

Physical Properties Analysis of Aqueous Blends of Potassium Carbonate and Piperazine as CO₂ Capture Solvent

By

Naathiya Mannar

15341

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

September 2014

Universiti Teknologi PETRONAS,
Bandar Seri Iskandar,
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Approved by,

(Dr. Bhajan Lal)

FYP Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NAATHIYA A/P MANNAR

ABSTRACT

It is widely known that carbon dioxide (CO₂) is one of the major greenhouse gas (GHG) contributors. It is very important for the industries, such as oil and gas, to reduce the amount of emission to the atmosphere. There have been many researches and studies conducted in order to come up with the most effective absorber for CO₂ capture. Potassium carbonate is being looked into by the industry as a potential solvent for absorption of CO₂ to replace alkanolamines due to its ability to resist oxidation degradation, low volatility due to its ionic structure and low binding energy. The introduction of promoter like piperazine to potassium carbonate helps to further enhance the CO₂ solubility effect by acting as catalyst to speed up the absorption process. In this project, the physical properties of aqueous blend solution of piperazine activated potassium carbonate are studied. The properties are measured over the wide range of temperature of (20-80) °C. The objectives of this project are;

1. To study on the effect of the temperature change on the properties of the blends (PC+PZ);
2. To study on effect of concentration change on the properties of the blends (PC+PZ).
3. To compare the results with the conventional blend solvent, Methyl-Diethanolamine (MDEA).

This project is an experimental based project and the time period given, the experimental work covers the physical properties analysis which consists of determination of the density and viscosity over various concentrations and temperature of the blends. Based on the observation of this project, the density and viscosity of piperazine activated aqueous potassium carbonate increases as the concentration of piperazine increases. It is also been noticed that the density and viscosity decreases with the increasing temperature.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

It is widely known that the increase in greenhouse gas (GHG) emissions to our atmosphere is the major contributor to global climate change. As the political and environmental demand increases, efficient methods for the CO₂ removal from the atmosphere will become increasingly important. There are many type of processes generate CO₂ which results in the release of acidic contaminants, eg. H₂S, SO_x, NO_x, CO₂. According to U. S. Environmental Protection Agency (EPA), combustion of fossil fuels accounts for 96 % of the total CO₂ emission in the US, with approximately 36% of total CO₂ emissions from electricity generation in coal-fired power plants. In the year 2007, the Intergovernmental Panel on Climate Change (IPCC) stated that global average temperature is likely to increase by between 1.1 and 6.4 during the 21st century.

1.1.1 Sources of Carbon Dioxide

Both natural and anthropogenic sources contribute to the ongoing emission of GHG, particularly CO₂. While natural emission from volcanoes, forest fires and biomass decomposition are significant, they are relatively constant from year to year. Man-made CO₂ emissions from power plants, manufacturing and automobiles have increased steadily since the industrial revolution and have become a major concern and a contributing factor to global warming.

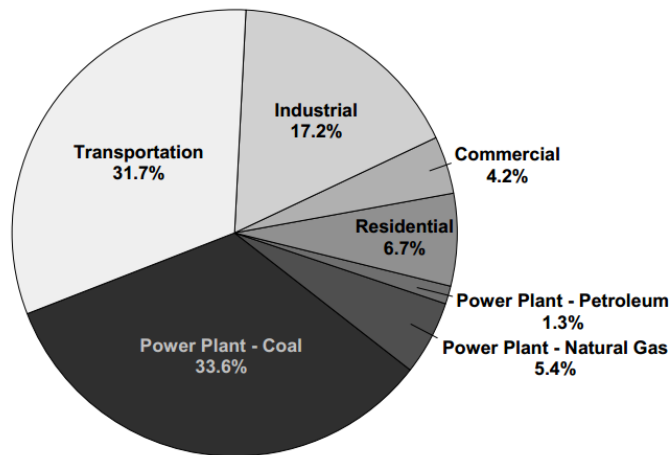
The major sources of man-made CO₂ emission showed in Table 1. Fossil fuel combustion accounts for >95% of the CO₂ emitted annually. The balance originates from processes such as iron and steel production, cement manufacturing and ammonia production.

