



CO₂ SOLUBILITY MEASUREMENTS AND MODELLING IN AMINE-NMP SOLVENT BLENDS

By

Rebecca-Lynn Dijkman

BSc. Eng. (Chemical Engineering)

University of KwaZulu-Natal

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Supervisor: Prof. Paramespri Naidoo

Co-supervisors: Dr. Wayne Michael Nelson & Dr. Khalid Osman

PREFACE

The investigation or study presented in this dissertation entitled “CO₂ SOLUBILITY MEASUREMENTS AND MODELLING IN AMINE-NMP SOLVENT BLENDS” was undertaken in the Thermodynamics Research Unit at the University of KwaZulu-Natal in the School of Engineering, Howard College Campus, Durban, South Africa.

This study was performed under the supervision of Prof. Paramespri Naidoo, Dr. Wayne Michael Nelson & Dr. Khalid Osman. This dissertation has been submitted as the full requirement for the award of the degree of Master of Science in Chemical Engineering. The study presented in this dissertation is my original work unless stated otherwise. This dissertation has not previously been submitted for a degree or examination at any other tertiary institute or university.

As the candidate’s supervisor, I, Prof. Paramespri Naidoo, agree to the submission of this dissertation.

	11 July 2022
Prof. Paramespri Naidoo	Date

As the candidate’s co-supervisor, I, Dr. Wayne Michael Nelson, agree to the submission of this dissertation.

	11 July 2022
Dr. Wayne Michael Nelson	Date

As the candidate’s co-supervisor, I, Dr. Khalid Osman, agree to the submission of this dissertation.

	11 July 2022
Dr. Khalid Osman	Date

DECLARATION- PLAGIARISM

I, Rebecca-Lynn Dijkman, student number 213527621, declare that

1. The research reported in this dissertation, except where otherwise indicated, is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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5. This dissertation does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the dissertation and in the References sections.

Signed:

Rebecca-Lynn Dijkman

Date

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ABSTRACT

In this study, solvent blends of monoethanolamine (MEA) or 2-(2-aminoethoxy)ethanol (DGA) with N-methyl-2-pyrrolidone (NMP) or water (H₂O) were selected for investigations of carbon dioxide (CO₂) solubility due to the high CO₂ absorption capacities of the individual solvents. A static synthetic apparatus, consisting of a stirred equilibrium vessel and a gas reservoir, each submerged in their own temperature-controlled environment, was used to measure the CO₂ solubility for the systems and conditions stated above. Isothermal solubility measurements were performed at 40 °C over a pressure range of 0.1 – 1.5 MPa for the systems of CO₂ in various solvent blends. These included 20% MEA–80% NMP, 30% MEA–70% NMP, 51% DGA–49% H₂O, 40% DGA–60% H₂O, 30% DGA–70% H₂O, 51% DGA–49% NMP, 40% DGA–60% NMP and 30% DGA–70% NMP (by mass). The recorded temperature-pressure-overall composition (T-P-z) data were converted to T-P-mole fraction (T-P-x) data. Results were displayed on pressure vs. CO₂ loading ($P-\alpha_{CO_2}$) graphs and compared to literature data. Further comparisons were made between the various solvent blends.

Thermodynamic modelling of the experimental data for the DGA systems was performed using MATLAB[®]. Due to a solvent blend of a water-lean amine and a physical solvent, two models were fitted to the experimental data by regression of the model parameters, and the results combined and displayed on $P-\alpha_{CO_2}$ graphs with the respective experimental data. The Posey-Tapperson-Rochelle model was used for DGA, and the Peng-Robinson equation of state (PR-EOS) with modified van der Waals-Berthelot mixing rules was used for NMP in water-lean cases. Only the Posey-Tapperson-Rochelle model was used for amine-water systems.

The results indicated that the water-lean blends, MEA-NMP and DGA-NMP, have a higher CO₂ loading at the same pressure when compared to the corresponding MEA-H₂O and DGA-H₂O blends. An increase from 30% DGA–70% H₂O to 40% DGA–60% H₂O (by mass) resulted in a viscosity increase of 0.65 Pa.s at 40 °C and an increase in CO₂ loading of 0.079 mol_{CO₂}/mol_{amine} at 0.63 MPa and 40 °C. Comparing the 30% MEA–70% NMP and 30% DGA–70% NMP (by mass) blends, it was observed that the DGA blend had an increase in CO₂ loading of 0.12 mol_{CO₂}/mol_{amine} at 0.24 MPa and 40 °C. Thermodynamic modelling for the CO₂–51DGA–49H₂O system gave a root mean square error of 3.75%, an absolute average deviation (AAD) of 98.24 and an average absolute relative deviation (AARD) of 22.69%, while modelling for the CO₂–51 wt% DGA–49 wt% NMP system gave a root mean square error of 0.61%, an AAD of 13.13 and an AARD of 2.94%. Based on the calculated error

and AARD, regression for the Posey-Tapperson-Rochelle and PR-EOS model parameters gave the closest results to the CO₂-30 wt% DGA-70 wt% NMP measured data.

From this work, it was concluded that in terms of the viscosity and CO₂ loading at 40 °C, the DGA-NMP blends show promise compared to the DGA-H₂O and MEA-NMP blends. The 40 wt% DGA-60 wt% NMP solvent blend was the best-performing DGA-NMP blend. Further experiments to determine the changes in viscosity and CO₂ loading of regenerated solvents for a range of DGA-NMP blends are recommended, and further modelling analyses for data prediction are recommended for continuation of this work.

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NOMENCLATURE

English letters

Symbol	Description	Units
A	PR-EOS parameter	-
a	Posey overall correction factor	-
a(T)	Attractive parameter for PR-EOS	-
B	PR-EOS parameter	-
b	Posey temperature correction factor	-
b(T)	Repulsive parameter for PR-EOS	-
C	PR-EOS parameter	-
c	Posey amine concentration factor	-
D	PR-EOS parameter	-
d	Posey amine concentration factor	-
E	PR-EOS parameter	-
K	Equilibrium constant	-
k	Mixing rule binary interaction parameter	-
l	Mixing rule binary interaction parameter	-
L_T	Gas loading	$\text{mol}_{\text{gas}}/\text{mol}_{\text{solvent}}$
m	Mixing rule binary interaction parameter	-
n	Number of moles	mol
P	Pressure	MPa
P_{CO_2}	Partial pressure of CO_2	MPa
R	Universal gas constant	$8.3144621 \text{ cm}^3 \cdot \text{MPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
T	Temperature	K or $^{\circ}\text{C}$
u	Combined standard uncertainty	-
U	Combined expanded uncertainty	-
v	Molar volume	(cm^3) per mol
V	Volume	cm^3
vol%	Composition in terms of percentage volume	-
w	Mass fraction	-
wt%	Composition in terms of mass percent	-
x	Mole fraction	-
X	Fraction of CO_2 in vapour phase	-
Z	Compressibility factor	-

Greek letters

Symbol	Description	Units
α	Coefficient of thermal expansion	-
$\alpha(T)$	Temperature-dependent constant for PR-EOS	-
α_{CO_2}	CO ₂ loading	mol _{CO₂} /mol _{amine}
∂V	Difference between measured and calculated volume	cm ³
κ	Parameter for PR-EOS	-
μ	Viscosity	cP or Pa.s
τ	Mixing rule binary interaction parameter	-
ω	Acentric factor	-

Subscripts

-	Negative ion charge
+	Positive ion charge
1,2,3	Component identification
cr	Critical
cal	Calibration
i,j	Species identification
L	Liquid phase
M	Molar
r	Residual
v	Vapour phase

Abbreviations

ACS	American Chemical Society
aq.	Aqueous
BV	Ball valve
CCS	Carbon capture and storage
CFBC	Circulating fluidised bed combustion
conc.	Concentration
CTL	Coal-to-liquid
DC	Direct current
DCL	Direct coal liquefaction
DDB	Dortmund Database
EC	Equilibrium cell
Elec-NRTL	Electrolyte NRTL
EOS	Equation of state
FBC	Fluidised bed combustion

FGD	Flue-gas desulphurisation
FTA	Fault tree analysis
GHG	Greenhouse gas
HAZOP	Hazard and operability
HSS	Heat stable salts
ICL	Indirect coal liquefaction
IGCC	Integrated gasification combined cycle
mol	Number of moles in solution
NV	Needle valve
P-CFBC	Pressurised circulating fluidised bed combustion
PFBC	Pressurised fluidised bed combustion
PR-EOS	Peng-Robinson equation of state
PTFE	Teflon, or polytetrafluoroethylene
PVC	Polyvinyl chloride
RK-EOS	Redlich-Kwong equation of state
SCR	Selective catalytic reaction
SS	Stainless steel
UPS	Uninterruptible Power Supply
VLE	Vapour-liquid equilibrium

Chemical names

[Apy][Tf ₂ N]	Allyl-pyridinium bis(trifluoromethylsulfonyl)imide
[bmin][Ac]	1-butyl-3-methyl-imidazolium acetate
[bmin][PF ₆]	1-butyl-3-methyl-imidazolium hexafluorophosphate
[Bpy][BF ₄]	1-butylpyridinium tetrafluoroborate
[P ₆₆₆₁₄]	Trihexyl(tetradecyl)-phosphonium imidazole
[Tf ₂ N]	(Trifluoromethylsulfonyl)imide-based IL
AMP	2-amino-2-methyl-1-propanol
CO ₃ ²⁻	Carbonate
COS	Carbonyl sulphide
DEA	Diethanolamine
DEG	Diethylene glycol
DGA	2-(2-aminoethoxy)ethanol or Diglycolamine®
DIPA	Di-isopropanolamine
DMMEA	Dimethyl-monoethanolamine
DMPEG	Polyethylene glycol dimethyl ether
DPEG	Dimethyl ether of polyethylene glycol

EDA	Ethylene diamine
EtOH	Ethanol
IL	Ionic liquid
MAPA	3-(methylamino)propylamine
MDA	1,8-p-menthanediamine
MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
MEG	Mono ethylene glycol
MEGMME	2-methoxyethanol
MeOH	Methanol
NFM	N-formylmorpholine
NMP	N-methyl-2-pyrrolidone
NO _x	Nitrogen oxides
PC	Propylene carbonate
PE	2-piperidineethanol
PEG200	Poly(ethylene glycol) 200
PZ	Piperazine
SO _x	Sulphur oxides
TEA	Triethanolamine

CHAPTER 1: INTRODUCTION

Coal is a primary source of fuel around the world, and some emissions from combustion or thermal decomposition of coal are carbon dioxide (CO₂), sulphur dioxide (SO₂), hydrogen sulphide (H₂S), nitrogen oxides (NO_x) and mercury. These gases have a detrimental effect on people and the environment, contributing to the effects of climate change (Le Quéré, *et al.*, 2021), acid rain, lung cancer, and cardiovascular disease (Wu, *et al.*, 2018). CO₂ emissions are the largest contributor to greenhouse gas (GHG) emissions, with many countries around the world committing to reduce their emissions *via* the guidelines set by the Kyoto Protocol in 1997 and the newer Paris Agreement in 2015 (Le Quéré, *et al.*, 2021).

The major industrial processes that contribute to CO₂ emissions are cement, iron and steel producers and fossil fuel power plants. Some challenges with the implementation of CO₂ removal in any of these processes are the high volume of flue gas produced, low CO₂ concentration, and trace components such as NO_x, SO₂ and particulate matter (Vega, *et al.*, 2018). Global CO₂ emissions were 34.9 GtCO₂ in 2021, which was an increase of 4.8% compared to 2020 (Liu, *et al.*, 2022). Global CO₂ emissions in 2020 were 34 GtCO₂ with a drop of 2.6 GtCO₂ from the previous year. This large reduction was an anomaly due to the COVID-19 pandemic, with an average reduction of 0.16 GtCO₂ per year since 2015 in the 64 countries that reduced their emissions. Since 2015, there was an average increase of 0.37 GtCO₂ per year in the 150 countries where emissions increased, resulting in a global net increase of 0.21 GtCO₂ per year. To reach the goals stated in the Paris Agreement, a reduction of 1 – 2 GtCO₂ per year is required (Le Quéré, *et al.*, 2021), therefore considerable work must still be done to further reduce CO₂ emissions.

There are three forms of clean coal technology to reduce the release of CO₂ and other harmful chemical by-products into the atmosphere: pre-combustion, in-combustion and post-combustion technologies. Some concerns surrounding these technologies are the economic viability, delivery timeframe, potential hidden costs due to social or environmental damage, and the viability and disposal cost of the compounds removed (Wu, *et al.*, 2018).

Pre-combustion technologies consist of coal gasification or liquefaction, where hazardous components such as sulphur and mercury can be removed prior to combustion. Coal gasification uses coal, water, and air/oxygen (O₂) at temperatures above 1000 °C to produce syngas (Wu, *et al.*, 2018), which contains mainly carbon monoxide (CO), hydrogen (H₂), CO₂, methane (CH₄) and water (H₂O) (Global CCS Institute, 2012). Coal liquefaction is used to convert coal to liquid fuels and petrochemicals.

There are two methods used for coal liquefaction: direct (DCL) and indirect (ICL) coal liquefaction. In-combustion technologies are made up of the optimisation of various aspects of existing coal combustion processes, and are used in a variety of industries. These processes include oxy-fuel combustion, fluidised bed combustion and supercritical combustion. Oxy-fuel combustion burns the fuel using pure O₂. Fluidised bed combustion suspends the solid fuel particles in a stream of gas or liquid. Supercritical combustion replaces the typical organic solvents with supercritical fluids such as CO₂ and water (Wu, *et al.*, 2018). Post-combustion technologies consist of treating the flue gas emissions from an oven, furnace, boiler or steam generator. Flue gas contains nitrogen (N₂), CO₂, water vapour, O₂, and small amounts of pollutants such as particulate matter, CO, NO_x, sulphur oxides (SO_x) and other sulphur compounds (Global CCS Institute, 2012). The particulate matter must first be removed before the pollutants can be removed. Technologies used to remove these pollutants include flue-gas desulphurisation (FGD) to remove sulphur compounds, selective catalytic reaction (SCR) to remove nitrogen compounds, and carbon capture and storage (CCS). CCS consists of capturing waste CO₂ and transporting it to a storage site (such as underground geological formations) where it will not be released into the atmosphere (Wu, *et al.*, 2018).

Post-combustion CO₂ capture technologies can be retrofitted to existing power plants and high-emission processes without changing the process itself, while in- and pre-combustion CO₂ capture technologies require a process redesign and construction to add the technology to the process. Therefore, post-combustion technologies are best suited to existing processes, while in- and pre-combustion technologies are best suited to new processes where they will be integrated into the plant design. Major contributors to CO₂ emissions are older existing processes, therefore urgent attention is being given to developing post-combustion capture technologies (Abdilahi, *et al.*, 2018). If countries are to meet the CO₂ emission goals set by the Paris Agreement, further improvements to the current CO₂ capture processes must be considered (Le Quéré, *et al.*, 2021). The two major challenges with post-combustion CO₂ capture are cost and scale. As of 2012, the increased cost of plant construction sometimes negated the savings achieved through advances in CO₂ capture technologies. A way to reduce costs in the future is the modification of current technologies, although newer methods developed have only been tested on a pilot-plant scale and have not been implemented in industry. Other challenges with post-combustion CO₂ capture are high water usage, impact on the environment and the feasibility of retrofitting existing plans to capture CO₂ (Global CCS Institute, 2012). However, the advantages outweigh the challenges, and post-combustion technologies are considered promising processes for CO₂ capture.

Post-combustion CO₂ capture is carried out using absorption (scrubbing), adsorption and gas membranes (Wu, *et al.*, 2018). Absorption uses a solvent to preferentially absorb one gas over others,

adsorption uses a solid to selectively adsorb gas molecules onto the surface of the material, and gas membranes allow certain particles or molecules to pass through the membrane, similar to the way a sieve works. The most common technology used for post-combustion CO₂ capture is scrubbing (absorption of a gas into a liquid solvent) using amine solvents (mainly monoethanolamine (MEA)) or a solvent containing sterically hindered amines (Blomen, *et al.*, 2009). Scrubbing is a mature technology that is widely used in nitrogen dioxide (NO₂) and SO₂ removal. It takes up less space than adsorbers and membranes, and, although chemical absorption processes require a large amount of energy, scrubbing has a lower energy requirement than adsorbers and membranes (Blomen, *et al.*, 2009). Additionally, CO₂ absorbers can easily be retrofitted to existing processes (Abdilahi, *et al.*, 2018), therefore scrubbing was the selected CO₂ capture process for this study, an example of which can be seen in Figure 1-1.

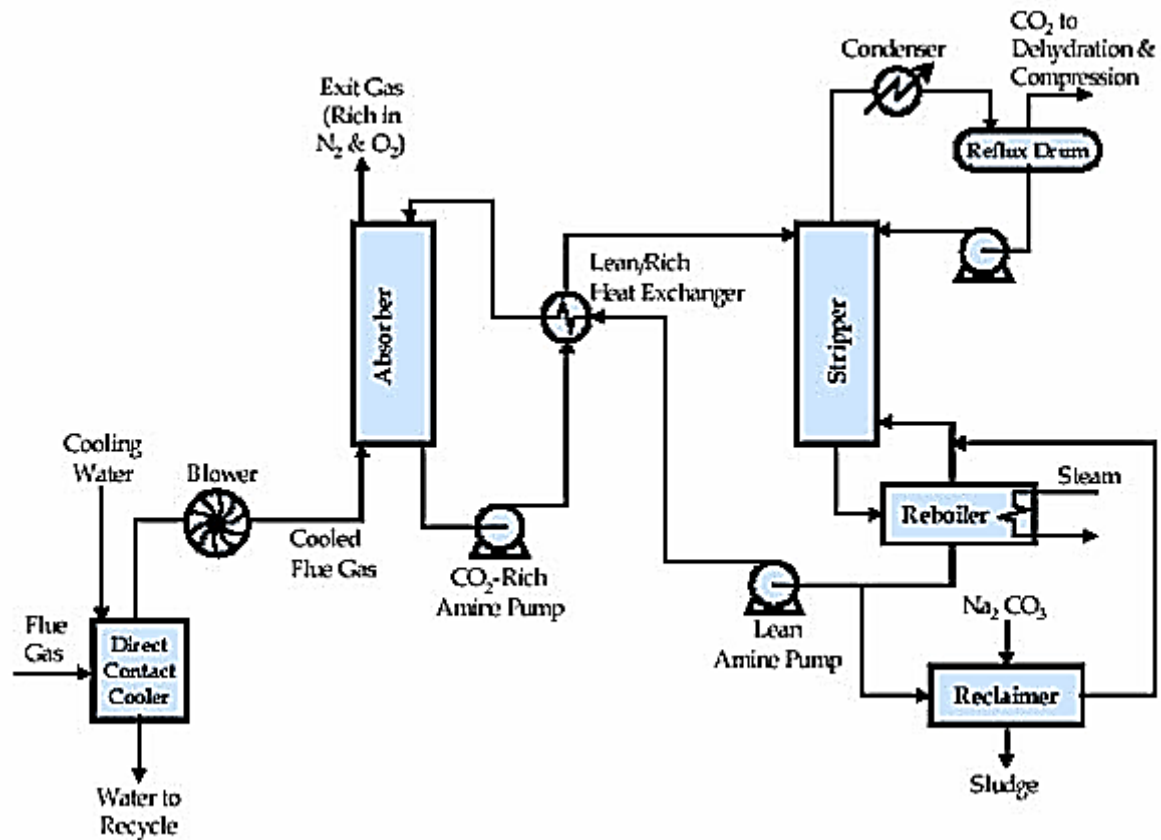


Figure 1-1: Scrubbing of CO₂ from flue gas with amines (Global CCS Institute, 2012)

In literature, various types of solvents are being tested for application for CO₂ capture. These are chemical solvents (such as MEA, 2-(2-aminoethoxy)ethanol (DGA) and N-methyldiethanolamine (MDEA)), physical solvents (such as N-methyl-2-pyrrolidone (NMP) and methanol (MeOH)), various ionic liquids (ILs), hybrid solvents such as potassium carbonates and amino acid salts, and solvent

blends of chemical and physical solvents or blends of chemical solvents and ILs. A chemical class of solvents widely used are alkanolamines, as they can absorb CO₂ at flue gas conditions (high volume, low CO₂ partial pressure gas at atmospheric pressure and high temperature) (Wang, *et al.*, 2017). These amine solvents react with CO₂ *via* a reversible reaction to form a carbonate salt. The solvent is then regenerated by heating in a stripping column. CO₂ capture using amine-based chemical solvents has been used in gas-treating plants since the 1950s, and is widely used in fossil-fuel power plants, cement factories, and iron and steel manufacturing (Vega, *et al.*, 2018). A drawback is the high energy requirements for solvent regeneration (due to dilution with water) and recirculation (due to high solvent viscosity). However, the technology for amines is already well established and much research is being carried out around solvent blends with amines (Wanderley, *et al.*, 2021).

Amine solvents are typically used to absorb CO₂ from streams containing gases such as O₂, N₂, hydrocarbons, and impurities such as mercaptans and H₂S. Primary amine solvents such as MEA are typically used, as they are effective even at low CO₂ partial pressures (Kohl & Nielsen, 1997). Chemical solvents have a high absorption rate due to absorption *via* chemical reactions. They are corrosive, therefore are diluted with water, which reduces the solvent absorption capacity and increases the solvent regeneration energy (Vega, *et al.*, 2018). Due to the corrosivity of MEA, alternative solvents with similar CO₂ absorption rates and capacity are being investigated. MDEA has been considered to be an alternative due to its lower corrosivity, but it has a slower absorption rate (Global CCS Institute, 2012). DGA is another amine that is effective at low CO₂ partial pressures and has a similar absorption rate to MEA without being as corrosive (Pacheco, *et al.*, 2000). Physical solvents such as NMP are also used for post-combustion CO₂ absorption, although the absorption capacity is lower than alkanolamines. Such solvents have a lower heat of regeneration since the pure solvent is used (Vega, *et al.*, 2018).

In recent years, solvent blends have become a promising area of interest in research regarding novel solvents for CO₂ absorption, where at least part of the water used to dilute the amine is replaced with another solvent. Solvent blends are easily tailored to meet specific viscosity, volatility, and regeneration energy requirements depending on the solvents used. Amine solvent blends were investigated in this study to attempt to minimise the drawbacks of amine solvents while also improving the overall solvent properties such as viscosity and CO₂ capacity. Therefore, amine-physical solvent blends were chosen for this study.

The consensus in literature is that DGA and 2-amino-2-methyl-1-propanol (AMP) are promising solvents to be used in solvent blends for CO₂ absorption (DDBST GmbH Online (2022), Dixit & Mollekopf (2014), Kohl & Nielsen (1997), Pacheco, *et al.* (2000), Wanderley, *et al.* (2021)). DGA has a much lower viscosity than AMP (43.851 cP at 20 °C for DGA compared to 185.311 cP at 20 °C for

AMP (Aspen, 2015)), which makes it an attractive amine (since lower viscosity results in lower pumping and regeneration energy requirements). DGA has a lower vapour pressure than MEA while maintaining the same reactivity and can be used in a more concentrated form with a lower solvent flow rate. Therefore, it is seen as a viable alternative to MEA (Pacheco, *et al.*, 2000). NMP is a widely used physical solvent for high-pressure absorption. NMP has a relatively low viscosity, and it has been used in amine solvent blends (Wanderley, *et al.*, 2021).

1.1. Aim and objectives

This study aims to investigate CO₂ solubility in new DGA-NMP solvent blends through measurements and modelling.

The following objectives were set:

1. Measurement of test systems at 40 °C (by mass):
 - a. CO₂-NMP
 - b. CO₂-30% MEA-70% H₂O
2. Measurement of new systems at 40 °C (by mass):
 - a. CO₂-20% MEA-80% NMP
 - b. CO₂-30% MEA-70% NMP
 - c. CO₂-51% DGA-49% H₂O
 - d. CO₂-51% DGA-49% NMP
 - e. CO₂-40% DGA-60% H₂O
 - f. CO₂-40% DGA-60% NMP
 - g. CO₂-30% DGA-70% H₂O
 - h. CO₂-30% DGA-70% NMP
3. Assess the regeneration and reuse of a selected DGA-NMP solvent blend
4. Regress measured data for new DGA-NMP systems in MATLAB[®] to obtain model parameters that can be used in possible future simulation work.

Mixtures of DGA and NMP at 40 °C for pressures between 0.1MPa and 1.5 MPa were considered for the following reasons:

1. There is a lack of information in literature regarding CO₂ solubility in DGA-NMP mixtures (DDBST GmbH Online (2022), Pacheco, *et al.* (2000), Wanderley, *et al.* (2021)).
2. Several literature sources report the solubility of solvent blends at 40 °C. This temperature was used so the solubility of CO₂ in DGA-NMP blends can be compared to literature.

3. DGA is commonly used with water in the composition range of 40 – 70% (Dixit & Mollekopf, 2014), and existing literature exists for DGA blends with a composition of 51%. A similar composition range was used so that comparisons can be made to literature and experimental data.
4. The performance of this solvent was also compared to other amines, specifically the MEA-H₂O and MEA-NMP blends, in order to draw comparisons between the blends with MEA and DGA.
5. Industry typically operates at atmospheric pressure, but the available literature data for CO₂ solubility in DGA-H₂O and DGA-NMP blends are above (Ebrahimejadhasanabadi, 2019) and below (Chen, *et al.*, 2011) atmospheric pressure. Therefore, pressures closer to atmospheric pressure were used in this study.

The use of NMP in solvent blends was considered to assess its performance against water-lean DGA blends. Data modelling was performed in MATLAB[®] using the Posey-Tapperson-Rochelle and Peng-Robinson Equation of State (PR-EOS) models. The data collected in the laboratory were used to predict solubility data for the new DGA-NMP water-lean solvent blends. The equipment used in the experiments was the same device reported by Ebrahimejadhasanabadi (2019).

The initial proposal of this research study was to modify the apparatus mentioned above for H₂S solubility measurements. The work by Dr Ebrahimejadhasanabadi proposed the development of an apparatus for measurements of systems including H₂S. However, due to delays in the acquisition and installation of the safety apparatus, the project aim and objectives were changed to those stated above. The possibility of using the new blends investigated in this study for acid gas (H₂S and CO₂) removal was also considered when selecting the diluent.

1.2. Overview

This dissertation is presented in six chapters with four appendices. The chapter contents are summarised below.

Chapter one provides a precise introduction to CO₂ capture technologies and the most common solvents used. The aim and objectives of this dissertation are stated, and an overview of the solvent blends tested is presented.

Chapter two reviews available literature covering CO₂ capture technologies, solvent selection criteria, old and new solvents used in CO₂ capture, comparison between the different types of solvents currently used, the regeneration of solvents and literature data from previous CO₂ solubility

measurements. Included in this chapter is a summary of the solvents selected for this study and the vapour-liquid equilibrium (VLE) equations required for the static synthetic equilibrium cell used in this study. The model selection and model equations for use in MATLAB[®] are then described.

Chapter three describes the equipment and materials used in this study. Calibration procedures, an in-depth look at the experimental procedures for the static synthetic equilibrium cell and the measurement procedures for physical properties are discussed. The uncertainty calculations carried out in this study are included at the end of this chapter.

Chapter four contains P - α_{CO_2} graphs of the processed experimental data for the two test systems, the MEA-H₂O and MEA-NMP systems, and the DGA-H₂O and DGA-NMP systems with experimental and modelled data. Included in this chapter are the VLE calculation methods, modelling methods, uncertainties, measured and collected physical properties, and the results from the model regression.

Chapters five and six contain the conclusions and recommendations respectively.

The Appendices contain supporting information for the main text. Appendix A contains various safety analyses including material safety data sheets (MSDS), a Fault Tree Analysis (FTA) and a Hazard and Operability (HAZOP) analysis. These analyses were performed with the intent to test H₂S solubility after adapting the current equipment. The safety analyses were conducted assuming the equipment modifications were in place, and a P&ID was developed. They were then adapted for use with any hazardous gas since, as mentioned in Section 1.1, the focus of this study was changed CO₂ absorption in new amine blends. These details are presented in Appendix A to inform the reader and for the purpose of future research endeavours. Appendix B contains more detailed uncertainty equations for the calculations detailed in Chapter 2 and some results from these calculations. Appendix C contains brief descriptions of what each MATLAB[®] file contains and how it is used. Appendix D contains the experimental and modelled VLE data in tables.

CHAPTER 2: LITERATURE REVIEW

The previous chapter introduced the concept of greenhouse gas emissions and CO₂ capture, and the methods and solvents used for CO₂ capture. With numerous options for processing methods, CO₂ capture techniques and solvents have received and continue to receive particular attention in this field of research. While the ultimate choices of capture method and solvents were stated in the previous chapter, this chapter contains a detailed literature review of CO₂ capture technologies, solvent selection criteria, common and new solvents used in CO₂ capture, a comparison between these different types of solvents and the regeneration capacity of solvents; all of which led to the focus of this study. Included in this chapter is a summary of the solvents selected for this study, VLE equations required for the static synthetic equilibrium cell used in this study, and model selection and equations used for data regression.

2.1. CO₂ capture technologies

Coal is widely used as a source of heat and energy. The burning (or combustion) of coal results in flue gas emissions containing species such as CO₂, SO₂, H₂S and NO_x, which are all damaging to people and the environment (Wu, *et al.*, 2018). A high volume of low-concentration CO₂ gas must be treated since CO₂ only makes up between 4 vol% and 15 vol% of the flue gas (Blomen, *et al.*, 2009). Pre-combustion, in-combustion and post-combustion technologies are used to remove these emissions to acceptable levels (Wu, *et al.*, 2018).

2.1.1. Pre-combustion technologies

Pre-combustion technologies consist of coal gasification or liquefaction, where hazardous components such as sulphur and mercury can be removed prior to combustion. Coal gasification is used on an industrial scale to produce syngas using coal, air and air/oxygen heated to above 1000 °C. During the coal gasification process, sulphur and mercury in the coal are released as H₂S and carbonyl sulphide (COS), and elemental mercury respectively, and must be removed from the flue gas. The syngas is then used for electricity production in an integrated gasification combined cycle (IGCC) power plant, or is used to produce methanol, gasoline and diesel (Wu, *et al.*, 2018). CO₂ is a by-product of coal gasification and must be removed from the gas before it is processed further (Koytsoumpa, *et al.*, 2018). Sulphur species such as H₂S are a major problem as it causes catalyst poisoning and affects downstream processes. Sulphur species removal is carried out using low-temperature desulphurisation

or absorption. Absorption is usually carried out at temperatures around 40 – 50 °C using organic or inorganic solvents and then heated before being sent to the gas turbines. These extra heating and cooling steps have led to research into alternatives, such as using adsorbents such as barium and calcium at temperatures above 600 °C (Wu, *et al.*, 2018).

Coal liquefaction is used to convert coal into liquid fuels and other petrochemicals. This is referred to as coal-to-liquid fuels (CTL). Direct coal liquefaction (DCL) converts the coal directly to liquid hydrocarbons using solvents or catalysts, and high pressure and temperature (Wu, *et al.*, 2018). Indirect coal liquefaction (ICL) consists of coal gasification to syngas, followed by conversion of the syngas into liquid hydrocarbons using processes such as the Fischer-Tropsch process (Koytsoumpa, *et al.*, 2018). Liquid hydrocarbons typically have a higher hydrogen:carbon ratio than coal, therefore DCL and ICL products have to undergo hydrogenation or carbon-rejection processes (Wu, *et al.*, 2018).

2.1.2. In-combustion technologies

In-combustion technologies involve the optimisation of various aspects of existing coal combustion processes. Modifications to the conventional coal combustion process are as follows (Wu, *et al.*, 2018, Koytsoumpa *et al.*, 2018):

- Oxy-fuel combustion burns the fuel using pure oxygen. The pure oxygen results in an increased flame temperature, therefore it is usually mixed with recycled flue gas or used in staged combustion. Nitrous oxide emissions are reduced since the nitrogen found in air is not present, and CO₂ is easier to remove as a result of the flue gas containing mainly water and CO₂. Other advantages include less heat lost in the flue gas and most gases in the flue gas can be condensed as a means of removal. In contrast, up to 15% of the energy produced by the coal-fired plant can be required to separate oxygen from air. Therefore, plants using oxy-fuel combustion cost more than those using traditional air-fired combustion.
- Fluidised bed combustion uses solid particles suspended in a flowing stream of gas or liquid, resulting in a fluid-like medium. This allows for combustion at lower temperatures and results in much lower SO₂ and NO_x emissions. Pollutants such as SO₂ and CO₂ are removed using limestone and adsorption respectively. The main types of fluidised bed combustion are atmospheric pressure (FBC), circulating (CFBC), pressurised (PFBC), and pressurised circulating (P-CFBC) fluidised bed combustion.
- Supercritical combustion uses supercritical fluids in place of organic solvents. Supercritical fluids have the properties of both gaseous and liquid phases. An advantage is that slightly less

fuel is used, thereby reducing GHG emissions. CO₂ and water are common supercritical fluids and are typically used for decaffeination and power generation respectively.

2.1.3. Post-combustion technologies

Post-combustion technologies consist of treating the flue gas emissions from an oven, furnace, boiler or steam generator (Wu, *et al.*, 2018). Flue gas composition differs depending on the type of fuel burnt, but it is typically made up of nitrogen (N₂), CO₂, water vapour and oxygen (O₂). Flue gas also has small amounts of pollutants such as particulate matter, CO, NO_x, SO_x and other sulphur compounds (Global CCS Institute, 2012). The particulate matter is removed *via* electrostatic precipitators or fabric filters before the pollutants are removed using a series of scrubbers and chemical processes. Technologies used to remove these pollutants include FGD to remove sulphur compounds, SCR to remove nitrogen compounds and CCS (Wu, *et al.*, 2018).

FGD is made up of several process sections to remove acid gases containing sulphur (such as H₂S, COS and carbon sulphide (CS₂)), and is typically carried out using wet scrubbing or dry injection. Wet scrubbing uses a slurry of alkaline sorbents to scrub acid gases after the gas has been passed through a fly ash removal device. Dry injection sprays alkaline sorbents into the absorption tower to absorb acid gases before the gas is passed through a particulate matter control device. SCR converts NO_x into N₂ and H₂O with the aid of a catalyst and a gaseous reductant such as anhydrous ammonia (NH₃). CCS is a term used for any process that captures CO₂ and includes the transportation of CO₂ to a storage site where it will not be released into the atmosphere, through underground storage in geological formations. This long-term storage is a relatively new concept in an effort to reduce the fossil fuel emissions that are produced by sources such as coal-fired power plants (Wu, *et al.*, 2018).

After removing most of the pollutants to prevent solvent degeneration, CO₂ capture is carried out at atmospheric pressure using a variety of chemical and physical separation processes, such as absorption, membranes, adsorption and cryogenic processes. Absorption is the most commonly used process in industry (Koytsoumpa, *et al.*, 2018). Although absorption is widely used, operational difficulties include solvent selection due to the low (atmospheric) pressure of the flue gas, solvent degradation and corrosion due to the presence of O₂, sulphur oxides and nitrogen oxides, and foaming, plugging and scaling of the equipment due to particulate matter (Global CCS Institute, 2012). Post-combustion technologies are best suited to existing processes, while in- and pre-combustion technologies are best suited to new processes where they will be integrated into the plant design. Post-combustion CO₂ capture is carried out using absorption (scrubbing), adsorption and gas membranes (Wu, *et al.*, 2018).

2.1.4. Absorption

Absorption uses a solvent to preferentially absorb one gas over others (Blomen, *et al.*, 2009). Absorption is classified according to the interaction between the gas and absorbent. There are three types: physical solutions, reversible reactions and irreversible reactions. Physical solvents selectively absorb a component from a gas mixture but do not react with the gas. The equilibrium concentration of the absorbed gas is dependent on the partial pressure of the gas in the gas phase. Chemical solvents can cause reversible or irreversible reactions. A reversible reaction occurs when a component in the absorbent reacts with a component from the gas phase and forms a loosely bonded product. The solvent can then be regenerated and the released gas can be sent for treatment or containment. An irreversible reaction occurs when a component in the absorbent reacts with a component in the gas phase and forms a product. The solvent cannot be regenerated very easily and the product is typically used elsewhere or disposed of (Kohl & Nielsen, 1997).

Chemical absorption is better suited to industrial processes that emit high volumes of flue gas with a low CO₂ concentration at atmospheric pressure, as it depends on the reactions between CO₂ and the components in the solvent. Physical absorption is better suited to processes that produce flue gases with a high CO₂ partial pressure at high flue gas pressures, as it depends on the solubility of CO₂ in the solution without any reactions taking place. For most processes that need to capture CO₂ from high-volume flue gas emissions, chemical absorption is better suited due to the low CO₂ concentration. Alkanolamines such as MEA are most commonly used (Vega, *et al.*, 2018).

In terms of solvent choice, the major drawback of using chemical absorption is its high-energy requirement. This comes mainly from the high energy requirements for solvent regeneration, resulting in a high reboiler duty. Three aspects of the absorber design are typically considered when looking at reducing the energy requirements: optimisation of operational parameters (reflux ratio, reboiler pressure etc.), modification of the process itself and development of better solvents (Wang, *et al.*, 2017).

A summary of a review performed by Le Moullec *et al.*, found in the work by Wang *et al.* (2017), stated that there are 20 process modifications that can be applied to the CO₂ scrubbing process. The factors that had the greatest effect on solvent regeneration energy were CO₂ loading in the CO₂-lean solvent, MEA concentration and reboiler pressure. Resistance to these modifications was due to the high energy requirement, which would increase the cost of the electricity produced. In turn, these modifications increased the cost and made the operability more complex (Wang, *et al.*, 2017). Therefore, it was seen that modifying the operational parameters does not seem feasible, as the small

reduction in the energy requirement is negated by the increase in capital cost and a more complex operation (Wang, *et al.*, 2017).

Improvements that can be applied to processes therefore usually focus on modifying or changing the solvent. Improvements to processes that use MEA can be categorised in three sections (Blomen, *et al.*, 2009):

- 1) Increasing MEA concentration: increasing the concentration of MEA in water results in an increase in capacity, which leads to a reduction in the solvent circulation rate and a decrease in operating costs. This also leads to a decrease in the heat requirement.
- 2) Introducing degradation and corrosion inhibitors: impurities in the flue gas cause solvent degradation. This leads to higher costs due to makeup solvent, waste disposal and higher energy demand. Degradation products often result in the solvent becoming corrosive, resulting in unplanned downtime due to repairs, loss of products and reduced equipment lifetime. Increasing the concentration of amines can cause a significant increase in corrosion, and inhibitors that prevent solvent degradation and corrosion can be added.
- 3) Replacing MEA with a new solvent: research thus far has been focused on solvents that have the following properties when compared to MEA: higher CO₂ capacity, lower regeneration energy, higher absorption and desorption rates, lower volatility, less degradation and lower corrosiveness.

In literature, the solvents that have been researched thus far are alternative alkanolamines, amino acid salts, sodium/potassium carbonate solutions (Na/K₂CO₃), NH₃ and blends of these solvents with piperazine (PZ) or ILs (Blomen, *et al.* (2009), Vega, *et al.* (2018), Wanderley, *et al.* (2021)). Alternative alkanolamines, or amines, such as MDEA and AMP seem to be gaining popularity (Blomen, *et al.*, 2009), as seen by the amount of data available in Tables 2-5 and 2-6 for solvent blends containing either of these solvents. Amino acid salts are solutions that are prepared via neutralisation of an amino acid using an organic or inorganic base solvent. Amino acids have the same functional group as an alkanolamine, therefore undergo a similar reaction in the presence of CO₂, but they do not deteriorate in the presence of O₂ (Songolzadeh, *et al.*, 2014). Potassium carbonate solutions are an example of an alkali salt of a weak acid. Compared to amines, these activated alkali salt solutions have a low cost, experience minimal solvent degradation, and can absorb CO₂ at high temperatures (Global CCS Institute, 2012).

NH₃ was used in a pilot plant process developed by Alstom, where it was chilled and used to absorb CO₂ from flue gas. It has been claimed that the process uses 50% of the energy required by the MEA

process (Blomen, *et al.*, 2009). PZ is a cyclic amine that is mixed with other solvents to speed up absorption and increase capacity. It can also be diluted with water and used for CO₂ absorption. PZ has a faster rate of absorption, greater CO₂ capacity, and much lower thermal and oxidative degradation compared to MEA (Xu & Rochelle, 2011). ILs are organic salts with an elevated boiling point and a low vapour pressure, and solvent regeneration requires comparatively less energy than alkanolamine processes (Vega, *et al.*, 2018). ILs are expensive and have high viscosities, therefore are typically mixed in small volumes with amines to reduce the typical disadvantages associated with amines (Ebrahimejadhasanabadi, 2019).

