23	1108.24	1101.98	1095.46
0.0826	0.548	1155.82	1150.85	1145.51	1139.83	1133.84	1127.58	1121.06
AMD		2.177 kg/m ³	AARD	0.09				
w ₁ =0.5								
0	0	1019.8	1014.5	1008.8	1002.8	996.5	989.9	983.1
0.0205	0.092	1052.5	1047.1	1041.4	1035.4	1029.0	1022.4	1015.5
0.0406	0.186	1083.7	1078.4	1072.7	1066.6	1060.3	1053.6	1046.7
0.062	0.29	1116.2	1110.9	1105.2	1099.1	1092.8	1086.2	1079.3
0.0825	0.395	1146.6	1141.3	1135.6	1129.6	1123.3	1116.7	1109.8
0.1013	0.495	1173.7	1168.5	1162.9	1156.9	1150.6	1144.0	1137.2
AMD	4.044	kg/m ³	AARD %	0.134117				

Correlation methods

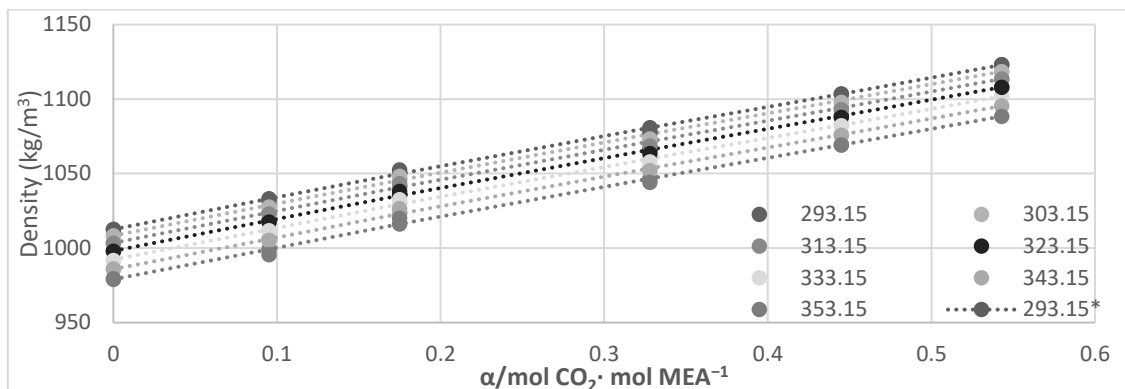


Figure 4.9 Density of CO₂-loaded MEA ($w_1=0.3$) solution at different CO₂ loadings and temperatures with AMD= 4.044 kg/m³ & AARD =0.13 % using Hartono et al. method

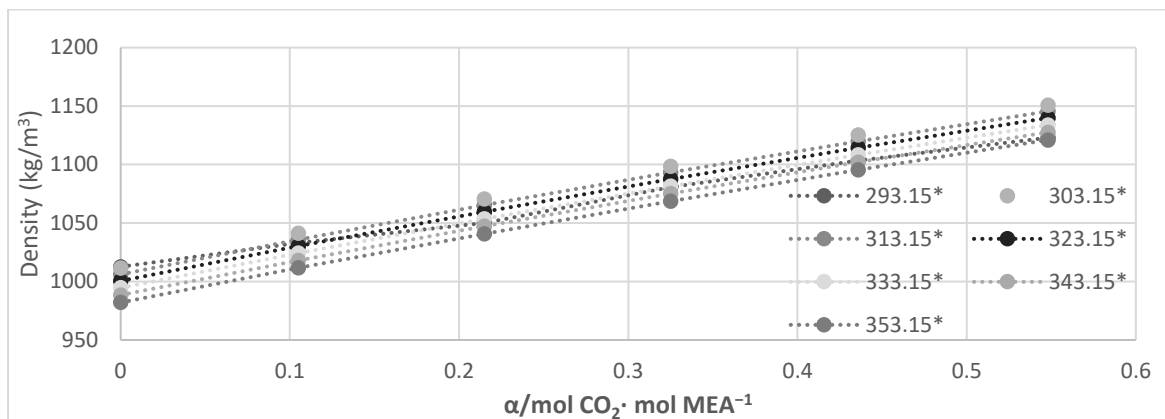


Figure 4.10 Density of CO₂-loaded MEA ($w_1=0.4$) solution at different CO₂ loadings and temperatures with AMD= 2.17 kg/m³ & AARD =0.09 % using Hartono et al. method.

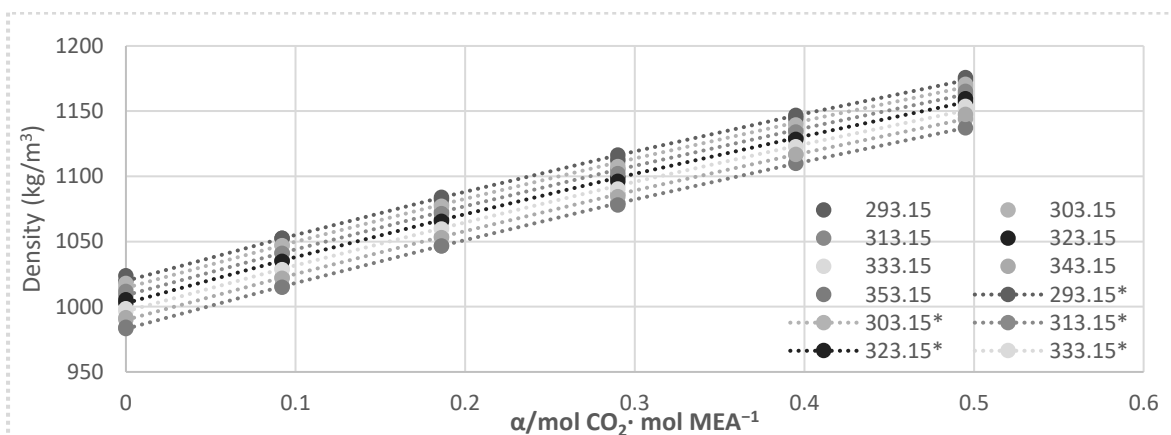


Figure 4.11: Density of CO₂-loaded MEA ($w_1=0.5$) solution at different CO₂ loadings and temperatures with AMD = 3.79 kg/m³ & AARD =0.16 % using Hartono et al. method.