Table 1 Annual CO₂ Emission in the United States in Tg CO₂ Eq.

Source	1999	2000	2001	2002
Fossil Fuel Combustion	5,488.8	5,673.6	5,558.8	5,611.0
Iron and Steel Production	64.4	65.7	59.1	54.4
Cement Manufacturing	40.0	41.2	41.4	42.9
Waste Combustion	17.6	18.0	18.8	18.8
Ammonia/Urea Production	20.6	19.6	16.2	17.7
Lime Production	13.5	13.3	12.8	12.3
Limestone/Dolomite Use	8.1	6.0	5.7	5.8
Gas Flaring	6.9	5.8	5.4	5.3
Aluminum Production	5.9	5.7	4.1	4.2
Soda Ash	4.2	4.2	4.1	4.1
Others	6.3	6.0	5.3	5.8
Total	5,676.3	5,859.0	5,731.8	5,782.4

Given the overwhelming percentage of emissions from fossil fuel combustion, it becomes useful to analyze this source as individual sectors for simplified classification. CO₂ emissions are shown in Figure 1 for four point-source sectors, including electricity generation and the residential, commercial, and industrial sectors (EPA, 2004). The transportation sector is also included.

Figure 1 CO₂ Emission from Fossil Fuel Combustion in the U.S., Total Emission: 5564.2 Tg CO₂ Eq.



Another important factor to consider is the efficiency of fuels for power production. The efficiency is directly related to the amount of fuel, and thus the amount of CO₂ produced, necessary to produce given quantities of electricity. Of the three main plant types, natural gas-fired plants are the most efficient (55 to 60%) and the cleanest burning in terms of carbon, producing 0.45 kg CO₂/kW-hr (IEA, 2001). Power production from petroleum fuels gives 0.80 kg CO₂/kW-hr.

Coal-fired plants produce the most carbon, approximately 0.96 kg CO₂/kW-hr, and is only 40 to 50% efficient.

It is clear that the largest potential application for CO₂ capture is coal-fired power plants. Coal combustion is a well-established technology accounting for 50% of the power in the U.S. The abundance of coal as a natural resource makes it a cheap, readily available fuel. In short, it is the largest contributor to overall CO₂ emissions and trends suggest an expanding share of the power production market. Improvements in capture technology for coal-fired power plants will be essential for making a significant impact on U.S. CO₂ emissions; therefore, most of the research presented in this work is targeted to conditions of coal-fired power plants.

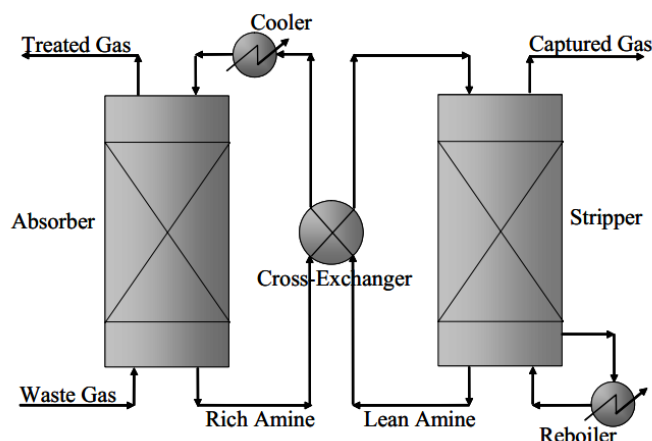
1.1.2 Carbon Dioxide Removal by Absorption/Stripping

One of the most researched, technologies for acid gas capture from waste gas streams is an absorber/stripper process that uses a circulated chemical solvent (Kohl and Reisenfeld, 1985). Processes such as this are currently used in ammonia production and natural gas treating. There are several variations of this flow sheet, including a temperature swing and an isothermal process.

In the most common absorption process, the temperature swing variation (Figure 2), a waste gas stream containing CO₂ enters the bottom of an absorber (Kohl and Reisenfeld, 1985). The CO₂ is removed and the treated gas exits the top of the column.