2.2. Solvent selection criteria

Several solvent characteristics are used to evaluate solvent performance for CO₂ absorption and economic feasibility (Vega, *et al.*, 2018, Mathias, *et al.*, 2013, Kohl & Nielsen, 1997, Songolzadeh, *et al.*, 2014, National Energy Technology Laboratory, 2018). These include:

- 1) CO₂ loading or absorption capacity: the amount of CO₂ that can be absorbed per mole of solvent. A high CO₂ capacity with a low heat of absorption is considered economically feasible. A high mass transfer rate and high reaction kinetics reduce the size of the equipment and increase capacity due to operation near equilibrium. The maximum CO₂ absorption capacity can be determined using the solubility of CO₂, which is presented as VLE curves for a specific temperature and range of pressures of CO₂ in the bulk gas.
- 2) Cyclic capacity: the difference in CO₂ loading between the rich solvent and the lean solvent. High rich solvent (used solvent) and low lean solvent (regenerated solvent) CO₂ loadings are considered favourable.
- 3) Chemical reactivity: the rate of CO₂ absorption from the bulk gas into the bulk liquid in terms of moles of CO₂ per second. A high mass transfer rate and fast reaction kinetics are considered economically feasible.
- 4) Degradation resistance: in the case of acid gas (CO₂ and H₂S) removal from flue gas, the presence of O₂, NO_x and SO₂ causes different solvents to degrade. Degradation can also be caused by elevated temperatures. The solvent degradation resistance for these cases is determined by looking at the amount of solvent lost under specific operating conditions. A low tendency for solvent degradation is considered economically favourable. This reduces the make-up solvent rate and allows for the operation of the regenerator at a higher temperature and pressure, which results in an increase in thermal efficiency.
- 5) Low viscosity: this reduces the energy required for pumping, and usually results in a faster mass transfer rate and a higher rate of heat transfer.

- 6) Low volatility: this reduces the solvent slip in the absorber, which results in a reduction in the capacity of the wash system.
- 7) Low environmental impact: as with all processes, the impact on the environment must be minimised. Solvents that produce toxic by-products and have losses due to high volatility must try to be avoided.
- 8) Low cost and readily available: solvents that can also absorb impurities and other harmful gases are preferred, as this can reduce or eliminate other steps and solvents.
- 9) Low tendency for fouling: this is related to the melting point of the solvent, which predicts whether it will precipitate out as a solid. Fouling can also be caused by the products of solvent degradation.
- 10) High chemical and thermal stability: this has an impact on the number of times a solvent can be regenerated. Higher stability means that fewer degradation products are formed and that the solvent will not readily vaporise.
- 11) Other factors such as exit gas content, selectivity for one acid gas over others, effect of water content on the feed, hydrocarbon absorption, cost and availability of the solvent, royalty cost, and thermal stability also influence solvent selection.

Some problems with amine solvents when used for post-combustion CO₂ capture include corrosion, solvent degradation, heat duty, and economy of the absorption and stripping columns due to a high heat of reaction. Alternative solvents aim to minimise or overcome these problems (Ume, *et al.*, 2011).

2.3. Solvents used in CO₂ capture

Some common solvents used for CO₂ capture are amine-based or contain amine functional groups. Since amine-based solvents are chemical solvents, they have a high absorption rate, leading to their popularity for low-pressure CO₂ absorption from flue gases (Mathias, *et al.*, 2013). Chemical solvents remove CO₂ via reaction with the gas. The CO₂ can then be released when the solvent is regenerated by heating (Global CCS Institute, 2012). Common chemical solvents used to remove CO₂ and H₂S from flue gases are aqueous solutions of alkanolamines. Two advantages of an aqueous alkanolamine solution are that the amines significantly improve the solubility of the acid gas in the aqueous phase, and the reactions of H₂S and CO₂ in the solvent result in a higher absorption rate. A disadvantage of using amines is that the reaction is highly exothermic, therefore large amounts of heat are required when regenerating the solvent (Austgen Jr, 1989). Further information about some of these amine solvents and other popular and promising solvents is contained in the following sections.

2.3.1. Conventional amine solvents

CO₂ absorption using amine-based chemical solvents has been used in gas-treating plants since the 1950s, where CO₂ absorbers are typically operated at 60 °C and atmospheric pressure. CO₂ capture processes that use amine solvents have therefore undergone extensive development over the years. Amines undergo a reversible reaction with CO₂ to form a carbonate salt. Since this reaction is reversible, the solvent can be regenerated *via* the release of CO₂ by heating the solution in a stripping column. Stripping columns used for solvent regeneration are typically operated at 120 °C with pressures varying between 0.18 and 0.3 MPa (Vega, *et al.*, 2018).

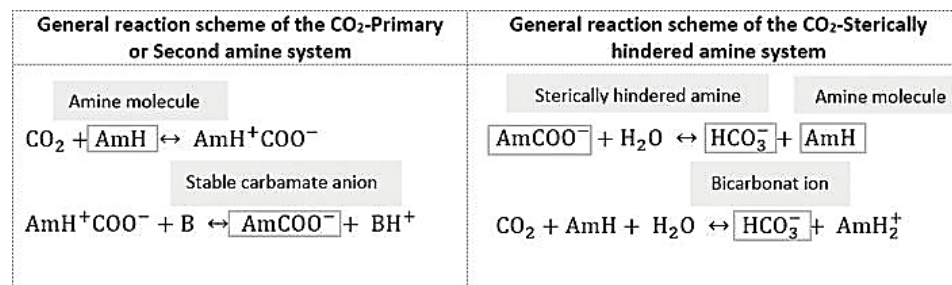
Alkanolamines (or amines) are derivatives of ammonia where one, two or three of the hydrogens are replaced by organic groups (Bauld, 2001). Alkanolamines are classified according to the number of substitutions on the central nitrogen atom. Amines with a single substituted atom are called primary amines, two substituted atoms are secondary amines, and three substituted atoms are tertiary amines (Global CCS Institute, 2012). Some examples of these different types of amines can be seen in Table 2-1, where the differences between the different types are easily identified. All these alkanolamines have at least one hydroxyl group and one amino group. The hydroxyl group reduces vapour pressure and increases the solubility of the amine in water, and the amino group provides the alkalinity that promotes the reactions with acid gases. These structural characteristics have an important role in the absorption capabilities of the various solvents used for acid gas removal (Vega, *et al.*, 2018), of which more detail can be found in Table 2-1.

Aqueous solutions of amine solvents remove acid gases (CO₂ and H₂S) by forming weak chemical bonds with the dissolved acid through acid-base reactions. These bonds are broken when heat is applied in the stripper to regenerate the solvent, which is then recycled back to the absorber (National Energy Technology Laboratory, 2018). CO₂ solubility in an amine solvent is typically expressed in terms of loading instead of mole fraction since the amine is diluted with water to improve viscosity (Wanderley, *et al.*, 2021). Solvent loading (α_{CO_2}) is the number of moles of absorbed CO₂ per mole of amine, so a higher loading reflects more moles of CO₂ absorbed. As can be seen in Table 2-1, diethanolamine (DEA) has the highest CO₂ loading, followed by MEA.

Table 2-1: Alkanolamines commonly used for acid gas absorption. Compiled from (Vega, *et al.*, 2018) and (Khakdaman, *et al.*, 2008)

Name and Classification	Monoethanolamine Primary amine	Diglycolamine ® or 2-(2-aminoethoxy) ethanol Primary amine	Diethanolamine Secondary amine	Di-isopropanolamine Secondary amine	Methyldiethanolamine Tertiary amine
Abbreviation	MEA	DGA	DEA	DIPA	MDEA
Structural Formulae	$\text{NH}_2\text{-CH}_2\text{-CH}_2\text{OH}$	$(\text{HO-C}_2\text{H}_4)\text{-O-(C}_2\text{H}_4\text{-NH}_2)$	$(\text{CH}_2\text{-CH}_2\text{OH})_2\text{NH}$	$(\text{CH}_3\text{-CHOHCH}_2)_2\text{NH}$	$\text{CH}_3\text{N(C}_2\text{H}_4\text{OH})_2$
3D Chemical Structure					
Industrial Processes	Natural gas and syngas purification	Syngas treatment	Natural gas treatment containing high levels of carbonyl sulphide (COS) and carbon sulphide (CS ₂)	Used in ADIP and Sulfinol for refinery gas treatment	URCASOL solvents and Claus plants (desulphurisation)
CO₂ loading (mol_{CO₂}/mol_{amine})	0.5	0.25 – 0.35	0.7 – 1	0.22 – 0.43	0.1 – 0.3
Selective absorption	None	None	H ₂ S under limited conditions	–	H ₂ S under most conditions
Aqueous solvent composition (wt%)	15 – 20	50 – 70	25 – 35	–	20 – 50

Key for 3D models: Grey – carbon, White – hydrogen, Red – oxygen, Blue – nitrogen. All images are from Vega *et al.* (2018)

Figure 2-1: General reaction scheme for CO₂-amine systems. Extracted from (Vega, *et al.*, 2018)

There are two differences between the CO₂ absorption performance for primary and secondary, and tertiary amines. The two main differences are the reaction rate and the reaction mechanism. Primary and secondary amines are very reactive and they form carbamates by reacting directly with the CO₂ via the Zwitterion mechanism (Vega, *et al.*, 2018), as seen in Figure 2-1. Although primary and secondary amines are very similar, secondary amines have a lower regeneration energy requirement (Global CCS Institute, 2012). Tertiary amines react comparatively slower; they form a bicarbonate ion and protonated amine by the hydration of CO₂ via base-catalysed hydration, and they show a low CO₂ absorption rate due to the indirect hydration reaction (Vega, *et al.*, 2018). Tertiary amines have an even lower regeneration energy requirement, do not as easily form degradation products, and have a lower corrosion rate, although the slow reaction rate is a serious drawback (Global CCS Institute, 2012).

Chemical solvents are seen to be a good option for CO₂ absorption on a small scale based on the reactions shown in Figure 2-1. The problems with chemical solvents at an industrial scale are (Vega, *et al.*, 2018):

- 1) A high energy requirement for solvent regeneration
- 2) Corrosion resistant materials and inhibitors are needed to prevent corrosion
- 3) The current CO₂ removal rate needs to be scaled up to meet emissions standards, and
- 4) Solvent degradation occurs when O₂, SO_x, hydrogen chloride, hydrogen fluoride, mercury and small particles are present

Traditionally, MEA has been used for CO₂ absorption and general acid gas removal due to it having the lowest relative cost compared to other alkanolamines, its fast reaction kinetics, and it works well at low pressures and CO₂ concentrations. MEA also has several disadvantages, leading to research into other possible amines and solvents. Secondary amines such as DEA have a lower heat of reaction than primary amines such as MEA, but they have the same problems as primary amines. Tertiary amines such as MDEA have slower reaction rates and therefore require a higher circulation rate, but they do have a lower heat of reaction, resulting in lower heat requirements. They also do not form degradation products as readily and have lower corrosion rates than primary and secondary amines (Global CCS Institute, 2012).

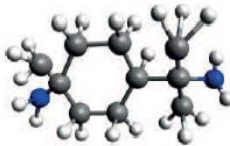
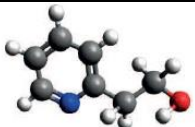
The most commonly used alkanolamines in the past several decades have been MEA and DEA, with DGA and MDEA also widely used. MEA, DEA and DGA react with H₂S and CO₂ in the aqueous phase, where H₂S reacts very quickly through a proton transfer mechanism. This results in only trace amounts of H₂S and a small fraction of CO₂ remaining in the gas. More recently, MDEA has been

favoured for the selective removal of H₂S from gases containing both H₂S and CO₂. This is due to MDEA reacting much more rapidly with H₂S than CO₂. H₂S reacts in the same way as before, through a proton transfer mechanism, while CO₂ has to react (slowly) with water before it can form bicarbonate. This in turn reduces the heat of reaction of MDEA when absorbing H₂S and CO₂ (Austgen Jr, 1989).

2.3.2. Sterically hindered amine solvents

Sterically hindered amines are formed by attaching an amino group to a tertiary carbon atom in a primary amine, or attaching to a secondary or tertiary carbon atom in a secondary amine, as shown in Table 2-2. Sterically hindered amines react directly with CO₂ to form carbamates with an intermediate to low stability due to a bulky substituent adjacent to the amino group (Global CCS Institute, 2012). This leads to a higher concentration of free-amine, which results in a lower regeneration energy requirement. The bulky substitute also slows down the overall reaction rate, and less stable carbamates can theoretically double the CO₂ capacity of the solvent. Based on the general reaction schemes shown in Figure 2-1, primary and secondary amines require two amine molecules for every one CO₂ molecule, while sterically hindered amines only require one amine molecule for every one CO₂ molecule. Therefore, theoretically, sterically hindered primary and secondary amines could have a higher CO₂ loading than conventional primary and secondary amines (Vega, *et al.*, 2018).

Table 2-2: Common sterically hindered amines. Reproduced from (Vega, *et al.*, 2018)

Name and Classification	Abbreviation	Structural Formulae	3D Chemical Structure
2-amino-2-methyl-1-propanol Sterically hindered primary amine	AMP	HO-CH ₂ -C-(CH ₃)(CH ₃)(NH ₂)	
1,8-p-menthane diamine Sterically hindered primary amine	MDA	CH ₃ NH ₂ -C ₆ H ₉ -C ₃ H ₆ NH ₂	
2-piperidineethanol Sterically hindered tertiary amine	PE	C ₂ H ₄ -NH-CH-(C ₂ H ₄ OH)-C ₂ H ₄	
Key for 3D models: Grey – carbon, White – hydrogen, Red – oxygen, Blue – nitrogen. All images are from Vega <i>et al.</i> (2018)			

2.3.3. Physical solvents

Absorption or stripping of acid gases can be carried out using physical solvents. Physical solvents are polar organic solvents used for economical bulk removal of CO₂ and H₂S, but they do not produce high purity gas (Global CCS Institute, 2012). Physical solvents are typically used when the acid gases have high partial pressures and low temperatures since they require a large driving force for mass transfer. An advantage of using physical solvents instead of chemical solvents is that the dissolved acid gases can be stripped from the solvent by reducing the partial pressure of the surrounding gas without needing to add large amounts of heat (Austgen Jr, 1989). Physical solvents are therefore best suited for use where there is a high CO₂ partial pressure, such as recovering CO₂ from IGCC (Global CCS Institute, 2012).

When screening for a physical solvent, one of the key parameters is the solubility of the gas to be absorbed. There are many suitable organic solvents when using this criterion, but there are additional criteria that need to be met for the physical solvent to be economically feasible. The physical solvent must have a high capacity for acid gases, low viscosity, low or moderate hygroscopicity (the tendency of a substance to absorb moisture from the surrounding atmosphere (Richardson, 2011)), low corrosivity, low reactivity with any components in the flue gas, low vapour pressure, and must be commercially available at a reasonably low cost (Kohl & Nielsen, 1997). The advantages, disadvantages, and absorption characteristics of physical solvents already used in industry can be seen in Table 2-3. A solvent commonly used in laboratories is NMP, which is associated with the PurisolTM process (Vega, *et al.*, 2018).

Table 2-3: Advantages, disadvantages and absorption characteristics of common physical solvents used in licensed processes. Compiled from (Vega, *et al.*, 2018), with species absorbed, selectivity and CO₂ solubility from (Burr & Lyddon, 2008)

Process	Selexol TM	Rectisol TM	Ipexol-2 TM	Fluor TM	Purisol TM	Sulfinol TM	Morphysorb TM
Chemical	Dimethyl ether of polyethylene glycol (DPEG)	Chilled MeOH	Refrigerated MeOH as part of Ifpex-2 TM	Propylene carbonate (PC)	NMP	A mixture of tetrahydrothiophene dioxide (Sulfolane) and DIPA or MDEA	N-formylmorpholine (NFM)
Licensors	UOP	Lurgi AG	Prosernat	Fluor Daniel, Inc.	Lurgi AG	Shell Oil Company	Krupp Uhde GmbH
Advantages	- Solvent regeneration without heating - Solvent is non-corrosive - Dry gas leaves the absorber	- Solvent does not foam	- High chemical and thermal stability - Solvent is non-corrosive	- High CO₂ solubility - Solvent regeneration without heating - Simple process operation - Solvent is non-corrosive	- Solvent does not foam - High chemical and thermal stability - Solvent is non-corrosive - Solvent has a low volatility	- High CO₂ capacity - Low solvent circulation rate - Effective over a wide range of acid gas partial pressures	- Solvent has a high acid gas loading capacity - Low energy requirement - Solvent is non-corrosive - Low capital and operating costs
Disadvantages	- High pressures are required for the best efficiency - Higher viscosity	- High refrigeration costs - High capital and operation costs	- High capital and operation costs - Amalgams form at low temperatures	- High solvent circulation rate - Solvent is expensive - Slow, irreversible reaction with CO₂ and H₂O above 90°C	- High cost due to compressor - High pressures are required for the best efficiency	- Solvent has foaming issues - Solvent is corrosive - Solvent regeneration requires heating	- New process, so there is not much experience with it
Species absorbed	H ₂ S, CO ₂ , mercaptans	H ₂ S, CO ₂ , COS	H ₂ S, CO ₂	CO ₂ , H ₂ S (low concentration)	H ₂ S, CO ₂	H ₂ S, CO ₂ , COS, mercaptans	H ₂ S, CO ₂ , COS, CS ₂ , mercaptans
Selective absorption	H ₂ S	H ₂ S	H ₂ S	CO ₂	H ₂ S	None	None
CO₂ solubility	0.485	0.425	-	0.455	0.477	-	Higher than Sulfinol TM

2.3.4. Ionic liquids

An alternative to amine-based solvents is a class of solvents called ionic liquids, or ILs, some of which can be seen in Table 2-4. These solvents are organic salts that have an elevated boiling point and low vapour pressure. ILs can selectively absorb CO₂, SO₂ and other acid gases and have relatively low energy requirements for solvent regeneration (Vega, *et al.*, 2018). This low regeneration energy is due to ILs absorbing CO₂ *via* physical absorption, and it is so low that a flash vessel could be used to separate CO₂ from the solvent (Ebrahimejadhasanabadi, 2019). Conventional ILs absorb CO₂ the same way as physical solvents and enhance solubility *via* Henry's Law-like behaviour. A major advantage is that they can be individually customised for a specific application, for example, flue gas treatment where there is a very low CO₂ concentration (Vega, *et al.*, 2018). Additionally, due to their low vapour pressures, the solvent loss to the flue gas can be assumed to be negligible (Ebrahimejadhasanabadi, 2019).

ILs have relatively high viscosities and become extremely viscous when CO₂ is absorbed, therefore are mixed with water to reduce the circulation energy. Amines can be mixed with ILs to decrease the viscosity of the IL without reducing the absorption capacity (Ebrahimejadhasanabadi, 2019). Another disadvantage is that ILs are expensive compared to common amine-based solvents. They are relatively new in industrial applications and the gaps in knowledge have to be bridged before they can be considered for large industrial applications (Vega, *et al.*, 2018). A literature search showed that ILs have gained popularity in the last 20 years, mainly due to their low volatility. Furthermore, pilot-scale results have been reported in 2021 by Wanderley, *et al.* (2021).

Table 2-4: Promising ILs for CO₂ absorption. Reproduced from (Vega, *et al.*, 2018)

Name	Abbreviation	Application	Viscosity (cP) (below 300 K)	CO ₂ loading (mol _{CO₂} /mol _{amine}) (above 1 MPa)
1-butylpyridinium tetrafluoroborate	[Bpy][BF ₄]	Post-combustion	150	<0.05 (ambient pressure)
Trihexyl(tetradecyl)-phosphonium imidazole	[P ₆₆₆₁₄]	Post-combustion	223 – 1077	0.3 – 0.91
1-butyl-3-methyl-imidazolium hexafluorophosphate	[bmin][PF ₆]	Post-combustion	–	0.75
(Trifluoromethylsulfonyl)imide-based IL	[Tf ₂ N]	Biogas/natural gas upgrading	–	0.66 – 0.84
1-butyl-3-methyl-imidazolium acetate	[bmin][Ac]	Biogas/natural gas upgrading	–	–
Allyl-pyridinium bis(trifluoromethylsulfonyl)imide	[Apy][Tf ₂ N]	Pre-combustion	17.7 – 28	–

Based on the CO₂ loading column in Table 2-4, the ILs containing the [BF₄], [PF₆] and [Tf₂N] anions can be observed to perform better than other anions, and this has been confirmed by Wanderley, *et al.* (2021). Generally, the anions in conventional ILs have a greater effect on absorption than the cations (Vega, *et al.*, 2018), therefore selecting the right anion is important. More information on ILs and their use in solvent blends for carbon capture can be found in the following articles and publications: Ebrahimejadhasanabadi (2019), Kumar, *et al.* (2014), Maginn (2007), Yokozeki, *et al.* (2008) and Zeng, *et al.* (2017).

2.3.5. New generation solvents

New-generation solvents proposed for CO₂ absorption focus on the reduction in energy usage, reduced make-up solvent, and improved CO₂ loading to ensure that chemical absorption is considered a cost-effective solution for industrial CCS. Most of the energy used for CCS in industry is consumed in the regeneration step. Water is typically added to amine solvents since it reduces the viscosity and corrosiveness of the solvent, although it also increases the energy consumption in the regeneration step (Vega, *et al.*, 2018). As a result, water-free solvents have become a major research area. Some water-free amine-diluent blends include MEA-NMP (Wanderley, *et al.*, 2018), DEA-PEG200 (poly(ethylene glycol) 200) (Li, *et al.*, 2014), MDEA-EtOH (ethanol) (Chen, *et al.*, 2015), and AMP-DEG (diethylene glycol) (Zheng, *et al.*, 2012), and many other water-free amine systems were referenced in Wanderley, *et al.* (2021).

Aminosilicones are another major research area as these solvents do not contain water and their hybrid nature has the potential to improve CO₂ capture (Lockwood, 2017). While the absorption capacity of aminosilicones is higher due to physisorption along with chemisorption, co-solvents are required to combat the possibility of solids forming and the increase in viscosity as more CO₂ is absorbed (Vega, *et al.*, 2018). Combinations of amines with superbase promoters, such as superbase ILs are also being investigated. These consist of blends of a primary amine with a strong non-nucleophilic base and can improve CO₂ capture efficiency by up to 30% (McCrellis, *et al.*, 2016). Although these combinations can increase capture efficiency and can be used at higher temperatures, they have the same problems as aminosilicones, such as solids formation and increased viscosity (Vega, *et al.*, 2018).

Another solvent that has been proposed as an alternative to alkanolamines is sodium carbonate (NaCO₃). CO₂ is absorbed as bicarbonate (HCO₃⁻), from which a sodium bicarbonate (NaHCO₃) precipitate is formed. The formation of the NaHCO₃ precipitate promotes bicarbonate formation, resulting in an improved CO₂ absorption capacity. NaCO₃ has a higher CO₂ loading capacity and a

lower reboiler duty than MEA, but it has a lower absorption rate (resulting in a greater absorption column height). Potassium carbonate is another solvent that does not contain any amine groups, and can be used as a promotor for amine-based solvents (Vega, *et al.*, 2018).

2.3.6. Solvent blends

Solvent blends are two or more solvents mixed together, with the solvents selected with the view to improve the characteristics and performance compared to the individual solvent blends' components (Vega, *et al.*, 2018). Aqueous alkanolamine solutions are also typically used for combined H₂S and CO₂ absorption (Global CCS Institute, 2012). Some advantages of blended amines include improved thermodynamic efficiency and a reduction in problems caused by degradation and corrosion. Furthermore, the blend can be tailored to a specific process to obtain optimum operation, thereby maintaining the high absorption rate of a single amine solvent while optimising other properties and reducing the energy required for solvent regeneration (Vega, *et al.*, 2018). The solvent properties can be optimised by reducing viscosity, increasing CO₂ capacity, increasing the rate of absorption and decreasing volatility (Wanderley, *et al.*, 2021).

Solvents that are mixed with amines in literature are physical solvents, ILs and other chemical solvents. Some physical solvents used in literature are NMP, propylene carbonate (PC), and methanol (MeOH) (Wanderley, *et al.*, 2021). Some ILs used in literature are [Tf₂N] and [bmin][PF₆]. Amines with fast reaction kinetics, such as MEA, DEA, and PZ, have been mixed with MDEA to speed up the reaction time while keeping a high CO₂ absorption capacity. Promising AMP blends for CO₂ capture found in literature were AMP-PZ, AMP-K₂CO₃, AMP-EDA (ethylenediamine), AMP-MAPA (3-(methylamino)propylamine) and AMP-DMMEA (dimethyl-monoethanolamine) (Vega, *et al.*, 2018). DGA is another primary amine that has been gaining attention, and can be used in place of MEA in solvent blends as it was found to be effective at low CO₂ partial pressures (Wanderley, *et al.*, 2021).

As mentioned in Section 2.3.5, water-lean solvent blends have gained popularity for CCS applications, although they were previously more often used in natural gas purification. Water-lean solvent blends are any form of amine solvent blend where water (the diluent) is replaced with another solvent to increase CO₂ absorption capacity, reducing regeneration energy requirements, and reducing volatility and viscosity. Some diluents include NMP, tetramethylene sulfolane (TMS), PC, mono ethylene glycol (MEG), MeOH, DEG and PEG200. Computational techniques can also be used to rapidly evaluate several possible blends to determine the optimum blend for a specific set of required properties (Wanderley, *et al.*, 2021).

A summary of the data for amine-based solvents and their blends available in the Dortmund Database (DDB) can be found in Tables 2-5 and 2-6. The DDB was used to verify the absence of data for a specific solvent blend after performing internet searches in August and October 2020 for published data on Elsevier, Wiley Online, American Chemical Society (ACS) and Taylor & Francis Online. This was verified by performing searches for DGA blends in the same journals and the DDB. Where the DDB data sets and data points differed from 2020, the previous values were also indicated. VLE data is needed for comparison to recorded experimental data, therefore literature data on density and heat capacities were not considered.

Not all possible blends are presented in Tables 2-5 and 2-6, as the emphasis was blends of MEA, MDEA, DGA, and AMP with water and/or NMP. The full database can be accessed online, which includes other physical solvents such as Sulfolane and MeOH instead of H₂O and/or NMP (DDBST GmbH Online, 2022). Based purely on Tables 2-5 and 2-6, some possible solvent blends missing are NMP-MDEA, H₂O-NMP-MEA, H₂O-NMP-DGA, H₂O-MEA-DGA, H₂O-MDEA-DGA, and H₂O-AMP-DGA. As indicated in Table 2-5, what was previously included as record number 1231 (NMP-CO₂-DGA) no longer exists in the database. These data have been referenced in Table 2-11 in Section 2.6 later in this chapter.

Table 2-5: Binary solvent blends with promising amines (DDBST GmbH Online, 2022)

DDB Record	DDB No.	Chemical name	No. of data sets	No. of data points
650	174	water	4	28
	284	N-methyl-2-pyrrolidone		
	1050	carbon dioxide		
744	174	water	269 (was 241 in 2020)	2204 (was 2012 in 2020)
	546	monoethanolamine		
	1050	carbon dioxide		
833	174	water	16	116
	1050	carbon dioxide		
	1839	diglycolamine		
837	174	water	316 (was 297 in 2020)	2338 (was 2206 in 2020)
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
839	174	water	145 (was 135 in 2020)	1174 (was 159 in 2020)
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
1231 (2020 DDB)	284	N-methyl-2-pyrrolidone	2	4
	1050	carbon dioxide		
	1839	diglycolamine		

Table 2-5 continued

DDB Record	DDB No.	Chemical name	No. of data sets	No. of data points
1298	284	N-methyl-2-pyrrolidone	10 (was 7 in 2020)	89 (was 44 in 2020)
	546	monoethanolamine		
	1050	carbon dioxide		
1301	284	N-methyl-2-pyrrolidone	10	65
	894	2,2'-diethanolamine		
	1050	carbon dioxide		
1304	284	N-methyl-2-pyrrolidone	20 (was 7 in 2020)	251 (was 56 in 2020)
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
1341	542	sulfolane	5 (was 4 in 2020)	58 (was 42 in 2020)
	546	monoethanolamine		
	1050	carbon dioxide		

Table 2-6: Ternary solvent blends with promising amines (DDBST GmbH Online, 2022)

DDB Record	DDB No.	Chemical name	No. of data sets	No. of data points
74	174	water	7	78
	284	N-methyl-2-pyrrolidone		
	1050	carbon dioxide		
	2187	n-methyldiethanolamine		
75	174	water	12	119
	284	N-methyl-2-pyrrolidone		
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
88	174	water	1	2
	542	sulfolane		
	546	monoethanolamine		
	1050	carbon dioxide		
93	174	water	24	304
	542	sulfolane		
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
94	174	water	16	134
	542	sulfolane		
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
109	174	water	6	42
	546	monoethanolamine		
	894	2,2'-diethanolamine		
	1050	carbon dioxide		

Table 2-6 continued

DDB Record	DDB No.	Chemical name	No. of data sets	No. of data points
114	174	Water	68	624
	546	monoethanolamine		
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
115	174	water	28 (was 19 in 2020)	197 (was 129 in 2020)
	546	monoethanolamine		
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
118	174	water	18	84
	546	monoethanolamine		
	1050	carbon dioxide		
	3865	piperazine		
143	174	water	49 (was 48 in 2020)	403 (was 399 in 2020)
	894	2,2'-diethanolamine		
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
144	174	water	32	241
	894	2,2'-diethanolamine		
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
173	174	water	30	275
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
	2189	2-amino-2-methyl-1-propanol		
176	174	water	127 (was 126 in 2020)	1095 (was 1089 in 2020)
	1050	carbon dioxide		
	2187	N-methyldiethanolamine		
	3865	piperazine		
197	174	water	93 (was 61 in 2020)	1005 (was 641 in 2020)
	1050	carbon dioxide		
	2189	2-amino-2-methyl-1-propanol		
	3865	piperazine		

Comparing the 2020 and 2022 data in the tables above, the system with the most recently included data points was H₂O-CO₂-AMP (record no. 839) in Table 2-5, with 1015 new points. This was followed by system H₂O-CO₂-AMP-PZ (record no. 197) in Table 2-6, with 364 new data points. This shows a significant rise and interest in data measurement of systems containing AMP in the past two years.

2.4. Comparison between physical and chemical solvents

Common chemical and physical solvents, including common mixtures of chemical and physical solvents used for CO₂ capture, are shown in Tables 2-7 and 2-8. Table 2-7 was reproduced from (Wiley VCH, 2015) and Table 2-8 was compiled from (SourGas (2016), Dash, *et al.* (2011), Dixit & Mollekopf (2014)). There are many more chemical and physical solvents to be found in literature. Those presented in Tables 2-7 and 2-8 are currently used in various industries or are areas of interest in research.

Table 2-7: Common chemical, physical and mixed solvents used for CO₂ capture. Reproduced from (Wiley VCH, 2015)

Trade name	Solvent	Licensors
Chemical absorption with aqueous amine solutions		
MEA	Monoethanolamine	Free process
DEA	Diethanolamine	Elf Aquitaine and others
DGA/Econamine	2-(2-aminoethoxy)ethanol	Fluor Daniel, Huntsman
DIPA	Di-isopropanolamine	Shell and others
MDEA	N-methyldiethanolamine	Free process
ADIP	DIPA or MDEA	Shell
Amine Guard/URCASOL	Formulated MDEA	UOP/Union Carbide
aMDEA	MDEA + activator	BASF
Gas Spec	Formulated MDEA	DOW Chemical
Flexsorb	Hindered amine	Exxon
Chemical absorption with alkaline solutions (hot potassium carbonate)		
Benfield	K ₂ CO ₃ + activator (DEA)	UOP
Catacarb	K ₂ CO ₃ + catalyst	Eickmeyer
Giammarco-Vetrocoke	K ₂ CO ₃ + activator (arsenic trioxide)	Giammarco
Vacasulf	K ₂ CO ₃ + NaOH	Krupp Uhde
Physical absorption		
Rectisol	Methanol	Linde/Lurgi
Selexol	DPEG	UOP
Purisol	NMP	Lurgi
Morphysorb	NFM	Krupp Uhde
Physical-chemical absorption		
Sulfinol D/M	Sulfolane + DIPA or MDEA	Shell
Amisol	MeOH + MEA, DEA or DETA	Lurgi

Presented in Table 2-7, physical solvents such as Rectisol (uses MeOH) and Selexol (uses DPEG) are used for high-purity syngas, while chemical solvents such as MDEA are used for lower purity syngas. Many amine-type chemical solvents are in use, but this is not always the case. Mixtures of physical and chemical solvents are already used by Shell in their Sulfinol process, where Sulfolane is mixed with either DIPA or MDEA (Wiley VCH, 2015).

Table 2-8: Comparison of some properties of selected physical and chemical solvents used for CO₂ capture. Compiled from (SourGas, 2016), with AMP from (Dash, *et al.*, 2011) and DGA from (Dixit & Mollekopf, 2014)

Solvent	MEA	DEA	MDEA	AMP	DGA	Selexol	Rectisol	Purisol	Sulfinol
Type	Chemical	Chemical	Chemical	Chemical	Chemical	Physical	Physical	Physical	Mixture
Solution strength (wt%)	10-20MEA with 80-90H ₂ O	25-30DEA with 70-75H ₂ O	35-50MDEA with 50-65H ₂ O	15-35AMP with 65-85H ₂ O	40-70DGA with 30-60H ₂ O	Mixture of DPEGs	Methanol or other organic solvents	NMP	30-40MDEA with 40-60 sulfolane and 5-15H ₂ O
Species removed	H ₂ S, CO ₂	H ₂ S, CO ₂	H ₂ S, CO ₂	CO ₂	CO ₂ , COS (partial)	H ₂ S, COS, CO ₂	H ₂ S, COS, CO ₂	H ₂ S, CO ₂	H ₂ S, CO ₂
Degradation conditions	Excessive temperatures, O ₂ , CO ₂ , COS and CS ₂	High temperatures, O ₂	High H ₂ S concentration	N/A	High temperatures, O ₂	N/A	N/A	N/A	N/A
Degradation products	Cause corrosion	N/A*	Cause corrosion	N/A	N/A	N/A	N/A	N/A	N/A
Losses	Vapourisation, chemical losses due to leaks, mechanical losses	N/A	N/A	N/A	N/A	N/A	Vapourisation	Vapourisation	N/A

*N/A is used when information was not available from the referenced literature source

Table 2-8 contains a summary of the solution strength, species removed, degradation conditions and products, and causes of solvent loss for common chemical and physical solvents used for CO₂ capture. Chemical solvents with the highest concentration are DGA and MDEA, while the physical solvents are typically used without dilution. Additionally, most solvents in the table also remove H₂S.

Chemical solvents can be corrosive, requiring stainless steel construction, and regeneration requires heat to be added, while physical solvents are favoured over chemical solvents when the process gas being treated has a high concentration of impurities or acid gases. Physical solvents are usually non-corrosive, and regeneration is often achieved by reducing the pressure without adding heat (Burr & Lyddon, 2008). Physical solvent processes are usually 2 to 3 times more expensive than chemical solvent processes due to refrigeration requirements and complex solution flashing, although the total energy usage for CCS processes can be similar for physical and chemical solvent processes. Since physical solvent processes have a higher power consumption, chemical solvent processes have a higher steam consumption due to the large amounts of heat required to regenerate the solvent (National Energy Technology Laboratory, 2018)

Physical solvent processes usually require a relatively high syngas pressure, high acid gas partial pressure, and/or low absorber operating temperature, and are typically more effective at high CO₂ partial pressures and low stream temperatures (National Energy Technology Laboratory, 2018). Solvent regeneration can be carried out *via* pressure throttling, but if sulphur species are present, heating is also required in the form of reboiler duties (Koytsoumpa, *et al.*, 2018). Due to the flue gas having a low CO₂ partial pressure and relatively high temperature, physical solvents do not seem to be competitive compared to chemical solvents for post-combustion CO₂ capture (National Energy Technology Laboratory, 2018). Chemical solvent processes usually operate slightly above ambient temperature and are typically more effective for use with lower acid gas partial pressure than physical solvents. The solvent is regenerated by heating to reverse the reaction and release stored CO₂ (Kohl & Nielsen, 1997).

Mixtures of physical and chemical solvents utilise the high purity of the treated gas from chemical solvents and the low energy requirements for regeneration of the physical solvents (Vega, *et al.*, 2018). These mixtures are generally effective over a wide range of acid gas partial pressures at approximately ambient temperatures. Solvent regeneration is different for each blend since the regeneration method used depends on the specific chemical and physical solvents present (National Energy Technology Laboratory, 2018).

2.5. Regeneration and reuse of solvents

Solvents regeneration is carried out to release the absorbed gas so that the solvent can be recycled and reused. The regeneration method depends on the type of solvent. The simplest method for regenerating the solvent is by flashing to atmospheric pressure or vacuum, depending on the operating pressure, or by stripping with an inert gas. This produces a solvent that still contains low levels of acid gases. Physical solvents are regenerated by flashing to atmospheric pressure, while chemical solvents are regenerated by applying heat to reverse the reactions. Solvent regeneration may require an additional step if there are other absorbed gases. For example, physical solvents typically co-absorb more H_2S than chemical solvents. A low H_2S concentration requires no additional regeneration steps, while higher concentrations require the addition of heat (Kohl & Nielsen, 1997).

After solvent regeneration, some absorbed gas remains in the solvent. For CO_2 capture, the CO_2 remaining in the solvent after regeneration is referred to as the lean loading of the solvent. An example is the use and regeneration of various MEA blends covered in Wanderley, *et al.* (2021). The solid stars in Figure 2-2 show the CO_2 loading of the regenerated MEG-MEA and MEGMME-MEA (2-methoxyethanol) blends after regeneration at 100 kPa and 120 °C. The MEG and MEGMME regenerated solvents were found to have a lean loading of $0.26 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$ and $0.05 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{MEA}}$ respectively. Comparing the solid and empty stars for the different blends, each solvent blend has its own lean loading, which is determined by the pressure at which the blend is regenerated (Wanderley, *et al.*, 2021).

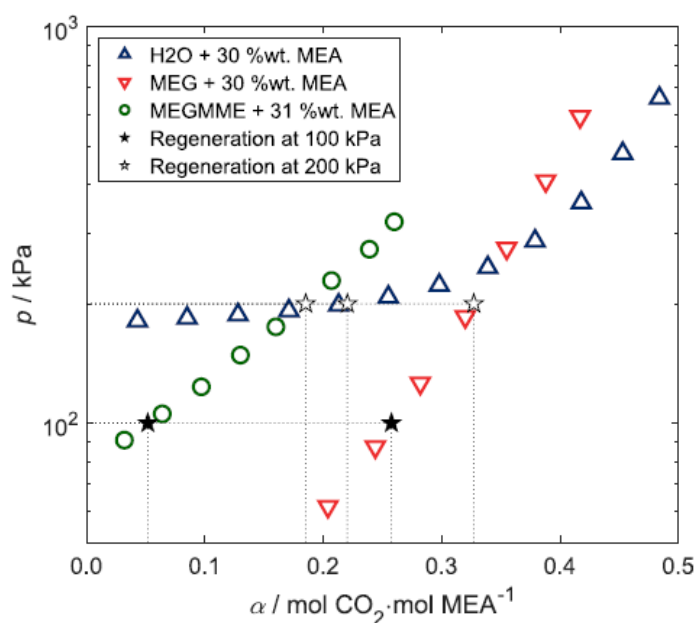


Figure 2-2: CO_2 loading in mixtures of MEA- H_2O , MEA-MEG, and MEA-MEGMME at 120 °C before and after solvent regeneration (Wanderley, *et al.*, 2021)

All amine solvents and amine solvent blends undergo degradation as a result of impurities being introduced in the flue gas feed or make-up streams. Flue gas impurities such as O_2 and SO_x can react with and degrade amines to form heat stable salts (HSS). O_2 degradation resistance varies greatly and depends on operating conditions (temperature and residence time) and solvent type, pH and concentration (ElMoudir, *et al.*, 2012). Bacon (1987) listed the degradation resistance of common amines from the most sensitive to the least sensitive to oxidation as follows: DIPA, DEA, MEA, DGA and MDEA. A lower sensitivity to oxidation indicates that the used solvent has lower levels of oxidation products, therefore DGA gives a lower concentration of oxidation products than MEA.

When regenerating a solvent for reuse, the concentration of degradation products increase and the following changes occur: a proportional increase in density, proportional increase in refractive index, decreased absorption capacity, increased viscosity, increased foaming and increased corrosivity (ElMoudir, *et al.*, 2012). Reza & Trejo (2006) performed degradation experiments on aqueous solvent blends containing varying mixtures of MDEA, DEA and AMP. CO_2 , H_2S , and blends thereof were used for measuring the change in solvent composition at 200 °C. It was observed that the solutions turned brown as degradation occurred, and solid degradation products were observed. Degradation products in solvents can result in increased energy, heating and cooling requirements, and fouling and blockages in equipment. These problems are addressed by either solvent cleaning and degradation prevention, or recycling and reclaiming (ElMoudir, *et al.*, 2012).

The guidelines for various contaminant and degradation product levels vary according to the amine used, but there are specific guidelines for the HSS anion levels as seen in Table 2-9. These levels determine how many times a solvent can be recycled, and they can be used to determine the best contaminant removal method (Haws, 2001). More information on contaminant removal methods can be found in ElMoudir, *et al.* (2012).