5 Result & Conclusion

5.1 Unloaded CO₂ Mixture

Density data for pure MEA was correlated from temperature 293.15-343.15 K and found to be inline with data produced by other researchers. Density data for other solutions like DEA, MDEA and AMP was found to be consistently low while compared with literature data throughout the same temperature range. The low value of density are mostly due to purity of the solutions.

Density for the binary system of aqueous MEA with 20-70 mass % MEA, aqueous PZ solutions with 1.74 -5.16 mass % PZ and aqueous MDEA solutions with 10-30 mass % MDEA were taken from temperature 298 K to 350 K. In all cases, densities decrease with increase in temperature and increases with increase in respective amine concentrations.

Ternary mixtures of MDEA, MEA & Water, PZ+AMP+Water and AMP+MEA+ Water at different mass fractions were measured from temperatures 293.15 K to 343.15 K. In all the cases densities decreases with increase in temperature. Also density increases, when the concentrations of MDEA, PZ and MEA increases in ternary mixture of MDEA +MEA +Water, PZ + AMP + WATER and AMP + MEA + WATER respectively.

5.2 Loaded CO₂ Mixture

Densities of 20-40 mass % MEA with CO₂ loading 0.1-0.5 % mass fraction solutions were also measures from temperature 298.15 K to 373.15 K. Densities of these solutions increased with increase in CO₂ loadings and were found to be higher than densities of unloaded aqueous MEA solutions at respective concentrations and temperature. In all cases, densities of loaded solutions increased rapidly at high loadings and lower temperatures but showed less effect at higher temperatures and low CO₂ loadings

Densities of PZ with CO₂ loaded solutions were also measures from temperature 293.15 K to 333.15 K. Densities of 6% mass MEA + 24 % mass AMP with CO₂ loading (0.1-0.50) mixture

were also correlated from temperature 298.15 K to 373.15 K. Densities of these solutions increased with increase in CO₂ loadings, with decrease in temperature.

5.3 Reliability of Mathematical Correlation Method Used

Different correlation has been studied and reproduced in this thesis & are discussed in relevant sections. The overall performance of mathematical correlation is evaluated using two statistical tools namely, Absolute Average Relative Deviation (AARD%), And Absolute Maximum Deviation (AMD) given by Equations (4.1) & Equation (4.2) respectively.

Absolute Average Relative Deviation:

$$AARD(\%) = \frac{100\%}{N} \sum_{i=1}^N \left| \frac{Y_i^E - Y_i^C}{Y_i^E} \right| \dots\dots\dots (5.1)$$

Absolute Maximum Deviation:

$$AMD = MAX|Y_i^E - Y_i^C| \dots\dots\dots (5.2)$$

Where

N=number of data points

Y_i^E, Y_i^C are measured property and Correlated property respectively.

On performing different models to correlate density data for various amines solutions, it was found that the AMD value for (MEA + Ethylene Glycol + H₂O) mixture to be 0.013 kgm⁻³ and AARD 0.007% using Jae-Hoon Song method. Similarly, density for MEA solution was calculated using Modified- Rackett equation and AARD was found to be 0.926%. The method of Samanta et al. for (PZ + H₂O) mixture, Henni et al. for (AMP+H₂O), Hartone et al. CO₂ unloaded for (MEA+H₂O) mixture and CO₂ loaded for (MEA + H₂O+ CO₂) mixture produced an AARD of 0.018%, 0.086%, 0.120% and 0.16% respectively, whereas AMD value of 0.060,1.812,3.441 and 3.790 kgm⁻³ respectively.

Result & Conclusion

Also, from Modified Tammann Tait equation for (PZ+ H₂O) mixture, the AARD was found to be 0.040% and AMD value of 1.075 kgm⁻³. The model of Setchenous method CO₂ loaded for (AMP + MEA + H₂O + CO₂) mixture produced an AMD value of 0.004 kgm⁻³ and AARD 0.180%.

Table 5.1: Correlation Method Applied In This Thesis

Correlation Method	Mixture	AARD (%)	AMD (kg/m ³)
Jae-Hoon Song Method	MEA+ Ethylene glycol+ H ₂ O	0.007	0.013
Modified Tammann-Tait equation	PZ+ H ₂ O	0.040	1.075
Modified Rackett equation	MEA	0.930	
Samanta et al. Method	PZ+H ₂ O	0.020	0.600
Henni et al. Method	AMP+ H ₂ O	0.090	1.812
Setchenows Method-CO ₂ Loaded	AMP + MEA+ H ₂ O+ CO ₂	0.180	0.004
Amudsen et al. Method	MEA + H ₂ O	2.960	12.420
Hartono et al. Method-CO ₂ Unloaded	MEA + H ₂ O	0.120	3.440
Hartono et al. Method-CO ₂ Loaded	MEA+H ₂ O+ CO ₂	0.130	4.045

Various measurements were performed by researchers at temperature between (294-449) K and pressure up to 100 MPa to find the density of aqueous solutions of carbon dioxide which has its respective benefits. The data calculated are also important in measuring of other important physiochemical parameters in the process . This thesis explains the detail study of density of various amines used in CO₂ Capture plant and their mixtures at different temperatures and various ways to correlate the values of density of unloaded binary, ternary mixtures & CO₂ loaded mixtures as well. Different correlation method is used for comparing experimental data's taken at different laboratories by various researchers which rely on the number of parameters for different mixtures. In this thesis, Jae-Hoon Song Method depicts the least deviation where as Amudsen et al. Method shows the highest AARD value.