A CO₂-lean solvent enters the top of the absorber and counter-currently contacts the gas phase in packing or on trays. The CO₂ is absorbed, and the rich solvent exits the absorber. The rich solvent is pre-heated in a cross exchanger and pumped to the top of a stripper. Heat, from intermediate or low pressure steam, is applied, regenerating the solvent. A concentrated CO₂ stream is recovered. Some heat is recovered from the lean solvent, though the solvent requires further cooling before its re-use in the absorber.

Figure 2 Absorber/Stripper Process Flow sheet



1.1.3 Solvents

Many solvents have been applied to gas treating, but the most effective are generally considered to be aqueous amines or hot potassium carbonate (hotpot) solvents. The variety of amines is endless, but some of the more common are shown in Table 2. Amines have an advantage over the hotpot process in that the absorption rate of CO₂ by amines is fast; however, the heat of absorption is also high. In contrast, absorption into potassium carbonate has a heat of absorption similar to physical solvents, but is limited by slow absorption rates.

Table 2 Common Amines in Gas Treating (Kohl and Riesenfeld, 1985)

Class	Name (Abbr.)	Structure
Primary Amine	Monoethanolamine (MEA)	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{N}\begin{matrix} \text{H} \\ \text{H} \end{matrix}$
	Diglycolamine® (DGA) ^a	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{N}\begin{matrix} \text{H} \\ \text{H} \end{matrix}$
Secondary Amine	Diethanolamine (DEA)	$\begin{matrix} \text{HO}-\text{CH}_2-\text{CH}_2 \\ \\ \text{HO}-\text{CH}_2-\text{CH}_2 \end{matrix} \text{N}-\text{H}$
	Diisopropanolamine (DIPA)	$\begin{matrix} \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CH}_3 \\ & & & \\ \text{CH} & & \text{CH} & \\ & & & \\ \text{OH} & & \text{H} & \\ & & & \\ & & \text{N} & \end{matrix}$
Tertiary Amine	Triethanolamine (TEA)	$\begin{matrix} \text{HO}-\text{CH}_2-\text{CH}_2 \\ \\ \text{HO}-\text{CH}_2-\text{CH}_2 \end{matrix} \text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$
	Methyldiethanolamine (MDEA)	$\begin{matrix} \text{HO}-\text{CH}_2-\text{CH}_2 \\ \\ \text{HO}-\text{CH}_2-\text{CH}_2 \end{matrix} \text{N}-\text{CH}_3$
Hindered Amine	Isobutanolamine (AMP)	$\begin{matrix} \text{CH}_3 \\ \\ \text{HO}-\text{CH}_2-\text{C} \\ \\ \text{CH}_3 \end{matrix} \text{N}\begin{matrix} \text{H} \\ \text{H} \end{matrix}$

a. Diglycolamine (DGA) is a registered trademark of Huntsman Chemical.

1.3.1.1 Potassium Carbonate/Piperazine for Carbon Dioxide Capture

This paper proposes a new blend, containing aqueous potassium carbonate and piperazine, for CO₂ capture from gas stream. The structure of PZ and its derivatives in aqueous solution with CO₂ are shown in Figure 3. Piperazine carbamate (PZCOO⁻) and piperazine dicarbamate (PZ(COO⁻)₂) are the products of the reaction with PZ. Protonated piperazine (PZH⁺) and protonated piperazine carbamate (H⁺PZCOO⁻) are known stable molecules at moderate pH. A diprotonated PZ exists below a pH of approximately 5.5, but conditions in this work never approach low pH, so this species is excluded from consideration.