Table 2-9: Heat stable salts anion guidelines. Reproduced from (Haws, 2001)

Organic HSS anions	Limit (ppm)	Inorganic HSS anions	Limit (ppm)
Acetate	1000	Chloride	500
Formate	500	Sulphate	500
Oxalate	250	Sulphite	500
Glycolate	500	Thiosulphate	10000
Malonate	500	Thiocyanate	10000
Succinate	1000		

2.6. Solvent selection for this study

As stated in the introduction, CO₂ capture using new amine-NMP blends was the focus of this study.

MEA, DEA and MDEA are the most popular alkanolamines proposed and used for CO₂ capture. DIPA was also popular in the 1960s, but has slowly been replaced with MDEA over time. DGA was first proposed for absorbing acid gases from process streams by Blohm and Riesenfeld in 1955, and has slowly regained some popularity in more recent years. DGA is a primary amine, so it has the same stability and reactivity as MEA, but also has the low vapour pressure and hygroscopicity of DEG, therefore it can be used in higher concentrations than MEA (Kohl & Nielsen, 1997). A higher amine concentration results in a higher CO₂ loading capacity (Plasynski & Chen, 2000), lower solvent circulation rate and steam consumption, resulting in a lower energy requirement when compared to MEA (Kohl & Nielsen, 1997).

There are many options for diluents, as outlined in Wanderley, *et al.* (2021). In literature to date, NMP has been found to be the best diluent in terms of increasing the CO₂ absorption rate. It also has a low viscosity and a low Henry's coefficient, which makes it a good option as a diluent for amine solvent blends (Wanderley, *et al.*, 2021). Detractors from using NMP are that it is toxic to reproductive organs and industry is moving away from using it. However, NMP was still used in research work (Ebrahimejadhasanabadi (2019), Wanderly, *et al.* (2020), Wanderley, *et al.* (2018), Yaun & Rochelle (2018), Pakzad, *et al.* (2018)), and its advantages outweigh its drawbacks for small-scale use in the controlled environment that laboratories offer.

Test systems are important as they show that literature results can be reliably reproduced. The test solvents selected were pure NMP and 30 wt% MEA–70 wt% H₂O. These CO₂ solubility measurements were tested at 40 °C. In this study, the CO₂ solubility data using new solvent blends was measured at low pressures, while literature typically contains measurements at higher pressures. Low pressure conditions were used since industry CO₂ capture processes operate at atmospheric pressure, and the equipment was able to measure pressures between 0.1 MPa and 4 MPa. A solvent matrix of the solvents selected and used in this study can be seen in Tables 2-10 and 2-11, with available literature data referenced for the specific solvents and solvent blends. Selected data from these tables can be seen in Figures 2-3 and 2-4, where the data are analysed.

Table 2-10: Summary of system conditions measured in literature for solvent blends of MEA or DGA with H₂O

Chemical	H ₂ O	
	System conditions	No. of data points
MEA	29.65% MEA: 0.09 – 1.69 MPa at 25 °C ^(a)	6
	10.34% MEA: 0.22 – 2.07 MPa at 40 °C ^(a)	5
	19.97% MEA: 0.20 – 1.91 MPa at 40 °C ^(a)	5
	29.65% MEA: 0.19 – 2.32 MPa at 40 °C ^(a)	7
	30% MEA: 0.10 – 0.21 MPa at 40 °C ^(b)	5
	30% MEA: 0.10 – 1.97 MPa at 40 °C ^(c)	7
DGA	51.32% DGA: 0.34 – 1.50 MPa at 25 °C ^(a)	5
	31.01% DGA: 0.19 – 2.10 MPa at 40 °C ^(a)	5
	51.32% DGA: 0.63 – 2.17 MPa at 40 °C ^(a)	5
	51% DGA: 2×10^{-5} – 5.79×10^{-3} MPa at 40 °C ^(e)	4
	60% DGA: 1.58×10^{-3} – 5.98 MPa at 50 °C ^(d)	20
	51% DGA: 1.5×10^{-4} – 2.69×10^{-2} MPa at 60 °C ^(e)	5
	51% DGA: 1.42×10^{-3} – 5.01×10^{-2} MPa at 80 °C ^(e)	4
	51% DGA: 6.25×10^{-3} – 1.8×10^{-2} MPa at 100 °C ^(e)	2
	60% DGA: 2.49×10^{-3} – 5.84 MPa at 100 °C ^(d)	26

All compositions are in terms of mass percent. (a) Ebrahimejadhasanabadi (2019), (b) Tong, Trusler, Maitland, Gibbins & Fennell (2012), (c) Shen & Li (1992), (d) Martin, Otto & Mather (1978), (e) Chen, Closmann & Rochelle (2011).

Table 2-11: Summary of system conditions measured in literature for solvent blends of MEA or DGA with NMP

Chemical	NMP	
	System conditions	No. of data points
NMP	0.56 – 0.98 MPa at 20 °C ^(b)	5
	0.13 – 1.91 MPa at 25 °C ^(a)	29
	0.29 – 2.03 MPa, 40 °C ^(a)	7
	0.66 – 1.12 MPa at 40 °C ^(b)	5
	0.38 – 2.58 MPa at 40 °C ^(c)	5
	0.27 – 2.09 MPa at 50 °C ^(a)	7
	0.36 – 2.02 MPa at 60 °C ^(a)	5
	0.70 – 1.12 MPa at 60 °C ^(b)	5
	0.29 – 1.96 MPa at 75 °C ^(a)	5
MEA	10.25% MEA: 0.21 – 1.74 MPa at 40 °C ^(a)	5
	20.32% MEA: 0.19 – 1.73 MPa at 40 °C ^(a)	5
	30.37% MEA: 0.33 – 2.30 MPa at 40 °C ^(a)	6
DGA	Unknown composition: 8.12×10^{-4} – 3.5×10^{-3} MPa at -10 °C ^(d)	2
	Unknown composition: 7.39×10^{-4} – 1.74×10^{-3} MPa at 25 °C ^(d)	2
	30.20% DGA: 0.26 – 1.89 MPa at 40 °C ^(a)	5
	49.64% DGA: 0.43 – 1.78 MPa at 40 °C ^(a)	5

All compositions are in terms of mass percent. (a) Ebrahimejadhasanabadi (2019), (b) Bohloul, Vatani & Peyghambarzadeh (2014), (c) Zubchenko, Shakhova & Ladygina (1985), (d) Provided by Dortmund Data Bank, DDB (2020) (not present in 2022 version): Rivas & Prausnitz (1979).

2.7. Solubility measurements in literature

The graphical representation of the performance of the solvent blends measured in this study are presented in plots of CO₂ loading vs system pressure, with the measured T-P-z data transformed to T-P- α_{CO_2} data using the iterative VLE calculation methods contained in Section 2.8.1.

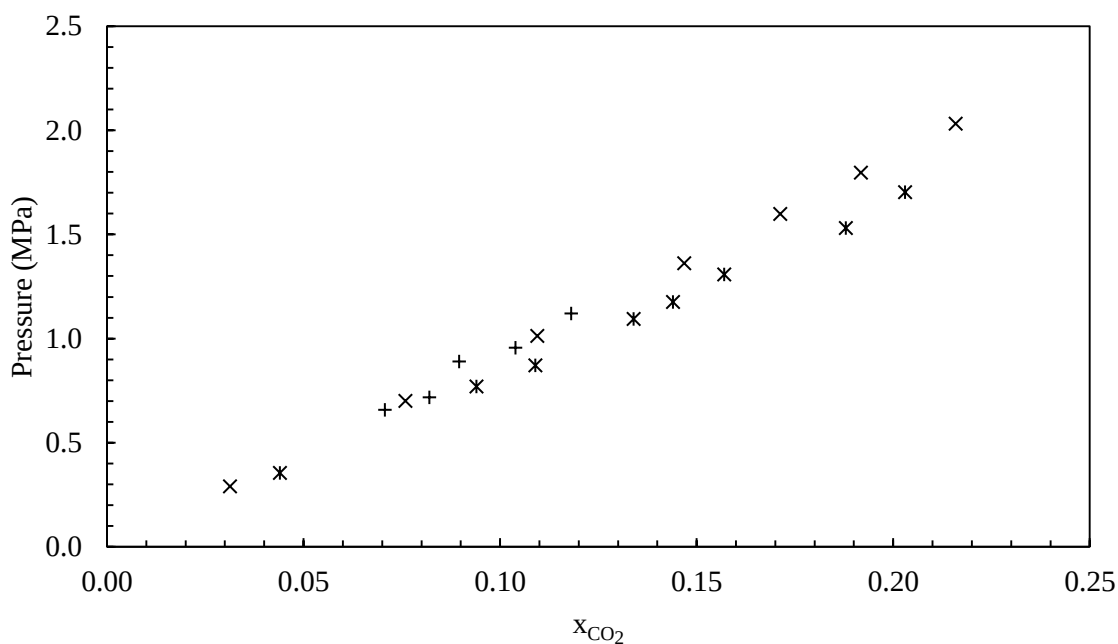


Figure 2-3: Literature data for CO₂ loading in NMP at 40 °C. × Ebrahiminejadhasanabadi (2019), + Bohloul, *et al.* (2014), * Zubchenko, *et al.* (1985)

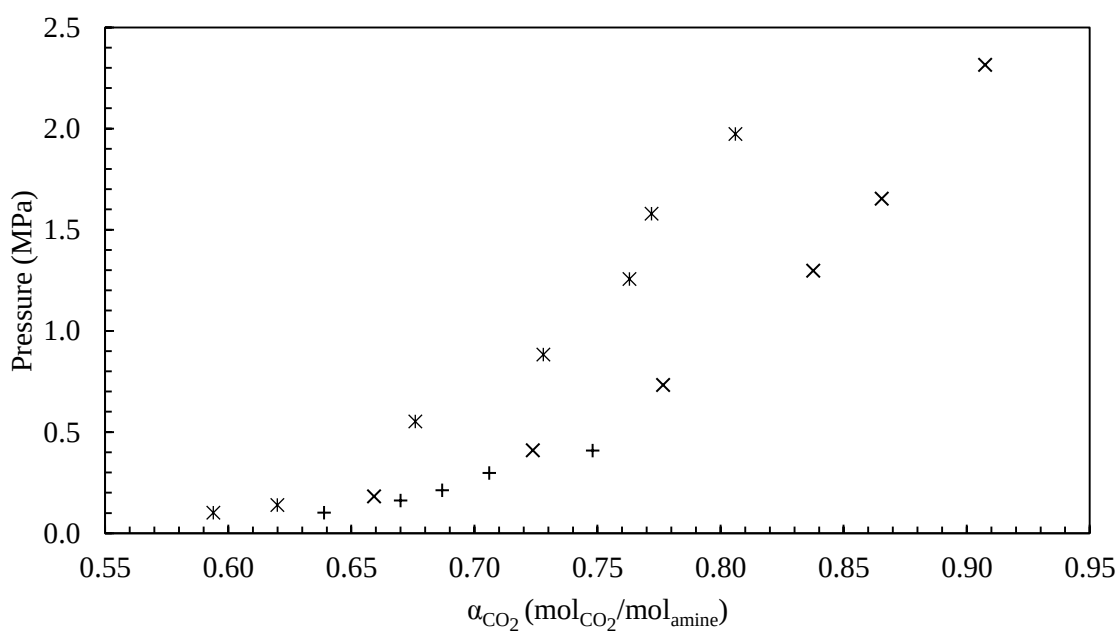


Figure 2-4: Literature data for CO₂ loading in MEA(1)-H₂O(2) at 40 °C. × Ebrahiminejadhasanabadi (2019) with $w_1=0.2965$, + Tong, *et al.* (2012) with $w_1=0.30$, * Shen & Li (1992) with $w_1=0.30$

Some literature data for the CO₂-NMP and CO₂-MEA-H₂O test systems are shown in Figures 2-3 and 2-4. These data were also listed in Tables 2-10 and 2-11. Although the X-axis was defined differently for amine blends, the results can be compared to pure solvents since the results are expressed as the number of moles of CO₂ per mole of active solvent. With water-lean amine blends, the CO₂ loading is calculated per mole of amine. Comparing the loading in Figure 2-3 and Figure 2-4, MEA has a much higher loading than NMP at similar pressures, and since MEA is a chemical solvent, it can absorb CO₂ at low pressures. The differences in the data trends are explained by the difference in the type of solvent. NMP is a physical solvent, therefore CO₂ is absorbed at a constant rate, and the solubility data has a linear trend as seen in Figure 2-3. MEA is a chemical solvent; due to the changing reaction rates, the slope of the solubility data increases to a fixed point, which depends on the solvent concentration and system temperature. This can be seen in Figure 2-4; the pressure increases slowly at lower CO₂ loadings, then increases rapidly as CO₂ loading increases and the saturation point is approached.

2.8. Modelling water-lean solvents

An important part of solvent research is process simulations, where it is necessary to have an accurate representation of the solubility of CO₂ in the selected amine solvent or amine solvent blend. It is difficult to model amine systems due to inconsistent published literature and the high number of ionic and molecular species produced during absorption (Barreau, *et al.*, 2006). As stated in Chunxi & Furst (2000), empirical expressions, excess Gibbs energy models, and Equations of State (EOS) have been used to model CO₂ solubility in aqueous MDEA solutions. Empirical expressions were found to provide an adequate representation of experimental data but had poor extrapolation capabilities. The accuracy of the excess Gibbs energy models and EOS depended on the specific models and equations used. Electrolyte systems are typically modelled using excess Gibbs energy models, while equations of state are better suited to the calculations of gas solubilities over a large pressure range (Chunxi & Furst, 2000). Since the CO₂ solubility data (T-P-z) recorded in this study was expected to have a pressure range of 0.1 – 1.5 MPa, an EOS was used for VLE calculations. A simple empirical model was used with the same base EOS for data regression for the water-lean CO₂ solubility data, again due to the expected pressure range of the recorded data.

2.8.1. VLE equations

The aim of VLE calculations is to determine the number of moles and composition of CO₂ absorbed in the liquid solvent. Knowing the T, P and initial solvent composition, an EOS is the most suitable method for calculating liquid composition and number of moles of absorbed CO₂. The experimental methods to obtain this data are detailed in Chapter 3. Using the static synthetic technique, the temperature, pressure, initial solvent composition and liquid volume are recorded. Once the overall composition is known, it is used to calculate the phase compositions and CO₂ solvent loading. These equations can be seen later in this section. The T-P- α_{CO_2} data are then used to perform modelling to predict the liquid phase composition for a specified temperature, pressure, and solvent blend for the DGA systems. These modelling equations can be seen in Section 2.8.2.

To determine the number of moles of CO₂ in the liquid phase, and knowing the number of moles of CO₂ initially available in the vapour phase, a suitable equation of state must be selected to calculate the mole fraction of CO₂ absorbed in the solvent. The equation selected was the PR-EOS, and the only constants needed are the gas constant, and the density and molar mass of each chemical in the system. The PR-EOS is commonly used and is suitable for a wide range of temperatures and pressures, and the third term (ω) makes it suitable for a variety of different classes of molecules (Koretsky, 2013). In addition, the PR-EOS was used for similar calculations using the same equipment in Ebrahimejadhasanabadi (2019), and it was used for modelling CO₂-NMP systems in literature (Bohloul, *et al.* (2014), Rajasingam, *et al.* (2004)).

When one component is present, the generic form of the PR-EOS must be used, with equations (2-1) to (2-6) taken from Bohloul, *et al.* (2014)

$$P = \frac{RT}{v-b(T)} - \frac{a(T)}{v(v+b(T))+b(v-b(T))} \quad (2-1)$$

Where

$$a(T) = \frac{0.457353\alpha(T)R^2T_{cr}^2}{P_{cr}} \quad (2-2)$$

$$b(T) = \frac{0.077796RT_{cr}}{P_{cr}} \quad (2-3)$$

$$\alpha(T) = [1 + \kappa(1 - T_r^{0.5})]^2 \quad (2-4)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \text{ for } \omega \leq 0.49 \quad (2-5)$$

$$\kappa = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 \text{ for } \omega \geq 0.49 \quad (2-6)$$

The virial form of the PR-EOS must be used for VLE calculations, as there are too many unknowns in the standard PR-EOS when using measured data. This equation is a dimensionless form in terms of a compressibility factor (Z) and other constants, and is derived from the standard PR-EOS. The calculations using the virial PR-EOS are performed on the vapour phase, and the results used to determine the CO₂ loading in the liquid phase. The virial PR-EOS is as follows, with equations (2-7) to (2-9) taken from Koretsky (2013).

$$Z^3 - CZ^2 + DZ - E = 0 \quad (2-7)$$

Where

$$C = 1 - B$$

$$D = A - 2B - 3B^2$$

$$E = AB - B^2 - B^3$$

Where

$$A = \frac{\alpha(T)a(T)P}{R^2T^2} \quad (2-8)$$

$$B = \frac{b(T)P}{RT} \quad (2-9)$$

Where $a(T)$, $b(T)$ and $\alpha(T)$ are the same as for the standard PR-EOS.

Since Z is unknown, a value must be estimated and iterative calculations performed to determine the true value of Z . There are many methods available for iterative calculations. The Newton-Raphson root-finding method was selected for iterative calculations since it is easy to implement in Excel when iterative calculations are enabled. The Newton-Raphson method is used to calculate Z_n until $Z_n - Z_{n-1} = 0$. The Newton-Raphson equation can be found in equation (2-10) (Smith, *et al.*, 2001).

$$Z_n = Z_{n-1} - \frac{f_n(Z)}{f'_n(Z)} \quad (2-10)$$

Where Z_n is the current value of Z

Z_{n-1} is the previous value of Z

$$f_n(Z) = Z^3 - CZ^2 + DZ - E \quad (2-11)$$

$$f'_n(Z) = 3Z^2 - 2CZ + D \quad (2-12)$$

The dimensionless form of the ideal gas equation (Koretsky, 2013) can then be used to calculate the number of moles of CO_2 in the vapour phase.

$$Z = \frac{nPV}{RT} \text{ or } n = \frac{PV}{ZRT} \quad (2-13)$$

Where n is the number of moles

R is the universal gas constant. The chosen version determines which units are used for the other variables

P is the pressure

V is the volume, and

T is the temperature

When more than one component is present, the same standard PR-EOS (2-1) is used, but the $a(T)$ and $b(T)$ terms are calculated using mixing rules (Koretsky, 2013). When the virial PR-EOS in equation (2-7) is used to calculate the CO_2 loading from the measured data, it is assumed that only the amine absorbs CO_2 . More details and fewer assumptions are required when performing data modelling (detailed in Section 2.8.2), hence mixing rules are needed to determine the extent of mixing of CO_2 in the diluent (NMP). The mixing rule depends on the types of components present, therefore an applicable mixing rule was researched for CO_2 absorption in NMP. Since this absorption is purely due to physical absorption, the mixing rule selected will determine the amount of CO_2 absorbed. Since a gas is being mixed with a liquid, there were concerns that the standard mixing rules would not be sufficient. Hence, the standard mixing rules such as those found in Koretsky (2013) were not considered, and more-complex mixing rules were researched.

The mixing rules from Bohloul, *et al.* (2014) were initially considered, but it was determined that more complex mixing rules must be investigated. As stated in Koretsky (2013), the van der Waals mixing rules can be used for both PR-EOS and RK-EOS. As stated by Osman (2014), the van der Waals-Berthelot mixing rules as used by Yokozeki (2001) were successfully applied to similar conditions as those used in Osman (2014). Therefore, it was determined that the van der Waals-Berthelot mixing rules would be used. The other PR-EOS equations and constants were kept unchanged.

The mixing rules used were adapted from Osman (2014), originally from the van der Waals-Berthelot mixing rules as used by Yokozeki (2001), and can be seen in equations (2-14) to (2-17).

$$a(T) = \sum_{i,j=1}^N \sqrt{a_i a_j} \left(1 + \frac{\tau_{ij}}{T}\right) (1 - k_{ij}) x_i x_j \quad (2-14)$$

$$b(T) = \frac{1}{2} \sum_{i,j=1}^N (b_i + b_j) (1 - m_{ij}) (1 - k_{ij}) x_i x_j \quad (2-15)$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j} \quad (2-16)$$

$$a_i = \frac{0.457353 R^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \quad (2-17)$$

Where N is the number of points, τ , k , m , and l are binary interaction parameters, and b_i is the same as $b(T)$ in equation (2-3).

Since the parameters in the mixing rules (l , k , m and τ) are all binary interaction parameters, $m_{ii} = 0$ and $m_{ij} = m_{ji}$ for all parameters except ' l ', where $l_{ii} = 0$ but $l_{ij} \neq l_{ji}$ (Osman, 2014). Therefore, for CO₂(1)-NMP(2), the mixing rules are expanded in equations (2-18) to (2-21).

$$k_{12} = \frac{l_{12} l_{21} (x_1 + x_2)}{l_{21} x_1 + l_{12} x_2} \quad (2-18)$$

$$k_{21} = \frac{l_{21} l_{12} (x_2 + x_1)}{l_{12} x_2 + l_{21} x_1} = k_{12} \quad (2-19)$$

$$a(T) = x_1^2 a_1 + 2 \sqrt{a_1 a_2} \left(1 + \frac{\tau_{12}}{T}\right) (1 - k_{12}) x_1 x_2 + x_2^2 a_2 \quad (2-20)$$

$$b(T) = x_1^2 b_1 + (b_1 + b_2) (1 - m_{12}) (1 - k_{12}) x_1 x_2 + x_2^2 b_2 \quad (2-21)$$

After calculating $a(T)$ and $b(T)$, the values can be substituted into equations (2-8) and (2-9), and the virial PR-EOS used as before. This form of the PR-EOS is used for the data regression in Section 2.8.2, where the $a(T)$ and $b(T)$ obtained from data regression are substituted into equation (2-1) to get the predicted model pressure.

2.8.2. Modelling equations

Data modelling consists of regressing for parameters in established models and then using those parameters and models to predict additional data for that specific system. This is performed after measuring data and performing VLE calculations. As shown in Tables 2-5 and 2-6 in Section 2.3.6, there are limited data for CO₂ solubility in water-free DGA-NMP blends, therefore modelling was investigated for the purpose of predicting solubility data for only the new DGA-NMP and DGA-H₂O data measured in this study. The literature search for existing models suitable for data regression of water-lean amine systems is detailed below.

According to Pakzad, *et al.* (2018), CO₂ only reacts with the amine when there is amine-NMP-H₂O present. NMP does not react with CO₂, as it is a physical solvent. DGA is a primary amine and reacts with CO₂, as it is a chemical solvent. As a result, two different types of models are needed to account for the different absorption mechanisms, where the results are combined to get an overall CO₂ loading for a specific pressure, as done in Ebrahimejadhasanabadi (2019) and Osman (2014). Since there is either NMP or H₂O present with DGA, there will be different reactions depending on the solvent. If there is water, the standard reactions for CO₂ in aqueous amine solvents can be used (Hu & Chakma, 1990). If there is no water, CO₂ will react directly with alkanolamines, but these reactions are not yet fully understood in literature (Wanderley, *et al.*, 2019).

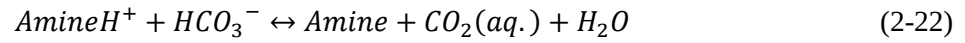
Osman (2014) had previously modified the Posey-Tapperson-Rochelle model for use with water-lean solvents, where water-lean amine blends replaced water with ILs. The more complicated models, such as the Deshmukh-Mather model, are more commonly used as they offer a high degree of accuracy. A drawback of the Deshmukh-Mather model is that the full set of reactions for the specific amine are required along with additional constants, as seen for the amine-H₂O system modelling in Ebrahimejadhasanabadi (2019). Since the exact reaction mechanism of CO₂ in water-lean DGA solvents is unknown, a simple model is more applicable for the water-lean CO₂-DGA reaction than other more complicated models. Therefore, the simple Posey-Tapperson-Rochelle model was selected for modelling CO₂ absorption in the DGA-diluent solvent blends used in this work.

A separate model is required for CO₂ absorption into NMP (Osman (2014), Ebrahimejadhasanabadi (2019)). Since the absorption is characterised by the dissolution of a gas into a liquid, an EOS with the appropriate mixing rules is applicable. The Redlich-Kwong equation of state (RK-EOS) was used by Osman (2014) since it had previously been proved appropriate for the temperatures and pressures he used. Since the temperatures and pressures to be used in this work (40 °C and 0.1 – 1.5 MPa) are within the range of those used by Osman (20 – 70 °C and 0.01 – 1.6 MPa), and the diluent is also a physical solvent, the RK-EOS could also be used in this work. Since it was previously stated in Section 2.8.1 that the Peng-Robinson EOS is suitable for use for CO₂ absorption in NMP (Ebrahimejadhasanabadi (2019), Bohloul, *et al.* (2014)), the replacement of the RK-EOS in Osman's code with the PR-EOS was investigated. This was further investigated by looking at modelling of CO₂ absorption in NMP in additional literature to determine the most common EOS used. Looking at other literature, it seems that the PR-EOS used by Bohloul, *et al.* (2014) for CO₂ absorption in NMP has also been used in other literature with standard and modified van der Waals mixing rules when there is no other solvent present (Rajasingam, *et al.*, 2004). The PR-EOS with the appropriate mixing rules can be found at the end of Section 2.8.1. The results from both models are then combined to get the overall solubility of CO₂ in the DGA-NMP blends.

Previous MATLAB[®] codes for the prediction of CO₂ solubility data in water-lean amine- IL solvents, developed by Osman (2014) in his PhD thesis, were used and adapted with permission for this study. Osman's work (Osman, 2014) was based on the Posey-Tapperson-Rochelle model for use with water-lean alkanolamine solvents found in Posey *et al.* (1996) and Dicko *et al.* (2010), and a generic non-electrolyte Redlich-Kwong equation of state (RK-EOS) for use with ILs found in Shiflett *et al.* (2005), with the van der Waals-Berthelot mixing rules found in Yokozeki (2001). As covered above, the PR-EOS was chosen to replace the RK-EOS. More details about the models used can be found in the section below, along with the PR-EOS and mixing rules already detailed in Section 2.8.1.

The Posey-Tapperson-Rochelle model is a simple empirical model introduced in Posey *et al.* (1996), where it was assumed that the reaction mechanism between CO₂ and any alkanolamine could be represented by one absorption reaction. Due to the absence of water in some of the DGA solvent blends tested here, the more complex models (such as the Deshmukh-Mather, Elec-NRTL, and Kent-Eisenberg models) cannot be used since the complete reaction mechanism is required. Even in more recent journals, chemical reactions for all water-lean solvents were still not fully realised (Wanderley, *et al.*, 2019), where a simple, single reaction was assumed for the reaction of CO₂ with an amine. Therefore, it was decided to use the Posey-Tapperson-Rochelle model as used by Osman (2014).

When modelling the results to be obtained in this study, it is assumed that CO₂ absorption into DGA consists of a single reaction shown in equation (2-22) (Osman, 2014).



The concentration of carbonate (CO₃²⁻) and hydroxide (OH⁻) ions is assumed to be negligible. Since CO₂ diffusion occurs in NMP instead of water, assuming that H₂O is present does not affect the accuracy of the predicted model (Osman, 2014).

The reaction shown in equation (2-29) above is then used to determine the equilibrium constant: this has been done previously in Posey *et al.* (1996) and Dicko *et al.* (2010). As stated by Osman (2014), the equilibrium constant is given by equation (2-23).

$$\ln(K_{CO_2}) = a + \frac{b}{T} + cL_TC^0_{AMINE} + d(L_TC^0_{AMINE})^{0.5} \quad (2-23)$$

Where $L_TC^0_{AMINE}$ is the concentration of amine, neglecting the presence of acid gases

$$L_TC^0_{AMINE} = \frac{Amine}{Amine + NMP}$$

‘a’ is an overall correction factor

‘b’ is a temperature correction factor, and

‘c’ and ‘d’ account for amine concentration in the solvent

Parameters ‘a’ to ‘d’ are found by regression of experimental data. MATLAB[®] is used in this study to perform the data regression with the code adapted from Osman (2014).

The partial pressure of CO₂ can then be predicted using equation (2-24), obtained from Osman (2014).

$$P_{CO_2} = P_{calc, Posey} = X_{CO_2} K_{CO_2} \frac{L_T}{(1-L_T)} \quad (2-24)$$

For the DGA-H₂O systems, the calculated pressures can then be compared to the experimental data. For the DGA-NMP systems, the calculated pressures are then added to those calculated using the PR-EOS, as detailed at the end of Section 4.2.2.

Whenever performing data regression, the modelled data must be compared to the measured data by calculating the root mean square error. This combined error for all the pressures is calculated using equation (2-25).

$$\text{error} = \sqrt{(P_{\text{calc},1} - P_{\text{CO}_2,1})^2 + (P_{\text{calc},2} - P_{\text{CO}_2,2})^2 + \dots + (P_i - P_{\text{CO}_2,i})^2} \quad (2-25)$$

Where P_{calc} is the calculated pressure using the respective model

P_{CO_2} is the experimental pressure

i is the number of recorded pressure points for that dataset

In summary, there are many solvents available and already in use for CO₂ capture, but improvements in energy use and desirable solvent properties are in demand. Chemical-physical solvent blends are a promising research area, as they can be tailored to have the best properties of both solvents. These amine blends can be tailored to reduce viscosity and solvent regeneration requirements by selecting an appropriate low-viscosity solvent and varying the solvent blend composition. DGA-NMP blends were selected for this study due to the potential of DGA as a replacement for MEA, the relatively low viscosity and heat capacity of NMP, and a lack of previous studies performed using these blends. This chapter also contained the VLE equations required to convert the recorded T-P-z data to T-P- α_{CO_2} data that could be plotted on a graph. Data regression was also researched for the new DGA-NMP/H₂O blends, and the selected models were described. The next chapter contains descriptions of the materials, equipment, and experimental procedures, along with the uncertainty calculations used in this study.

CHAPTER 3: EXPERIMENTAL WORK

In the previous chapter, DGA-NMP blends were selected due to their promise and the absence of both measured and modelled data in literature. VLE equations were detailed using the PR-EOS and the Posey-Tapperson-Rochelle model with the PR-EOS and van der Waals-Berthelot mixing rules were selected for data regression of the measured DGA-NMP/H₂O data. The materials and equipment used, as well as an in-depth explanation of the experimental procedures for the static synthetic equilibrium cell are presented in this chapter. Further details of the measurement of physical properties, which were required to characterise solvents, and the uncertainty calculation methods used are also reported.

3.1. Experimental techniques in literature

There are different classifications for the types of equipment used for VLE measurements. They are classified according to the way in which equilibrium is reached (static or dynamic methods) and the way in which the composition of the phases at equilibrium is obtained (synthetic or analytical methods). Static methods consist of loading a solvent and gas into an evacuated equilibrium cell, which is then sealed, and stirring the solvent at isothermal conditions until equilibrium is reached. Dynamic methods consist of circulating a gas and/or solvent through an equilibrium cell until equilibrium is reached. Synthetic methods involve the measurement of bubble or dew points, or total pressure measurements at equilibrium in the equilibrium cell. Requirements for this method include known solvent composition and the use of a suitable thermodynamic model. Analytical methods involve the sampling and analysis of a gas and/or solvent at equilibrium either directly from an equilibrium cell (using spectroscopic or gravimetric methods) or from outside an equilibrium cell (using chromatographic, refractometric, titration or pressure drop methods). Requirements for this method include apparatus for removing gas and/or solvent samples, and the relevant sample analysis apparatus (Ebrahimejadhasanabadi, 2019).

The focus of this study was on the measurement and modelling of new water-lean DGA-NMP blends. As such, the previous chapter did not present an in-depth literature review of equipment and experimental techniques used for VLE measurements since the equipment used in this study was previously constructed by Ebrahimejadhasanabadi (2019). For more information on the development of the equipment used in this study, the reader is referred to Ebrahimejadhasanabadi (2019), and for in-depth information on different VLE measurement techniques, the reader is referred to Christov & Dohrn (2002), Dohrn, *et al.* (2010) and Bazyleva, *et al.* (2021).

3.2. Materials

The chemicals used in this study are listed in Table 3-1, along with the details of the purities, suppliers, densities, refractive indices and purification method used. Experimental data were compared to those in literature. This ensured that the chemicals used were of required purity. When using any chemicals, the MSDS for the respective chemical must first be consulted for handling, safety and disposal methods. Summaries of the MSDS for CO₂, H₂S, NMP, MEA, and DGA can be found in Appendix A: Safety Analysis. Also in Appendix A are the FTA and HAZOP analysis.

Table 3-1: Chemicals used in this study

Component	CAS number	Supplier	Phase	Supplier purity (wt%)	Density (g.cm ⁻³) at 293.15 K		Refractive index at 293.15 K		Purification
					Literature	Exp ¹	Literature	Exp ²	
CO ₂	214-38-9 ^g	Afrox	Gas	99	N/A	N/A	N/A	N/A	None
H ₂ O	7732-18-5 ^a	Laboratory supply of distilled water ³	Liquid	N/A	0.9982 ^a	N/A	1.333 ^a	N/A	Degassed
NMP	872-69-3 ^b	Merck	Liquid	≥ 99.5	1.03 ^b	1.0333	1.4684 ^b	1.4690	Degassed
MEA	141-07-4 ^c	Sigma Aldrich	Liquid	≥ 99	1.0180 ^c	1.0189	1.4541 ^c	1.4530	Degassed
DGA	929-06-6 ^d	Sigma Aldrich	Liquid	98	1.0572 ^d	1.0469 ^e	1.460 ^f	1.4561 ^e	Degassed

a – d: National Center for Biotechnology Information (2022); e: Recorded at 303.15 K; f: ChemicalBook (2017); g: AFROX (2020); N/A: Not applicable or not measured

1: Anton Paar, DSA 5000M, U(T) = 0.02 K, U(density) = 0.0002 g.cm⁻³

2: Atago, RX-7000α, U(T) = 0.02 K, U(refractive index) = 0.001

3: Produced using a Q5 Ultrapure (Millipore) purifier

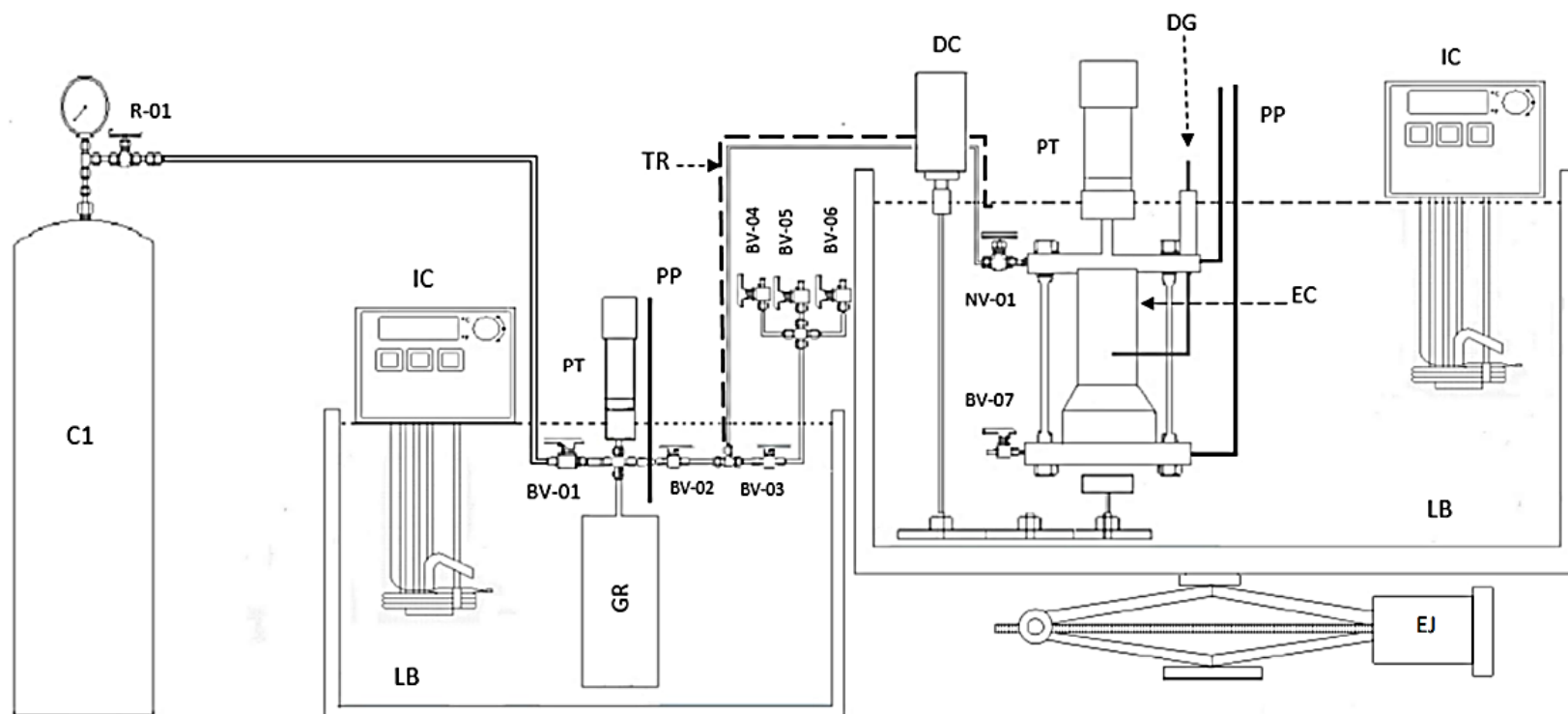


Figure 3-1: Schematic of the static synthetic apparatus. BV: ball valve, C1: Gas cylinder, DC: DC motor, DG: depth gauge, EC: equilibrium cell, EJ: electronic jack, GR: gas reservoir, IC: immersion circulator, LB: liquid bath, NV: needle valve, PP: platinum resistance temperature probe, PT: pressure transmitter, R: regulator, TR: temperature regulation, BV-04, BV-05 and BV-06 are connected to vacuum pump, release cylinder and trap respectively. Extracted from (Ebrahiminejadhasanabadi, 2019)

3.3. Equipment description

A static synthetic apparatus reported by Ebrahimejadhasanabadi (2019) for her PhD thesis was used with a slight modification for solubility measurements in this study. A schematic diagram of the apparatus used can be seen in Figure 3-1, which consists of an equilibrium cell, constructed from a sapphire tube between two 316L stainless steel (SS) flanges, and sealed with two O-rings. The volume of the cell is 43.82 cm^3 . The bottom flange has a single Swagelok ball valve (BV) (1/8" SS, 40G series) for solvent loading and drainage, and the top flange has a single Parker needle valve (NV) (1/8" SS, 10V series) for gas loading and release. The ball valve has a 'dead' volume of 0.035 cm^3 , which was subtracted from the total solvent volume. A depth gauge is fitted on the outside of the equilibrium cell and attached to the top flange. Stirrer blades form part of an internal mixer, which contains a nickel-coated neodymium ring magnet and ceramic ball bearings housed in a 316L SS ring. A direct current (DC) brush motor, with an adjustable DC power supply (MASTECH: HY3005D-3, VA 131008667), is mounted above the housing for the equilibrium cell and runs the internal mixer *via* a magnetic coupling. The equilibrium cell housing is suspended from the top of a large water bath with two glass viewing windows. This housing also holds the drive shaft, gears, and neodymium ring magnet to drive the mixer.

Two modifications were made to the equipment as shown in Figure 3-1 during the course of this study. Dr Nelson changed the stirring brushes and mixer blades detailed in Ebrahimejadhasanabadi (2019) at the end of 2019. The brushes were replaced with a ceramic ball bearing and an additional o-ring due to the brushes wearing down quickly, and the new blades increased the volume. Secondly, an Uninterruptible Power Supply (UPS) was installed so that experiments could be continued during power interruptions. This was connected to the fume hood fan, water baths, data acquisition unit, and DC motor, with the intent to connect the computer at a later stage.

The gas reservoir (316L SS) has a working capacity of 137.09 cm^3 with a 4-way union fitting welded on the top, and is submerged in a small water bath. The working capacity includes the interior reservoir volume, the pressure transmitter, 4-way union fitting, and the volumes of the lines (1/8" 316L SS) and fittings from the ball valve before the gas reservoir (1/4" SS, Swagelok 40G series) to the equilibrium cell fitting. All other ball valves are 1/8" SS Swagelok 40G series.

For the equilibrium cell pressure and temperature measurements, a pressure transmitter (WIKA, P-30, 4 MPa maximum, 0.05% total span accuracy) is sealed in a 1/4" SS pipe fitting welded to the top flange, and there are holes for temperature probes in the flanges. This transmitter is capable of reliably measuring equilibrium cell pressures between 0.1 MPa and 4 MPa. There are two temperature probes

(100 Ω platinum resistance, 316L SS coating) with 90-degree bends, and each is placed in the holes on the top and bottom flanges. The signals from the pressure and temperature sensors are sent to a data acquisition unit (Agilent, 34972A), which is linked to a computer where the pressure and temperature readings are displayed and recorded. For the gas reservoir temperature and pressure measurements, a temperature probe (100 Ω platinum resistance, 316L SS coating) is placed in a hole in the gas reservoir frame, and a pressure transmitter (WIKA, P-30, 2.5 MPa maximum, 0.05% total span accuracy) is fixed in a 1/4" SS pipe fitting connected to the 4-way union fitting. This pressure transmitter is capable of reliably measuring gas reservoir pressures between 0 MPa and 2.5 MPa. The signals from the pressure and temperature sensors are also sent to the data acquisition unit linked to the computer, where all the pressure and temperature readings are displayed and recorded.