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Appendices

Appendix A: Task description

Appendix B: Jae-Hoon Song Method

Appendix C: Modified Tamman Tait

Appendix D: Modified Rackett Equation

Appendix E: Samanta et al. Method

Appendix F: Henni et al. Method

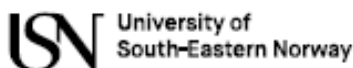
Appendix G: Setschenow-type correlation

Appendix H: Amundsen et al Method

Appendix I: Hartono et al. Method-Unloaded CO₂

Appendix J: Hartono et al. Method-Loaded CO₂

Appendix A: Task description



Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: literature review and correlation of density for amines relevant for CO₂-capture process

USN supervisor: Zulkifli Idris

External partner: Dag A. Eimer

Task background:

Carbon dioxide (CO₂) is considered as one of the main contributors to the global warming and removal of CO₂ from industrial gas streams has become even more important due to the focus on reduction of greenhouse gas emissions.

Amine based chemical absorption processes is the main method for removal of CO₂. The well-known amine for this purpose is ethanolamine (MEA) and it has been used as an important industrial absorbent due to its rapid reaction rate, relative low cost and thermal stability. However, other amines are also being considered in an attempt to lower capture costs. There is a shortage of physiochemical data of such solutions, be it unloaded or loaded with CO₂. Such data are important for good chemical engineering design of most units in a CO₂ capture plant affecting both CO₂ capture rate and energy management.

Good work in this area may be published in journals, and many papers like this have been published in the past based on thesis work. There is a strong research group at USN working on CO₂ capture. The candidate would in practice be a member of this group while working on this project.

Task description:

The student will first be guided to perform a literature survey for relevant publications using scientific search engines. Densities for unloaded and CO₂-loaded amine solutions found in literature will be analysed using suitable correlation methods. The literature data shall be correlated by fitting parameters to appropriate models such that these models can account for mixture densities at various temperatures, amine concentrations and CO₂ loadings. It is important for use in simulation work that data are available in the form of convenient mathematical models. In the thesis, a discussion on suitability of each method chosen will be discussed.

Student category: EET or PT students

The task is suitable for online students (not present at the campus): Yes

*if an online student chooses this project, a discussion with supervisors will be arranged such that details of task description will be modified.

Practical arrangements:

USN has online subscription to relevant search engines and journals.

Appendices

Supervision:

As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and signature):

Student (write clearly in all capitalized letters): PRADEEP BARAL

Student (date and signature): Jan 30, 2021



Appendix B: Jae-Hoon Song Method

```

temp = [303.15,313.15,323.15,333.15,343.15]
a1 = [0.8586,1.0015,1.0712,1.1432,1.1754,1.2681]
a2 = [13.152*10**-4,6.0500*10**-4,3.5236*10**-4,0.6656*10**-4,-0.1060*10**-4,-
4.4704*10**-4]
a3 = [-2.7857*10**-6,-1.7857*10**-6,-1.5000*10**-6,-1.1429*10**-6,-1.0714*10**-
6,0.4286*10**-6]
def func1():
    j = 0;
    i = 0
    while j < 5:
        density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
        print(density)
        j+=1
def func2():
    j = 0;
    i = 1
    while j < 5:
        density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
        print(density)
        j+=1
def func3():
    j = 0;
    i = 2
    while j < 5:
        density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
        print(density)
        j+=1
def func4():

```

```

j = 0;
i = 3
while j < 5:
    density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
    print(density)
    j+=1
def func5():
    j = 0;
    i = 4
    while j < 5:
        density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
        print(density)
        j+=1
def func6():
    j = 0;
    i = 5
    while j < 5:
        density = a1[i]+(a2[i]*temp[j])+(a3[i]*(temp[j]**2))
        print(density)
        j+=1
print("at 0 84.7-----")
func1()
print("at 15 69.7-----")
func2()
print("at 30 54.7-----")
func3()
print("at 45 49.7-----")
func4()
print("at 60 24.7-----")
func5()