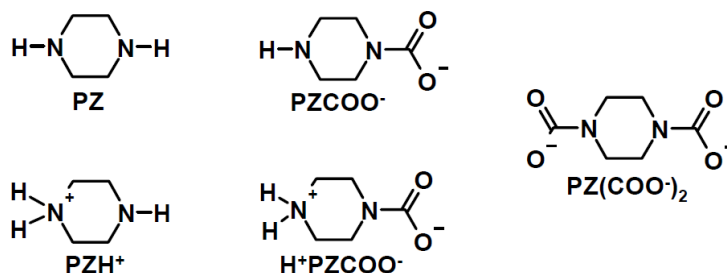


Figure 3 Structures of Piperazine in the Presence of CO₂

The solvent holds several advantages over traditional amines. First, because PZ is a diamine, the solvent can react with two moles of CO₂ per mole of amine. Coupled with the potassium carbonate in solution, which provides an additional sink for storage of the absorbed CO₂, the solvent has the potential for a higher CO₂ capacity than other amines. Also, the two amine functional groups will favourably affect the rate of absorption. Second, the amine has a high pKa, similar to that of MEA. A high pKa generally translates into a fast rate of absorption. Third, the large quantity of carbonate/bicarbonate in solution serves as a buffer, reducing the protonation of the amine and leaving more amine available for reaction with CO₂.

1.2 Problem Statement

There are several critical questions been addressed to develop a better understanding of K⁺/PZ mixtures as applied to CO₂. While quantifying specific performance characteristics, it becomes beneficial to further develop the underlying fundamental science.

Thus so far, studies have been published in the thermodynamics of polyamines or salt-amines mixtures. Of fundamental interest in the understanding of the thermodynamics is a description of amine specification with CO₂ and, for PZ, and identification of differences resulting from unique, heterocyclic ring structure. In promoted K₂CO₃ systems, the impact of high ionic strength on equilibrium is largely unknown. An effective thermodynamic representation of K⁺/PZ will improve the fundamental understanding of other amine solutions and mixtures.

1.3 Objective of Study

The objectives of this paper are:

1.3.1 To determine the physical properties, viscosity and density, of a new aqueous blend of potassium carbonate and piperazine at various temperatures.

1.4 Scope of Study

The scope of this paper encompasses, to extend of identifying the physical properties of individual solvents, PZ, K₂CO₃ and H₂O, and also the mixtures. The properties which are focused on this paper are viscosity and density. That is, the temperature range interest is from 20 to 80°C and the concentration of PZ 2 to 10 % whereas the concentration of K₂CO₃ ranges from 5 to 25%.

A basic study of the solid solubility of K⁺/PZ mixtures was initiated to determine viable solvent compositions. Physical properties, such as density and viscosity, are being measured and studied to improve modelling and interpretation of fluid dependent parameters.

CHAPTER 2

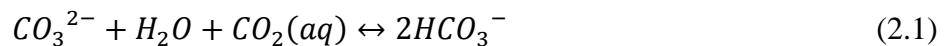
LITERATURE REVIEW

2.1 PROPERTIES OF SOLVENTS FOR CO₂ ABSORPTION

2.1.1 Potassium Carbonate

The value of potassium carbonate as a CO₂ absorbent has been recognized since the early 1900's. The process evolved over the years into a viable commercial process, often used in treating synthesis gas (Benson and Field, 1959). The preferred embodiment is a 40 wt% K₂CO₃ solution in an isothermal absorber/stripper at 100°C and 15 to 20 atm.

Much of the commercial validation was done by Benson *et al.* (1954) and Benson *et al.* (1956). These two studies show important pilot plant characterization of hot potassium carbonate (hotpot) versus aqueous MEA and conclude that, under specific configurations, hotpot is an efficient CO₂ absorbent. The absorption of CO₂ into aqueous K₂CO₃ is commonly represented by the overall reaction



though the reaction is usually described in terms of two parallel, reversible reactions.



Since the reaction with hydroxide is the rate-limiting step, the reaction rate is represented as a second order rate expression.

$$r_{CO_2} = k_{OH^-}[OH^-][CO_2] \quad (2.4)$$

This reaction, though important to the solution equilibrium, is generally much slower than aqueous amines, limiting its application in processes requiring a high percentage

of removal. It is often advantageous to add a promoter to increase the absorption rate. The energy required to reverse the reaction is typically less than that required for amine solvents.

2.1.1.1 Physical/Chemical Properties of Potassium Carbonate

Pure potassium carbonate is a solid at room temperature. The appearance of the substance and some physicochemical properties are mentioned in the Table 3.