Both water baths are filled with distilled water until the gas reservoir or equilibrium cell, fittings and lines are covered, although other temperature control fluids could be used. The temperature of both water baths is set and controlled using an immersion circulator (Grant, TX-150). The water from the gas reservoir water bath is circulated through rubber tubes covering the stainless-steel lines from the gas reservoir to the equilibrium cell to ensure the gas temperature of the working volume is constant.

Auxiliary equipment includes an electric jack, three DC power units, a vacuum pump and glass round-bottom flasks and fittings. The equipment is mounted on a trolley that is housed within a fume hood. The vacuum pump (Edwards, RV3) is used for degassing solvents and evacuating the gas reservoir, equilibrium cell and connecting lines, and the round-bottom vacuum flasks and fittings are used for mixing and loading solvents into the equilibrium cell. A mass balance (Ohaus Explorer, maximum weight 6100 g, readability = 0.01 g) and balancing cylinder are used to determine the mass of liquid in the equilibrium cell. The balancing cylinder is a polyvinyl chloride (PVC) pipe or plastic container used to separate the magnet on the bottom of the equilibrium cell from the weighing plate of the mass balance. A more accurate mass balance (Ohaus Explorer, maximum weight 450 g, readability = 0.001 g) was used to weigh the solvent and round-bottom vacuum flasks before and after mixing.

The density, viscosity and sound velocity of solvents are measured using the Anton Paar densimeter (DSA 5000M) with the Lovis Micro Viscometer (2000ME) attachment. Calibrations are performed by a technician when the units are serviced. The Anton Paar densimeter measures density ($U(\text{density}) = 0.0002 \text{ g.cm}^{-3}$) and sound velocity ($U(\text{sound velocity}) = 0.7 \text{ m.s}^{-1}$) via an isothermal U-tube, and the Lovis attachment measures viscosity ($U(\text{viscosity}) = 0.003 \text{ mPa.s}$) via the 'falling sphere' method. The micro viscometer capillary tubes available are not suitable for the high viscosities of the regenerated solvents. The alternative viscosity measurement apparatus requires a volume of at least 50 cm^3 . This is also not suitable since the total volume of the equilibrium cell is only 43.82 cm^3 .

The refractive index of solvents is measured using the Atago refractometer (RX-7000 α , (U(refractive index) = 0.001) with its own temperature control module. These instruments are available in the third floor Thermodynamics Laboratory in the Chemical Engineering Building at UKZN Howard College campus.

Additional equipment required for H₂S measurements was also researched, and some preliminary sizing was done. This was performed since the original scope of this study was to measure systems with H₂S. This was also one of the proposed objectives for Ebrahiminejadhasanabadi's work. However, there were significant delays that resulted in the change of the scope of this study. The details for the equipment and sizing can be found at the beginning of Appendix A. This equipment was also used to draw up a P&ID, FTA and HAZOP analysis. These items can also be found in Appendix A.

3.4. Experimental methods

3.4.1. Procedure for washing and drying the equilibrium cell

The inside and outside of the equilibrium cell were washed with distilled water before and after running any measurements. The outside of the equilibrium cell was wiped with paper towels and then dried using compressed air. The inside of the equilibrium cell was rinsed with acetone, and then connected to the vacuum pump and evacuated for approximately 10 minutes (when no liquid could be seen in the equilibrium cell).

After performing solubility measurements, the equilibrium cell was removed from the water bath and the outside dried as before. The equilibrium cell was then drained into a beaker and disposed of, and the inside was washed with a suitable wash liquid. Distilled water was used for the amine-water and amine-NMP solvent blends since the solvents and reaction products were readily soluble in water. Acetone was then used to rinse and dry the equilibrium cell after washing thoroughly with water. After rinsing with acetone, the equilibrium cell was connected to the vacuum pump and evacuated for approximately 10 minutes to dry the acetone and check there was no liquid in the joints, O-rings or ball valve.

3.4.2. Leak tests

There were two different types of leak tests performed: a quick test to check for leaks after changing the O-rings and a longer, overnight leak test. After changing the O-rings, the equilibrium cell was filled with CO₂ to its maximum transducer pressure (4 MPa), and then Snoop[®] was used or the cell was immersed in water to check the joints for leaks. All lines that are often connected and disconnected should be regularly checked for leaks.

An overnight leak test was carried out before each set of solubility measurements. This was necessary to determine if there were any slow leaks in the gas reservoir or equilibrium cell. The names of the respective valves can be found in Figure 3-1. The overnight leak test procedure is as follows:

1. The computer and data acquisition unit were switched on.
2. The gas reservoir water bath was set to 50 °C and the equilibrium cell water bath was set to the required temperature. All solubility measurements were carried out at 40 °C, therefore the water bath was set to 40 °C.
3. All valves were closed and all connections checked.
4. The inside and outside of the equilibrium cell were washed as described in Section 3.4.1.
5. The cell was evacuated using the vacuum pump and placed in the housing above the water bath once it had reached the set temperature.
6. The temperature-regulated gas line was connected to valve NV-01, using Teflon (PTFE) thread tape to ensure a proper seal as the ferrule seal becomes damaged/worn-down over time. The two temperature sensors were then put in place and the pressure transducer data cable was connected.
7. Valve BV-03 was opened and all other valves closed, then the vacuum pump was connected to valve BV-04 and the gas lines evacuated.
8. All valves were closed and the vacuum pump disconnected before valve R-01 on the CO₂ cylinder was opened.
9. Valves BV-02 and BV-03 were used to slowly load gas into the gas reservoir, and valve BV-05 was opened several times to ensure there was no air in the lines. Gas was only vented after connecting the lines for the first time. All valves were closed once the required pressure was reached in the gas reservoir.
10. Once equilibrium was reached in the gas reservoir, valve BV-02 was opened and gas was slowly added to the equilibrium cell using NV-01.
11. The valves were then closed, and the water bath was raised using the electronic jack until the top flange of the equilibrium cell was completely submerged.

12. More gas was then added to the equilibrium cell until the highest pressure to be measured in the subsequent solubility test was reached. If the gas reservoir pressure was equal to the equilibrium cell, valve NV-01 was closed and more gas loaded into the gas reservoir.
13. All valves were closed, and the pressure and temperature readings on the computer were observed until equilibrium was reached in the gas reservoir and equilibrium cell.
14. The leak test was left running overnight. The 12-hour leak rate was used to determine if the gas leakage rate was acceptable. It was considered acceptable if it was below 0.05 kPa/hr due to the time required for the solubility tests (Ebrahiminejadhasanabadi, 2019).
15. Once the leak test was completed the following morning, the water bath was lowered, the gas released from the equilibrium cell using valve NV-01 and BV-05, the equilibrium cell was removed from the housing, and the outside of the cell dried. If the leak rate was acceptable, and no water got into the cell when releasing the gas, the cell was evacuated in readiness for the solubility test.

3.4.3. Sensor calibration procedures

The calibrations originally carried out in Ebrahiminejadhasanabadi (2019) were used. These calibrations were then verified in July 2019, and the existing calibrations were used unless stated otherwise. The new equilibrium cell volume was measured after the mixer was changed. The temperature and pressure sensor calibrations were verified if the equipment had not been used for three months, or every three months when using the equipment continuously. The last time these calibrations were verified was the 2nd of March 2021, before the last solubility data were measured. The validity of the temperature and pressure calibrations was tested by performing a test system measurement with a single solvent (NMP). This also ensured sufficient familiarity with the equipment and ensured the correct techniques were developed. A new depth gauge calibration was performed on the 12th of October 2020. There was no need for further verification since it only needed to be verified every six months.

3.4.3.1. Temperature probe calibration

The three temperature probes (T_{101} and T_{102} for the equilibrium cell, and T_{104} for the gas reservoir) were calibrated against a standard digital temperature probe (WIKA instruments, CTH 6500). The temperature probe calibration procedure is as follows:

1. The small water bath was set to 25 °C. The standard probe and the three temperature probes were held together and partially immersed in the water bath.

2. Once the set temperature was reached, and all the temperature probes displayed an almost constant temperature, the readings were recorded for 2 minutes. The average was calculated for each of the temperature probes.
3. The water bath temperature was raised by 5 °C and step (2) repeated until a temperature of 55 °C was reached.
4. The displayed temperature on the standard probe was converted to the true temperature using the probe's calibration chart from WIKA.
5. The temperature of the probe was plotted against the true temperature, and a linear calibration equation was determined for each temperature probe. The uncertainty of each calibration equation ($\partial T_{\text{calibration}}$) was the maximum difference between the calculated and true temperature. These equations were used to calculate the true temperature during solubility measurements.

3.4.3.2. Pressure transducer calibration

Two gauge pressure transducers (P_{121} for the equilibrium cell and P_{122} for the gas reservoir) were calibrated against a standard pressure transmitter (MENSOR CPC 800, 25 MPa), with each pressure transducer calibrated individually. The transmitter pressure is the gauge pressure, and must be added to the measured atmospheric pressure. The pressure transducer calibration procedure is as follows:

1. The respective pressure transducer and standard pressure transmitter were connected to the equilibrium cell or gas reservoir.
2. The valves on the equilibrium cell were opened and the pressure transmitter was set to 'vent' to obtain the atmospheric pressure reading. The pressure transmitter should show zero, but if it does not, this value is taken to be the uncertainty of the transmitter.
3. The pressure transmitter was set to 5 bar (0.5 MPa). Once the pressure transducer reading was constant for approximately 10 minutes, the transducer pressure was recorded for 2 minutes and the average calculated.
4. The set pressure of the pressure transmitter was increased by 5 bar and step (3) repeated.
5. Step (4) was repeated until an equilibrium cell pressure of 35 bar (3.5 MPa) and a gas reservoir pressure of 20 bar (2 MPa) were reached.
6. The pressure of the pressure transmitter was decreased by 5 bar, and step (3) was repeated until atmospheric pressure was reached. The pressure transmitter was then set to 'vent' again and the uncertainty calculated using the maximum correlation deviation. The true pressure was calculated by subtracting the average of the two uncertainties of the pressure transducer determined in this step and step (2).

7. The transducer pressure was plotted against the transmitter pressure, and a linear calibration equation was determined for each pressure transducer. The uncertainty of each calibration equation ($\partial P_{\text{calibration}}$) was the maximum difference between the calculated and true pressure. These equations were used to calculate the true pressure during solubility measurements.

3.4.3.3. Depth gauge calibration

A depth gauge calibration was necessary as each user will read the liquid level slightly differently, which will introduce errors to the results. The liquid level is read by adjusting the gauge until the bottom of the plate is in line with the bottom of the liquid meniscus, and the offset of the top bar is measured using an electronic calliper. The depth gauge calibration procedure is as follows:

1. The large water bath was used to regulate the temperature of the water in the equilibrium cell to ensure an accurate volume was calculated. The water bath was set to 30 °C and the corresponding density of water was obtained from Engineering ToolBox (2003).
2. The equilibrium cell was weighed when it was empty. Distilled water was then added until the level was seen in the sapphire cylinder, and the cell was weighed again.
3. The equilibrium cell was placed in the housing above the large water bath, the two temperature sensors put in place, and the bath raised until the top flange was covered. Care was taken to ensure the handle of the needle valve was not submerged in the water.
4. Once the temperatures had stabilised and been recorded, the liquid level was measured using the electronic calliper.
5. The water bath was then lowered, the temperature sensors removed and the equilibrium cell removed and dried.
6. Steps (2) to (5) were repeated, weighing before and after water was added, until the equilibrium cell was almost full.
7. The average temperature over all the points was used to obtain the density of water at atmospheric pressure from Engineering ToolBox (2003).
8. The true volume was plotted against the depth gauge volume, and a linear calibration equation was determined. The uncertainty of the calibration equation ($\partial V_{\text{calibration}}$) was the maximum difference between the calculated and true volume. This equation was used to calculate the true volume during solubility measurements. The data points were then used to determine an equation that was used in the solubility measurements.

3.4.4. Procedures for adding solvents to the equilibrium cell

Before degassing the solvents and adding them to the equilibrium cell, the computer, data acquisition unit and heater controllers for the water baths were switched on. The water bath temperatures were set and allowed to reach the set temperature before the equilibrium cell was submerged. Since the equilibrium cell has valves only on one side, it is not perfectly balanced. Therefore, when weighing the cell and balancing cylinder, four readings were taken, rotating the cell 90° each time, and the average used as the mass of solvent loaded into the cell. Since it was difficult to balance the round-bottom vacuum flask with attached fittings, and most readings did not stabilise when it was rotated, it was kept on the mass balance in a large beaker and the solvent was added to the flask.

3.4.4.1. Single solvent

The procedure for degassing a single solvent and adding it to the equilibrium cell is as follows:

1. If an acceptable leak rate (0.05 kPa/hr) was obtained after the leak test, a round-bottom vacuum flask and valve and connecting lines were washed and dried. Pieces (b), (d) and (e) as seen in Figure 3-2 and piece (f) as seen in Figure 3-3 were used.
2. The solvent was weighed in the round-bottom vacuum flask before and after adding the solvent using the smaller mass balance.
3. The glass vacuum attachment (pieces (d) and (e) in Figure 3-2) was attached to the vacuum flask using high-vacuum grease.
4. The solvent was degassed using the vacuum pump and vacuum connector, and the vacuum flask closed until the solvent was added to the equilibrium cell.
5. The equilibrium cell was evacuated and then weighed using the balancing cylinder and mass balance.
6. The vacuum line (piece (b) in Figure 3-2) was re-attached to the equilibrium cell and the cell kept under constant vacuum when adding the solvent.
7. The round-bottom vacuum flask was connected to valve BV-07 and the yellow valve opened.
8. Once the solvent (at least) covered the stirrer blades, all the valves were closed and the round-bottom vacuum flask disconnected. The remaining solvent in the round-bottom vacuum flask was kept for density, viscosity, and refractive index measurements.
9. The vacuum line was disconnected from valve NV-01 and the equilibrium cell weighed to determine the mass of solvent added to the cell.
10. Solubility measurements were then carried out according to the procedure in Section 3.4.5.

3.4.4.2. Solvent blend

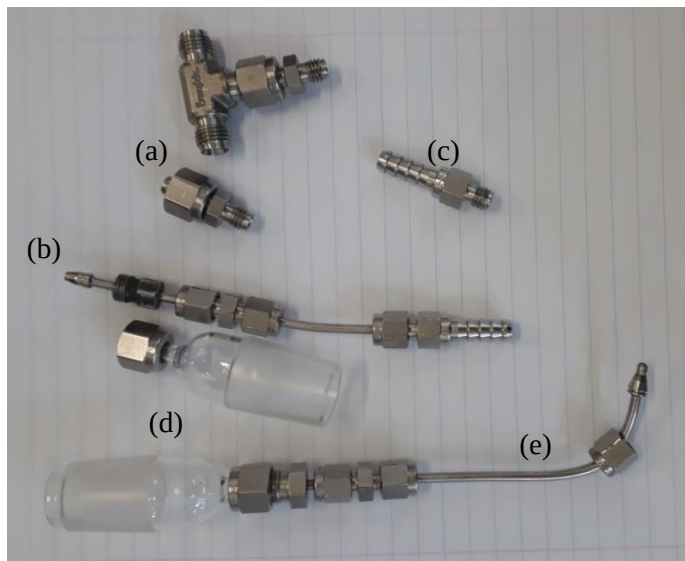


Figure 3-2: Glass fittings and line connectors. (a) T-piece and 1/4"-1/8" reducer; (b) Vacuum line and connector to valve NV-01; (c) Removable vacuum fitting; (d) Glass vacuum seal for round-bottom vacuum flask; (e) Connector to (c) and/or valve BV-07 on the equilibrium cell



Figure 3-3: Setup for mixing two degassed solvents under vacuum, where (f) is the yellow valve for the round-bottom vacuum flask

Each solvent was degassed separately before mixing. A round-bottom vacuum flask, valve, and glass fitting were needed for each solvent. Each solvent was first degassed using the same procedure as steps 1-4 in Section 3.4.4.1. The procedure below for mixing two degassed solvents was then followed.

- 1) Each degassed solvent in its own round-bottom vacuum flask, with all the fittings and under vacuum, was weighed to ensure an accurate final mass was recorded.

- 2) The solvents were mixed according to increasing volatility to reduce solvent evaporation, and the least volatile solvent was placed in the bottom flask.
- 3) The two round-bottom flasks were connected using piece (a) in Figure 3-2. An example of the setup can be seen in Figure 3-3. The gas line with a ball valve was connected to the vacuum pump using piece (c) in Figure 3-2.
- 4) The connecting lines were degassed, and then the ball valve was closed.
- 5) First, the bottom yellow valve was opened, then the top valve opened and the solvents were mixed. The time taken for the solvents to mix depended on the viscosity of the top solvent. Once all the solvent from the top round-bottom vacuum flask had been added to the bottom flask, the yellow valves were closed and the flasks disconnected.
- 6) The mixed solvent was then weighed and the solvent composition calculated.
- 7) As before, the equilibrium cell was evacuated and then weighed using the balancing cylinder and mass balance.
- 8) The vacuum line (piece (b) in Figure 3-2) was re-attached to the equilibrium cell but the valve NV-01 was kept closed.
- 9) The round-bottom vacuum flask was connected to valve BV-07 and the air removed from the connecting lines by opening valve NV-01. This valve was then closed again, but valve BV-07 was kept open.
- 10) As before, the yellow valve was slowly opened and used to control the rate of solvent added to the equilibrium cell. When solvent stopped being drawn into the cell, valve NV-01 was opened and closed to help draw in the solvent.
- 11) As before, once the solvent (at least) covered the stirrer blades, all the valves were closed and the round-bottom vacuum flask disconnected. The remaining solvent was kept for density, viscosity, and refractive index measurements.
- 12) The vacuum line was disconnected from valve NV-01 and the equilibrium cell weighed to determine the mass of solvent added to the cell. The estimated mass of solvent stuck in the ball valve was subtracted from this mass since it did not come into contact with the CO₂ in the equilibrium cell.
- 13) Solubility measurements were then carried out according to the procedure in Section 3.4.5.

3.4.5. Procedure for solubility measurements

It must be noted that the pressure recorded from the pressure sensor is the gauge pressure, therefore the atmospheric pressure must also be recorded for each point and added to the measured pressure.

Before starting this procedure, the equilibrium cell was washed (Section 3.4.1), the overnight leak test completed (Section 3.4.2), the computer, data acquisition unit and heater controllers for the water baths were switched on, and the solvent added to the cell (Section 3.4.4). Depending on the volatility of the solvent or solvent blend, vaporisation can occur when the equilibrium cell is under vacuum and in its housing above and in the water bath. Therefore, it is important to carry out steps 1-5 as quickly as possible to minimise vaporisation. Additionally, gas is added before immersing the equilibrium cell in the water bath to prevent solvent vapourisation as it heats up.

1. The equilibrium cell was placed in its housing and the temperature-regulated gas line connected to valve NV-01 using PTFE thread tape to ensure a proper seal. The two temperature sensors were then put in place and the pressure sensor data cable was connected.
2. Gas was loaded into the gas reservoir as before (steps 7-9 in Section 3.4.2). The temperature and pressure of the gas reservoir were recorded.
3. The water bath was raised using the electronic jack until the bottom flange of the equilibrium cell was covered in water to ensure the stirrer did not splash when it was switched on.
4. A positive pressure is recommended before the water bath is raised to minimise the vapourisation of solvent. The stirrer was switched on, valve BV-02 opened, and valve NV-01 used to slowly add some gas to the equilibrium cell. The voltage on the stirrer was slowly increased until an appreciable vortex is formed. The voltage was different for each solvent and solvent blend, and was set to approximately 4 V for the DGA-NMP blends.
5. The valves were then closed, the stirrer stopped, and the water bath raised until the top flange of the equilibrium cell was completely submerged and the liquid level and depth gauge could be seen through the glass viewing port.
6. The stirrer was started and valves BV-02 and NV-01 were used to add more gas until the required pressure was reached. This process was different depending on the type of solvent. Amine solvents and blends absorbed a lot more CO₂ at low pressures, and sometimes there was not enough gas loaded into the gas reservoir to record the first point. If this happened, the valves were closed, the equilibrium temperature and pressure in just the gas reservoir recorded, more gas was loaded into the reservoir, and the temperature and pressure recorded again before more gas was added to the equilibrium cell.

7. Once the desired pressure was reached, all the valves were closed and the equilibrium temperature and pressure of the gas reservoir recorded. More gas was loaded into the gas reservoir as necessary.
8. Once equilibrium was reached in the equilibrium cell, the stirrer was switched off and the liquid level, temperature, and pressure were recorded. The time taken to reach equilibrium depended on the solvent or solvent blend used.
9. Steps 6-8 were repeated until a sufficient number of points had been recorded. The water bath was lowered and the pressure in the equilibrium cell slowly released using valve NV-01. Depending on the solvent viscosity, the solvent could bubble vigorously and rapidly expand to the top of the cell. This was to be avoided as solvent could get into the pressure sensor and needle valve if it bubbles up too high. Therefore, the pressure was released slowly and in stages until atmospheric pressure was reached.
10. Valve NV-01 was closed, the equilibrium cell removed from the housing, and the outside of the cell dried before draining the solvent. If needed for future tests, the solvent was stored.
11. The inside of the equilibrium cell was then washed as before in Section 3.4.1.

3.4.6. Measuring density, viscosity, sound velocity and refractive index

Where possible, the density, viscosity, and sound velocity were measured using the Anton Paar apparatus with the Lovis micro viscometer attachment. Both were described at the end of Section 3.3. A syringe without a needle was used to add any liquid into the apparatus, and the internal fan was used to purge any liquid from the apparatus. Any liquid purged from the apparatus was discarded of in a conical flask unless a sample was kept for further analysis. Before use, the apparatus was thoroughly cleaned using acetone, and if the discarded liquid was still discoloured, the temperature was set to 40 °C to aid in the cleaning process. After cleaning, the internal fan was switched on to dry the apparatus.

Properties at each of the required temperatures were measured using one sample of approximately 3.5 cm³ for just the density and sound velocity measurements, and one sample of 7 cm³ when viscosity was also measured. After cleaning and drying the apparatus, the sample was added and the temperature was set. Once the set temperature was reached, and the density and sound velocity were recorded. The micro viscometer attachment was not working during most of the experimental investigations. Once the attachment has been repaired, it was found that the glass capillaries available were not suitable for the more viscous liquids such as the DGA-NMP blends before and after use, and before and after regeneration and reuse. Therefore, only two DGA-H₂O solvent blend viscosities could be measured. When measuring the viscosity, the same procedure used for measuring density and sound velocity was followed, but the setting was changed to also measure viscosity.

The refractive index of the solvents before use was measured using the Atago RX-7000 α at the same temperatures as the density, viscosity and sound velocity. The apparatus was cleaned with acetone, then the sample was added, the temperature set and four readings taken once the temperature had stabilised. The average of these readings was then calculated and reported as the refractive index.

3.5. Uncertainty calculations

Whenever data are measured and then used for calculations, there is an uncertainty associated with the data, which needs to be reported. There are different calculation methods depending on the type of data. Temperature and pressure sensors, mass balances, and instruments used to measure density, viscosity and refractive index all have an instrument accuracy or uncertainty quoted by the manufacturer. Calibrations performed for temperature and pressure sensors and depth gauge have an uncertainty determined by the difference between the measured and actual values. Finally, equations used for calculations introduce uncertainties that also have to be calculated and accounted for. The law of propagation of uncertainty is used to account for a number of standard uncertainties for various sources, and is the basis for equations (3-1) and (3-2) (JCGM , 2008). This is beyond the scope of this study, therefore the equations as obtained from Nelson (2012) were used. The methods described by NIST, as also used by Ebrahiminejadhanabadi (2019) and Nelson (2012), were used.

The combined standard uncertainty ($u_c(\theta)$) and the combined expanded uncertainty ($U_c(\theta)$) equations are general expressions for the calculation of uncertainty. The coverage factor k creates an interval within which it is confidently believed that all values of θ will lie. A coverage factor of 2 is typically used, which creates an interval with a 95% confidence interval (Nelson, 2012).

$$u_c(\theta) = \pm \sqrt{\sum_i u_i(\theta)^2} \quad (3-1)$$

$$U_c(\theta) = k u_c(\theta) \quad (3-2)$$

A coverage factor of 2 was used in this study.

The uncertainties used in equation (3-1) depend on the type of data used. There are two types of uncertainties. Type A uncertainties are determined using statistical methods and are not used in this study. Type B uncertainties are determined using other methods and are made up of variables that have an equal likelihood to appear anywhere within the distribution. The rectangular distribution model is the most common and is used for all uncertainties in this study.

The rectangular distribution model is expressed in equation (3-3) as found in Nelson (2012).

$$u_i(\theta) = \frac{b}{\sqrt{3}} \quad (3-3)$$

Where b is half the width of the interval. In this study, the calibration equations for pressure, temperature, volume, and liquid level had a value of b set as the maximum error between the calculated and measured value.

When there are other measured quantities ($\bar{\alpha}_i$), the law of propagation of uncertainty is used, where $u_i(\theta)$ is calculated by combining the standard uncertainties of all measured variables ($u(\bar{\alpha}_i)$) using the root-sum-squares method in equation (3-4) (Nelson, 2012).

$$u_i(\theta) = \sqrt{\left[\left(\frac{\partial \theta}{\partial \bar{\alpha}_1} \right)_{\bar{\alpha}_i \neq 1} u(\bar{\alpha}_1) \right]^2 + \left[\left(\frac{\partial \theta}{\partial \bar{\alpha}_2} \right)_{\bar{\alpha}_i \neq 2} u(\bar{\alpha}_2) \right]^2 + \dots + \left[\left(\frac{\partial \theta}{\partial \bar{\alpha}_n} \right)_{\bar{\alpha}_i \neq n} u(\bar{\alpha}_n) \right]^2} \quad (3-4)$$

Estimates for the uncertainties of the calibrations, water bath temperatures, sensors, measured and calculated volumes, and number of moles can be found in Chapter 4 Section 4.6. More in-depth equations used for the uncertainty calculations can be found in Appendix B.

In summary, the materials, equipment, experimental procedures and uncertainty calculations have been detailed in this chapter. The results of the measured data are presented in Chapter 4, along with the VLE calculation and data regression methods used. The results from the data regression are also presented in the following chapter.

CHAPTER 4: RESULTS AND DISCUSSION

Previous chapters in this dissertation contained literature data pertaining to CO₂ capture and the materials and equipment used in this study. Chapter 2 contained literature reviews on CO₂ capture technologies and common solvents used for CO₂ capture *via* absorption. It was concluded that DGA-NMP blends were promising and had not been well studied in literature, therefore were selected for this study. Also contained in Chapter 2 were the equations used to convert the recorded P-T-z data to P-T- α_{CO_2} data that could then be plotted on a graph, as well as the model selections for data regression for the new DGA-NMP/H₂O data. The PR-EOS was selected with an iterative Newton-Raphson method for conversion of the data, and the Posey-Tapperson-Rochelle model and the PR-EOS with van der Waals-Berthelot mixing rules were used for data regression, the results of which can be seen in this chapter. Chapter 3 contained details of the materials used, a description and diagram of the equipment used, and the experimental procedures followed to record the data presented in this chapter.

This chapter presents the experimental VLE data along with a discussion of the results obtained. Included are the VLE and data regression calculations, and the measured and collected physical properties of the pure solvents and solvent blends. Data modelling was also carried out using the experimental data obtained for the DGA-H₂O and DGA-NMP systems. These results and a discussion thereof can be found with the relevant measured data throughout this chapter.

VLE data are an important tool for characterising the solubility of a gas in a solvent and the behaviour of a solvent blend with varying compositions. It is the first step when considering a solvent for use in any capacity in industry or simulations, as VLE data are required for rigorous distillation, absorption and stripping columns design using McCabe-Thiele methods. As already detailed in Section 3.4.3, a test system was performed to verify the validity of the calibrations and measurement techniques used. This also ensured that data measured for the selected solvents and solvent blends would be valid without having to perform repeatability tests, saving time and chemicals. The data obtained were then compared to literature data for the same system (Bohloul, *et al.* (2014), Chen, *et al.* (2011), Shen & Li (1992), Tong, *et al.* (2012) and Zubchenko, *et al.* (1985)), along with data obtained by the previous user of the equipment (Ebrahiminejadhasanabadi, 2019).

CO₂-NMP was chosen for a test system as there are several literature datasets available, it is a physical solvent (quick to reach equilibrium), and it was readily available in the laboratory. A list of

the test systems and their conditions can be seen in Table 4-1. DGA was chosen since it has similar properties when compared to MEA. Thus, it should be able to be used in current CO₂ capture with only minor adjustments, and it is far less corrosive than MEA. NMP is already used in other physical-chemical solvent blends due to its lower viscosity, as was seen in Table 2-5. Therefore, NMP was selected for mixing with DGA. Finally, DGA-NMP blends were measured, as there have been limited studies performed using these blends. As presented in Table 2-5, there are no published DGA-NMP data available online in 2022. The previous user of the equipment used in this study (Ebrahimejadhasanabadi, 2019) had measured some DGA-NMP blends. The data were obtained from her PhD thesis and were recorded at 40 °C for pressures between 0.262 MPa and 1.893 MPa. The compositions of the solvent blends and their conditions measured in this study can be seen in Table 4-2.

Table 4-1: Overview of test systems measured in this work

System	Solvent Composition	Temperature (°C)	Pressure Range (MPa)
CO ₂ -NMP	NMP = 1	40	0.43-1.60
CO ₂ -MEA(1)-H ₂ O(2)	w ₁ /w ₂ = 0.2960/0.7040	40	0.17-0.74

Table 4-1 lists the test systems and their conditions tested in this work. Pure NMP was first tested to ensure the correct measurement procedures were followed and to verify that data could be reproduced. These results and a discussion thereof can be seen in Figure 4-4. The MEA-H₂O blend was then tested to ensure solvents could be mixed correctly, giving the required composition, and to verify that chemical solvent data could also be reproduced. These results and a discussion thereof can be seen in Figure 4-5.

Table 4-2: Overview of new solvent blends and their conditions measured in this work

System	Solvent Composition	Temperature (°C)	Pressure Range (MPa)
MEA systems			
CO ₂ -MEA(1)-NMP(2)	w ₁ /w ₂ = 0.2990/0.7010	40	0.25-1.46
	w ₁ /w ₂ = 0.1803/0.8197	40	0.30-1.14
DGA systems			
CO ₂ -DGA(1)-H ₂ O(2)	w ₁ /w ₂ = 0.5106/0.4894	40	0.17-1.09
	w ₁ /w ₂ = 0.3998/0.6002	40	0.19-0.87
	w ₁ /w ₂ = 0.3025/0.6975	40	0.23-0.92
DGA systems			
CO ₂ -DGA(1)-NMP(2)	w ₁ /w ₂ = 0.5096/0.4904	40	0.11-0.79
	w ₁ /w ₂ = 0.4001/0.5999	40	0.12-1.14
	w ₁ /w ₂ = 0.3015/0.6985	40	0.16-0.69
Regenerated solvents			
CO ₂ -DGA(1)-NMP(2)	w ₁ /w ₂ = 0.4001/0.5999	40	0.57-1.18
	w ₁ /w ₂ = 0.3015/0.6985	40	0.26-0.92

Table 4-2 lists the new solvent blends and the conditions at which they were measured. The CO₂-MEA-NMP systems were measured first, then the CO₂-DGA-H₂O and corresponding CO₂-DGA-NMP systems were measured, and finally, the regenerated solvent systems were measured.

4.1. Calibration results

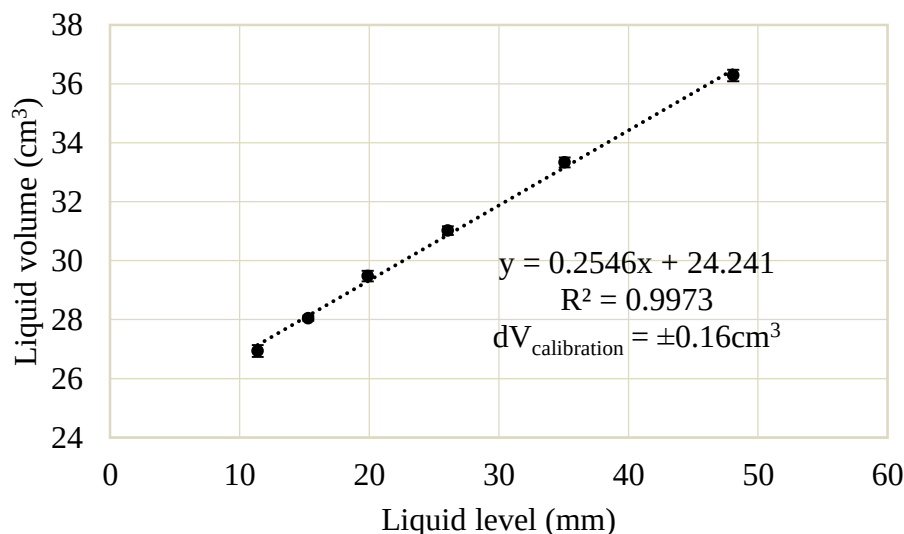


Figure 4-1: Depth gauge calibration graph with error bars

$$V_{liquid}(cm^3) = 0.2546V_{measured} + 24.241; \partial V_{calibration} = \pm 0.16cm^3 \quad (4-1)$$

The depth gauge calibration procedure in Section 3.4.3.3 was followed, and the graph in Figure 4-1 was generated using the recorded information. The resulting equation, seen in equation (4-1), was used to calculate the liquid volume in the equilibrium cell at each equilibrium point for all test systems and new solvent blend systems. The deviation from the measured volume was calculated for each point. This was calculated by finding the absolute difference between the measured volume and the volume calculated using equation (4-1). This is shown as the error bars in Figure 4-1. The average of these differences gave the overall $\partial V_{calibration}$. Figure 4-1 shows a linear trend as expected, as calibration plots typically have a linear trend. Although the $\partial V_{calibration}$ was higher than expected, when used for the CO₂-NMP test system it gave results acceptable when compared to those recorded by Ebrahimejadhanabadi (2019), as shown in Figure 4-4. Therefore, it was acceptable to use the derived equation to calculate volume in the other measurements performed in this study.

As stated in Section 3.4.3, the results obtained previously for the temperature and pressure calibrations were used in this study and were verified using the CO₂-NMP test system. These calibration equations for each of the temperature probes and pressure transmitters can be found in equations (4-2) to (4-6). T_{101} , T_{102} and P_{121} are for the equilibrium cell, and T_{104} and P_{122} are for the gas reservoir.

$$T_{101}(^{\circ}\text{C}) = 0.9966T_{\text{measured}} - 2.6427; \partial T_{\text{calibration}} = \pm 0.02^{\circ}\text{C} \quad (4-2)$$

$$T_{102}(^{\circ}\text{C}) = 0.9966T_{\text{measured}} - 2.2418; \partial T_{\text{calibration}} = \pm 0.02^{\circ}\text{C} \quad (4-3)$$

$$T_{104}(^{\circ}\text{C}) = 0.9986T_{\text{measured}} - 1.2531; \partial T_{\text{calibration}} = \pm 0.01^{\circ}\text{C} \quad (4-4)$$

$$P_{121}(\text{bar}) = 1.0016P_{\text{measured}} - 0.0314; \partial P_{\text{calibration}} = \pm 0.009\text{bar} \quad (4-5)$$

$$P_{122}(\text{bar}) = 1.0007P_{\text{measured}} - 0.0076; \partial P_{\text{calibration}} = \pm 0.001\text{bar} \quad (4-6)$$

4.2. Calculations

4.2.1. VLE calculation methods for measured data

When performing VLE calculations using the measured data, it was assumed that the volume of DGA, NMP and MEA in the vapour phase were negligible. This assumption is reasonable due to the pressure range used for experimental measurements (0.1 – 1.5 MPa). Thus, it was assumed that only CO₂ was present in the vapour phase. This assumption was verified by comparing the vapour pressures of MEA, H₂O, DGA and NMP. The vapour pressures are as follows: MEA at 20°C = 5.3×10⁻⁵ MPa; H₂O at 0°C = 8.15×10⁻² MPa; DGA at 20°C < 1.33×10⁻⁶ MPa; and NMP at 25°C = 4.6×10⁻⁵ MPa (National Center for Biotechnology Information, 2022). The vapour pressure of water at 40°C was subtracted from the equilibrium cell pressure to obtain the true pressure, but was not included in the vapour phase composition as it was considered a diluent that did not react with CO₂. A flash calculation was performed in Aspen to verify the validity of the assumption that only CO₂ is present in the vapour phase. This was performed in Aspen (2015) using a Flash Vessel and the PR-EOS for the 51.06 wt% DGA–48.94 wt% H₂O blend at pressures between 0.1 MPa and 1.5 MPa. The mole fraction of H₂O in the vapour phase was found to be 0.06 at 0.1 MPa, 0.013 at 0.5 MPa, 0.007 at 1 MPa, and 0.005 at 1.5 MPa. Since these fractions were so low, the assumption that only CO₂ is in the vapour phase at equilibrium is valid.

VLE calculations depend on how many components are present. Due to the nature of the measured data, the virial PR-EOS (2-7) was used with the Newton-Raphson numerical root-finding method. The calculation of the compressibility factor, *Z*, requires iterative calculations with an initial estimate for *Z*, hence iterative calculations were enabled in Excel for simplified calculations. In order to use the virial PR-EOS, it must be assumed that the volumes of the liquid components in the vapour phase are negligible. Therefore, it was assumed that only CO₂ is present in the vapour phase, i.e. only one component is present. This assumption holds for low-pressure measurements (Ebrahimejadhasanabadi, 2019). A flow diagram of the calculation method used can be seen in

Figure 4-2, with additional required equations stated on the following page. Whenever calculations are performed using measured data, the associated uncertainty must be calculated. These calculations can be found in Section 3.5.

Solubility measurements using the static synthetic technique were carried out by loading gas into the equilibrium cell, recording the equilibrium T, P and liquid volume, and then loading more gas. Using this technique, the number of moles loaded into the cell each time must be calculated. The number of moles of CO₂ loaded into the equilibrium cell was obtained using equation (4-7) after calculating $n_{GR,before}$ (number of moles in the gas reservoir (GR) before loading into the equilibrium cell) and $n_{GR,after}$ (number of moles in the GR after loading into the equilibrium cell), where 1 is before loading and 2 is after loading.

$$n_{loaded} = n_{GR,before} - n_{GR,after} = \frac{P_1 V_{GR}}{R Z_1 T_1} - \frac{P_2 V_{GR}}{R Z_2 T_2} \quad (4-7)$$

$$n_{total\ loaded} = n_{loaded} + n_{total\ previously\ loaded} \quad (4-8)$$

The number of moles of CO₂ in the vapour and liquid phases in the equilibrium cell at equilibrium was then determined after calculating the compressibility of the vapour phase (Z_v) in the equilibrium cell at equilibrium.

The volume of gas in the vapour phase (V_v) was calculated using volume of liquid in the equilibrium cell (V_{liq}), which was previously calculated using calibration equation (4-1).

$$V_v = V_{cell} - V_{liq} \quad (4-9)$$

Where V_{cell} is the volume of the equilibrium cell. The number of moles of CO₂ in the vapour phase was then calculated.

$$n_{CO_2,v} = \frac{y_{CO_2} P_{eq} V_v}{R Z_v T_{eq}} \quad (4-10)$$

The number of moles of CO₂ absorbed in the liquid phase at equilibrium can then be calculated.

$$n_{CO_2,L} = n_{total\ loaded} - n_{CO_2,v} \quad (4-11)$$

If it was a pure solvent, the composition (x_{CO_2}) was calculated using equation (4-12) below.

$$x_{CO_2} = \frac{n_{CO_2,L}}{n_{solvent}} \quad (4-12)$$

If it was a solvent blend, the CO₂ loading (α_{CO_2}) was calculated using equation (4-13).

$$\alpha_{CO_2} = \frac{n_{CO_2,L}}{n_{amine}} \quad (4-13)$$

Other equations needed for the VLE calculations include the calibration equations for the liquid volume and the temperature and pressure sensors, and can be found in Chapter 3 Section 3.4.3.