```

```
print("at 84.7-----")  
func6()
```

Appendices

Appendix C: Modified Tamman Tait

```

import math
temp = [293.15,313.15,333.15,353.15,373.15,393.15]
P = [0.1,0.5,1,2,5,10,15,20,30,40,50,60,70,80,90,100,110,120,130,140]

#different parameters value
Ao = 867.144
A1 = 1.2366
A2 = -0.00262
Bo = -161.649
B1 = 3.2407
B2 = -0.00568
C = 0.12572
#at t=293.15 and at different pressure
def func_293():
    i = 0
    print("-----at temperature = 293.15 -----")
    while i < 20:
        Density = (Ao + (A1*temp[0])+(A2*temp[0]**2))/(1-
C*math.log((Bo+B1*temp[0]+B2*temp[0]**2+P[i])/(Bo+B1*temp[0]+B2*temp[0]**2+0.1)
))
        print(Density)
        i+=1
def func_313():
    i = 0
    print("-----at temperature = 313.15 -----")
    while i < 20:
        Density = (Ao + (A1*temp[1])+(A2*temp[1]**2))/(1-
C*math.log((Bo+B1*temp[1]+B2*temp[1]**2+P[i])/(Bo+B1*temp[1]+B2*temp[1]**2+0.1)
))
        print(Density)
        i+=1
def func_333():
    i = 0
    print("-----at temperature = 333.15 -----")
    while i < 20:
        Density = (Ao + (A1*temp[2])+(A2*temp[2]**2))/(1-
C*math.log((Bo+B1*temp[2]+B2*temp[2]**2+P[i])/(Bo+B1*temp[2]+B2*temp[2]**2+0.1)
))
        print(Density)
        i+=1

```

```

def func_353():
    i = 0
    print("-----at temperature = 353.15----- ")
    while i < 20:
        Density = (Ao + (A1*temp[3])+(A2*temp[3]**2))/(1-
C*math.log((Bo+B1*temp[3]+B2*temp[3]**2+P[i])/(Bo+B1*temp[3]+B2*temp[3]**2+0.1)
))
        print(Density)
        i+=1
def func_373():
    i = 0
    print("-----at temperature = 373.15 -----")
    while i < 20:
        Density = (Ao + (A1*temp[4])+(A2*temp[4]**2))/(1-
C*math.log((Bo+B1*temp[4]+B2*temp[4]**2+P[i])/(Bo+B1*temp[4]+B2*temp[4]**2+0.1)
))
        print(Density)
        i+=1
def func_393():
    i = 0
    print("-----at temperature = 393.15----- ")
    while i < 20:
        Density = (Ao + (A1*temp[5])+(A2*temp[5]**2))/(1-
C*math.log((Bo+B1*temp[5]+B2*temp[5]**2+P[i])/(Bo+B1*temp[5]+B2*temp[5]**2+0.1)
))
        print(Density)
        i+=1

func_293()
func_313()
func_333()
func_353()
func_373()
func_393()

```

Appendix D: Modified Rackett Equation

```
T = [298.15,303.15,308.15,313.15,318.15,323.15,328.15,333.15]
```

```
#T = [25,30,35,40,45,50,55,60]
```

```
Tc = 636.73
```

```
#Tc = 363.58
```

```
def func():
```

```
    i=0
```

```
    while i < 8:
```

```
        Tr = T[i]/Tc
```

```
        print(Tr)
```

```
        i+=1
```

```
func()
```

```
#Zra = 0.2491
```

```
#Zra = [0.092,0.092,0.092,0.062,0.0914,0.091,0.091,0.090]
```

```
Zra = 0.09162673281056866
```

```
Pc = 67.84
```

```
#R = 1.348
```

```
R = 8.314
```

```
#R = 82.134
```

```
Tr = [0.4682518492924787,
```

```
0.47610447128296135,
```

```
0.48395709327344394,
```

```
0.4918097152639266,
```

```
0.4996623372544092,
```

```
0.5075149592448919,
```

```
0.5153675812353744,
```

```
0.523220203225857]
```

```
#k = 1+((1-Tr)**(2/7))
def func1():
    i = 0
    while i < 8:
        density1 = ((R*Tc)/Pc)*(Zra**((1+((1-Tr[i])**((2/7))))))
        density = 1/density1
        print(density)
        i+=1
func1()
```

Appendix E: Samanta et al. Method

```
temp = [298,303,308,313,318,323,328,333]
```

```
W = [1.74,3.45,5.16,6.88]
```

```
A0 = 0.7550
```

```
B0 = 1.8866*10**(-3)
```

```
C0 = -3.6056*10**(-6)
```

```
A1 = 3.1716*10**(-4)
```

```
B1 = 7.0006*10**(-7)
```

```
C1 = -6.1337*10**(-10)
```

```
A2 = 3.5437*10**(-5)
```

```
B2 = -1.7548*10**(-7)
```

```
C2 = 2.2115*10**(-10)
```

```
def func1():
```

```
    j = 0
```

```
    i = 0
```

```
    while i < 8:
```

```
        density1 = (A0+B0*temp[i]+C0*temp[i]**2)
```

```
        density2 = (A1*W[j]+(B1*W[j])*temp[i]+(C1*W[j]**1)*temp[i]**2)
```

```
        density3 = (A2*(W[j]**2))+((B2*W[j]**2)*temp[i])+(C2*(W[j]**2)*temp[i]**2)
```

```
        fdensity = density1+density2+density3
```

```
        print(fdensity)
```

```
        i+=1
```

```
def func2():
```

```
    j = 1
```

```
    i = 0
```

```
    while i < 8:
```

```
        density1 = (A0+B0*temp[i]+C0*temp[i]**2)
```

```
        density2 = (A1*W[j]+(B1*W[j])*temp[i]+(C1*W[j]**1)*temp[i]**2)
```

```
        density3 = (A2*(W[j]**2))+((B2*W[j]**2)*temp[i])+(C2*(W[j]**2)*temp[i]**2)
```

```
        fdensity = density1+density2+density3
```

```
        print(fdensity)
```

```
        i+=1
```

```
def func3():
```

```
    j = 2
```

```
    i = 0
```

```
    while i < 8:
```

```
        density1 = (A0+B0*temp[i]+C0*temp[i]**2)
```

```
        density2 = (A1*W[j]+(B1*W[j])*temp[i]+(C1*W[j]**1)*temp[i]**2)
```

```
        density3 = (A2*(W[j]**2))+((B2*W[j]**2)*temp[i])+(C2*(W[j]**2)*temp[i]**2)
```

```
        fdensity = density1+density2+density3
```

```

    print(fdensity)
    i+=1
def func4():
    j = 3
    i = 0
    while i < 8:
        density1 = (A0+B0*temp[i]+C0*temp[i]**2)
        density2 = (A1*W[j]+(B1*W[j])*temp[i]+(C1*W[j]**1)*temp[i]**2)
        density3 = (A2*(W[j]**2))+((B2*W[j]**2)*temp[i]+(C2*(W[j]**2)*temp[i]**2)
        fdensity = density1+density2+density3
        print(fdensity)
        i+=1
#at 1.74
print("at 1.74-----")
func1()
#at 3.45
print("at 3.45-----")
func2()
#at 5.16
print("at 5.16-----")
func3()
#at 6.88
print("at 6.88-----")
func4()