Table 3 Physicochemical Properties of Potassium Carbonate

Physical State	Solid (Powder)
Colour	White
Density	2.43 g/cm ³ (19°C)
Melting Temperature	891°C
Boiling Temperature	The substance decomposes at high temperature
Molecular Weight	138.2 g/mol
Water Solubility	Very Soluble

Potassium carbonate dissociates completely in water into potassium (K⁺) and carbonate ions (CO₃²⁻). The dissolution in water is exothermic, so vigorous reaction can occur when potassium carbonate is added to water. The vapour pressure of the substance is very low and a melting point cannot be determined, as the substance decomposes at high temperature.

2.1.2 Piperazine

Some work has been done previously on aqueous PZ and its behaviour with CO₂. Ermatchkov *et al.* (2003) present speciation data from High Nuclear Magnetic Resonance (HNMR) experiments for 0.1 to 1.45 m PZ and CO₂ loadings of 0.1 to 1.0 mol CO₂/mol PZ. The temperature ranges from 10 to 60°C. This data set is essential for establishing a basis for a model of PZ thermodynamics, defining equilibrium constants and temperature dependences. Kamps *et al.* (2003) report total pressure data of CO₂/PZ mixtures from 40 to 120°C.

Unfortunately, most of this data are above loadings of 1.0 mol CO₂/mol PZ limiting its use in this work. Aroua and Salleh (2004) give equilibrium CO₂ partial pressure data for aqueous PZ under similar conditions (20 to 50°C and loadings > 0.8). Again, the high loading data are of limited use in modelling PZ at absorber/stripper conditions.

There is some research on PZ as a promoter in amines. Dang (2001) gives data for the absorption rate of CO₂ into PZ/MEA. The thermodynamics are represented by a simple equilibrium model based on previously determined equilibrium constants, but the work does show that PZ is an effective rate promoter for MEA. Bishnoi (2000) presents data on PZ/MDEA and rigorously models the thermodynamics and reaction rate. While information applicable to K₊/PZ is limited, the work of Bishnoi provides a foundation for the modelling and interpretation presented in this paper.

2.1.2.1 Physical/Chemical Properties of Piperazine

Table 4 Physicochemical Properties of Piperazine

Physical State	Solid
Density	146 g/cm ³ (19°C)
Melting Temperature	108-112°C
Boiling Temperature	145-146°C
Molecular Weight	86.13 g/mol

2.1.3 Amine-Promoted Potassium Carbonate

The process of CO₂ removal by absorption into K₂CO₃ has been used in natural gas treating and ammonia production for many years. The process has a low heat of absorption, making solvent regeneration more energy efficient. The rate of absorption is slow and absorber performance suffers. To counteract the slow absorption rates, amines can be added in small quantities to promote the hotpot process. The following discussion summarizes important work in the development of these solvents. A list of the investigations of the more common amine-promoters is presented in Table 3.

Table 5 Selected Studied of Amine-Promoted K₂CO₃

Amine	[Amine] (kmol/m ³)	[K ₂ CO ₃] (kmol/m ³)	T (°C)	Source	Method	Thermo	Rates
MEA	0.1	2	25	Shrier and Danckwerts (1969)	Stirred Cell	Yes	Yes
	1.0	0.4 – 1.0	11 – 25	Laddha and Danckwerts (1982)	Stirred Cell	No	Yes
	0.1	2.75	100	Mahajani and Danckwerts (1982)	BaCl	Yes	No
	0.1	2.75	100	Mahajani and Danckwerts (1983)	Stirred Cell	No	Yes
DEA	0.1	2	25	Shrier and Danckwerts (1969)	Stirred Cell	Yes	Yes
	1.0	0.4 – 1.0	11 – 25	Laddha and Danckwerts (1982; 1982)	Stirred Cell	No	Yes
	0.1	2.75	100	Mahajani and Danckwerts (1982)	BaCl	Yes	No
	0.0 – 0.314	2.75	100	Mahajani and Danckwerts (1983)	Stirred Cell	No	Yes
	0.6	2.0	40 – 120	Sartori and Savage (1983)	Autoclave/ Wetted-Sphere	Yes	Yes
	0.3 – 0.7	5.0	50 – 100	Tseng <i>et al.</i> (1988)	Wetted-sphere	No	Yes
DIPA	0.6	2.0	90	Bosch <i>et al.</i> (1989)	Modeling	-	-
	0.1	2.75	100	Mahajani and Danckwerts (1982)	BaCl	Yes	No
	0.101	2.75	100	Mahajani and Danckwerts (1983)	Stirred Cell	No	Yes
TEA	0.097	2.75	100	Mahajani and Danckwerts (1983)	Stirred Cell	No	Yes