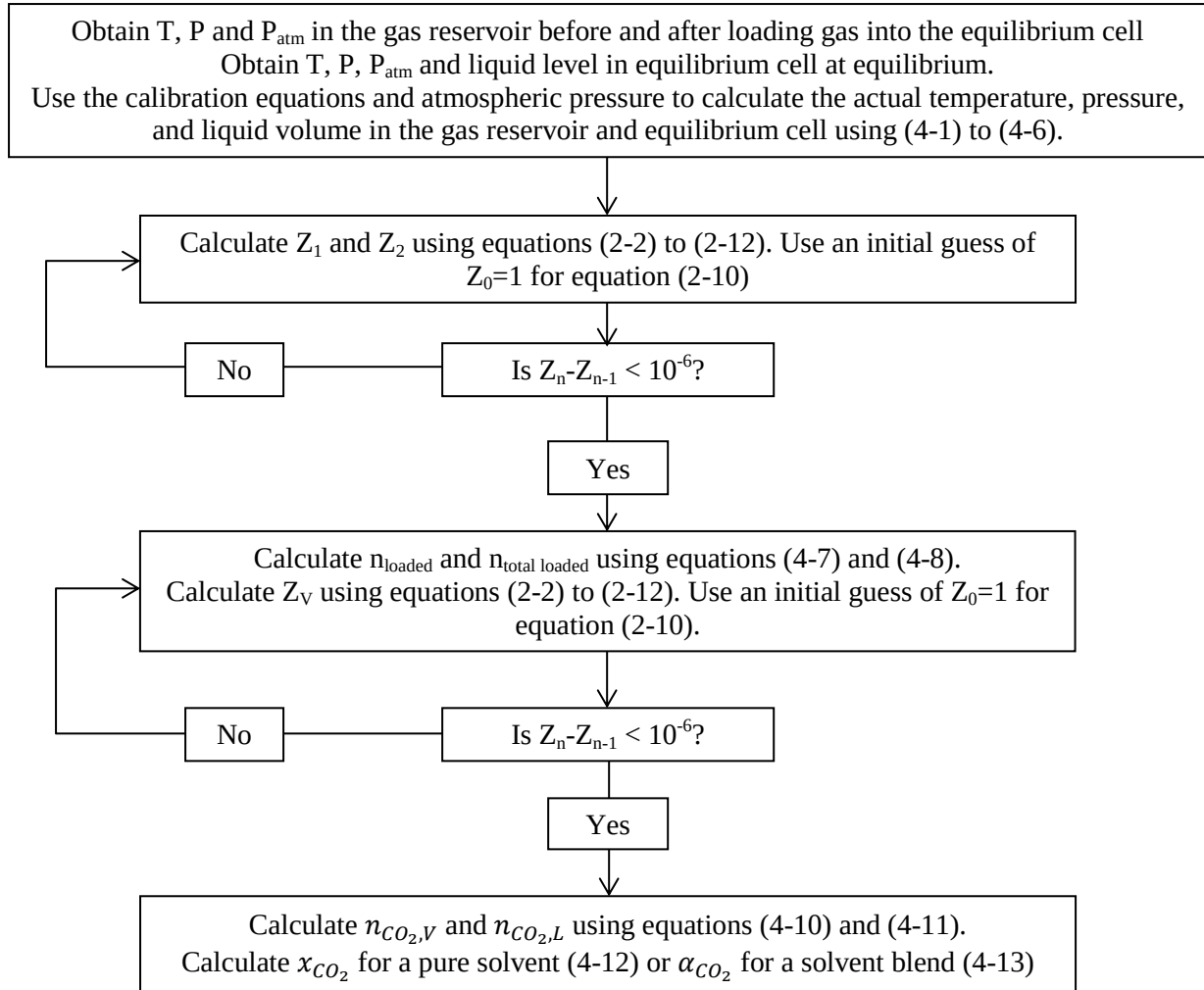


Figure 4-2: Flow diagram for VLE calculations

The calculation methods for a pure solvent and a solvent blend are essentially the same, with the differences outlined in Table 4-3.

Table 4-3: Calculating CO₂ in the liquid phase for pure solvent vs. solvent blend

Pure solvent	Solvent blend
The number of moles of the pure solvent in the equilibrium cell is calculated	The number of moles of each solvent in the equilibrium cell is calculated
The mass of solvent in the EC ball valve BV-07 is calculated using the density of the pure solvent	The mass of solvent in the EC ball valve BV-07 is calculated using the approximated mixture density $\rho_{mix} = \rho_1 x_{m,1} + \rho_2 x_{m,2}$, where x_m is the mass fraction
The X-axis values are calculated as follows: $x_{CO_2} = \frac{n_{CO_2,L}}{n_{CO_2,L} + n_{solvent}}$	The X-axis values are calculated as follows: $mol_{CO_2}/mol_{amine} = \alpha_{CO_2} = n_{CO_2,L}/n_{amine}$

4.2.2. Data regression

Data regression was performed using the measured solvent composition data and the selected model to predict the system pressure for a specified solvent loading. These composition data were obtained using the measured data, the VLE calculation method detailed in Section 4.2.1, and the selected models detailed in 2.8.2. When developing the PR-EOS section of the MATLAB[®] code, the mixing rules from Bohloul, *et al.* (2014) were initially used, where the absorption of CO₂ into NMP was modelled. When running the code with these mixing rules, the PR-EOS section of the code gave a combined calculated pressure that varied greatly compared to the experimental pressure. A possible reason for this is that there are too few parameters, as there is also DGA in the mixture. Another possible reason is an error in the code, but this was checked and ruled out. As a result, more-complex mixing rules were investigated. The van der Waals-Berthelot mixing rules were selected using the rationale covered at the end of Section 2.8.1.

When performing data regression, the absolute average deviation (AAD) and average absolute relative deviation (AARD) for the modelled pressure are also calculated. These were calculated using equations (4-14) (Ebrahimejadhasanabadi, 2019) and (4-15) (Bohloul, *et al.*, 2014) respectively.

$$AAD = \frac{1}{N} \sum_{i=1}^n |P_{calc} - P_{exp}|_i \quad (4-14)$$

$$AARD(\%) = \frac{100}{N} \sum_{i=1}^n \left| \frac{P_{calc} - P_{exp}}{P_{exp}} \right|_i \quad (4-15)$$

Where P_{calc} and P_{exp} are the calculated (modelled) and experimental (measured) pressure of CO₂ in the vapour phase.

Figure 4-3 shows the calculation procedure followed when the Posey code file is run. The corresponding descriptions of the MATLAB® code files and functions can be found in Appendix C: MATLAB® Files. The key equations referenced in Figure 4-3 and used in the MATLAB® file named Posey_modelling are as follows:

$$n_{CO_2,d} = n_d \frac{n_{d,before} \frac{x_{CO_2,before}}{x_{d,before}}}{n_{d,before}} \quad (4-16)$$

Where $n_{CO_2,d}$ is the number of moles of CO₂ in the diluent

n_d is the number of moles of diluent

$x_{d,before}$ is the mole fraction of the diluent before loading more CO₂

$x_{CO_2,before}$ is the mole fraction of CO₂ in the solvent before loading more CO₂

$$n_{CO_2,s} = n_s \frac{x_{CO_2}}{1-x_{CO_2}} \quad (4-17)$$

Where $n_{CO_2,s}$ is the number of moles of CO₂ in the solvent

n_s is the number of moles of solvent

x_{CO_2} is the mole fraction of CO₂

$$n_{CO_2,a} = n_{CO_2,s} - n_{CO_2,d} \quad (4-18)$$

Where $n_{CO_2,a}$ is the number of moles of CO₂ in the amine

After performing the data regression, the parameters in equation (2-18) to (2-21) were then substituted into equation (2-1) to calculate the pressure at each point, $P_{calc,PR-EOS}$.

The error from the PR-EOS with mixing rules was also calculated using equation (2-25), where the calculated pressure is now the combined CO₂ partial pressure from both models. The combined CO₂ partial pressure from both models at each point is calculated using equation (4-19) below, where the pressure from each model is weighted using the overall mole fraction of the respective component.

$$P_{calc} = P_{calc,Posey} \frac{n_{DGA}}{n_{DGA}+n_{H_2O}+n_{NMP}} + P_{calc,PR-EOS} \frac{n_{NMP}}{n_{DGA}+n_{H_2O}+n_{NMP}} \quad (4-19)$$

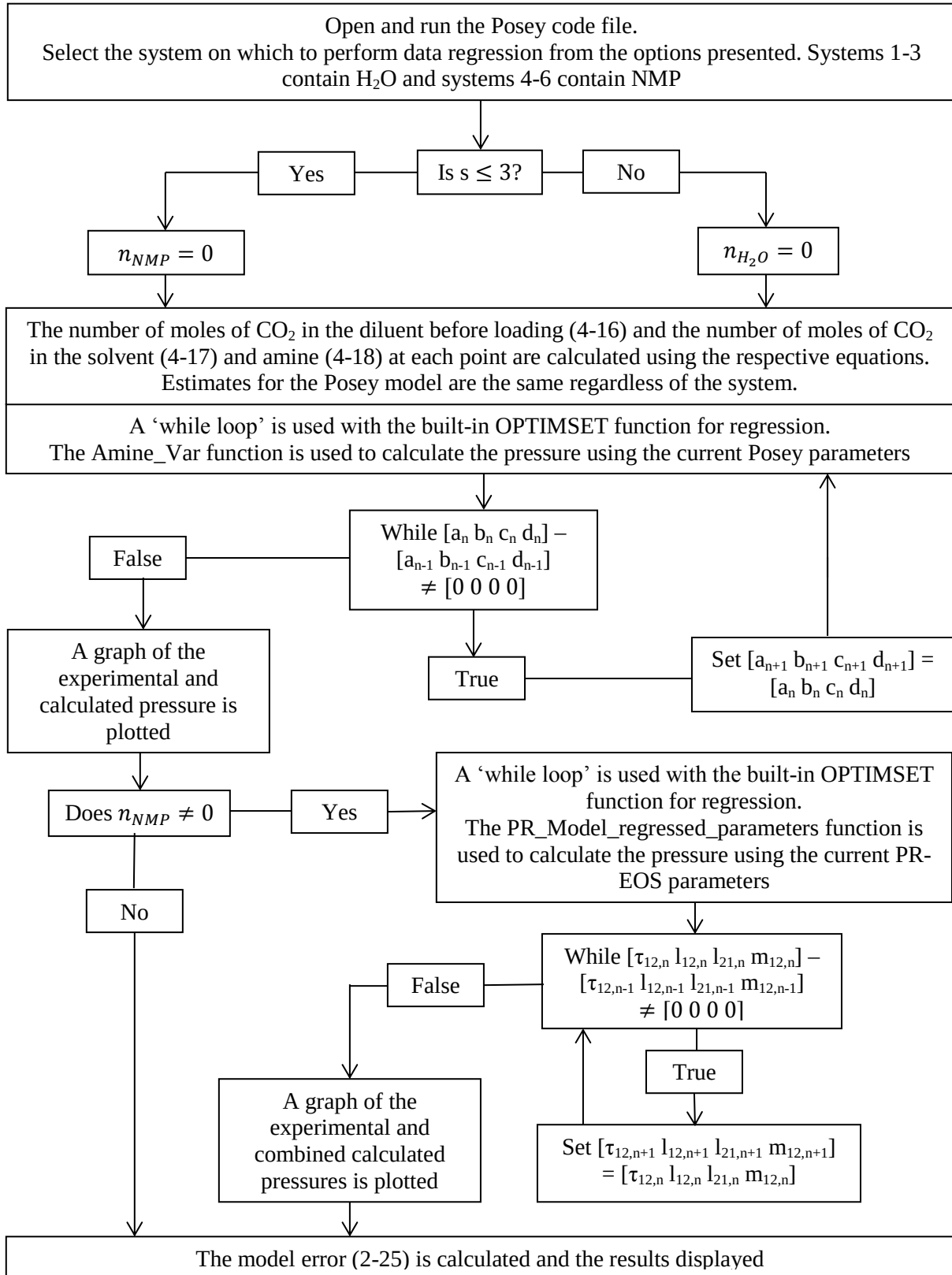


Figure 4-3: Calculation method for performing data regression

4.3. Test systems

4.3.1. CO₂-NMP test system

NMP is a physical solvent used in the Purisol® process licensed by Lurgi. It is a physical solvent, so it absorbs CO₂ quickly and is easily regenerated by flashing to atmospheric pressure or degassing under vacuum (Vega, *et al.*, 2018). NMP was selected as a test system since it is used in some industries for CO₂ capture, it absorbs CO₂ quickly, is often used for research work in laboratories, and there are extensive data available in various journals (Ebrahimejadhasanabadi (2019), Bohloul, *et al.* (2014) and Rajasingam, *et al.* (2004)). This measured data, along with the uncertainties, can be found in Table D-1 in Appendix D. The error bars are too small to be seen in Figure 4-4, therefore the system uncertainties for the CO₂-NMP systems measured in this study on 8 October 2020 and 2 March 2021 are $U(x_{CO_2}) = 0.31\%$ and $U(x_{CO_2}) = 0.15\%$ respectively.

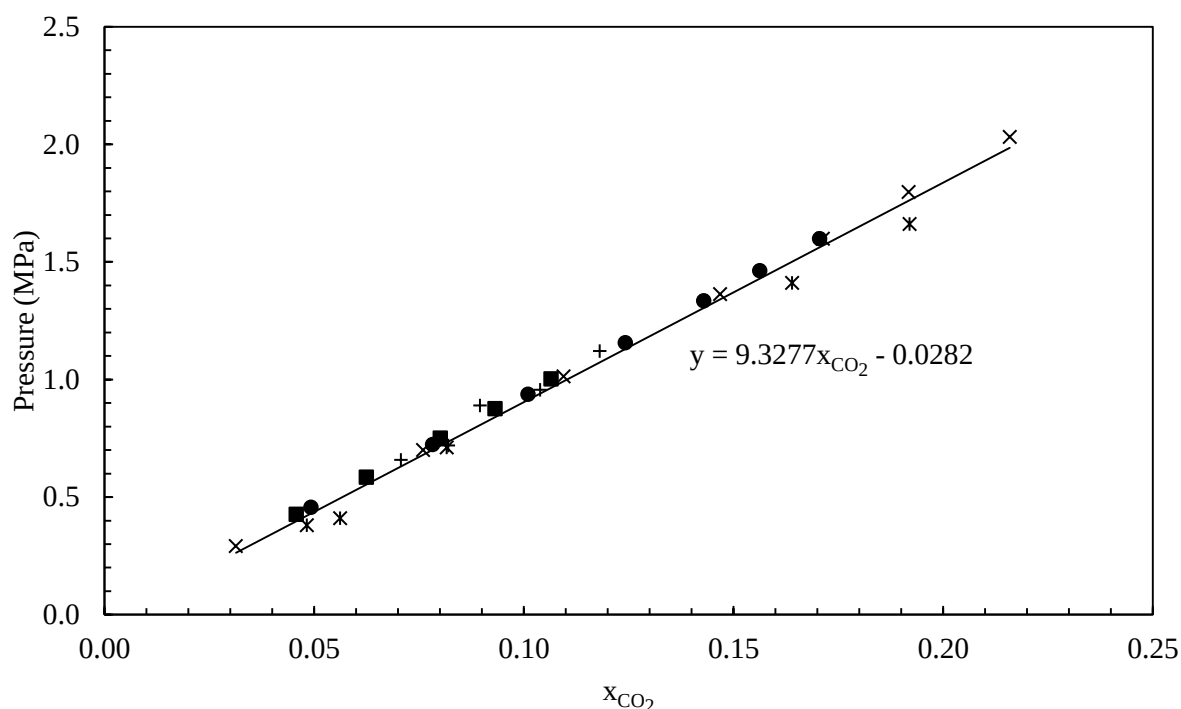


Figure 4-4: Solubility data of CO₂ in NMP at 40 °C. ● This work (8/10/2020), ■ This work (2/03/2021), × Ebrahimejadhasanabadi (2019), + Bohloul, *et al.* (2014), * Zubchenko, *et al.* (1985). The trendline for the combined literature data is shown as a solid line.

As seen in Figure 4-4, the data measured at different times compared favourably with data measured by Ebrahimejadhasanabadi (2019). This was to be expected, as the same equipment and experimental procedures were used. The fact that the new data compared favourably to Ebrahimejadhasanabadi (2019) was also used to verify the validity of the sensor calibrations. The measured data also compared favourably with Bohloul, *et al.* (2014) for most pressures. Although, slight differences between the measured data and other literature data from Bohloul, *et al.* (2014) and

Zubchenko, *et al.* (1985) can also be seen in Figure 4-4. The data from Zubchenko *et al.* (1985) shows the most deviation from the measured and literature data. Although all CO₂ solubility in NMP data should be the same due to pure CO₂ and NMP being used, slight differences are to be expected. Possible reasons for this are differences in measurement methods, ambient laboratory conditions, instrument sensitivities, NMP preparation methods, and different chemical suppliers, leading to different gas and solvent purities. Bohloul, *et al.* (2014) measured data with a static synthetic equilibrium cell and a similar experimental technique, but the equilibrium cell had a volume of 320 cm³. The Zubchenko, *et al.* (1985) data was obtained from Ebrahimejadhasanabadi (2019), but the journal article could not be found online. Thus, the measurement methods cannot be compared to the other literature sources here.

The system uncertainties for the literature sources are not available in the cited literature, therefore the root mean square error was calculated. When all the literature data was combined into one dataset and the linear trend line plotted, an equation was obtained as shown in Figure 4-4. This equation was then used to calculate the pressure for each measured x_{CO_2} , and a root mean square error of 10.15% was calculated. Given the variation of the literature data, this error between the literature and measured data is acceptable. Taking into account the differences outlined above, the data obtained for the test system CO₂-NMP showed that the experimental technique employed produced reliable results, and that the sensor calibrations were valid.

4.3.2. CO₂-MEA-H₂O test system

MEA is a chemical solvent commonly used for CO₂ capture from flue gas in various industries. It is a primary amine commonly mixed with water and regenerated by heating in a reboiler or stripping column (Vega, *et al.*, 2018). A test system with a solvent blend of 30 wt% MEA–70 wt% H₂O was measured to ensure the correct mixing procedure was followed, since the procedure for charging the equilibrium cell with a mixed solvent is more complicated. This procedure is detailed in Chapter 3 Section 3.4.4.2, and the tabulated data and uncertainties can be found in Table D-2 in Appendix D.

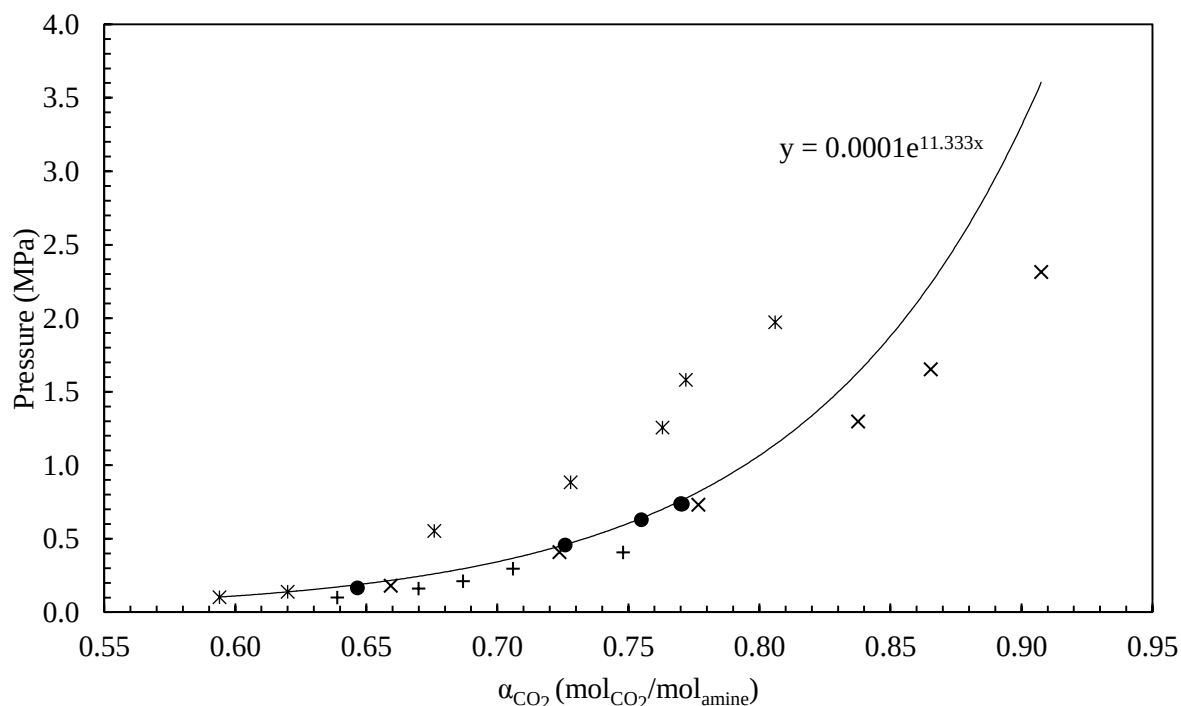


Figure 4-5: Solubility data of CO₂ in MEA(1)-H₂O(2) at 40 °C for $w_1/w_2=0.3/0.7$. ● This work with $w_1=0.2960$, × Ebrahiminejadhasanabadi (2019) with $w_1=0.2965$, + Tong, *et al.* (2012) with $w_1=0.30$, * Shen & Li (1992) with $w_1=0.30$. The trendline for the combined literature data is shown as a solid line.

The error bars are too small to be seen in Figure 4-5, therefore the system uncertainty is stated here instead. The uncertainty for the CO₂-29.60MEA-70.40H₂O system measured in this study is $U(\alpha_{CO_2}) = 0.23\%$. As with the CO₂-NMP test system, it was expected that the data measured would compare well with that recorded by Ebrahiminejadhasanabadi (2019). As seen in Figure 4-5, the measured data are similar to that measured by Ebrahiminejadhasanabadi (2019), who had a system uncertainty of 6.51%. All the datasets show the same exponential trend, which is due to the chemical reactions. At low pressures, most datasets are similar with the differences being more pronounced at higher pressures.

The data published in Shen & Li (1992) does not correlate closely with other literature data (Ebrahiminejadhasanabadi (2019) and Tong, *et al.* (2012)) or the data measured in this study. The discrepancies between the datasets could be due to even only small differences in solvent composition, chemical mixing methods, degassing procedures, chemical and gas purities, and different data collection and processing methods. Different equipment should not have an appreciable effect on the data in Figure 4-5, but the type of equipment used will affect the uncertainty of the data. Tong, *et al.* (2012) measured data using a static analytic apparatus, where a GC was used to analyse the liquid phase. This method could reduce the uncertainty of the liquid phase composition, and subsequently the CO₂ loading, since the only uncertainties are due to the equipment. Shen & Li

(1992) measured data above 0.2 MPa using a static synthetic method in a batch equilibrium cell with a volume of 500cm³ for pressures between 0.2 and 2 MPa. Since this is a larger cell volume, the uncertainty of the liquid phase composition will be higher. This could be why the CO₂ loading at pressures above 0.2 MPa are different to the other literature data presented in Figure 4-5. Pressures below 0.2 MPa were measured using a dynamic analytic, vapour-recirculation equilibrium cell, with the liquid phase analysed using a GC and nitrogen added for very low CO₂ pressures for pressure stabilisation. This method could reduce the uncertainty of the liquid phase composition. This could be why the CO₂ loading for pressures below 0.2 MPa correspond well with the other literature data and the data measured in this study.

The system uncertainty for the literature sources cited could not be accessed since the data was obtained from Ebrahimejadhasanabadi (2019), and only the abstracts could be accessed online. Thus, the literature data was combined into one dataset and the exponential trend line was plotted, as shown in Figure 4-5. This equation was then used to calculate the pressure for each measured α_{CO_2} , and a root mean square error of 24.79% was obtained for the combined literature data. Given the variation of the literature data, this value is acceptable. Taking into account the differences outlined above, the data obtained for the test system of CO₂–30 wt% MEA–70 wt% H₂O showed that the solvent mixing technique that was used produced reliable results.

4.4. CO₂-MEA systems

In this section, measured CO₂-MEA-NMP solubility data are compared to Ebrahimejadhasanabadi's data (previously recorded using the same equipment). The measured CO₂-MEA-NMP data are also compared to the CO₂-MEA-H₂O test system data to evaluate the performance when replacing the H₂O with NMP in the solvent blend. The tabulated data and uncertainties for the CO₂-MEA systems can be found in Table D-2 in Appendix D.

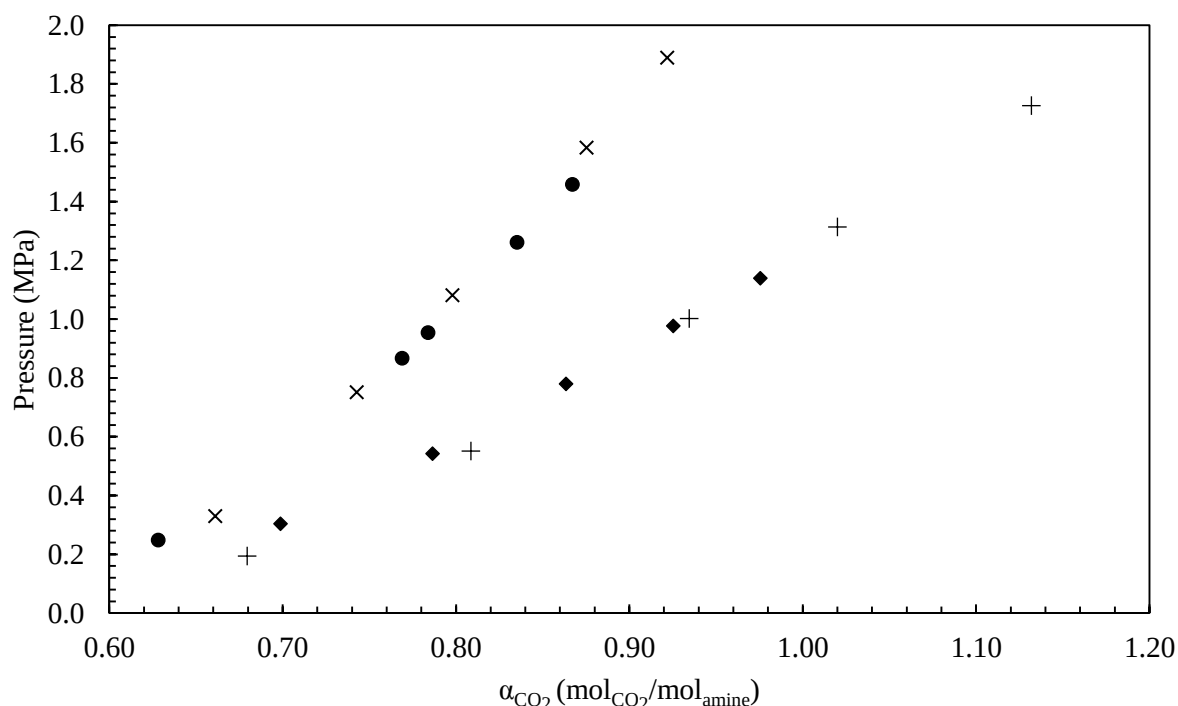


Figure 4-6: Solubility data of CO₂ in MEA(1)-NMP(2) at 40 °C. ● This work with $w_1=0.2990$, ◆ This work with $w_1=0.1803$, × Ebrahiminejadhanabadi (2019) with $w_1=0.3037$, + Ebrahiminejadhanabadi (2019) with $w_1=0.2140$

Figure 4-6 presents measured and literature CO₂ solubility data in MEA(1)-NMP(2) at 40 °C for pressures between 0.19 MPa and 2.30 MPa. The system uncertainties for these blends can be found below Figure 4-7. As seen in Figure 4-6, both solvent blends correlate well with the data recorded by Ebrahiminejadhanabadi. The slight differences in the data are only due to the slightly different compositions. When comparing the measured data at $w_1=0.1803$ and the $w_1=0.2140$ data from Ebrahiminejadhanabadi (2019) in Figure 4-6, the discrepancies between the datasets seem to change as the pressure and CO₂ loading increase, and the measured data seem to have a more linear trend. A more linear trend is due to a higher NMP concentration in the solvent blend, resulting in the absorption being more characterised by physical absorption than chemical absorption.

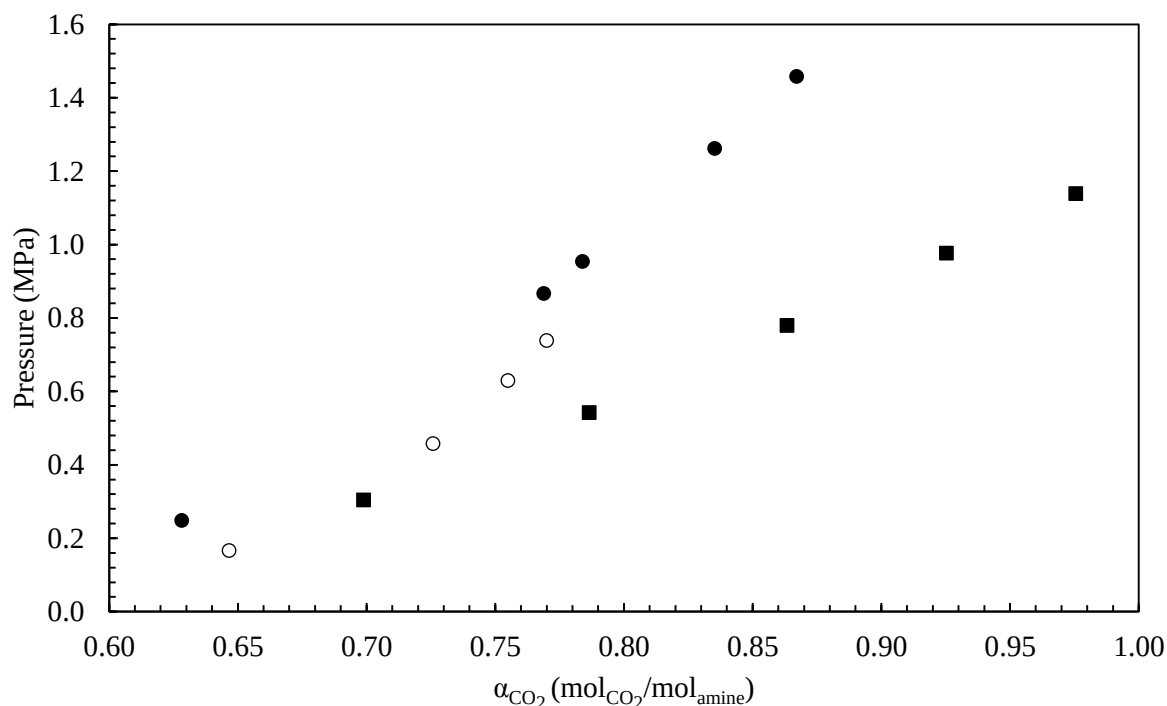


Figure 4-7: Solubility data of CO₂ in MEA(1)-H₂O(2) and MEA(1)-NMP(3) at 40 °C. ○ This work with $w_1/w_2=0.2960/0.7040$, ● This work with $w_1/w_3=0.2990/0.7010$, ■ This work with $w_1/w_3=0.1803/0.8179$

Figure 4-7 presents measured CO₂ solubility in MEA(1)-H₂O(2) and MEA(1)-NMP(3) for pressures between 0.17 MPa and 1.46 MPa. The error bars are too small to be seen in Figure 4-7, therefore the system uncertainties are stated here for reference. The system uncertainties for the CO₂-29.60MEA-70.40H₂O, CO₂-29.90MEA-70.10NMP and CO₂-18.03MEA-81.98NMP systems measured in this study are $U(\alpha_{CO_2}) = 0.23\%$, $U(\alpha_{CO_2}) = 1.39\%$ and $U(\alpha_{CO_2}) = 0.82\%$ respectively.

When comparing all the MEA systems in Figure 4-7, it appears that a higher MEA concentration leads to a more exponential solubility trend. This is expected; as can be seen in Figure 4-4, CO₂ solubility in pure NMP has a linear trend due to physical absorption; therefore, a higher NMP concentration will result in absorption closer to physical absorption, while a higher MEA concentration will show a trend closer to that of MEA-H₂O solvents. When looking at the measured data with $w_1/w_2=0.2960/0.7040$ and $w_1/w_3=0.2990/0.7010$ in Figure 4-7, it appears that replacing water with NMP results in a more linear trend. If the trends for both solvent blends were continued, the water blend would reach its CO₂ saturation point faster than the NMP blend; this shows that NMP absorbs more CO₂ than water. This was expected, as pure NMP is used in industry for high-pressure CO₂ absorption since it easily absorbs CO₂ at high pressures (Wiley VCH, 2015). Finally, the trends for the MEA-NMP blends seem to be a combination of the exponential trend of a MEA-H₂O blend and the linear trend of pure NMP. This is due to chemical absorption occurring at lower pressures and physical absorption only having an observable effect at higher pressures.

4.5. CO₂-DGA systems

DGA is a primary amine, and similar to MEA, it is characterised by relatively fast CO₂ absorption. An advantage of DGA over MEA is that DGA and its reaction products are less corrosive (Kohl & Nielsen (1997), ElMoudir, *et al.* (2012)). After an extensive literature search, it was found that there is little data on CO₂ absorption using DGA-NMP blends (DDBST GmbH Online, 2022). NMP was selected to replace water as it has a higher CO₂ capacity and lower heat of vapourisation (Vega, *et al.*, 2018). There is substantial data available for CO₂ absorption in solvent blends with various amines at 40 °C; therefore it was decided to test these DGA-NMP blends at the same temperature for uniformity, and so that comparisons can be made to these other systems in the future. Data regression was also carried out for the new DGA-NMP/H₂O blends so that the models can be used for simulation work in the future.

4.5.1. CO₂-DGA-H₂O

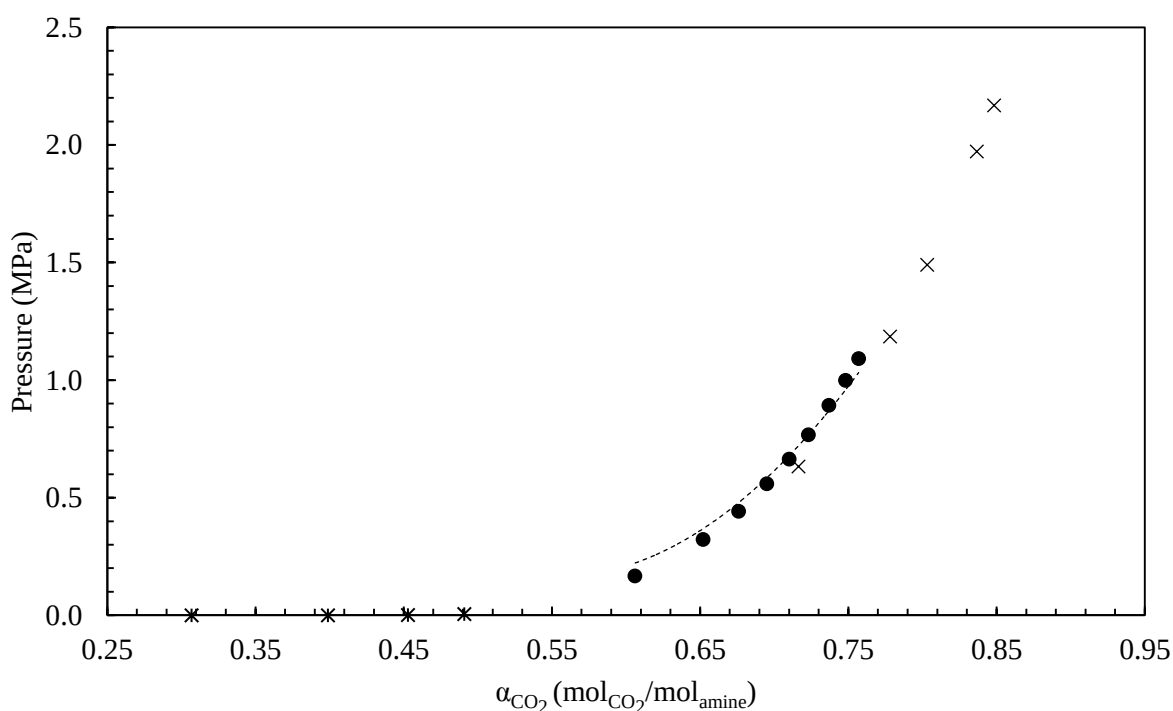


Figure 4-8: Solubility data of CO₂ in DGA(1)-H₂O(2) at 40 °C for $w_1/w_2=0.51/0.49$. ● This work with $w_1=0.5106$, * Chen, *et al.* (2011) with $w_1=0.51$, x Ebrahimejadhasanabadi (2019) with $w_1=0.5132$. Posey-Tapperson-Rochelle model predictions shown by dashed line.

Figure 4-8 presents the measured, literature and modelled CO₂ solubility in DGA(1)-H₂O(2) at 40 °C for pressures between 0.0002 MPa and 2.17 MPa. The tabulated data and uncertainties for the measured data can be found in Table D-3 in Appendix D. The error bars are too small to be seen in Figure 4-8, therefore the system uncertainty for the CO₂-51.06DGA-48.94H₂O system measured in

this study is $U(\alpha_{CO_2}) = 0.49\%$. A discussion of the model predictions can be found in Section 4.5.2 and Section 4.8.

As shown in Figure 4-8, the measured data in this study corresponds well to that recorded by Ebrahimejadhasanabadi (2019), who had a system uncertainty of 5.9%. Although there is not much overlap between the datasets, they seem to have the same trend. The data recorded by Ebrahimejadhasanabadi also seem to fit well with the model predictions. Figure 4-8 includes the results of Chen, *et al.* (2011), which show data at very low pressures ranging from 0.0002 to 0.006 MPa. Such low pressures cannot be measured accurately using the current pressure transducer since it has a limit on vacuum pressure readings. As such, pressures lower than the minimum recorded in Figure 4-9 (0.11 MPa) cannot be reliably reported. Since measured pressures for the system were higher than those recorded by Chen, *et al.* (2011), the two datasets cannot be compared without predicting the data trend. Finally, the measured data seem to have a similar exponential trend as amine-water blends, as previously seen in Figure 4-5. CO₂ absorption in amine-water solvents is characterised by a comparatively large number of moles of gas initially being absorbed, with the moles absorbed decreasing past a particular point for a particular amine. This trend can be seen in Figure 4-8 since the slope of the measured data increases as the number of moles of CO₂ per mole of DGA increases.

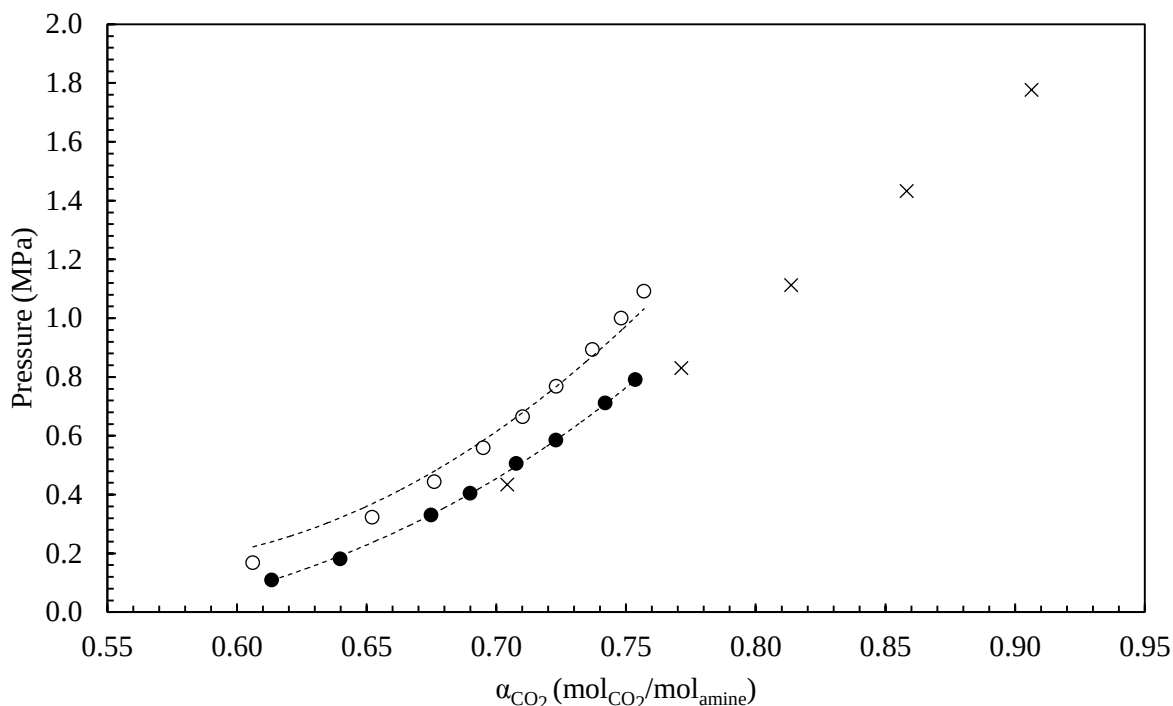
4.5.2. CO₂-DGA-H₂O/NMP

Figure 4-9: Solubility data of CO₂ in DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for $w_1=0.51$ and $w_2=w_3=0.49$. ● This work with $w_1/w_2=0.5096/0.4904$, × Ebrahimejadhasanabadi (2019) with $w_1/w_2=0.4964/0.5036$, ○ This work with $w_1/w_3=0.5106/0.4894$. Posey-Tapperson-Rochelle and PR-EOS combined model predictions shown by dashed line.