```

Appendix F: Henni et al. Method

```
#parametric values
X2 = [0,0.0503,0.0704,0.1005,0.2006,0.2939,0.4075,0.4982,0.5996,0.7028,0.8016,0.9001,1]
Ao = [0.99664,0.99578,0.99203,0.98794,0.98311,0.97819]
A1 = [0.05597,0.00862,-0.01389,-0.05063,-0.08256,-0.13097]
A2 = [-0.71889,-0.42705,-0.46712,-0.35228,-0.24621,0.00477]
A3 = [1.442,0.64412,0.99755,0.83676,0.66740,0.08077]
A4 = [-1.26103,-0.29992,-0.87903,-0.77954,-0.65025,-0.03857]
A5 = [0.41698,-0.35576,0.29021,0.26908,0.23148,0.894]

def func_25():
    i=0
    j=0
    while j < 13:
        density =
        (Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
        +(A5[i]*X2[j]**5)
        print(density)
        j+=1

def func_30():
    i=1
    j=0
    while j < 13:
        density =
        (Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
        +(A5[i]*X2[j]**5)
        print(density)
        j+=1

def func_40():
    i=2
    j=0
    while j < 13:
        density =
        (Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
        +(A5[i]*X2[j]**5)
        print(density)
        j+=1

def func_50():
```

```

i=3
j=0
while j < 13:
    density =
(Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
+(A5[i]*X2[j]**5)
    print(density)
    j+=1

def func_60():
    i=4
    j=0
    while j < 13:
        density =
(Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
+(A5[i]*X2[j]**5)
        print(density)
        j+=1

def func_70():
    i=5
    j=0
    while j < 13:
        density =
(Ao[i]*X2[j]**0)+(A1[i]*X2[j]**1)+(A2[i]*X2[j]**2)+(A3[i]*X2[j]**3)+(A4[i]*X2[j]**4)
+(A5[i]*X2[j]**5)
        print(density)
        j+=1
print("-----at 25-----")
func_25()
print("-----at 30 C-----")
func_30()
print("-----at 40-----")
func_40()
print("-----at 50-----")
func_50()
print("-----at 60-----")
func_60()
print("-----at 70-----")
func_70()

```

Appendix G: Setschenow-type correlation

```

import matplotlib.pyplot as plt
import math
temp = [293.15,298.15,303.15,308.15,313.15,318.15,323.15,328.15,333.15,338.15,343.15]

#for 27 3 70
a1_27 = 2.376
b1_27 = -0.00006204
a2_27 = -3.7
b2_27 = -0.03917
x4_27 = [0.0059, 0.0125, 0.0200, 0.0349, 0.0407]
Do_27 = [1000.8,998.2,995.6,992.7,989.7,986.7,983.5,980.2,976.8,973.3,969.7]
#at 21 9 70
def func_27_1():
    i = 0
    while i < 11:
        D1_27 =
Do_27[i]*math.exp(((a1_27+(b1_27*temp[i]))*x4_27[0])+((a2_27+(b2_27*temp[i]))*x4_27[0]**2))
        print(D1_27)
        i+=1
def func_27_2():
    i = 0
    while i < 11:
        D1_27 =
Do_27[i]*math.exp(((a1_27+(b1_27*temp[i]))*x4_27[1])+((a2_27+(b2_27*temp[i]))*x4_27[1]**2))
        print(D1_27)
        i+=1
def func_27_3():
    i = 0
    while i < 11:
        D1_27 =
Do_27[i]*math.exp(((a1_27+(b1_27*temp[i]))*x4_27[2])+((a2_27+(b2_27*temp[i]))*x4_27[2]**2))
        print(D1_27)
        i+=1
def func_27_4():
    i = 0
    while i < 11:
        D1_27 =
Do_27[i]*math.exp(((a1_27+(b1_27*temp[i]))*x4_27[3])+((a2_27+(b2_27*temp[i]))*x4_27[3]**2))
        print(D1_27)
        i+=1
def func_27_5():
    i = 0
    while i < 11:

```

```

    D1_27 =
Do_27[i]*math.exp((((a1_27+(b1_27*temp[i]))*x4_27[4])+((a2_27+(b2_27*temp[i]))*x4_27[4]**2))
    print(D1_27)
    i+=1
func_27_1()
print("_____")
func_27_2()
print("_____")
func_27_3()
print("_____")
func_27_4()
print("_____")
func_27_5()