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

As per the studies done before based the literature review, the blends of K_2CO_3/PZ will change the physical properties towards the CO_2 absorption. The properties vary as the temperature varies. Thus, a clear understanding on the study and vital objectives must be known. As per discussed in 1.3, the main aim of this study is to determine the physical properties, viscosity and density, of a new aqueous blend of potassium carbonate and piperazine at various temperatures. The next step is to analyze the related case and study on the blending composition, density and viscosity of blends to aid in CO_2 absorption.

There is some of the parameter of individual and mixture solvents are considered. Suggested methods of carrying this study are presented in the tables below.

3.1.1 Chemicals and Equipment needed



Table 6 List of Chemical required

Chemical	Purity (%)	Suggested Supplier
Piperazine	99.9	Merck, Malaysia
Potassium Carbonate	99	Merck, Malaysia

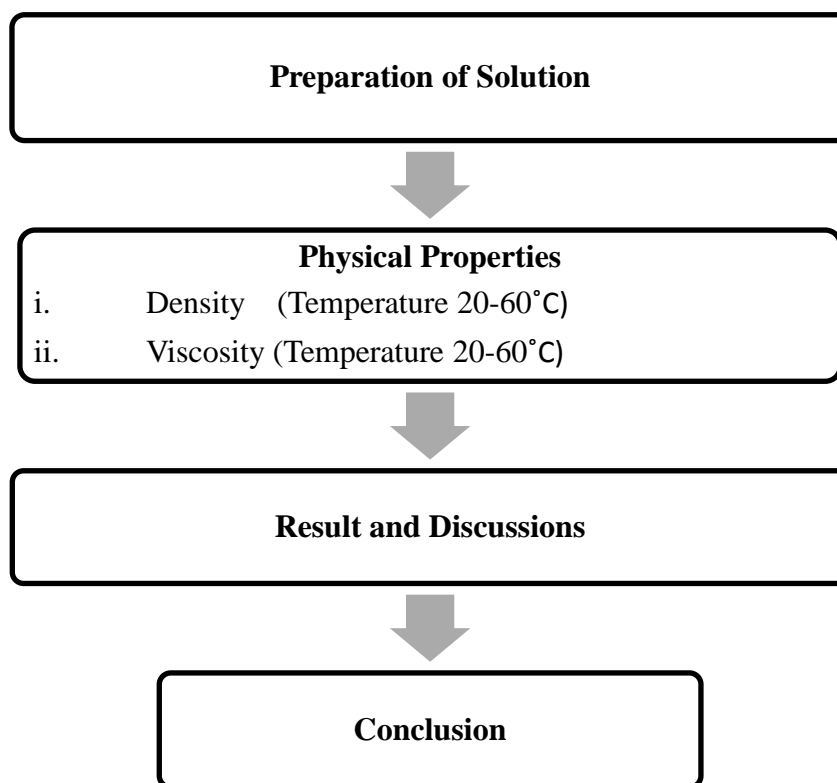
The main reagent for this project is potassium carbonate ($\geq 99\%$ purity) and promoter piperazine ($\geq 99\%$ pure) was obtained from Benua Sains Sdn Bhd, Malaysia. Different blends of PC+PZ will be prepared using distilled water. The blending ratio of aqueous PC/PZ will be approximately 2% to 25% of mass fraction and prepared gravimetrically using and analytical balance (Mettler Toledo AS120S) with an accuracy of $\pm 0.0001g$.