Figure 4-9 presents measured, literature and modelled CO₂ loading in DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for pressures between 0.17 MPa and 1.09 MPa. The tabulated data and uncertainties for the measured data shown in Figure 4-9 can be found in Table D-3 in Appendix D. The error bars are too small to be seen in Figure 4-9. The system uncertainties for the CO₂-51.06DGA-48.94H₂O and CO₂-50.96DGA-49.04NMP systems measured in this study are $U(\alpha_{CO_2}) = 0.49\%$ and $U(\alpha_{CO_2}) = 1.38\%$ respectively. A discussion of the model predictions can be found below Figure 4-12 and in Section 4.8.

Figure 4-9 shows that the data measured in this study correlates well with the measured data of Ebrahimejadhasanabadi (2019), who had a system uncertainty of 6.25%. In theory, due to the very close composition, same temperature, and use of a similar equipment, the points should be almost indistinguishable from each other. The difference could be due to the installation of a different mixer in 2019, increasing the equilibrium cell volume, or a slightly different mixing method. Since each person has a preferred procedure when deciding which chemical is added to the other, the actual vs. estimated masses will be slightly different for each person mixing solvents, even if the same apparatus is used.

All datasets in Figure 4-9 can be seen to follow the same exponential trend at lower pressures, regardless of whether water or NMP were used. NMP is more suited to absorption at higher pressures than DGA; this could be why the absorption trend is initially closer to that of DGA in water. The same observation cannot be made when comparing the MEA-H₂O and MEA-NMP datasets in Figure 4-7, since not enough points were recorded at the lower pressures. It would be interesting to observe the performance of other amine blends where water is replaced with NMP and compare that to the DGA-NMP blends measured in this study.

As observed for the MEA-NMP blends, the trends for all the datasets in Figure 4-9 seem to be a combination of the exponential trend of a DGA-H₂O blend and the linear trend of pure NMP. When looking at the measured data with $w_1/w_2=0.5096/0.4904$ and $w_1/w_3=0.5106/0.4894$ in Figure 4-9, the DGA-H₂O system has a slightly lower CO₂ loading than the NMP system at the same pressure. This was expected since NMP absorbs more CO₂ than water, which is why pure NMP is used in industry in the Purisol process (Wiley VCH, 2015). It can also be observed that replacing H₂O with NMP seems to further increase the CO₂ loading for higher pressures; this can be seen in the greater difference in loading between the H₂O and NMP systems as the pressure is increased.

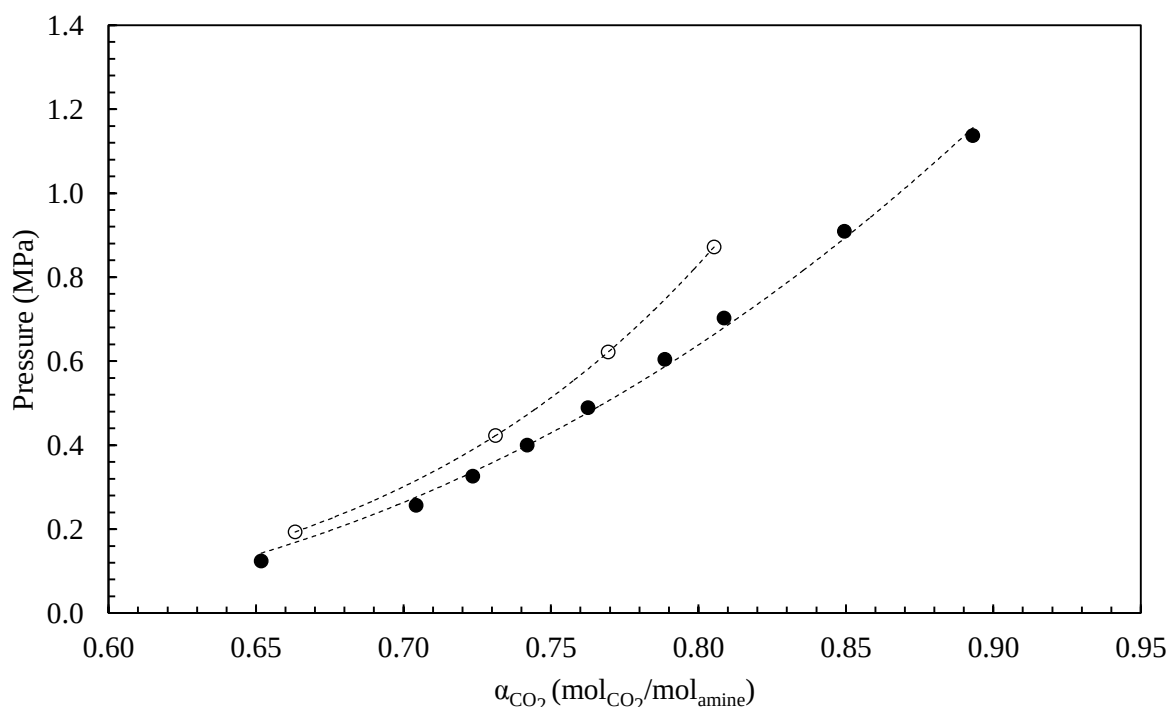


Figure 4-10: Solubility data of CO₂ in DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for $w_1=0.40$ and $w_2=w_3=0.60$. ● This work with $w_1/w_2=0.4001/0.5999$, ○ This work with $w_1/w_3=0.3998/0.6002$. Posey-Tapperson-Rochelle and PR-EOS combined model predictions shown by dashed line.

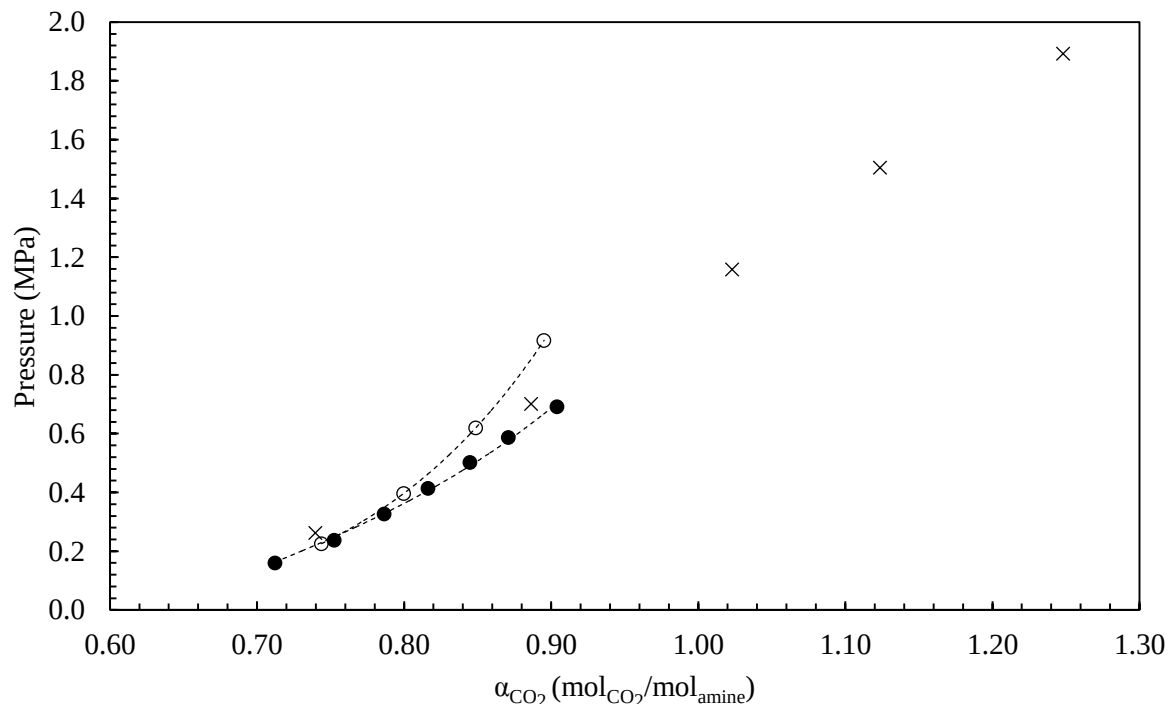


Figure 4-11: Solubility data of CO₂ in DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for $w_1=0.30$ and $w_2=w_3=0.70$. ● This work with $w_1/w_2=0.3015/0.6985$, × Ebrahimejadhasanabadi (2019) with $w_1/w_2=0.3020/0.6980$, ○ This work with $w_1/w_3=0.3025/0.6975$. Posey-Tapperson-Rochelle and PR-EOS combined model predictions shown by dashed line.

Figure 4-10 presents the measured and literature CO₂ solubility in DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for pressures between 0.12 MPa and 1.14 MPa. Figure 4-11 presents the measured, literature and modelled CO₂ solubility DGA(1)-NMP(2) and DGA(1)-H₂O(3) at 40 °C for pressures between 0.16 MPa and 1.89 MPa. The tabulated data and uncertainties for the measured data shown in Figures 4-10 and 4-11 can be found in Table D-3 in Appendix D. The error bars are too small to be seen in both these figures, therefore the system uncertainties are stated here. From Figure 4-10, the system uncertainties for the CO₂-39.98DGA-60.02H₂O and CO₂-40.01DGA-59.99NMP system are $U(\alpha_{CO_2}) = 0.21\%$ and $U(\alpha_{CO_2}) = 1.80\%$ respectively. From Figure 4-10, the system uncertainties for the CO₂-30.25DGA-69.75H₂O and CO₂-30.15DGA-69.85NMP system are $U(\alpha_{CO_2}) = 0.18\%$ and $U(\alpha_{CO_2}) = 1.03\%$ respectively.

As shown in Figure 4-10, the $w_1/w_2=0.3015/0.6985$ data measured in this study correlate well with the $w_1/w_2=0.3020/0.6980$ measured by Ebrahimejadhasanabadi (2019), who had a system uncertainty of 6.44%. Slight differences in the two datasets are due to slight differences in the solvent compositions. These differences solidify the fact that even differences in DGA composition as small as 0.05% can have an effect on the DGA-NMP equilibrium data. As shown in Figures 4-10 and 4-11, the trends for all the DGA-NMP blends seem to be closer to the linear trend of pure NMP than the exponential trend of a DGA-H₂O blend. This effect becomes more pronounced for the blends with a higher NMP

concentration, and is due to the higher concentration and due to NMP absorbing CO_2 at higher pressures. In addition, due to the steeper slope of the DGA- H_2O trend lines, these blends will reach their CO_2 saturation point sooner than the DGA-NMP blends. This is expected, since H_2O does not absorb CO_2 . The DGA-NMP blends also had a higher $\text{mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}$ value at the same pressure when compared to the respective DGA- H_2O blends; this can be seen in Figures 4-9 to 4-11.

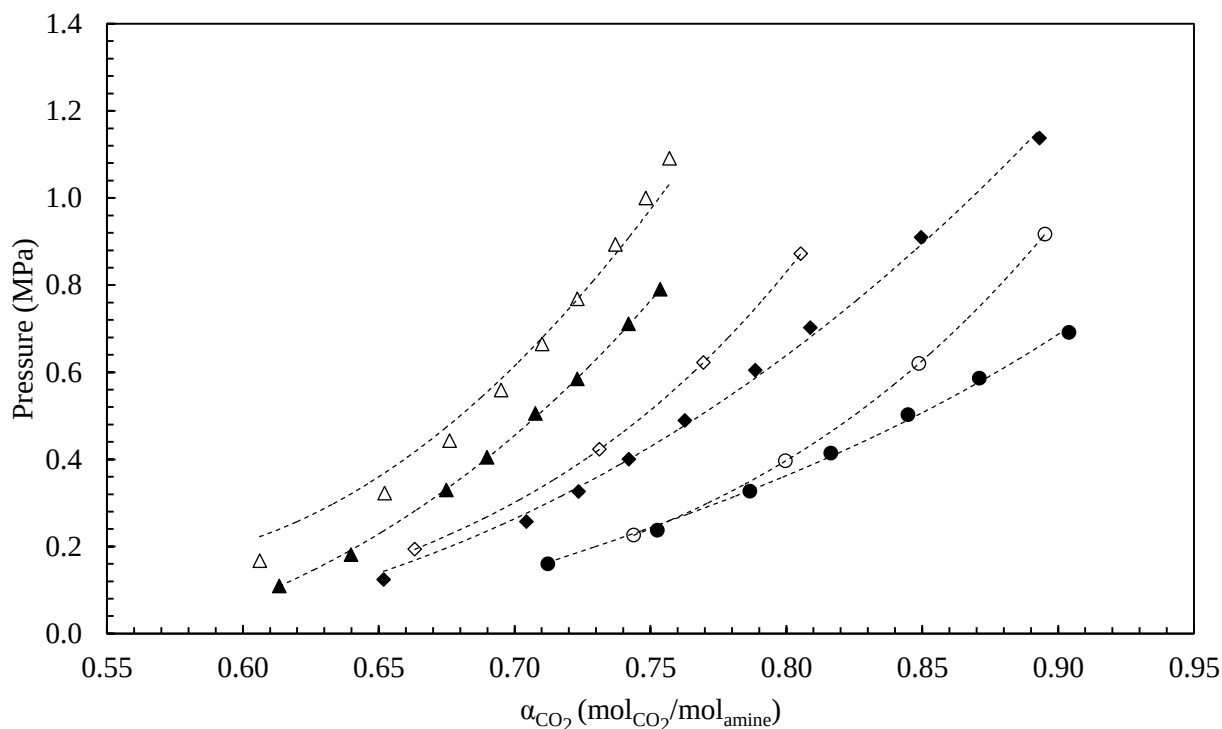


Figure 4-12: Solubility data of CO_2 in DGA(1)-NMP(2) and DGA(1)- H_2O (3) at 40 °C.

▲ $w_1/w_2=0.5096/0.4904$, △ $w_1/w_3=0.5106/0.4894$, ◆ $w_1/w_2=0.4001/0.5999$, ◇ $w_1/w_3=0.3998/0.6002$, ● $w_1/w_2=0.3015/0.6985$, ○ $w_1/w_3=0.3025/0.6975$. Posey-Tapperson-Rochelle and PR-EOS combined model predictions shown by dashed line.

Figure 4-12 presents the measured and modelled CO_2 solubility in DGA(1)-NMP(2) and DGA(1)- H_2O (3) at 40 °C for pressures between 0.11 MPa and 1.15 MPa. The tabulated data and uncertainties for the measured data can be found in Table D-3 in Appendix D. As shown in Figure 4-12, all the DGA- H_2O systems had a lower loading at the same pressure when compared to the respective DGA-NMP system. Since the CO_2 loading is calculated only in terms of moles of CO_2 absorbed per mole of DGA, the amount of CO_2 absorbed by any other solvent present is not shown in these graphs. Since NMP absorbs more CO_2 than water, this would account for the higher loading when comparing the respective DGA-NMP and DGA- H_2O systems.

It can be observed in Figure 4-12 that for both diluents, as the amount of DGA in the blend is increased, the data follows a more exponential trend, with the DGA- H_2O blends having a more exponential trend than their corresponding DGA-NMP blends. As stated in the analysis of Figure 4-7,

the blends with water are expected to have a more exponential trend as water does not absorb CO_2 , so the saturation point will be reached faster than the blends containing NMP. If the datasets continue to follow the trends in Figure 4-12, the DGA-NMP blends will ultimately absorb more CO_2 than the DGA- H_2O blends before the saturation point is reached. Comparing the $w_1/w_2=0.3015/0.6985$, $w_1/w_2=0.4001/0.5999$, and $w_1/w_2=0.5096/0.4904$ in Figure 4-12, an increased NMP composition results in a more linear trend. For solvent blends with a NMP mass fraction greater than 0.5, it can be seen that the trend is almost the same as that of pure NMP.

When performing the experiments for the DGA(1)-NMP(2) systems, it was observed that a higher DGA concentration resulted in a more viscous solvent before and after absorption. It was necessary to keep as much of the solvent as possible for regeneration and retesting (discussed in Section 4.5.3). This became a problem for the $w_1=0.5096/w_2=0.4904$ solvent blend, as it was difficult to add to and remove from the cell. This resulted in solvent loss for this blend, as well as the other DGA-NMP blends that were kept for regeneration and retesting.

An increase in viscosity occurs when CO_2 is absorbed in any water-lean solvent (Wanderley, *et al.*, 2021). A method to decrease the viscosity would be to add water to the blend, and this can be done with the current mixing method in Section 3.4.4.2 by repeating the solvent degassing and mixing step. When mixing more solvents, it is important to mix them in the order of increasing volatility to ensure that the mass recorded is as accurate as possible. To decrease the solvent viscosity, DGA could be mixed with a different solvent with lower viscosity. This could be the basis for future work, where the effect of different diluent solvents on the viscosity of the blend after absorption could be investigated. In terms of the observed solvent viscosity and measured CO_2 loading, the best-performing solvent of the three DGA-NMP blends was the $w_1/w_2=0.4001/0.5999$ blend, with the $w_1/w_2=0.3015/0.6985$ blend a close second. Further investigations to develop quantifiable correlations between solvent viscosity and solvent composition, and solvent viscosity and solvent performance should be carried out.

Comparing the model predictions to the experimental data in Figure 4-12, the DGA(1)- H_2O (3) blend with $w_1/w_3=0.5106/0.4894$ deviates the most from the measured data. Some inaccuracy is expected since the Posey-Tapperson-Rochelle model does not account for the specific CO_2 -DGA reaction mechanisms. The reaction mechanisms between CO_2 and the amine depend on the type of amine (primary, secondary or tertiary). This is not accounted for in the Posey-Tapperson-Rochelle model since the reaction mechanism is reduced to a single, generic reaction, regardless of the type of amine used (Osman, 2014). In addition, higher DGA concentrations lead to a higher equilibrium constant, which affects the equation used for regression of the Posey-Tapperson-Rochelle parameters. These parameters are shown as variables A-D in Table 4-6. Finally, the parameter initialisation figures were

taken from Osman (2014), where they were used for water-lean amine- IL mixtures, so these initial estimates may not be suitable. These initial estimates were not changed since the intent behind the modelling of the experimental data was to provide predictions for the DGA-NMP systems. Furthermore, the Posey-Tapperson-Rochelle model with these parameter estimates performed well for the other DGA-H₂O and DGA-NMP blends. Further discussion of the model parameters, AAD and AARD can be found in Section 4.8.

In summary, CO₂ absorption in DGA-NMP shows promise when compared to the same solvent composition with DGA-H₂O. As a result, varying compositions of the DGA-NMP blends were tested and then compared against the same composition with DGA-H₂O. The best-performing DGA-NMP blends were then regenerated and tested again, then compared to the measured data previously obtained for that specific blend. Regeneration tests would have to be carried out many times, with GC or NMR analysis done on the solvent before and after each regeneration step. This repeated regeneration and reuse of a single solvent blend can be used to determine what reaction products build up over time, the CO₂ remaining after each regeneration, and how long the solvent can be used before the residual CO₂ levels become too high for effective absorption.

4.5.3. CO₂-DGA-NMP solvent regeneration and reuse

Solvent regeneration and reuse was carried out on the 30.15% DGA–69.85% NMP and 40.01% DGA–59.99% NMP (by mass) blends. Since the solvent blends stated in Figure 4-12 contain DGA, a chemical solvent, and chemical solvents absorb more CO₂ than physical solvents, it was decided that solvent regeneration should be carried out by heating under vacuum (Zhang, *et al.*, 2017). This was done by placing the vacuum flask in a water bath set at 50 °C for short intervals to ensure gradual heating, and to make sure that the solvent did not get too hot. The process was stopped using the same criteria used when degassing the pure solvents. The first DGA(1)-NMP(2) blend selected for regeneration was $w_1=0.3015$ since it gave the highest CO₂ loading at the lowest pressure.

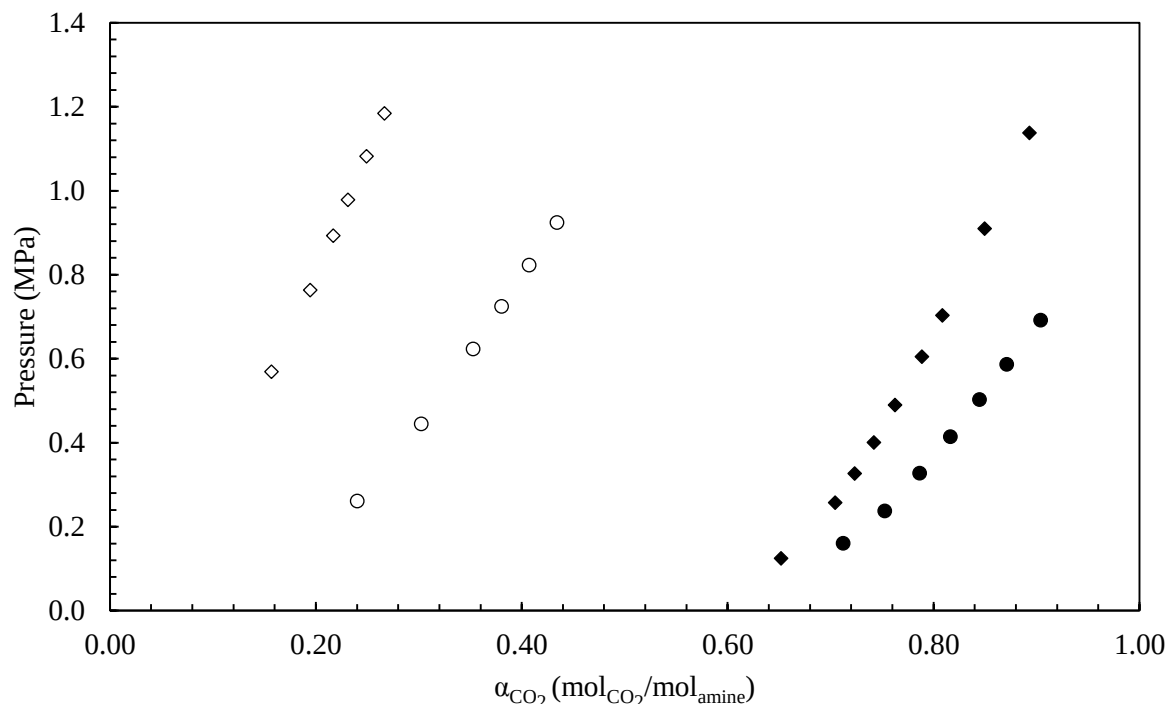


Figure 4-13: Solubility data of CO₂ in regenerated DGA(1)-NMP(2) at 40 °C. ● This work with $w_1=0.3015$, ○ Regenerated $w_1=0.3015$, ◆ This work with $w_1=0.4001$, ◇ Regenerated with $w_1=0.4001$

Figure 4-13 presents measured CO₂ solubility in new and regenerated DGA(1)-NMP(2) blends at 40 °C for pressures between 0.12 MPa and 1.18 MPa. There were problems encountered when regenerating the DGA-NMP solvent blends, as it was difficult to determine from literature the regeneration method for physical-chemical solvent blends. Usually, chemical solvents are regenerated by heating, and physical solvents are regenerated by flashing to atmospheric pressure. Therefore, solvent regeneration was first carried out for the $w_1=0.3015$ blend by heating under vacuum in a round-bottom vacuum flask.

There was an appreciable difference in the liquid level in the equilibrium cell for regeneration by heating under vacuum. This could have certainly resulted in a change in concentration of the solvent blend, hence altering the performance as observed in Figure 4-13. It was critical to determine the cause of the solvent loss because if the composition changed, the regeneration and reuse test results would be invalid. It was therefore decided to test regeneration two ways to determine if the solvent loss was due to evaporation (change in composition) or just general losses in the glassware (unchanged composition). Evaporation results in a change in composition since the solvents evaporate at different rates. This is due to their different vapourisation pressures. Solvent loss in glassware does not result in a change in composition since there is no phase change. The assumption of perfect mixing is then valid. Solvent regeneration was carried out by heating under vacuum ($w_1=0.3015$) and regeneration by degassing under vacuum ($w_1=0.4001$). After regenerating the $w_1=0.4001$ blend, it was

observed that there was still appreciable solvent loss when compared to the initial solvent mass in the equilibrium cell for the testing of CO₂ solubility.

A number of steps were followed when determining the reason for the solvent loss of the regenerated blends (lean solvent) and the subsequent reasons for the results shown in Figure 4-13:

1. The boiling points of NMP and DGA were checked. They were found to be above 200 °C at atmospheric pressure (Sigma-Aldrich (2022) and Sigma-Aldrich (2021)). A pressure-temperature interactive nomograph (Merck, 2022) was used to determine that the vacuum pressure used in the laboratory was not low enough to have a significant effect on the boiling point of the individual chemicals. Therefore, the solvent loss was not due to evaporation.
2. The solvent left in the glassware was then checked. Due to the increased viscosity of the used DGA-NMP blends, it was difficult to retrieve all the solvent from the equilibrium cell after measurements. Solvent was also left behind in each piece of glassware used. Since the solvent loss was due to solvent remaining in the glassware, the composition of the lean solvent did not change.
3. The assumptions used for the VLE calculations were then checked. When performing the VLE calculations, it is assumed that the number of moles of CO₂ initially in the solvent is zero. This assumption holds for the new solvent, but is not valid when using regenerated solvents since there is still some CO₂ in the lean solvent. As a result, the offset in the datasets between the new and regenerated solvents can be attributed to residual CO₂ in the lean solvent. This cannot be accounted for using the current calculation method.
4. Ways to account for the remaining CO₂ in the lean solvents were then investigated. The CO₂ in the lean solvent can be determined using a GC, but that method cannot be used to rectify the data already collected. Instead, the VLE calculations were modified for the regenerated solvents. An initial number of moles of CO₂ was estimated and iterated for until the regenerated solvent results were sufficiently close enough to the new solvent results. In future work, a GC could be used to determine the concentration of CO₂ in the lean solvent.

Using the estimation method stated above, it was estimated that the $w_1=0.3015$ blend (regenerated by heating under vacuum) contained 0.04 mol CO₂ and the $w_1=0.4001$ blend (regenerated by degassing under vacuum) contained 0.065 mol CO₂. The different methods yielded a difference in CO₂ lean loading of 2.5%. Although these values were estimated, it can be concluded that regenerating a mixed solvent by heating under vacuum desorbed more CO₂ than just degassing under vacuum.

4.5.4. Comparison of the CO₂-DGA/MEA-NMP systems

When selecting a possible replacement solvent, it is important to compare the performance of the two solvents at the same temperature, pressure, and composition.

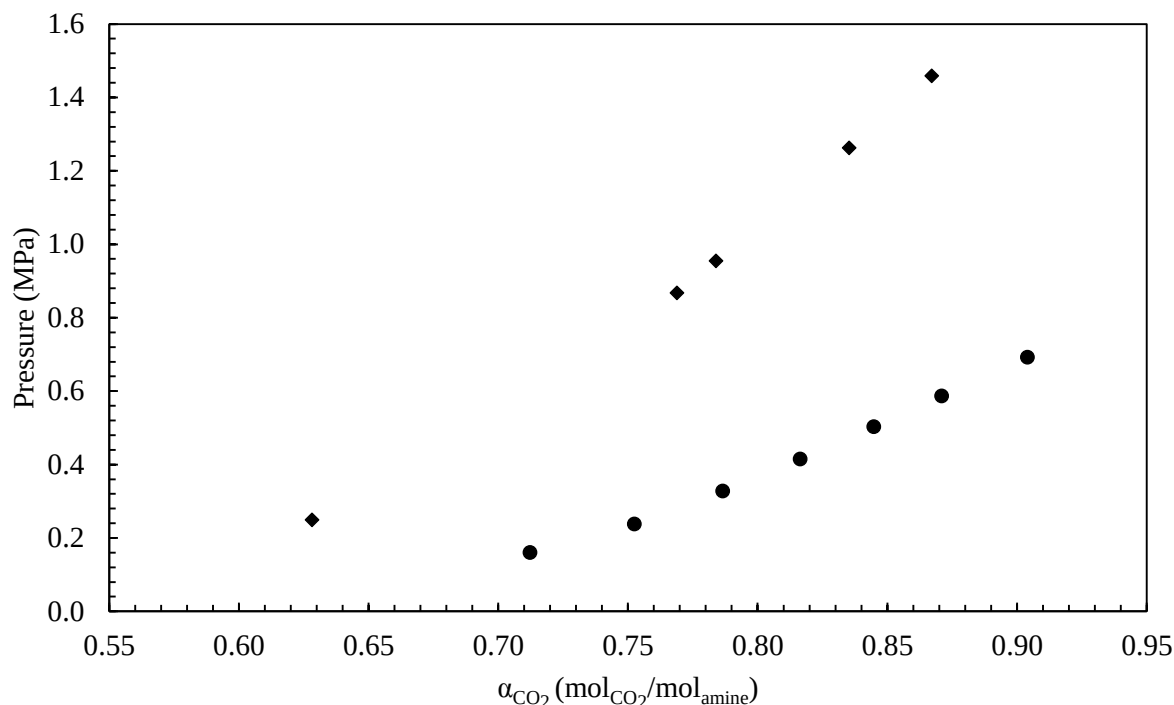


Figure 4-14: Solubility data of CO₂ in MEA(1)-NMP(2) and DGA(3)-NMP(2) at 40 °C.

◆ $w_1/w_2=0.2990/0.7010$, ● $w_3/w_2=0.3015/0.6985$

Figure 4-14 presents measured CO₂ solubility in MEA(1)-NMP(2) and DGA(3)-NMP(2) at 40 °C for pressures between 0.16 MPa and 1.46 MPa. Comparing the MEA-NMP and DGA-NMP systems in Figure 4-14, the loading for the DGA system is much higher for the same pressure compared to the MEA system. The loading is calculated from the number of moles of CO₂ loaded into the equilibrium cell and the height of the liquid level, therefore a higher loading means that more moles of CO₂ were absorbed by the solvent. Therefore, a higher loading at the same pressure means that more CO₂ was absorbed by the DGA system compared to the MEA system. The MEA-NMP system in Figure 4-14 displays a more exponential trend compared to the DGA-NMP system. In amine solvents, larger amounts of CO₂ are initially absorbed, with the number of moles absorbed decreasing as the CO₂ already in the solution increases. Since DGA initially absorbs more CO₂, by the time a similar pressure to the MEA system is reached, DGA has absorbed more CO₂ and the gradient is lower. Comparing the trends of the two systems in Figure 4-14, if the trends continue, the MEA system will reach saturation before the DGA system; as such, DGA should be able to absorb a larger amount of CO₂ overall. Purely based on CO₂ capacity, DGA could be an alternative to MEA, but the heat of regeneration, regeneration studies, and further viscosity studies should be carried out.

4.6. Uncertainties

Uncertainty calculations were carried out for all systems in this study using the method in Chapter 3 Section 3.5, and the equations in Appendix B: Uncertainty Calculations. Estimates for the uncertainties of the calibrations, water bath temperatures, sensors, measured and calculated volumes, and number of moles can be found in Table 4-4. These were estimated using equation (3-3).

Table 4-4: Sources of uncertainty, type of distribution and estimated uncertainty

Source of uncertainty	Distribution	Estimate
Temperature		
Water bath circulator $u(T_{\text{cont}})$ (K)	Rectangular	0.003
Water bath non-uniformity $u(T_{\text{bath}})$ (K)	Rectangular	0.005
Calibration for gas reservoir $u(T_{\text{calib},T104})$ (K)	Rectangular	0.001
Calibration for equilibrium cell $u(T_{\text{calib},T101,T102})$ (K)	Rectangular	0.01
Standard temperature probe $u(T_{\text{standard}})$ (K)	Rectangular	0.01
Pressure		
Calibration for gas reservoir $u(P_{\text{calib},P121})$ (bar)	Rectangular	0.0052
Calibration for equilibrium cell $u(P_{\text{calib},P122})$ (bar)	Rectangular	0.0006
Standard pressure transmitter $u(P_{\text{standard}})$ (bar)	Normal	0.0083
Volume of the gas phase in the equilibrium cell		
Calibration for depth gauge $u(V_{\text{calib}})$ (cm ³)	Rectangular	0.2
Repeatability of volume measurement $u(V_{\text{repeat}})$ (cm ³)	Rectangular	0.12
Total volume of equilibrium cell $u(V_{\text{cell}})$ (cm ³)	None	0.0313
Total composition z_i		
Volume of gas reservoir $u(V_{\text{GR}})$ (cm ³)	None	0.05140
Pressure of gas reservoir $u(P_{122})$ (bar)	None	0.0084
Temperature of gas reservoir $u(T_{104})$ (bar)	None	0.013
Compressibility factor of vapour phase in gas reservoir before and after loading $u(Z_1)$ and $u(Z_2)$	Rectangular	$0.006Z_v$
Liquid phase solubility α_i		
Pressure of equilibrium cell $u(P_{121})$ (bar)	None	0.0098
Volume of gas phase in equilibrium cell $u(V_v)$	None	0.12
Compressibility of vapour phase $u(Z_v)$	Rectangular	$0.006Z_{\text{eq}}$
Temperature of equilibrium cell $u(T_{\text{cell}})$ (K)	None	0.012
Uncertainty of number of moles of solvent $u(n_{\text{solvent}})$ (mol)	None	0.0002

The main results from these calculations were the uncertainty of the overall mole fraction of CO₂ in the system ($U(z_{CO_2})$) and the uncertainty of CO₂ loading in the solvent ($U(\alpha_{CO_2})$). The system uncertainties for each solvent blend can be found in the discussion of the respective figures in the previous sections. The individual uncertainties for each point were too small to be viewed on the relevant figures when they were plotted as error bars. Therefore, the uncertainties for each point in all the systems measured in this study can be found in the respective tables in Appendix D. Graphs of the uncertainties for individual points can be found in Appendix B in Figures B-1 and B-2, along with a brief discussion of the results.

4.7. Density, viscosity, sound velocity and refractive index of all solvents and solvent blends

Table 4-5 shows the experimental, predicted physical properties of the pure chemicals and solvent blends used in this study, along with the literature data for the pure solvents. The properties for some of the blends were not measured due to the unavailability of the Anton Paar apparatus for certain measurements. The excluded blends were 29.60% MEA–70.40% H₂O, 29.90% MEA–70.10% NMP, 18.03% MEA–81.79% NMP, and 51.06% DGA–48.94% H₂O (by mass), and most viscosities were not measured.

Table 4-5: Density, viscosity, sound velocity and refractive index of pure chemicals and solvent blends with NMP(1), MEA(2), DGA(3), and H₂O(4)

Temperature (°C)	Source	Density (g.cm ⁻³) ¹	Viscosity (cP) ²	Sound velocity (m.s ⁻¹) ¹	Refractive index ³
NMP					
20	Experimental	1.033343	-	1566.53	1.4690025
	Aspen	0.010392	2.080199	1524	-
25	Literature ^a	1.027	1.65	-	1.4690
40	Experimental	1.017383	-	1437.2	1.460875
	Aspen	0.01023	1.450282	1524	-
MEA					
20	Experimental	1.01886	-	1734.96	1.453015
	Aspen	0.016634	24.16671	1524	-
25	Literature ^b	1.0180 ^d	18.95	-	1.4541 ^d
40	Experimental	1.003302	-	1669.94	1.44499
	Aspen	0.016385	9.979487	1524	-
DGA					
20	Literature	1.0572 ^c	-	-	1.460 ^e
30	Experimental	1.046854	-	1606.97	1.4560875
	Aspen	9.96E-03	27.31473	1524	-

Table 4-5 continued

Temperature (°C)	Source	Density (g.cm ⁻³) ¹	Viscosity (cP) ²	Sound velocity (m.s ⁻¹) ¹	Refractive index ³
DGA-NMP with w₃/w₁=0.5096/0.4904					
20	Experimental	1.044334	-	1596.15	1.4644175
	Aspen	1.030685	9.403513	1524	-
30	Experimental	1.03577	-	1561.41	1.4599325
	Aspen	1.021792	6.766821	1524	-
40	Experimental	1.02717	-	1527.97	1.456165
	Aspen	1.012821	4.979253	1524	-
DGA-NMP with w₃/w₁=0.4001/0.5999					
20	Experimental	1.040443	-	1583.56	1.465375
	Aspen	1.027611	6.748629	1524	-
30	Experimental	1.031803	-	1514.45	1.4610375
	Aspen	1.018849	5.009729	1524	-
40	Experimental	1.02323	-	1456.27	1.4569375
	Aspen	1.010027	3.796311	1524	-
DGA-NMP with w₃/w₁=0.3015/0.6985					
20	Experimental	1.039244	-	1578.42	1.4665325
	Aspen	1.026298	5.024022	1524	-
30	Experimental	1.035	-	1522.84	1.46205
	Aspen	1.017647	3.834096	1524	-
40	Experimental	1.012746	-	1477.24	1.457785
	Aspen	1.008935	2.982418	1524	-
DGA-H₂O with w₃/w₄=0.3998/0.6002					
25	Experimental	1.036335	4.101	1674.48	1.3876525
	Aspen	2.004548	1.323814	1965.308	-
30	Experimental	1.03322	3.4469	1721.83	1.386125
	Aspen	1.999242	1.173855	1992.374	-
40	Experimental	1.026621	2.5299	1680.83	1.3098175
	Aspen	1.987768	0.937504	2038.337	-
DGA-H₂O with w₃/w₄=0.3025/0.6975					
25	Experimental	1.027434	2.8731	1686.79	1.37352
	Aspen	1.874687	1.173136	1803.676	-
30	Experimental	1.025459	2.6095	1684.7	1.372795
	Aspen	1.870298	1.044594	1824.522	-
40	Experimental	1.019903	1.8766	1650.93	1.3711125
	Aspen	1.860611	0.841049	1858.748	-

a-c: National Centre for Biotechnology Information (2022); d: Data at 20 °C; e: ChemicalBook (2017)
 1: Anton Paar, DSA 5000M, U(T) = 0.02 K, U(density) = 0.0002 g.cm⁻³, U(sound velocity) = 0.7 m.s⁻¹;
 2: Lovis Micro Viscometer, 2000ME, U(T) = 0.02 K, U(viscosity) = 0.003 mPa.s;
 3: Atago, RX-7000α, U(T) = 0.02 K, U(refractive index) = 0.001

Most viscosities for the solvents and solvent blends were not measured since the Anton Paar micro viscometer attachment was offline for an extended period. Once it was repaired, it was found that the capillaries were unsuitable for the viscosities of most solvent blends tested. The other viscometer available required at least 50 cm³, which is greater than the volume of the equilibrium cell. Unfortunately, the Anton Paar with its current setup is unsuitable for the measurement of the properties of chemicals with higher viscosities, therefore the DGA-NMP blends before and after regeneration could not be measured. As a result, the only viscosities measured were two of the DGA-H₂O blends.

As can be seen in Table 4-5, the experimental densities and refractive indices of the pure chemicals were comparable to those in literature. Considering the properties for the DGA(3)-NMP(1) blends, it is observed that a greater NMP mass fraction results in slightly lower density, sound velocity and a slightly higher refractive index. This is expected since NMP has a lower density and sound velocity and a higher refractive index than DGA. Based on these properties, the $w_3/w_1=0.3015/0.6985$ blend is the most favourable. Considering the properties for the DGA(3)-H₂O(4) blends, it is observed that a greater H₂O mass fraction lower density, viscosity and refractive index, but higher sound velocity. The lower values for density, viscosity and refractive index were expected, since these properties are all relative to water. The $w_3/w_4=0.3025/0.6975$ blend shows a decreasing sound velocity with an increasing temperature, following the same trend as the DGA-NMP blends. Conversely, the $w_3/w_4=0.3998/0.6002$ blend does not show a clear trend as the temperature increases. The highest sound velocity is at 30 °C, followed by those at 40 °C and 20 °C. Since there is no clear trend, it is assumed that there were errors with the measurement. These errors could be due to the temperature not stabilising properly before recording the properties, impurities in the water used for the blend, or improper cleaning of the device before starting these measurements.

Aspen and the Elec-NRTL model were used to obtain approximate physical properties at the required temperatures and atmospheric pressure for the pure and mixed chemicals. The Elec-NRTL model accounts for interaction parameters and solution chemistry, whereby all molecular and ionic liquid-phase species are determined. It is a well-developed model that has been used in other industries (Osman, 2011), and is relatively easy to use in Aspen. The Elec-NRTL model was selected as it has been used extensively in literature to predict CO₂ solubility in amine-H₂O blends (Austgen, *et al.* (1989), Austgen, *et al.* (1991), Wappel, *et al.* (2008), Osman (2011)). The Elec-NRTL model was selected in Aspen, and the pure and binary interaction parameters were automatically generated. The mixture properties were then estimated at the same temperatures as the measured properties for the various solvent blends in Table 4-5.

As can be seen in Table 4-5, the Elec-NRTL model did not accurately predict the physical properties of any of the pure chemicals or DGA-H₂O solvent blends, but DGA-NMP blends had the most accurate predictions. Since the measured properties compared favourably with those found in literature, it was determined that the predicted properties were inaccurate. This is most likely due to the use of the automatically generated pure and binary interaction parameters instead of searching for those determined in literature. Furthermore, the 2015 version of Aspen was used, therefore the built-in databases may not be up to date, resulting in sometimes inaccurate results. Finally, if not all the components are entered into Aspen before selecting the property method, some components will be excluded from the pure and binary interaction parameters. Even if these parameters are then cleared and then retrieved again, the programme has problems retrieving all the parameters for the components added after choosing the property method. The Aspen results were merely used as a guideline for the measured physical properties therefore these values were retained.