```

Appendix H: Amundsen et al Method

T = [298.15,313.15,323.15,343.15,353.15]

```
def forx():
    molMea = 61.08
    molH2O = 18.015
    massMea = [20,30,40,50,70,90,100]
    massH2O = [80,70,60,50,30,10,0]
    i = 0
    while i < 7:
        x1=(massMea[i]/molMea)/((massMea[i]/molMea)+(massH2O[i]/molH2O))
        print(x1)
        #x2=(massH2O[i]/molH2O)/((massMea[i]/molMea)+(massH2O[i]/molH2O))
        #print(x2)
        i+=1
forx()
```

```
x1 = [0.06867173652009834,
0.11221851932600367,
0.16431796415378302,
0.22776408116821548,
0.4076516510691946,
0.7263624756400778,
1.0]
x2 = [0.9313282634799016,
0.8877814806739963,
0.835682035846217,
0.7722359188317846,
0.5923483489308053,
0.27363752435992206,
0.0]
A0 = [-2.5263,-2.4787,-2.4630,-2.4541,-2.4070]
A1 = [0.7404,0.6135,0.5338,0.4324,0.4664]
A2 = [0.5698,0.6018,0.6420,0.7030,0.5390]
A3 = [-1.6062,-1.2561,-0.9870,-0.6392,-0.7186]
def forvel():
    i=0
    j=0
    while i < 7:
```

```

    Ve = (x1[i]*x2[i])*(A0[j]+(A1[j]*(x1[i]-x2[i]))+(A2[j]*((x1[i]-
x2[i])**2)))+(A3[j]*((x1[i]-x2[i])**3)))
    print(Ve)
    i+=1
def forve2():
    i=0
    j=1
    while i < 7:
        Ve = (x1[i]*x2[i])*(A0[j]+(A1[j]*(x1[i]-x2[i]))+(A2[j]*((x1[i]-
x2[i])**2)))+(A3[j]*((x1[i]-x2[i])**3)))
        print(Ve)
        i+=1
def forve3():
    i=0
    j=2
    while i < 7:
        Ve = (x1[i]*x2[i])*(A0[j]+(A1[j]*(x1[i]-x2[i]))+(A2[j]*((x1[i]-
x2[i])**2)))+(A3[j]*((x1[i]-x2[i])**3)))
        print(Ve)
        i+=1
def forve4():
    i=0
    j=3
    while i < 7:
        Ve = (x1[i]*x2[i])*(A0[j]+(A1[j]*(x1[i]-x2[i]))+(A2[j]*((x1[i]-
x2[i])**2)))+(A3[j]*((x1[i]-x2[i])**3)))
        print(Ve)
        i+=1
def forve5():
    i=0
    j=4
    while i < 7:
        Ve = (x1[i]*x2[i])*(A0[j]+(A1[j]*(x1[i]-x2[i]))+(A2[j]*((x1[i]-
x2[i])**2)))+(A3[j]*((x1[i]-x2[i])**3)))
        print(Ve)
        i+=1
print("-----Ve at 25*C-----")
forve1()
print("\n\n-----Ve at 40*C-----")
forve2()
print("\n\n-----Ve at 50*C-----")
forve3()
print("\n\n-----Ve at 70*C-----")

```

```
forve4()
print("\n\n-----Ve at 80*C-----")
forve5()
```

```
#ve at 25*C
```

```
Ve_25 = [-0.10935500679915254,
-0.2000980443065921,
-0.31315409921600523,
-0.4399398779688015,
-0.635914008073433,
-0.44191437004830797,
-0.0
```

```
]

```

```
#ve at 40*C
```

```
Ve_40 = [-0.11216065283083632,
-0.19990423295647594,
-0.30748592059377333,
-0.4276856540204842,
-0.6190293820793982,
-0.436111798113282,
-0.0]
```

```
#ve at 50*C
```

```
Ve_50 = [-0.1158946634162542,
-0.20227954762358294,
-0.30667624329261206,
-0.42283526045322467,
-0.6117620013451086,
-0.4335622794907192,
-0.0
```

```
]

```

```
#ve at 70*C
```

```
Ve_70 = [-0.12110761711812873,
-0.20606681874392285,
-0.30678263014121915,
-0.41825250709110273,
-0.6051172280788767,
-0.4320181601160727,
-0.0]
```

```
#ve at 80*C
```

```
Ve_80 = [-0.12451665561279361,
-0.2101389858344268,
-0.3103006122701247,
-0.4195213502626378,
```

```

-0.5964903917254837,
-0.42774250077305437,
-0.0]
D = -5.35162*10**-7
E = -4.51417*10**-4
F = 1.19451
M1 = 61.08
M2 = 18.015
def forv1():
    i=0
    while i<5:
        v1 = M1/((D*(T[i]**2))+(E*T[i])+F)
        print(v1)
        i+=1
def forv2():
    i=0
    while i<5:
        v1 = M2/((D*(T[i]**2))+(E*T[i])+F)
        print(v1)
        i+=1
#for v1 at different temp
print("v1 at different temp")
forv1()
print("\n\n v2 at fifferent temp")
forv2()

V1 =
[60.335005097087546,61.03915157924624,61.526075682475636,62.54416502627282,63.07
6406157819356]
V2 =
[17.795270412967128,18.002952123446644,18.14656603503272,18.44684238618705,18.60
3822150181987]
def forV1():
    i=0
    j=0
    while i<7:
        V = Ve_25[i]+(x1[i]*V1[j]+x2[i]*V2[j])
        print(V)
        i+=1
def forV2():
    i=0
    j=1
    while i<7:

```

```

        V = Ve_40[i]+(x1[i]*V1[j]+x2[i]*V2[j])
        print(V)
        i+=1
def forV3():
    i=0
    j=2
    while i<7:
        V = Ve_50[i]+(x1[i]*V1[j]+x2[i]*V2[j])
        print(V)
        i+=1
def forV4():
    i=0
    j=3
    while i<7:
        V = Ve_70[i]+(x1[i]*V1[j]+x2[i]*V2[j])
        print(V)
        i+=1
def forV5():
    i=0
    j=4
    while i<7:
        V = Ve_80[i]+(x1[i]*V1[j]+x2[i]*V2[j])
        print(V)
        i+=1
print("V at different ratio ")
forV1()
print("\n\nV at different ratio ")
forV2()
print("\n\nV at different ratio ")
forV3()
print("\n\nV at different ratio ")
forV4()
print("\n\nV at different ratio ")
forV5()

```

```

V1 = [20.607192858030782,
22.36891840743357,
24.47215891268786,
27.044354118466682,
34.50074948492087,
48.25262304114861,
60.335005097087546]
V2 = [20.84616202047087,

```

```

22.63250647083856,
24.767086882346003,
27.37736689544841,
34.927700505267126,
48.826720704188126,
61.03915157924624]
V3 = [21.00961762849673,
22.812270829133276,
24.96792250299732,
27.604024930957067,
35.21853276403977,
49.22225177511127,
61.526075682475636]
V4 = [21.35397449065066,
23.189311820354607,
25.386042036897255,
28.072376052193427,
35.818071540070115,
50.04546466802292,
62.54416502627282,
]
V5 = [21.533315065909605,
23.384330692285936,
25.60116600270492,
28.313558033595147,
36.13665405648334,
50.47929586730774,
63.076406157819356]

```

```

def fun1():
    i=0
    j=0
    while i < 7:
        d = (x1[i]*M1+x2[i]*M2)/V1[i]
        print(d)
        i+=1
def fun2():
    i=0
    j=1
    while i < 7:
        d = (x1[i]*M1+x2[i]*M2)/V2[i]
        print(d)
        i+=1

```

```
def fun3():
    i=0
    j=2
    while i < 7:
        d = (x1[i]*M1+x2[i]*M2)/V3[i]
        print(d)
        i+=1
def fun4():
    i=0
    j=3
    while i < 7:
        d = (x1[i]*M1+x2[i]*M2)/V4[i]
        print(d)
        i+=1
def fun5():
    i=0
    j=4
    while i < 7:
        d = (x1[i]*M1+x2[i]*M2)/V5[i]
        print(d)
        i+=1
print("-----at 25 C-----")
fun1()
print("-----at 40 C-----")
fun2()
print("-----at 50 C-----")
fun3()
print("-----at 70 C-----")
fun4()
print("-----at 80 C-----")
fun5()
```

Appendix I: Hartono et al. Method-Unloaded CO₂

```

T = [293.15,303.15,313.15,323.15,333.15,343.15,353.15,363.15]
x1 = [0.1122,0.1643,0.2278,0.3067,0.4077,0.5412,0.7264,1]
x2 = [1-0.1122,1-0.1643,1-0.2278,1-0.3067,1-0.4077,1-0.5412,1-0.7264,0]
k1 = 683.5
k2 = 1.344*10**5
k3 = -1.089*10**4
k4 = 145.2
k5 = 567.9
import math

def func1():
    j = 0
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func2():
    j = 1
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func3():
    j = 2
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func4():
    j = 3
    i = 0
    while i < 8:

```

```

    density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
    print(density)
    i+=1
def func5():
    j = 4
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func6():
    j = 5
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func7():
    j = 6
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
def func8():
    j = 7
    i = 0
    while i < 8:
        density =
(k1+((k2*x2[j])/T[i]))*math.exp((k3/T[i]**2)+((k4*x1[j])/T[i])+(k5*(x1[j]/T[i])**2))
        print(density)
        i+=1
print("at x1 = 0.1122-----")
func1()
print("at x1 = 0.1643-----")
func2()
print("at x1 = 0.02278-----")
func3()
print("at x1 = 0.3067-----")

```

```
func4()
print("at x1 = 0.4077-----")
func5()
print("at x1 = 0.5412-----")
func6()
print("at x1 = 0.7264-----")
func7()
print("at x1 = 1-----")
func8()
```

Appendix J: Hartono et al. Method-Loaded CO₂

```

import math
T = [293.15,303.15,313.15,323.15,333.15,343.15,353.15,363.15]
#x1 = [0.1122,0.1643,0.2278,0.3067,0.4077,0.5412,0.7264,1]
#x2 = [1-0.1122,1-0.1643,1-0.2278,1-0.3067,1-0.4077,1-0.5412,1-0.7264,0]

x2_2 = [1-0.1643-0,1-0.1122-0.0105,1-0.1122-0.0193,1-0.1122-0.0355,1-0.1122-0.0476,1-
0.1122-0.0547]
#at w1 = 0.3
x1_1 = 0.1122
x2_1 = [1-0.1122-0,1-0.1122-0.0105,1-0.1122-0.0193,1-0.1122-0.0355,1-0.1122-0.0476,1-
0.1122-0.0547]
x3_1 = [0,0.0105,0.0193,0.0355,0.0476,0.0574]
a1_1 = 0.6802
a2_1 = 0.001951
a3_1 = -2.97*10**-6
a4_1 = 2.346
#at w1 = 0.4
x1_2 = 0.1643
x2_2 = [1-0.1643-0,1-0.1643-0.0170,1-0.1643-0.0341,1-0.1643-0.0507,1-0.1647-0.0669,1-
0.1647-0.0826]
x3_2 = [0,0.0170,0.0341,0.0507,0.0669,0.0826]
a1_2 = 0.7731
a2_2 = 0.001354
a3_2 = -2.015*10**-6
a4_2 = 2.164
#at w1 = 0.5
x1_3 = 0.2278
x2_3 = [1-0.2278-0,1-0.2278-0.0205,1-0.2278-0.0406,1-0.2278-0.0620,1-0.2278-0.0825,1-
0.2278-0.1013]
x3_3 = [0,0.0205,0.0406,0.0620,0.0825,0.1013]
a1_3 = 0.7506
a2_3 = 0.001494
a3_3 = -2.237*10**-6
a4_3 = 2.015

k1 = 683.5
k2 = 1.344*10**5
k3 = -1.089*10**4
k4 = 145.2