4.8. Modelling results

As outlined in Chapter 2 Section 2.8.2, the data regression for obtaining the parameters for the Posey-Tapperson-Rochelle and PR-EOS was carried out in MATLAB[®] using the experimental data reported in Section 4.5. The Posey-Tapperson-Rochelle model was used for the DGA-H₂O systems since only chemical absorption occurred. The DGA-NMP systems were modelled using a combination of the Posey-Tapperson-Rochelle model and PR-EOS model with van der Waals-Berthelot mixing rules since they contain hybrid solvents. Thus, the Posey-Tapperson-Rochelle model was used to model the chemical absorption of CO₂ in DGA and the PR-EOS was used to model the physical absorption of CO₂ in NMP. The modelled data can be seen in Figures 4-8 to 4-12 as a dashed line, and the fit of the model for each solvent blend is discussed below Figure 4-12. The regressed model parameters, root mean square error, AAD and AARD can be found in Table 4-6. The calculated model parameters (a, b, c, d) were used for the Posey-Tapperson-Rochelle model and the binary interaction parameters (ℓ_{12} , ℓ_{21} , τ_{12} , m_{12}) were used for the van der Waals-Berthelot mixing rules with the PR-EOS for the respective DGA-H₂O and DGA-NMP blends. As detailed in equation (2-23) in Section 2.8.2, 'a' is an overall correction factor, 'b' is a temperature correction factor, and 'c' and 'd' account for amine concentration in the solvent.

Table 4-6: Model (a, b, c, d) and binary interaction (ℓ_{12} , ℓ_{21} , τ_{12} , m_{12}) parameters for predicting CO₂ solubility in DGA(1)-H₂O(2) and DGA(1)-NMP(3) blends using the Posey-Tapperson-Rochelle and PR-EOS models with van der Waals-Berthelot mixing rules and calculated model error, AAD and AARD

System (wt%)	a	b	c	d	ℓ_{12}	ℓ_{21}	τ_{12}	m_{12}	Root mean square error (%)	AAD (Pressure)	AARD (%) (Pressure)
DGA-H ₂ O with w ₁ /w ₂ =51.06/48.94	-3.73E+03	1.09E+06	-1.12E+05	1.10E+04	-	-	-	-	3.75	98.24	22.69
DGA-H ₂ O with w ₁ /w ₂ =39.98/60.02	8.44E+03	-2.65E+06	-2.11E+03	211.6094	-	-	-	-	0	0	0
DGA-H ₂ O with w ₁ /w ₂ =30.25/69.75	-1.37E+04	4.25E+06	-9.24E+04	8.43E+03	-	-	-	-	0	0	0
DGA-NMP with w ₁ /w ₃ =50.96/49.04	120.0745	-6.53E+04	-3.08E+03	1.07E+03	0.4723	1.70E+12	1.14E+03	71.7358	0.61	13.13	2.94
DGA-NMP with w ₁ /w ₃ =40.01/59.99	-1.81E+03	5.56E+05	-2.39E+03	629.6433	0.5272	2.27E+13	1.30E+03	40.4107	0.99	20.68	6.10
DGA-NMP with w ₁ /w ₃ =30.15/69.85	1.42E+03	-4.54E+05	-3.39E+03	682.8007	0.5018	9.65E+12	1.31E+03	41.2171	0.46	7.22	2.14

As observed in Figure 4-12, the Posey-Tapperson-Rochelle model generally provides adequate pressure predictions when compared to the measured data. Comparing all the DGA-H₂O blends, the model predictions for the 51.06 wt% DGA–48.94 wt% H₂O blend show the most deviation from the measured pressures. Firstly, the model predicts higher pressures than the measured data at lower CO₂ loadings, with the greatest deviation at a loading of 0.61 mol_{CO₂}/mol_{amine}. The model then predicts the same pressure as the measured data at 0.72 MPa and a loading of 0.72 mol_{CO₂}/mol_{amine}. Finally, the model predicts lower pressures than the measured data after the intersection point at a loading of 0.72 mol_{CO₂}/mol_{amine}. Although the predicted pressure fits the measured data at loadings above 0.7 mol_{CO₂}/mol_{amine}, the inaccuracy at the lower loadings increases the AARD. This results in this blend having the greatest AARD of the DGA-H₂O blends, with a value of 22.69%. As explained previously in Section 4.5.2, reasons for the high AARD include simplification of the CO₂-DGA reactions to a single reaction, higher DGA concentrations, and the use of standard parameter initialisation figures. Thus, this AARD is acceptable given the simplicity of the Posey-Tapperson-Rochelle model and the complexity of CO₂ absorption in DGA.

As seen in Table 4-6, the 39.98% DGA–60.02% H₂O and 30.25% DGA–69.75% H₂O (by mass) blends have a Root mean square error, AAD and AARD of zero. Since both these systems only had four points, the model provided a best-fit prediction that was the same as the measured pressure. Therefore, there was no apparent error between the predicted and measured pressure. Since there cannot be any comparison between the predicted and measured results, it is recommended that data regression only be carried out for systems containing more than 5 points. As seen in Table 4-6, all the DGA-H₂O systems had a much larger temperature correction factor (*b*) than the solvent concentration parameter. Literature shows that the Posey-Tapperson-Rochelle model used alone can produce very accurate predicted data. These studies used data collected at temperatures between 90 and 120 °C (Dicko, *et al.* (2010), Osman (2014), Posey, *et al.* (1996)). The DGA-H₂O data predicted at 40°C in this study was inaccurate in comparison, possibly due to the much larger temperature correction factor. In contrast, the predicted DGA-NMP data was accurate compared to the measured data. This can suggest that the Posey-Tapperson-Rochelle model is not as accurate at lower temperatures unless combined with other models.

As observed in Figure 4-12, the combined Posey-Tapperson-Rochelle model and PR-EOS model with van der Waals-Berthelot mixing rules provides predicted pressures close to the measured data. Comparing all the DGA-NMP blends, the model predictions for the 40.01 wt% DGA–59.99 wt% NMP blend show the most deviation from the measured pressures. Compared to the measured data, the predicted pressures are slightly above, below and then above the measured pressure as the loading

increases. These deviations increase the AARD of this blend compared to the other DGA-NMP blends, resulting in an AARD of 6.10%. A possible reason for this is that the 40.01 wt% DGA blend has the largest pressure range and highest pressure. This could indicate that the combined model does not predict pressures as accurately at higher system pressures. As seen in Table 4-6, the predicted data for the 30.15 wt% DGA–69.85 wt% NMP blend were closest to the measured data, with an AARD of 2.14. The combined model provided accurate predictions for the DGA-NMP blends, with an average AARD of 3.73%.

Based on the average AARD, the Posey-Tapperson-Rochelle and PR-EOS models with the selected mixing rules are suitable for predicting CO₂ solubilities in water-lean DGA-NMP solvent blends. These models could be further improved by customising the Posey-Tapperson-Rochelle parameter initialisation figures for each blend, and adjusting the conditions for the MATLAB[®] regression functions. Further work to improve data prediction could include other more accurate models, such as the Deshmukh-Mather model, which would require an in-depth investigation into the reactions that occur in DGA-H₂O and DGA-NMP blends.

In summary, the results from the CO₂ solubility tests in NMP, MEA-H₂O, MEA-NMP, DGA-H₂O and DGA-NMP solvents and solvent blends were displayed and discussed in this chapter, along with the modelled data of the DGA-H₂O and DGA-NMP solvent blends. Solvent regeneration was briefly investigated, and the performance of the models discussed. It was concluded that the 40.01 wt% DGA–59.99 wt% NMP system performed the best with an acceptable viscosity, and that the data regression produced sufficient results for all DGA systems.

CHAPTER 5: CONCLUSION

CO₂ capture using amine solvent blends is a growing area of research. The aim of this study was to investigate CO₂ solubility in new DGA-NMP solvent blends.

A static synthetic apparatus was used to measure T-P-z data for CO₂ in various pure and mixed solvents. The two test systems measured showed that literature results could be reliably reproduced using the existing calibrations and the experimental and VLE calculation methods used in this study. It can therefore be concluded that the apparatus and associated experimental methods, the conversion of the measured T-P-z data to the plotted T-P-x and T-P- α data, and the calculated uncertainties were suitable.

New solubility measurements were successfully carried out at 40 °C for a pressure range of 0.1 – 1.5 MPa. Analysis of the data showed that the MEA-NMP blend had a higher CO₂ loading at the same pressure when compared to the respective MEA-H₂O blend, with a trend closer to that of NMP when the blend had more NMP. New data for different compositions of the DGA-NMP blends were produced. Taking into account the solvent viscosity and CO₂ loading, the best-performing solvent blends were the 40.01% DGA–59.99% NMP and 30.15% DGA–69.85% NMP (by mass). At 0.697 MPa, these solvents had CO₂ loadings of 0.809 mol_{CO₂}/mol_{amine} and 0.904 mol_{CO₂}/mol_{amine} respectively.

To assess the regeneration and reuse of the two best-performing solvent blends, the used solvent was heated under vacuum (30.15 wt% DGA–69.85 wt% NMP) and degassed under vacuum (40.01 wt% DGA–59.99 wt% NMP). However, problems with the regeneration procedure, inability to measure viscosity, and the lack of composition analysis of the solvent resulted in inconclusive results. When comparing the two regenerated solvents, the 30.15 wt% DGA blend had a CO₂ lean loading that was 2.5% lower than the 40.01 wt% DGA blend. Therefore, although limited data were recorded, it can be concluded that heating under vacuum resulted in a greater CO₂ capacity when reusing the solvent for CO₂ solubility measurements.

The density, viscosity, sound velocity and refractive index of the pure solvents and solvent blends were measured. It was found that the experimental densities and refractive indices of the pure chemicals were comparable to those in literature, and the viscosity of the DGA-H₂O blends decreased with increased H₂O composition. Aspen and the Elec-NRTL model were used to approximate the

measured physical properties. The Elec-NRTL model did not provide accurate physical property predictions.

Data regression of the new data measured for the DGA-H₂O and DGA-NMP blends were successfully implemented in MATLAB[®] using The Posey-Tapperson-Rochelle model and PR-EOS model with van der Waals-Berthelot mixing rules. The average AARD for the DGA-NMP systems was 3.73%, but the AARD values for the DGA-H₂O systems varied from 0% to 22.69%. Given the simplicity of the Posey-Tapperson-Rochelle model, and the complexity of CO₂ absorption in DGA, the model provided sufficient CO₂ solubility data predictions.

CHAPTER 6: RECOMMENDATIONS AND FUTURE WORK

In this study, new CO₂ solubility data in DGA-H₂O and DGA-NMP blends were measured using the static synthetic method. In terms of further uses for the apparatus, since it is contained in its own fume hood with a UPS, and it was originally designed for adaptation for use with H₂S, this work could be continued with other hazardous gases. Preliminary investigations into work with H₂S has been carried out, and some of this information can be found in Appendix A. Furthermore, the DGA blends investigated in this study could possibly be applied to CO₂-H₂S gas blends. Improvements to the experimental method could include GC analysis of the solvent blend before and after use to determine the exact solvent composition and to help identify the reaction products.

It was concluded that water-lean DGA-NMP blends show promise for the replacement of MEA-H₂O blends currently in use, since DGA is less corrosive than MEA and NMP provides additional CO₂ absorption capacity. Additional investigations into the use of NMP as a replacement for water in amine blends could be performed by mixing NMP with other promising amines, to determine if it has the same effect on absorption capacity. In terms of DGA as a potential replacement for MEA, DGA could be mixed in water-lean blends with other solvents such as PEG200 or DEG, which have already been mixed with other amines in other literature.

Solvent regeneration and reuse was attempted but only provided limited results. Repeated solvent regeneration and reuse tests with DGA solvent blends could be carried out with GC analysis of the solvent before and after regeneration. This would enable determination of the reaction products that build up over time, how much CO₂ remains in solution after regeneration, and how long the solvent can be used before the residual CO₂ and degradation product levels become too high for effective absorption.

Density, sound velocity and refractive index measurements were carried out. Limited viscosity measurements were recorded due to the unsuitability of the current capillaries for high viscosity solvent measurements. Thus, it is recommended that suitable capillaries or a suitable micro viscometer be sourced for measurement of viscosities for all the solvent blends. This would enable the measurement of viscosity before and after CO₂ solubility measurements to determine if there is a correlation between the solvent viscosity before and after absorption. Further investigation into the correlation between solvent viscosity and solvent performance could be carried out for various DGA-NMP blends. All physical properties were estimated using Aspen and the Elec-NRTL model, but poor

results were obtained. These results could be improved by using literature pure and binary interaction parameters.

Data regression was carried out for these new blends using the Posey-Tapperson-Rochelle and PR-EOS models. It was concluded that these models performed sufficiently, but they could be improved. Further work could include the development of other more accurate models such as the Deshmukh-Mather model, which has a high degree of accuracy without greatly increasing the computation time. Using models such as this would require an in-depth investigation into the reaction mechanism of CO₂ in DGA-NMP blends, since these models require a full set of reactions along with other constants.

CHAPTER 7: REFERENCES

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APPENDIX A: SAFETY ANALYSIS

As with any operation in the laboratory, there are also hazards and safety aspects associated with the static synthetic equilibrium cell and chemicals used in this study. This appendix contains the material safety data sheets (MSDS) for the chemicals used, a Fault Tree Analysis, and a HAZOP study conducted for selected procedures detailed in Chapter 3 Section 3.4.

When H_2S was initially considered, modifications for the current apparatus had to be designed to address safety concerns, since the H_2S levels must be kept below 10 ppm TLV (Mamrosh, *et al.*, 2008). An emergency cylinder and H_2S trap were sized for quick release and slow release, respectively, from the equilibrium cell and gas reservoir. The emergency cylinder was designed to be able to hold all the gas in the apparatus. The H_2S trap was sized to hold an excess volume of NaOH solution with a high pH, where the gas from the apparatus would slowly be bubbled through the solution, and the outlet would be placed high in the fume hood. Additional experimental procedures required for safe operation are listed below:

- A large N_2 cylinder required for flushing the apparatus after using H_2S
- H_2S to be decanted into a small cylinder kept in the fume hood to reduce the volume of gas stored in the laboratory
- Power backup sourced for the fume hood fan to ensure constant air removal
- H_2S detector placed in the fume hood and on the person working with the apparatus
- Respirator used when performing hazardous operations and kept at the workstation for emergencies
- H_2S resistant gloves required whenever using the apparatus
- Schedule placed in the laboratory and, as far as possible, work was to be carried out when there were not any other people in the laboratory.
- Another person required in the building who knew how to use the apparatus, was aware that H_2S was being used, and knew the emergency protocols if there was a leak in the laboratory.

Finally, a Fault Tree Analysis and HAZOP study were performed with H_2S in mind, and both were adapted for use with any hazardous gas, including CO_2 , and the current apparatus with modifications included for hazardous gases. The modifications included were an emergency cylinder, trap, scrubber, and detectors.

A.1. MSDS

When working with any chemicals, a MSDS should be consulted for possible hazards and required handling and disposal measures. Tables A-1 and A-2 contain summaries of the MSDS data compiled from AFROX (2022), AFROX (2020), Sigma-Aldrich (2022), Sigma-Aldrich (2020) and Sigma-Aldrich (2021) for CO₂, H₂S, NMP, MEA and DGA respectively.

Table A-1: MSDS for gases used in this work, compiled from (AFROX, 2022) for CO₂ and (AFROX, 2020) for H₂S

Chemical species	CO ₂	H ₂ S
Phase	Gas (compressed)	Gas
Hazard identification	- Gas under pressure - Rapid release through a valve may result in the formation of dry ice - Asphyxiant in high concentrations - Corrosive to steel in the presence of water - May increase respiration and heart rate, and dry ice may cause frostbite - Odourless - Heavier than air, and will displace oxygen in enclosed spaces - Use in adequately ventilated spaces	- Gas under pressure - Low concentrations (15-50 ppm) lead to irritation of mucous membranes, headaches, dizziness and nausea. - Higher concentrations (200-300 ppm) may lead to respiratory arrest and unconsciousness - Concentrations above 700ppm may be fatal - Eye and skin contact also lead to irritation - Detection by odour (rotten egg smell) is unreliable therefore a sensor is required - Use in well-ventilated spaces in a forced ventilation system and/or in a fume hood - Gas can form an explosive mixture with air, so avoid discharging directly to the air
Health effects	- Stimulant and depressant of the central nervous system - Can cause harm <i>via</i> exposure to eyes and skin (dry ice) and inhalation (gas) - Performance impaired during prolonged exposure to 3% concentration in air - Laboured breathing, headache, dizziness and sweating occur during prolonged exposure at 7.6% concentration in air - Unconsciousness occurs at 10% concentration within 1 minute - TWA: 5 000 ppm - STEL: 15 000 ppm - IDLH: 40 000 ppm	- Eye irritation caused by inhalation for 30 minutes between 20 – 50 ppm in air, with slightly higher concentrations resulting in upper respiratory tract irritation and possible pulmonary oedema - Headache, dizziness, excitement, staggering and gastroenteric disorder caused by inhalation for 30 minutes at 500 ppm - Respiratory paralysis caused by inhalation for 30 minutes above 600 ppm - Human detection is unreliable at higher concentrations due to a rapid onset of olfactory fatigue - Repeated exposure to the eyes can lead to conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision - TLV: 10 ppm - STEL: 15 ppm

Table A-1 continued

Chemical species	CO ₂	H ₂ S
Firefighting measures	- Container may explode if heated - Gas does not burn; extinguish the surrounding fire with an appropriate extinguishing agent - Stop gas leak if safe to do so and continuously spray with water from a safe distance until the container remains cool - A self-contained breathing apparatus (SCBA) should be used in enclosed spaces	- Container may explode if heated - Gas burns; thermal decomposition product is SO₂. All known extinguishing agents are suitable - Stop gas leak if safe and continuously spray water onto the container from a safe distance until it remains cool - Do not extinguish a leaking gas flame unless necessary. Spontaneous and/or explosive re-ignition is possible - SCBA and chemically protective clothing should be used
Accidental release and disposal measures	- Evacuate and ventilate the area, prevent accumulation in low-lying areas if possible, and do not enter the area without SCBA - When safe to do so, prevent further leakage by sealing the container - Area is cleaned via adequate ventilation - Dispose of gas by venting to the atmosphere in a well-ventilated place	- Evacuate and ventilate the area, eliminate ignition sources, and do not enter the area without SCBA - Keep the area clear of personnel and free from ignition sources until the gas has dissipated into the atmosphere - Area is cleaned by good ventilation - Dispose of gas by scrubbing or flaring through a suitable burner before releasing it to the atmosphere - Do not discharge gas where it could accumulate and become dangerous - Combustion products should be scrubbed before releasing into the atmosphere
Handling and storage	- Only trained and experienced persons should handle the containers - Move containers using appropriate means and ensure they are not damaged - Secure containers in an upright position against a wall or container stand and close valves when not in use - Wear appropriate eye, hand and feet protection based on operation and anticipated exposure levels - SCBA may be required based on anticipated exposure levels - Store in a well-ventilated area below 50 °C - Store away from moisture and sources of heat and/or ignition - Check the container periodically for condition and leaks	- Purge air from the system before introducing gas - Keep away from water sources - Only trained and/or experienced persons should handle the containers with appropriate personal protective equipment (PPE) for the operation - Move containers using appropriate means and ensure they are not damaged - Use the 'first-in-first-out' inventory system - Secure containers in an upright position to prevent them from falling - Store container below 50 °C away from static discharge - Store away from ignition sources, flammable or combustible materials in a dry, well-ventilated storage space constructed from non-combustible materials on a firm, level floor - Do not store containers with other containers of O₂ or any other highly combustible or oxidising materials

Table A-1 continued

Chemical species	CO₂	H₂S
Environmental effects	- No ecological damage, but may contribute to the greenhouse effect when discharged in large quantities	- Do not allow gas to enter sewers or storm-water drains - Toxic to water organisms

Table A-2: MSDS for chemicals used in this work, compiled from (Sigma-Aldrich, 2022) for NMP, (Sigma-Aldrich, 2020) for MEA, and (Sigma-Aldrich, 2021) for DGA

Chemical species	NMP	MEA	DGA
Phase	Liquid	Liquid	Liquid
Hazard identification	- Colourless liquid with an amine-like odour - May damage an unborn child, therefore there are restrictions regarding who is able to work with the chemical - If inhaled, move to fresh air. If eye/skin contact occurs, wash thoroughly with water. If ingested, drink water. In all cases, consult the relevant health care specialist. - NMP vapour is heavier than air and can enter water systems this way - Wear eye, hand and body protection when working with the chemical, and wash hands and face afterwards - Oxidising agents may cause ignition or formation of vapours, and violent reactions are possible with strong acids and bases - Various plastics are incompatible with the chemical	- Clear, colourless liquid with an amine-like odour - Harmful if swallowed, comes into contact with skin or vapour is inhaled - Avoid release into the environment as it has long-lasting effects - Wear appropriate PPE (hand, body, eye and face protection). Throw away gloves after use and wash hands - If swallowed, rinse mouth. If inhaled, move to fresh air. If skin contact occurs, change clothing and wash with water. If eye contact occurs, wash thoroughly with water and immediately call a poison centre/doctor. In all cases, consult the relevant health care specialist. - Absorbs CO₂ from the air, causing it to turn yellow as more is absorbed - Chemical is stable under normal conditions. Avoid exposure to moisture, heat, sparks, flames and electrostatic discharge - Incompatible materials include strong acids, strong oxidising agents, iron, copper, brass and rubber - MEA vapour accumulates in low-lying areas and can enter the environment this way	- Contact with skin and eyes can cause severe burns and eye damage - Wear appropriate PPE (hand, body, eye and face protection). Throw away gloves after use and wash hands - If swallowed, rinse mouth and drink a maximum of 2 glasses of water, but do not induce vomiting or attempt to neutralise. If inhaled, move the person to fresh air. If chemical comes into contact with eyes or skin, remove contaminated clothing and wash for several minutes. In all cases, immediately contact the relevant health specialist - Vapour is heavier than air and may spread along the floor - Liquid is chemically stable under ambient conditions - If chemical comes into contact with nitrites, nitrates or nitrous acid, nitrosamines may be formed. Chemical also can undergo an exothermic reaction in the presence of strong oxidising agents and acids

Table A-2 continued

Chemical species	NMP	MEA	DGA
Health effects	- Single exposure may cause respiratory irritation - Contact with eyes can cause serious irritation and contact with skin will cause irritation - Prolonged or repeated exposure may lead to vomiting, diarrhoea and abdominal pain - Bone marrow irregularities have also been observed in humans	- Harmful if swallowed, inhaled or comes into contact with skin and eyes - Inhalation may result in respiratory irritation - Single exposure to eyes and skin will cause serious eye damage and skin burns - Repeated exposure can cause liver irregularities in humans	- Contact with skin will cause burns - Contact with eyes will cause severe irritations and severe eye damage - Chemical is extremely harmful to tissue in the mucous membranes and upper respiratory tract. Inhalation can result in a burning sensation, inflammation and spasm of the larynx and bronchi, pneumonitis, pulmonary oedema, and laryngitis - Repeated or prolonged exposure can cause cough, wheezing, shortness of breath, headaches and nausea
Firefighting measures	- Water foam, CO₂ or dry powder are suggested extinguishing agents, with no unsuitable agents given - Liquid is combustible. Combustion products include carbon oxides, nitrogen oxides and nitrous gases. In the event of a fire, these hazardous gases or NMP vapour may be released - Vapour forms an explosive mixture with air under intense heating - SCBA and protective clothing are required if entering danger area to extinguish the fire - If the container is surrounded by fire, remove from the area and spray with water until it is cool	- Water spray, alcohol-resistant foam, dry chemical or CO₂ are suitable extinguishing agents - Do not use a water jet as an extinguishing agent - Liquid is combustible. Combustion products include carbon oxides and nitrogen oxides - SCBA and suitable PPE should be worn when fighting the fire - Avoid breathing in vapour - If unopened container is surrounded by fire, remove it from the area when possible and cool with water spray - Accumulated vapour can form an explosive mixture at high-enough concentrations	- Water foam, CO₂ or dry powder are suggested extinguishing agents, with no unsuitable agents given - Liquid is combustible. Combustion products include carbon oxides and nitrogen oxides. These products may be formed in the event of a fire - DGA vapour forms an explosive mixture with air under intense heating - SCBA and protective clothing are required when entering the danger area to fight the fire - Suppress vapour or gas with a water spray or jet - Prevent water used to extinguish the fire from entering water sources

Table A-2 continued

Chemical species	NMP	MEA	DGA
Firefighting measures	- Suppress gas/vapour/mist with water - Prevent water used to extinguish the fire from entering water sources		
Accidental release and disposal measures	- Do not breathe in vapour, avoid contact with liquid and ensure adequate ventilation - Persons performing clean-up must wear Butyl-rubber gloves, safety glasses, protective clothing and a respirator - Keep spill away from heat and sources of ignition - After a large spill evacuate the area, cover drains and collect, bind and pump off large spills - Clean up using a liquid-absorbent material and dispose of properly <i>via</i> normal chemical disposal procedures - Do not let product enter drains	- Do not inhale vapour or gas and avoid contact with the liquid - Depending on the expected contact with liquid, personnel performing clean-up must wear tightly-fitting safety goggles with a face shield if necessary, chloroprene gloves, protective body suit or protective clothing, and a respirator or SCBA - After a large spill ventilate the area, cover drains, remove all other sources of ignition and evacuate personnel - Clean up using a non-combustible absorbent material and place in a sealed container for disposal according to regulation - Do not let product enter the drains and prevent discharge into the environment if possible - Prevent further spillage when safe to do so - Dispose of surplus and waste chemicals through a licensed chemical disposal company. Keep in its own container and do not mix with other waste	- Persons performing clean-up must not breathe in vapour and avoid direct contact with the liquid by wearing the appropriate PPE - Butyl-rubber gloves should be used if full contact with skin is expected - After a large spill evacuate the area, ventilate the area, cover drains, and collect, bind and pump off spills - For smaller spills, clean up the affected area with a liquid-absorbent material - Do not let the product enter the drains - Dispose of properly per normal chemical handling procedures and through a registered chemical disposal company

Table A-2 continued

Chemical species	NMP	MEA	DGA
Handling and storage	- Work with liquid in a fume hood, do not inhale and avoid generating vapour - When working, keep liquid away from open flames, hot surfaces and sources of ignition, including static discharges - Wear appropriate PPE and change contaminated clothing immediately. Also, wash hands and face after working with liquid - Store away from light in a well-ventilated area, and keep the container closed when not in use - Store in an area at room temperature, accessible only by authorised or qualified persons	- Avoid contact with skin and eyes and avoid inhalation of vapour - Keep away from sources of ignition and take measures to prevent the build-up of electrostatic discharge - Wear appropriate PPE and change contaminated clothing immediately. Use a respirator when vapour may be generated - Store in a cool, dry, well-ventilated place, and keep the container sealed and in an upright position when not in use - Wash hands before taking a break and at the end of the day	- Wear protective tightly fitting safety goggles, nitrile rubber gloves and protective clothing - An appropriate respirator is only required when vapours are generated - Keep the container tightly closed when not in use - Store away from sources of heat
Environmental effects	- Do not let product enter drains - Toxic to fish (above 500 mg·L⁻¹), aquatic invertebrates (4.897 mg·L⁻¹) and algae (672.8 mg·L⁻¹) - Liquid is readily biodegradable	- Do not let product enter the environment - Toxic to fish (above 349 mg·L⁻¹), aquatic invertebrates (above 65 mg·L⁻¹), algae (above 1 mg·L⁻¹) and bacteria (above 1 mg·L⁻¹) - Long-lasting effects in environment - Biodegradable over 21 days under aerobic conditions	- Do not allow product to enter drains - Toxic to fish (above 460 mg·L⁻¹), aquatic invertebrates (above 190 mg·L⁻¹), algae (above 162 mg·L⁻¹) and bacteria (110 mg·L⁻¹) - Readily biodegradable and is easily eliminated from water

A.2. Fault tree analysis

A FTA is a diagram showing a sequence of events that may result in a hazard. The likelihood of the hazard occurring is also included in the discussion of the FTA (Nelson, 2012). When compiling the FTA, the following process was followed: First, possible ways that CO₂ or a dangerous gas could be released into the laboratory were considered. Then the causes of these events were considered. Lastly, this information was compiled to form the FTA.

The results of the FTA can be seen in Figure A-1, where the causes for gas release into the fume hood, insufficient air removal rate in the fume hood and gas release into the laboratory can be seen. The probabilities of the events in Figure A-1 were then sorted into a low, moderate, and high probability of occurrence as follows:

- Low probability: cylinder rupture, leak in cylinder, leak along line, leak in extraction pipe, extraction fan not working properly, insufficient air removal from fume hood, leak from fume hood into lab.
- Moderate probability: leak in equilibrium cell, leak in gas reservoir, leak from valve, leak into fume hood, fume hood window not closed properly.
- High probability: leak in equilibrium cell due to insufficient sealing.

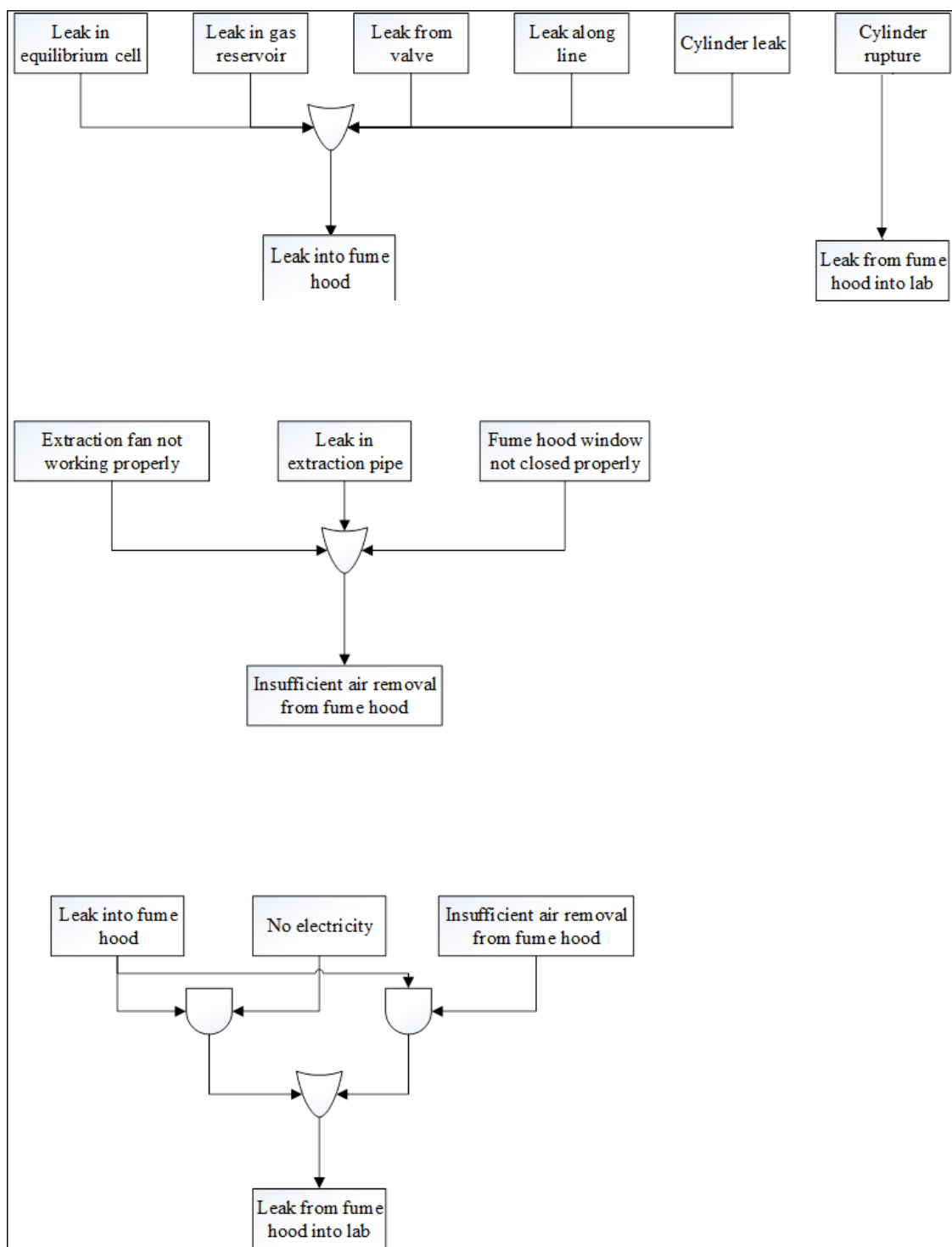


Figure A-1: Fault tree analysis

A.3. HAZOP

A HAZOP is usually compiled by following the steps in Figure A-2.

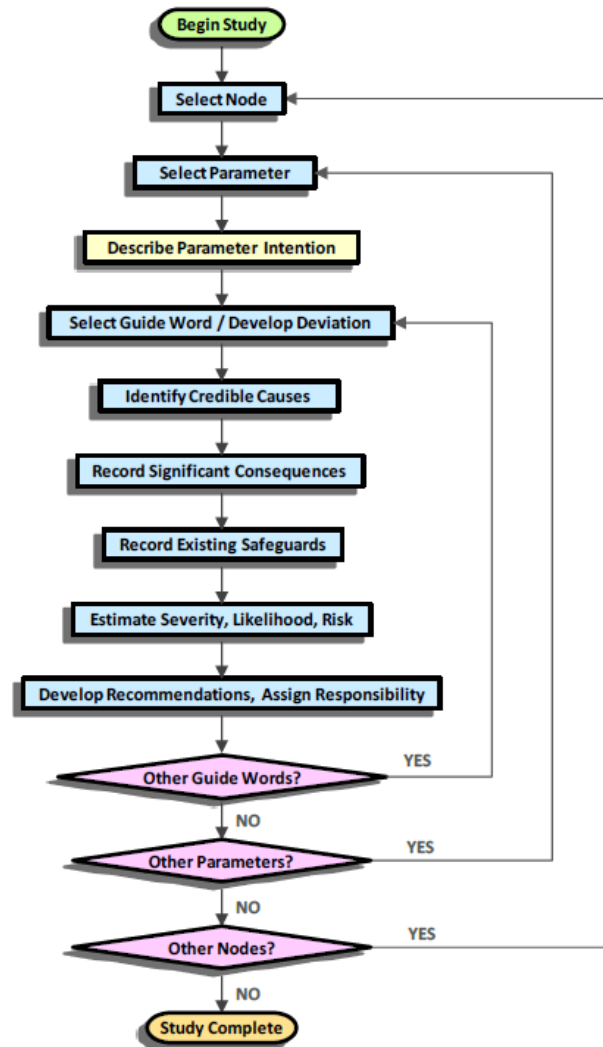


Figure A-2: Typical HAZOP process, extracted from (Eichleay, 2015)

This approach is usually applied to the pipes linking major equipment until all the equipment has been covered. For each deviation, there can be multiple local causes and consequences, knock-on effects on local and linked systems, and multiple or no mitigating factors. A complete P&ID is required before starting the HAZOP. Additional resources required may be a PFD, mass and energy balance data, equipment datasheets, cause and effect diagrams and MSDS for hazardous materials (Limb, 2009). The most common guide words used to describe the most common deviations are shown in Table A-3.

Table A-3: Typical HAZOP deviation matrix, extracted from (Eichleay, 2015)

Design Parameter	Guide Word						
	More	Less	None	Reverse	Part Of	As Well As	Other Than
Flow	High Flow	Low Flow	No Flow	Back Flow or Misdirected	Wrong Amount	Added Component	Wrong Component
Pressure	High Pressure	Low Pressure	Vacuum				
Temperature	High Temp	Low Temp					
Level	High Level	Low Level	No Level				
Agitation	Too Much	Too Little					
Reaction	High Rate	Low Rate	No Reaction	Decompose	Incomplete	Side Reaction	Wrong Reaction
Time	Too Much	Too Little					
Step	Step Late	Step Early	Missed Step	Back Step	Partial Step	Extra Action	Wrong Action
Composition	High Concentration	Low Concentration	None			Extra Component	Wrong Component
Phase	Too Many	Too Few	Single	Inversion	Emulsion		
Addition	Too Much	Too Little					
Mixing	Too Much	Too Little	None				

The same experimental methods described in Chapter 3 were used to perform the HAZOP analysis. The HAZOP was carried out on the current equipment, but with modifications made for use with hazardous gases. The additions considered were according to the additional equipment required if H₂S were to be used. These modifications were detailed at the beginning of this chapter.

The HAZOP was carried out for the different parts of the experimental procedure since no liquid or gas was flowing through the system for most of the operations. The operations analysed were adding solvent to the equilibrium cell, loading gas into the gas reservoir, loading gas into the equilibrium cell, and solubility measurements. General hazards when performing these operations were also considered.

The P&ID before the HAZOP study is shown in Figure A-3. The HAZOP studies for the procedures above can be seen in Tables A-4 to A-7. The P&ID after implementing changes suggested by the HAZOP study is shown in Figure A-4.

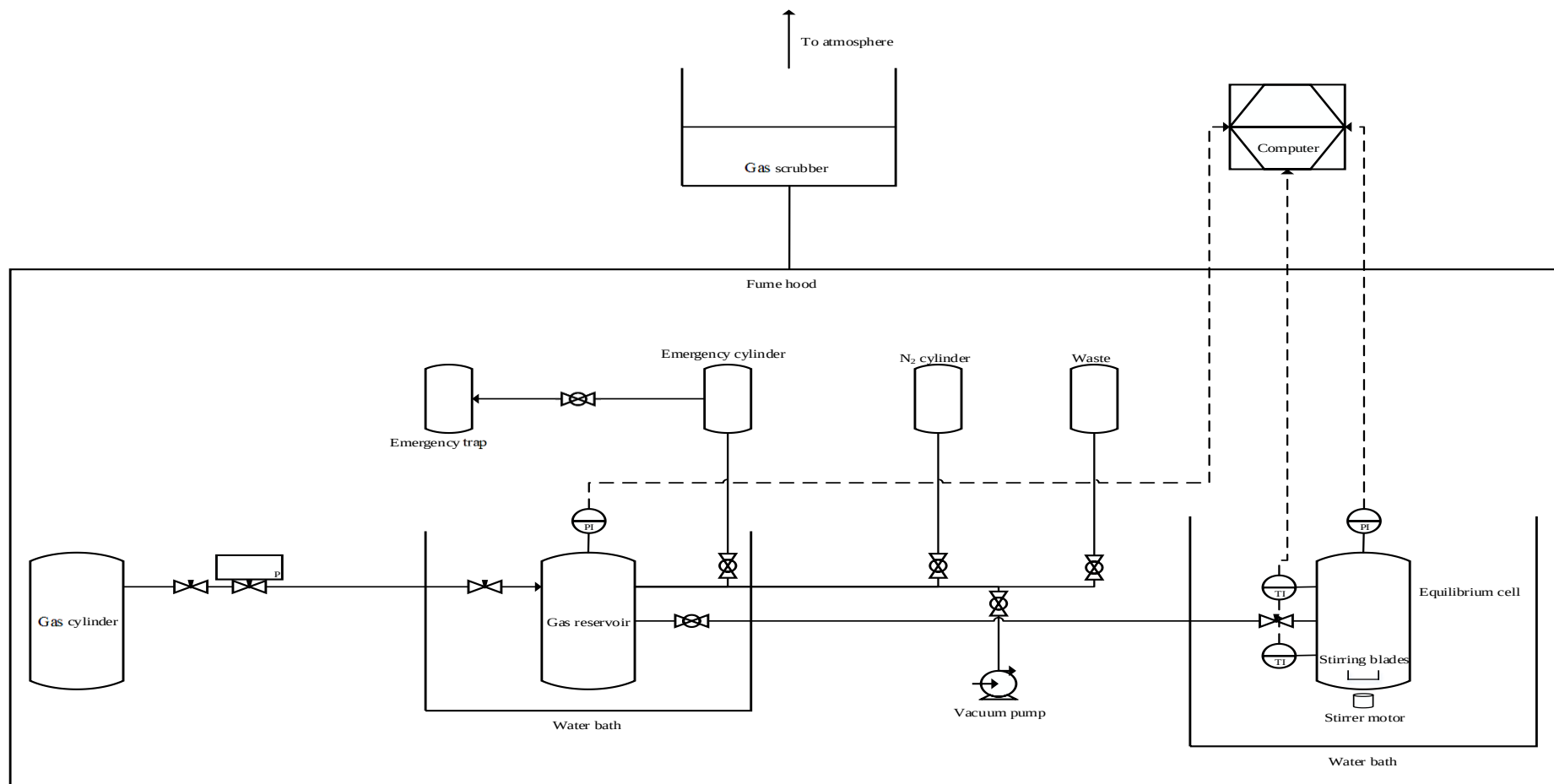


Figure A-3: P&ID for hazardous gas operation before HAZOP

Table A-4: Adding solvent to the equilibrium cell

Adding solvent to the equilibrium cell					
Equipment: Charging vessel and attachments, equilibrium cell			Intention: Add solvent to equilibrium cell for test system		
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Liquid	Less	- Leak in valves - Valves not closed properly - Bolts not connected properly - Leak in equilibrium cell	- Spillage of potentially hazardous liquids	- Bolts tightened using spanner - Leak test performed before each test system run	- Check and re-check all bolts are tightened properly, and all valves are closed properly

Table A-5: Loading gas into the gas reservoir

Loading gas into the gas reservoir					
Equipment: Gas cylinder, gas reservoir, pressure transducer, connecting lines and valves			Intention: Fill gas reservoir with gas to be later transferred to the equilibrium cell		
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Pressure	Less	- Leak in any of the valves between the gas cylinder and the gas reservoir - Leak in gas reservoir - Leak in the lines from the gas cylinder to the gas reservoir	- Release of dangerous gas - Loss of gas when performing tests on test systems	- Leak test - Pressure constantly logged and monitored on computer using pressure transducers	- Install gas detector in fume hood if using a dangerous gas - Check pressure transducers are operating in the expected pressure range

Table A-5 continued

Loading gas into the gas reservoir					
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Pressure	More	- Failure of the two valves on the gas cylinder - Failure of the two valves from the gas cylinder to the gas reservoir - A high pressure on the second valve on the gas cylinder due to a leaking valve - Failure of operator to note pressure	- Overpressure of the gas reservoir will lead to the pressure transducer being damaged	- Pressure gauges on both valves on the gas reservoir - Pressure constantly logged and monitored on computer using pressure transducers	- Check pressure on gas cylinder pressure gauge valves before filling gas cylinder - Check pressure transducers are operating in the expected pressure range
Temperature	Less	- Malfunction of heater in gas reservoir water bath	- Incorrect data obtained - May cause some gas to condense in the gas reservoir and in the line to the equilibrium cell	- Current temperature displayed on heater	- Monitor temperature on heater
	More	- Malfunction of the heater in gas reservoir water bath	- Incorrect data obtained - May cause some solvent to vaporise in equilibrium cell	- Current temperature displayed on heater	- Monitor temperature on heater

Table A-6: Loading gas into the equilibrium cell

Loading gas into the equilibrium cell					
Equipment: Gas reservoir, equilibrium cell, connecting lines and valves			Intention: Add gas to the equilibrium cell		
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Pressure	Less	- Leak in any of the valves between the gas reservoir and equilibrium cell - Leak in the gas reservoir or equilibrium cell	- Release of dangerous gas	- Leak test - Pressure constantly logged and monitored on computer using pressure transducers	- Install gas detector in fume hood if using a dangerous gas - Check pressure transducers are operating in the expected pressure range
	More	- Needle valve not closed properly - Failure of valve between the gas reservoir and equilibrium cell - Failure of needle valve	- Gas slowly leaks into equilibrium cell, equilibrium will not be reached - Overpressure will not occur since the maximum pressure of the gas reservoir is lower than the equilibrium cell	- Pressure constantly logged and monitored on computer using pressure transducers - Ball valves are used, which are either fully open or fully closed, reducing the possibility of a slow leak	- Check needle valve is properly closed after gas added to equilibrium cell - Check pressure transducer is operating in the expected pressure range
Temperature	Less	- Malfunction of the heater in equilibrium cell water bath - Malfunction of chiller	- Incorrect data obtained - Gas may condense in equilibrium cell	- Current temperature displayed on heater - Temperature sensors on equilibrium cell	- Monitor temperature on heater - Check temperature sensors are operating as expected

Table A-6 continued

Loading gas into the equilibrium cell					
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Temperature	More	- Malfunction of the heater in the water bath	- Higher temperature may cause some of the solvent in the equilibrium cell to vaporise	- Current temperature displayed on heater	- Monitor temperature on heater - Check temperature sensors are operating as expected
Liquid	Less	- Leak in equilibrium cell - Failure of ball valve on equilibrium cell	- Loss of solvent	- Leak test	- Check liquid level between gas loadings

Table A-7: Solubility measurements

Solubility measurements					
Equipment: Gas cylinder, gas reservoir, equilibrium cell, connecting lines and valves			Intention: Obtain VLE data for different systems		
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Pressure	Less	- Leak from any of the valves or connecting lines - Leak in gas reservoir - Leak in equilibrium cell	- Release of dangerous gas	- Leak test - Pressure constantly logged and monitored on computer using pressure transducers	- Check pressure transducers are operating in the expected pressure range

Table A-7 continued

Solubility measurements					
Keywords	Deviation	Causes	Consequences	Safeguards	Recommendations
Pressure	More	- Gas cylinder valve not fully closed and none of the valves between the gas cylinder and gas reservoir and the gas reservoir and equilibrium cell are closed	- Overpressure of the entire system - Pressure transducers will be damaged	- Pressure gauge on both gas cylinder valves - Pressure constantly logged and monitored on computer using pressure transducers - Leak test	- Check all valves are properly closed after loading - Check pressure transducers are operating in the expected pressure range
Temperature	Less	- Malfunction of heaters in water baths - Malfunction of chiller	- Incorrect data obtained - May cause some gas to condense in the gas reservoir and in the line to the equilibrium cell	- Temperature sensor on equilibrium cell - Current temperature displayed on heaters	- Monitor temperature on heaters - Check temperature sensors are operating as expected
	More	- Malfunction of the heaters in the water baths	- Higher temperature may cause some of the solvent in the equilibrium cell to vaporise	- Current temperature displayed on heater	- Monitor temperature on heater - Check temperature sensors are operating as expected
Liquid	Less	- Leak in equilibrium cell - Failure of ball valve on equilibrium cell	- Loss of solvent	- Leak test	- Check whether liquid level in equilibrium cell decreases between gas loadings - Check valve properly closed after loading

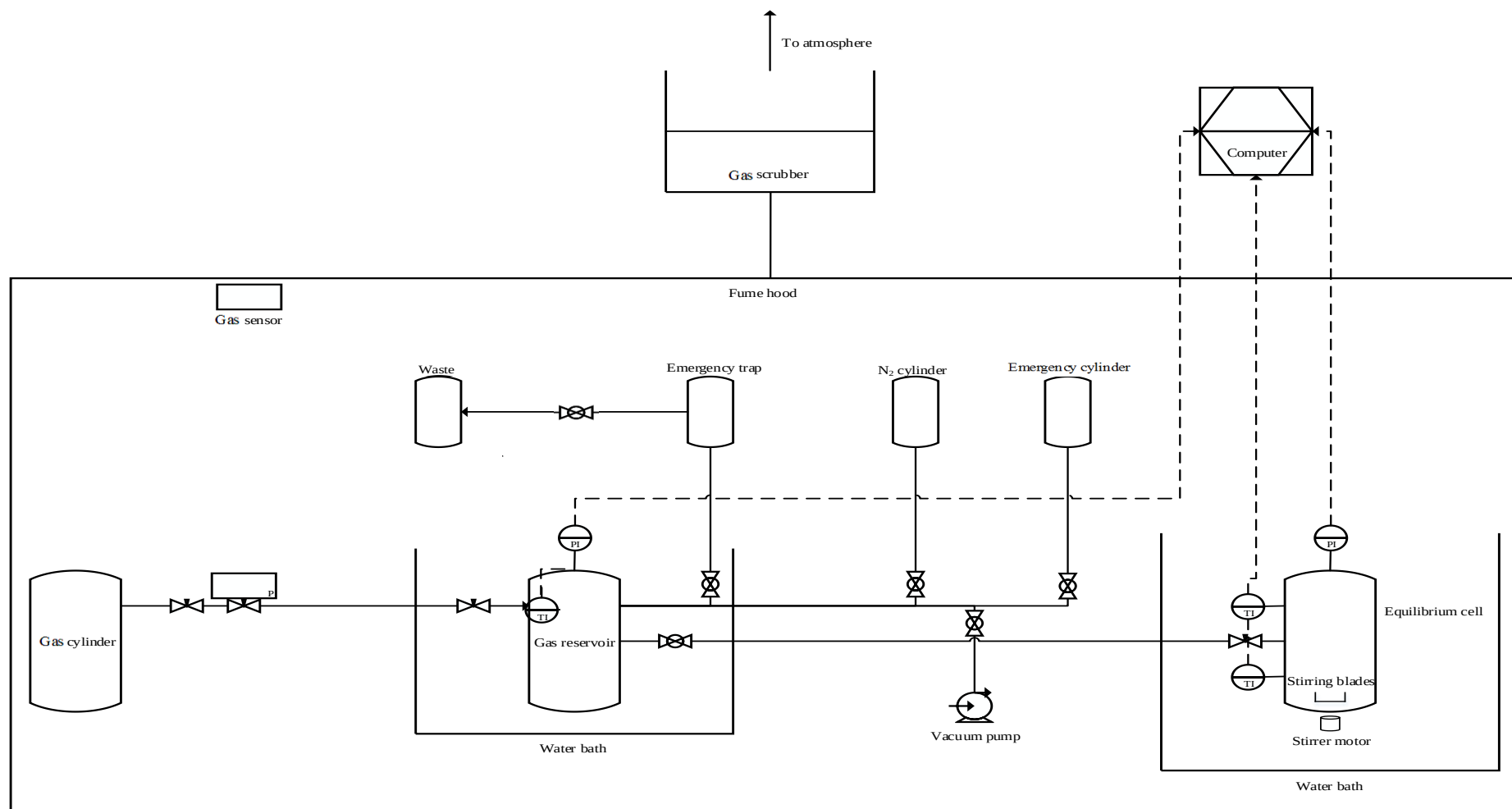


Figure A-4: P&ID for hazardous gas operation after HAZOP

APPENDIX B: UNCERTAINTY CALCULATIONS

This chapter contains further detailed equations used for the uncertainty calculations described in Chapter 3 Section 3.5.

B.1. Temperature and pressure

Uncertainty for the temperature reading recorded from the temperature sensors on the equilibrium cell (T_{101} and T_{102}) and the gas reservoir (T_{104})

$$u(T_{101,102,104}) = \sqrt{u(T_{cont})^2 + u(T_{bath})^2 + u(T_{calib})^2 + u(T_{standard})^2} \quad (B-1)$$

Where $u(T_{cont})$ is due to the accuracy of the water bath temperature controller

$u(T_{bath})$ is due to the non-uniformity of the temperature of the gas in the gas reservoir, and is only used for T_{104}

$u(T_{calib})$ is due to the calibration equations for the respective temperature sensor

$u(T_{standard})$ is due to the accuracy of the standard digital temperature probe

Uncertainty for the pressure reading recorded from the pressure sensors on the equilibrium cell (P_{121}) and the gas reservoir (P_{122})

$$u(P_{121,122}) = \sqrt{u(P_{calib})^2 + u(P_{standard})^2} \quad (B-2)$$

Where $u(P_{calib})$ is due to the calibration equations for the respective pressure sensor

$u(P_{standard})$ is due to the accuracy of the standard pressure transmitter

Uncertainty for the temperature reading recorded for the equilibrium cell

$$u(T_{cell}) = \sqrt{0.5^2 \times u(T_{101})^2 + 0.5^2 \times u(T_{102})^2} \quad (B-3)$$

B.2. Calculated variables

Uncertainty for the calculated gas volume

$$u(V_{gas}) = \sqrt{u(V_{liquid})^2 + u(V_{cell})^2} \quad (B-4)$$

Where $u(V_{gas})$ is the uncertainty of the volume of CO₂ in the vapour phase

$$\begin{aligned} u(V_{liquid}) &\text{ is the uncertainty of the volume of the liquid phase} \\ &= \sqrt{u(V_{calib})^2 + u(V_{repeat})^2} \end{aligned} \quad (B-5)$$

$u(V_{cell})$ is the uncertainty of the equilibrium cell volume, from the calculation of the total cell volume. This was previously found to be $u(V_{cell}) = 0.0313$ (Ebrahimejadhasanabadi, 2019)

Uncertainty for the total number of moles of CO₂ in the system

$$u(n_{t,CO_2}) = \sqrt{u(n_{t,CO_2}^0)^2 + u(n_{t,CO_2,injected})^2} \quad (B-6)$$

Where $u(n_{t,CO_2})$ is the uncertainty of the total number of moles of CO₂ loaded into the equilibrium cell

$u(n_{t,CO_2}^0)$ is the uncertainty of the total number of moles of CO₂ in the system from the previous point

$u(n_{t,CO_2,injected})$ is the uncertainty of the number of moles of CO₂ loaded into the equilibrium cell from the gas reservoir

Uncertainty for the number of moles of CO₂ in the liquid phase

$$u(n_{liquid}) = \sqrt{u(n_{t,CO_2})^2 + u(n_{gas})^2} \quad (B-7)$$

Where $u(n_{liquid})$ is the uncertainty of the number of moles of CO₂ in the liquid phase

$u(n_{gas})$ is the uncertainty of the number of moles of CO₂ in the vapour phase

Uncertainty for the number of moles of CO₂ in the vapour phase using the law of propagation of uncertainty

$$u(n_{gas}) = \sqrt{\left(\frac{V_V y_{CO_2}}{TRZ_V}\right)^2 \times \left(\frac{u(P_{121})}{10}\right)^2 + \left(\frac{P}{10 y_{CO_2}}\right)^2 \times u(V_V)^2 + \left(\frac{P}{10 V_V y_{CO_2}}\right)^2 \times u(Z_V)^2 + \left(\frac{P}{10 V_V y_{CO_2}}\right)^2 \times u(T_{cell})^2} \quad (B-8)$$

Where V_V is the volume of the vapour phase (cm³)

y_{CO_2} is the mole fraction of CO₂ in the vapour phase

T is the temperature of the equilibrium cell (K)

R is the standard gas constant (m³.Pa.K⁻¹.mol⁻¹)

Z_V is the calculated compressibility of the vapour phase

$u(P_{121})$ is the uncertainty of the pressure transducer on the equilibrium cell

P is the pressure in the equilibrium cell (bar)

$u(T_{cell})$ is the combined uncertainty of both temperature probes on the equilibrium cell

Uncertainty for the number of moles of gas loaded into the equilibrium cell from the gas reservoir using the law of propagation of uncertainty

$$u(n_{t,CO_2,injected}) = \left\{ \left(\frac{1}{R} \left[\frac{P_1}{Z_1 T_1} - \frac{P_2}{Z_2 T_2} \right] \right)^2 \times u(V_{GR})^2 + \left(\frac{V_{GR}}{R} \left[\frac{1}{Z_1 T_1} + \frac{1}{Z_2 T_2} \right] \right)^2 \times \left(\frac{u(P_{122})}{10} \right)^2 \right\}^{\frac{1}{2}} + \left\{ \left(\frac{V_{GR}}{R} \left[\frac{P_1}{Z_1 T_1^2} + \frac{P_2}{Z_2 T_2^2} \right] \right)^2 \times u(T_{104})^2 + \left(\frac{V_{GR}}{R} \frac{P_1}{T_1 Z_1^2} \right)^2 \times u(Z_1)^2 + \left(\frac{V_{GR}}{R} \frac{P_2}{T_2 Z_2^2} \right)^2 \times u(Z_2)^2 \right\}^{\frac{1}{2}} \quad (B-9)$$

Where P_1 is the pressure in the gas reservoir before loading gas into the equilibrium cell (bar)

P_2 is the pressure in the gas reservoir after loading gas into the equilibrium cell (bar)

Z_1 is the compressibility factor of CO_2 in the gas reservoir before loading gas into the equilibrium cell

Z_2 is the compressibility factor of CO_2 in the gas reservoir after loading gas into the equilibrium cell

T_1 is the temperature in the gas reservoir before loading gas into the equilibrium cell (K)

T_2 is the temperature in the gas reservoir after loading gas into the equilibrium cell (K)

$u(V_{GR})$ is the uncertainty of the volume of CO_2 in the gas reservoir. This was previously found to be $u(V_{GR}) = 0.05140$ (Ebrahimejadhasanabadi, 2019)

V_{GR} is the volume of the gas reservoir (cm^3)

$u(P_{122})$ is the uncertainty of the pressure transducer on the gas reservoir

Uncertainty for the composition of the liquid phase using the law of propagation of uncertainty

$$u(x_{\text{CO}_2}) = \sqrt{\left(\frac{1}{n_{t,\text{CO}_2} + n_{\text{solvent}}} - \frac{n_{t,\text{CO}_2}}{(n_{t,\text{CO}_2} + n_{\text{solvent}})^2}\right)^2 \times u(n_{t,\text{CO}_2})^2 + \left(\frac{n_{t,\text{CO}_2}}{(n_{t,\text{CO}_2} + n_{\text{solvent}})^2}\right)^2 \times u(n_{\text{solvent}})^2} \quad (\text{B-10})$$

Where $u(x_{\text{CO}_2})$ is the uncertainty of the composition of CO_2 in the liquid phase

$u(n_{\text{solvent}})$ is the uncertainty of the number of moles of solvent added to the equilibrium cell using gravimetric analysis. This was found to be $u(n_{\text{solvent}}) = 0.0002$

The combined standard uncertainty of the overall liquid composition of CO_2 $U(x_{\text{CO}_2})$ is calculated as follows

$$U(x_{\text{CO}_2}) = 2u(x_{\text{CO}_2}) \quad (\text{B-11})$$

Uncertainty for the overall composition of the liquid phase using the law of propagation of uncertainty

$$u(z_{CO_2}) = \sqrt{\left(\frac{1}{n_{liquid}+n_{solvent}} - \frac{n_{liquid}}{(n_{liquid}+n_{solvent})^2}\right)^2 \times u(n_{liquid})^2 + \left(\frac{n_{liquid}}{(n_{liquid}+n_{solvent})^2}\right)^2 \times u(n_{solvent})^2} \quad (B-12)$$

Where $u(z_{CO_2})$ is the uncertainty of the overall composition of CO_2 in the liquid phase

The combined standard uncertainty of the overall liquid composition of CO_2 $U(z_{CO_2})$ is calculated as follows

$$U(z_{CO_2}) = 2u(z_{CO_2}) \quad (B-13)$$

Uncertainty for the solubility of CO_2 in a solvent using the law of propagation of uncertainty

$$u(\alpha_{CO_2}) = \sqrt{\left(\frac{1}{n_{solvent}}\right)^2 \times u(n_{t,CO_2})^2 + \left(\frac{1}{n_{solvent}}\right)^2 \times u(n_{gas})^2 + \left(\frac{n_{t,CO_2}-n_{gas}}{n_{solvent}}\right)^2 \times u(n_{solvent})^2} \quad (B-14)$$

Where $u(\alpha_{CO_2})$ is the uncertainty of the solubility of CO_2 in the solvent

$n_{solvent}$ is total the number of moles of solvent initially loaded into the cell

n_{t,CO_2} is the total number of moles of CO_2 in both phases

n_{gas} is the number of moles of CO_2 in the vapour phase

The combined standard uncertainty of the solubility $U(\alpha_{CO_2})$ is calculated as follows

$$U(\alpha_{CO_2}) = 2u(\alpha_{CO_2}) \quad (B-15)$$

B.3. Uncertainties

The uncertainties found in Tables D-1 to D-3 can be seen in the figures on the following page. These uncertainties could not be plotted as error bars since they were too small to be seen on the pressure vs. CO_2 loading graphs in Chapter 4.

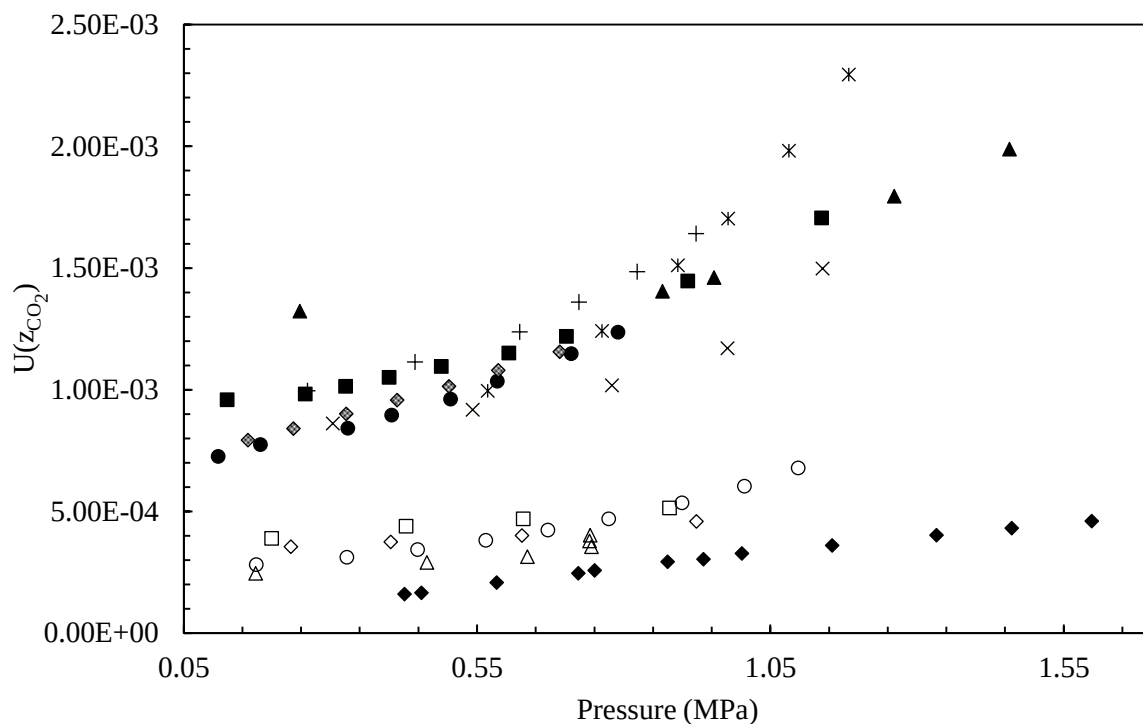


Figure B-1: $U(z_{CO_2})$ for the solvents and solvent blends containing NMP(1), MEA(2), H₂O(3) and DGA(4). $\blacklozenge$ $w_1=1$, $\triangle$ $w_2/w_3=0.2960/0.7040$, $\blacktriangle$ $w_2/w_1=0.2990/0.7010$, $\times$ $w_2/w_1=0.1803/0.8198$, $\circ$ $w_4/w_3=0.5106/0.4894$, $\bullet$ $w_4/w_1=0.5096/0.4904$, $\square$ $w_4/w_3=0.3998/0.6002$, $\blacksquare$ $w_4/w_1=0.4001/0.5999$, $*$ $w_4/w_1=0.4001/0.5999$ regenerated, $\diamond$ $w_4/w_3=0.3025/0.6975$, $\blacklozenge$ $w_4/w_1=0.3015/0.6985$, $+$ $w_4/w_1=0.3015/0.6985$ regenerated

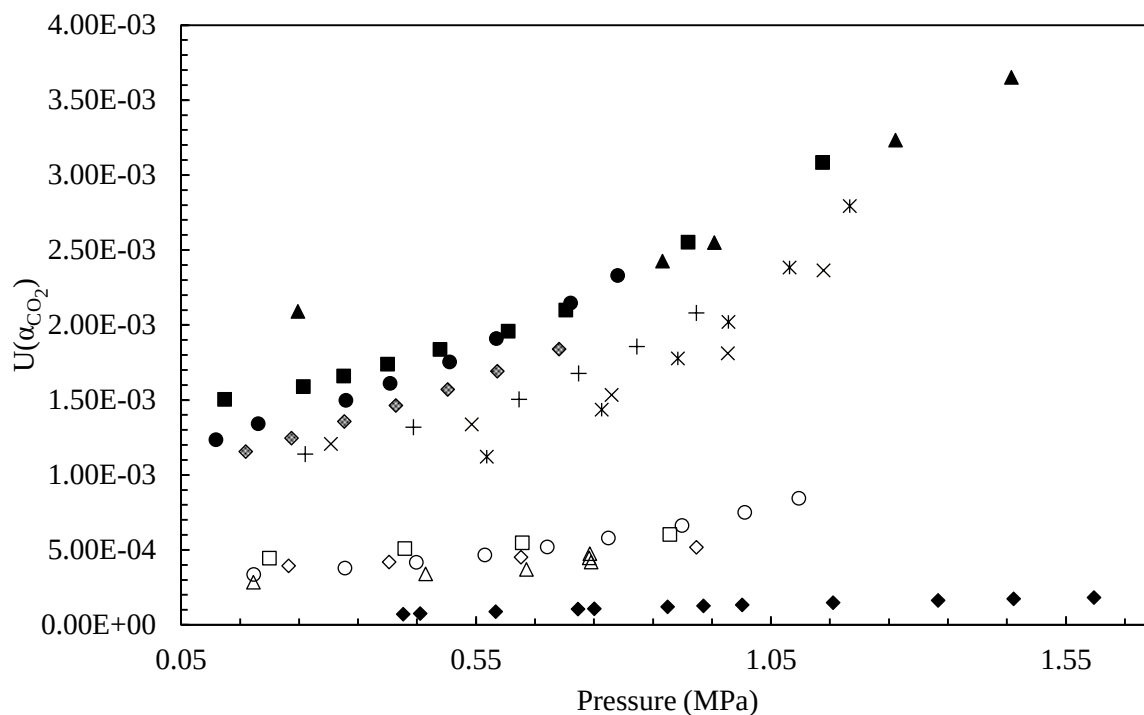


Figure B-2: $U(\alpha_{CO_2})$ for the solvents and solvent blends containing NMP(1), MEA(2), H₂O(3) and DGA(4). $\blacklozenge$ $w_1=1$, $\triangle$ $w_2/w_3=0.2960/0.7040$, $\blacktriangle$ $w_2/w_1=0.2990/0.7010$, $\times$ $w_2/w_1=0.1803/0.8198$, $\circ$ $w_4/w_3=0.5106/0.4894$, $\bullet$ $w_4/w_1=0.5096/0.4904$, $\square$ $w_4/w_3=0.3998/0.6002$, $\blacksquare$ $w_4/w_1=0.4001/0.5999$, $*$ $w_4/w_1=0.4001/0.5999$ regenerated, $\diamond$ $w_4/w_3=0.3025/0.6975$, $\blacklozenge$ $w_4/w_1=0.3015/0.6985$, $+$ $w_4/w_1=0.3015/0.6985$ regenerated

Comparing Figure B-1 and Figure B-2, $U(\alpha_{CO_2})$ is slightly higher than $U(z_{CO_2})$ for the respective system at the same pressure, although these differences are not large enough to have an appreciable effect on the calculated loading or overall composition. In both figures, the pure NMP solvent has the lowest uncertainty due to no solvent mixing and simpler composition calculations, while the 29.90 wt% MEA–70.10 wt% NMP blend has the highest uncertainty due to the highest measured pressure of the water-lean solvent blends. It can also be observed that as pressure increases, the uncertainty increases. This is due to more gas compression occurring at higher pressures. Therefore, the measurements are more accurate at lower pressures. In both figures, the solvent blends containing water have lower uncertainties than the respective water-lean blend. Since the calculations to transform the measured T-P-z data to T-P- α_{CO_2} data are only in terms of the amine, any CO_2 absorption by the NMP is neglected. The calculations are valid since the results are only in terms of the amine; however, uncertainties are introduced as a result. A recommendation for reducing the uncertainty is to use the minimum possible pressure in the gas reservoir when loading the equilibrium cell with gas from the reservoir. Since higher pressures cause the gas to be compressed more, there is a greater uncertainty for the number of moles added to the equilibrium cell.

APPENDIX C: MATLAB® FILES

The following sections have the same names as the MATLAB® code files and give a brief description of what each code file contains.

C.1. Posey_modelling

This is the main code file, which uses the Posey-Tapperson-Rochelle model to determine CO₂ loading in solvents containing an amine. For ease of use, the code pulls the user-selected data from the Data_Bank code, uses the relevant functions to calculate the system pressure, then plots the results with the experimental data in a P - α_{CO_2} graph and displays the regressed parameters. If the selected system contains water, the Amine_Var function is used to regress for the Posey-Tapperson-Rochelle parameters and the calculated pressure is plotted against the experimental pressure. If the selected system contains NMP, the Amine_Var function is used to regress for the Posey-Tapperson-Rochelle model parameters, the PR_Model_regressed_parameters function is used to regress for the PR-EOS mixing rule parameters, and the combined calculated pressure is plotted against the experimental pressure.

C.2. Data_Bank

This code file stores the experimental data for each system referenced in the main code file. It also contains the densities and critical properties of each chemical in all the systems. The molar volume of CO₂ in the vapour phase, calculated previously from experimental data using the virial from of the PR-EOS, was used to calculate the density of CO₂ at each data point.

C.3. Amine_Var

This function contains the equations for the Posey-Tapperson-Rochelle model. The regression is carried out in the main code file using a built-in function and this function in order to calculate the value of the regressed parameters and pressure after each iteration. The calculated pressure is then used in the main code file.

C.4. PR_Model_regressed_parameters

This function contains the equations for the PR-EOS and its constants, and the equations for the mixing rules from Osman (2014) as described in Section 2.8.1. The regression is carried out in the main code file using a built-in function and this function to calculate the parameters and pressure after each iteration. This calculated pressure is then added to the pressure calculated using the Posey-Tapperson-Rochelle model in the main code file.

APPENDIX D: EXPERIMENTAL AND MODELLED VLE DATATable D-1: Experimental solubility data of CO₂ in NMP

T (K)	P (MPa)	V_v (cm³)	n_{CO₂,L} (mol)	n_{solvent} (mol)	z_{CO₂}	U(z_{CO₂})	x_{CO₂}	U(x_{CO₂})
313.33	0.427	14.75	0.0143	0.2979	0.0532	0.0002	0.0457	0.0001
313.31	0.455	13.49	0.0157	0.3029	0.0564	0.0002	0.0493	0.0001
313.33	0.584	14.52	0.0199	0.2979	0.0723	0.0002	0.0625	0.0001
313.31	0.723	13.05	0.0257	0.3029	0.0886	0.0002	0.0782	0.0001
313.33	0.751	14.30	0.0259	0.2979	0.0921	0.0003	0.0801	0.0001
313.34	0.875	14.14	0.0306	0.2979	0.1066	0.0003	0.0932	0.0001
313.32	0.936	12.71	0.0340	0.3029	0.1136	0.0003	0.1010	0.0001
313.34	1.001	13.90	0.0355	0.2979	0.1213	0.0003	0.1065	0.0001
313.33	1.155	12.34	0.0430	0.3029	0.1387	0.0004	0.1243	0.0001
313.33	1.333	12.02	0.0505	0.3029	0.1586	0.0004	0.1430	0.0002
313.34	1.461	11.79	0.0561	0.3029	0.1727	0.0004	0.1563	0.0002
313.34	1.598	11.50	0.0623	0.3029	0.1876	0.0005	0.1705	0.0002

U(T) = 0.02 K, U(P) = 0.002 MPa, System uncertainty: U(NMP) = 0.15%

APPENDIX D: EXPERIMENTAL AND MODELLED DATA

Table D-2: Experimental solubility data of CO₂ in MEA(1)/H₂O(2) and MEA(1)/NMP(3)

T (K)	P (MPa)	V _v (cm ³)	n _{CO₂,L} (mol)	n _{solvent} (mol)	z _{CO₂}	U(z _{CO₂})	α _{CO₂}	U(α _{CO₂})
w₁/w₂=0.2960/0.7040								
313.27	0.173	14.69	0.0923	1.2936	0.0673	0.0002	0.6466	0.0003
313.26	0.465	14.41	0.1036	1.2936	0.0759	0.0003	0.7259	0.0003
313.28	0.636	14.33	0.1078	1.2936	0.0793	0.0003	0.7550	0.0004
313.27	0.745	14.28	0.1099	1.2936	0.0811	0.0004	0.7700	0.0004
313.24	0.742	14.06	0.1100	1.2936	0.0811	0.0004	0.7706	0.0004
313.27	0.743	14.23	0.1099	1.2936	0.0811	0.0004	0.7702	0.0005
w₁/w₃=0.2990/0.7010								
313.31	0.248	15.99	0.0829	0.3227	0.2075	0.0013	0.6283	0.0021
313.29	0.866	15.33	0.1015	0.3227	0.2487	0.0014	0.7689	0.0024
313.31	0.954	15.24	0.1035	0.3227	0.2531	0.0015	0.7840	0.0025
313.32	1.261	15.03	0.1103	0.3227	0.2678	0.0018	0.8353	0.0032
313.33	1.458	14.88	0.1145	0.3227	0.2767	0.0020	0.8671	0.0036
w₁/w₃=0.1803/0.8179								
313.31	0.304	17.84	0.0547	0.2973	0.1603	0.0009	0.6989	0.0012
313.28	0.543	17.64	0.0615	0.2973	0.1800	0.0009	0.7865	0.0013
313.28	0.780	17.37	0.0675	0.2973	0.1970	0.0010	0.8634	0.0015
313.30	0.977	17.19	0.0724	0.2973	0.2102	0.0012	0.9253	0.0018
313.30	1.139	17.03	0.0763	0.2973	0.2206	0.0015	0.9755	0.0024

U(T) = 0.02 K, U(P) = 0.002 MPa. System uncertainties: U(w₁=0.2960) = 0.23%, U(w₁=0.2990) = 1.39%, U(w₁=0.1803) = 0.82%

APPENDIX D: EXPERIMENTAL AND MODELLED DATA

Table D-3: Experimental and modelled solubility data of CO₂ in DGA(1)/H₂O(2) and DGA(1)/NMP(3)

T (K)	P ^{exp} (MPa)	P ^{model} (MPa)	V _v (cm ³)	n _{CO₂,L} (mol)	n _{solvent} (mol)	z _{CO₂}	U(z _{CO₂})	α _{CO₂}	U(α _{CO₂})
w₁/w₂=0.5106/0.4894									
313.35	0.174	0.000	18.61	0.0774	0.8418	0.0855	0.0003	0.6062	0.0003
313.30	0.328	0.334	18.44	0.0833	0.8418	0.0923	0.0003	0.6522	0.0004
313.33	0.449	0.592	18.39	0.0863	0.8418	0.0962	0.0003	0.6761	0.0004
313.34	0.565	0.462	18.33	0.0888	0.8418	0.0993	0.0004	0.6950	0.0005
313.31	0.671	0.712	18.28	0.0907	0.8418	0.1019	0.0004	0.7101	0.0005
313.30	0.774	0.831	18.23	0.0923	0.8418	0.1043	0.0005	0.7231	0.0006
313.30	0.899	0.820	18.19	0.0941	0.8418	0.1068	0.0005	0.7371	0.0007
313.27	1.006	1.088	18.14	0.0956	0.8418	0.1089	0.0006	0.7482	0.0007
313.29	1.097	0.904	18.08	0.0967	0.8418	0.1106	0.0007	0.7570	0.0008
w₁/w₂=0.3998/0.6002									
313.34	0.200	0.194	13.33	0.0794	1.1684	0.0644	0.0004	0.6633	0.0004
313.31	0.429	0.423	13.14	0.0876	1.1684	0.0713	0.0004	0.7312	0.0005
313.34	0.629	0.622	13.00	0.0921	1.1684	0.0755	0.0005	0.7695	0.0005
313.35	0.878	0.872	12.87	0.0964	1.1684	0.0795	0.0005	0.8053	0.0006
w₁/w₂=0.3025/0.6975									
313.35	0.233	0.226	14.30	0.0646	1.2559	0.0499	0.0004	0.7438	0.0004
313.30	0.403	0.396	14.16	0.0695	1.2559	0.0540	0.0004	0.7997	0.0004
313.33	0.626	0.620	14.04	0.0737	1.2559	0.0579	0.0004	0.8487	0.0004
313.36	0.924	0.917	13.98	0.0778	1.2559	0.0620	0.0005	0.8952	0.0005
w₁/w₃=0.5096/0.4904									
313.32	0.109	0.111	16.18	0.0839	0.2764	0.2343	0.0007	0.6134	0.0012
313.31	0.181	0.183	16.15	0.0875	0.2764	0.2428	0.0008	0.6398	0.0013
313.30	0.330	0.353	15.91	0.0923	0.2764	0.2545	0.0008	0.6749	0.0015
313.31	0.404	0.400	15.86	0.0944	0.2764	0.2595	0.0009	0.6899	0.0016

APPENDIX D: EXPERIMENTAL AND MODELLED DATA

Table D-3 continued

T (K)	P ^{exp} (MPa)	P ^{model} (MPa)	V _v (cm ³)	n _{CO₂,L} (mol)	n _{solvent} (mol)	z _{CO₂}	U(z _{CO₂})	α _{CO₂}	U(α _{CO₂})
w₁/w₃=0.5096/0.4904									
313.30	0.505	0.468	15.80	0.0968	0.2764	0.2655	0.0010	0.7077	0.0018
313.32	0.585	0.596	15.77	0.0989	0.2764	0.2706	0.0010	0.7230	0.0019
313.33	0.711	0.724	15.66	0.1015	0.2764	0.2770	0.0011	0.7420	0.0021
313.34	0.790	0.779	15.58	0.1031	0.2764	0.2809	0.0012	0.7536	0.0023
w₁/w₃=0.4001/0.5999									
313.32	0.124	0.132	15.60	0.0715	0.2840	0.2027	0.0010	0.6518	0.0015
313.32	0.257	0.329	15.43	0.0772	0.2840	0.2171	0.0010	0.7044	0.0016
313.33	0.326	0.309	15.27	0.0793	0.2840	0.2225	0.0010	0.7235	0.0017
313.32	0.400	0.395	15.22	0.0814	0.2840	0.2277	0.0011	0.7420	0.0017
313.32	0.489	0.450	15.14	0.0836	0.2840	0.2335	0.0011	0.7626	0.0018
313.30	0.604	0.600	15.03	0.0865	0.2840	0.2408	0.0012	0.7886	0.0020
313.31	0.703	0.675	14.95	0.0887	0.2840	0.2464	0.0012	0.8088	0.0021
313.31	0.910	0.912	14.79	0.0932	0.2840	0.2576	0.0014	0.8496	0.0025
313.30	1.138	1.148	14.57	0.0979	0.2840	0.2693	0.0017	0.8931	0.0031
w₁/w₃=0.4001/0.5999 after solvent regeneration									
313.32	0.568	-	18.92	0.0165	0.2713	0.0709	0.0010	0.1571	0.0011
313.29	0.763	-	18.74	0.0204	0.2713	0.0877	0.0012	0.1946	0.0014
313.31	0.892	-	18.64	0.0227	0.2713	0.0978	0.0015	0.2170	0.0018
313.32	0.978	-	18.60	0.0242	0.2713	0.1042	0.0017	0.2314	0.0020
313.33	1.081	-	18.51	0.0261	0.2713	0.1120	0.0020	0.2495	0.0024
313.32	1.184	-	18.56	0.0279	0.2713	0.1197	0.0023	0.2667	0.0028
w₁/w₃=0.3015/0.6985									
313.34	0.160	0.159	14.53	0.0610	0.2961	0.1729	0.0008	0.7122	0.0012
313.33	0.237	0.261	14.44	0.0645	0.2961	0.1818	0.0008	0.7525	0.0012

APPENDIX D: EXPERIMENTAL AND MODELLED DATA

Table D-3 continued

T (K)	P ^{exp} (MPa)	P ^{model} (MPa)	V _v (cm ³)	n _{CO₂,L} (mol)	n _{solvent} (mol)	z _{CO₂}	U(z _{CO₂})	α _{CO₂}	U(α _{CO₂})
w₁/w₃=0.3015/0.6985									
313.32	0.327	0.316	14.30	0.0674	0.2961	0.1894	0.0009	0.7866	0.0014
313.33	0.414	0.409	14.21	0.0699	0.2961	0.1961	0.0010	0.8164	0.0015
313.34	0.502	0.486	14.15	0.0724	0.2961	0.2024	0.0010	0.8448	0.0016
313.35	0.586	0.586	14.04	0.0746	0.2961	0.2082	0.0011	0.8710	0.0017
313.32	0.691	0.700	13.97	0.0774	0.2961	0.2153	0.0012	0.9040	0.0018
w₁/w₃=0.3015/0.6985 after solvent regeneration									
313.35	0.261	-	18.62	0.0188	0.2710	0.0710	0.0010	0.2402	0.0011
313.32	0.444	-	18.47	0.0237	0.2710	0.0904	0.0011	0.3026	0.0013
313.33	0.623	-	18.36	0.0277	0.2710	0.1062	0.0012	0.3529	0.0015
313.34	0.724	-	18.17	0.0298	0.2710	0.1146	0.0014	0.3806	0.0017
313.34	0.823	-	18.03	0.0319	0.2710	0.1225	0.0015	0.4071	0.0019
313.34	0.924	-	18.02	0.0340	0.2710	0.1307	0.0016	0.4344	0.0021

U(T) = 0.02 K, U(P^{exp}) = 0.002 MPa. System uncertainties: U(w₁=0.5106) = 0.49%, U(w₁=0.5096) = 1.38%, U(w₁=0.3998) = 0.21%, U(w₁=0.4001) = 1.80%, U(w₁=0.4001 regenerated) = 1.15%, U(w₁=0.3025) = 0.18%, U(w₁=0.3015) = 1.03%, U(w₁=0.3015 regenerated) = 0.96%