```

k5 = 567.9

```
# density at w1 = 0.3-----
def func1():
    i=0
    j=0
    while i < 7:
        density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[0]))*(k1+((k2*x2_1[0])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
        print(density)
        i+=1
def func2():
    i=0
    j=5
    while i < 7:
        density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[1]))*(k1+((k2*x2_1[1])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
        print(density)
        i+=1
def func3():
    i=0
    j=5
    while i < 7:
        density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[2]))*(k1+((k2*x2_1[2])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
        print(density)
        i+=1
def func4():
    i=0
    j=5
    while i < 7:
        density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[3]))*(k1+((k2*x2_1[3])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
        print(density)
        i+=1
def func5():
    i=0
    j=5
    while i < 7:
```

```

    density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[4]))*(k1+((k2*x2_1[4])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
    print(density)
    i+=1
def func6():
    i=0
    j=5
    while i < 7:
        density =
(a1_1+(a2_1*T[i])+(a3_1*T[i]**2)+(a4_1*x3_1[5]))*(k1+((k2*x2_1[5])/T[i]))*math.exp((k
3/T[i]**2)+((k4*x1_1)/T[i])+(k5*(x1_1/T[i])**2))
        print(density)
        i+=1
#density at w1 = 0.4-----
def func2_1():
    i=0
    j=0
    while i < 7:
        density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
        print(density)
        i+=1
def func2_2():
    i=0
    j=1
    while i < 7:
        density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
        print(density)
        i+=1
def func2_3():
    i=0
    j=2
    while i < 7:
        density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
        print(density)
        i+=1
def func2_4():

```

```

i=0
j=3
while i < 7:
    density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
    print(density)
    i+=1
def func2_5():
    i=0
    j=4
    while i < 7:
        density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
        print(density)
        i+=1
def func2_6():
    i=0
    j=5
    while i < 7:
        density =
(a1_2+(a2_2*T[i])+(a3_2*T[i]**2)+(a4_2*x3_2[j]))*(k1+((k2*x2_2[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_2)/T[i])+(k5*(x1_2/T[i])**2))
        print(density)
        i+=1

#density at w1 = 0.5-----
def func3_1():
    i=0
    j=0
    while i < 7:
        density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
        print(density)
        i+=1
def func3_2():
    i=0
    j=1
    while i < 7:

```

```

    density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
    print(density)
    i+=1
def func3_3():
    i=0
    j=2
    while i < 7:
        density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
        print(density)
        i+=1
def func3_4():
    i=0
    j=3
    while i < 7:
        density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
        print(density)
        i+=1
def func3_5():
    i=0
    j=4
    while i < 7:
        density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
        print(density)
        i+=1
def func3_6():
    i=0
    j=5
    while i < 7:
        density =
(a1_3+(a2_3*T[i])+(a3_3*T[i]**2)+(a4_3*x3_3[j]))*(k1+((k2*x2_3[j])/T[i]))*math.exp((k3
/T[i]**2)+((k4*x1_3)/T[i])+(k5*(x1_3/T[i])**2))
        print(density)
        i+=1

print("-----at w1 =0.3 and x3 = 0-----")

```

```

func1()
print("-----at w1 =0.3 and x3 = 0.0105-----")
func2()
print("-----at w1 =0.3 and x3 = 0.0193-----")
func3()
print("-----at w1 =0.3 and x3 = 0.0355-----")
func4()
print("-----at w1 =0.3 and x3 = 0.0476-----")
func5()
print("-----at w1 =0.3 and x3 = 0.0574-----")
func6()
print("\n\n density at w1 = 0.4")
print("-----at w1 =0.4 and x3 = 0-----")
func2_1()
print("-----at w1 =0.4 and x3 = 0.0170-----")
func2_2()
print("-----at w1 =0.4 and x3 = 0.0341-----")
func2_3()
print("-----at w1 =0.4 and x3 = 0.0507-----")
func2_4()
print("-----at w1 =0.4 and x3 = 0.0669-----")
func2_5()
print("-----at w1 =0.4 and x3 = 0.0826-----")
func2_6()
print("\n\n density at w1 = 0.5")
print("-----at w1 =0.5 and x3 = 0-----")
func3_1()
print("-----at w1 =0.5 and x3 = 0.0205-----")
func3_2()
print("-----at w1 =0.5 and x3 = 0.0406-----")
func3_3()
print("-----at w1 =0.5 and x3 = 0.0620-----")
func3_4()
print("-----at w1 =0.5 and x3 = 0.0825-----")
func3_5()
print("-----at w1 =0.5 and x3 = 0.1013-----")
func3_6()

```