Equipments for the physical properties experiment:

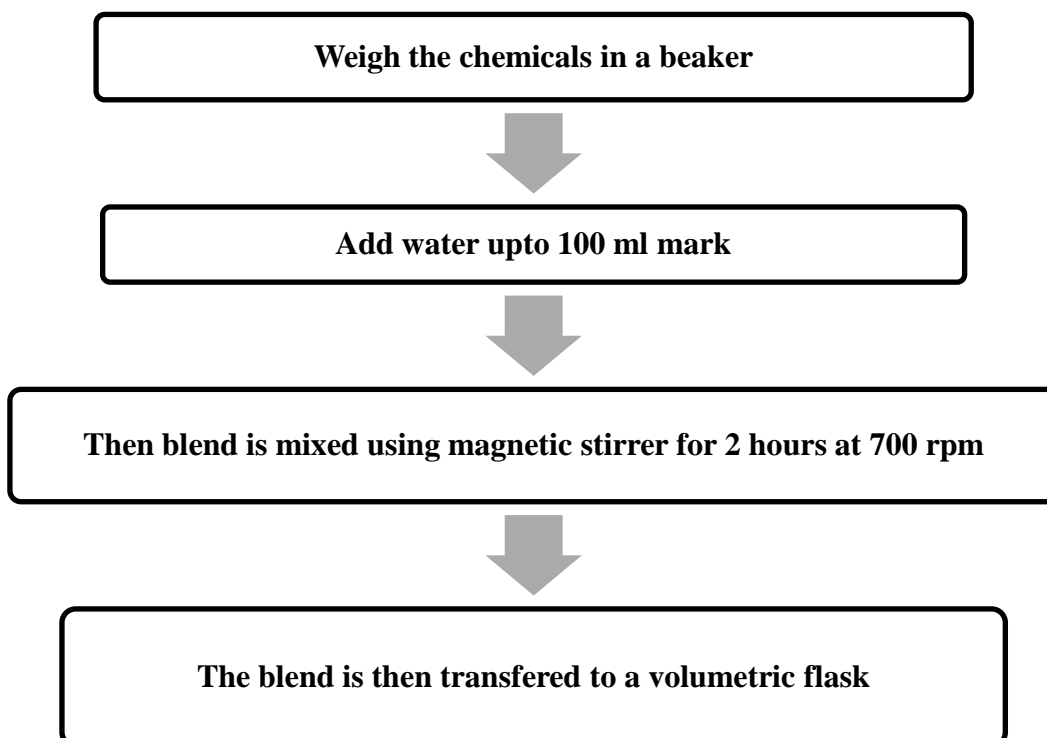
Table 7 List of equipment required

Measurement	Equipment	Availability
Density	<p data-bbox="612 423 1123 456">Mettler Toledo Density Meter (DM 40)</p>  <p data-bbox="639 517 1118 965">The image shows a white Mettler Toledo DM 40 density meter. It consists of a main unit with a blue handle on the right and a separate digital display unit. The display unit shows a reading of 0.9995. The Mettler Toledo logo is visible on the front of the main unit.</p>	<p data-bbox="1270 423 1382 510">Block 5, Level G</p>
Viscosity	<p data-bbox="520 1043 1182 1077">Digital Anton Par microviscometer (Lovis-2000M)</p>  <p data-bbox="523 1093 1214 1592">The image shows a digital Anton Par microviscometer (Lovis-2000M). It is a white, boxy device with a digital display on the front and a sample compartment on the right side. The device is set against a dark background with a blue light effect.</p>	<p data-bbox="1262 1272 1390 1359">Block N, RCCO₂C</p>

3.2 Project Activities



3.2.1 Preparation of solution



3.2.2 Concentration of the blends

There are 35 blends in total:

Table 8: Concentration of the blends

Binary Blends	
2 % Piperazine (PZ) + 98 % H ₂ O	5 % Potassium Carbonate (PC) + 95 % H ₂ O
4 % PZ + 96 % H ₂ O	10 % PC + 90 % H ₂ O
6 % PZ + 94 % H ₂ O	15 % PC + 85 % H ₂ O
8 % PZ + 92 % H ₂ O	20 % PC + 80 % H ₂ O
10 % PZ + 90 % H ₂ O	25 % PZ + 75 % H ₂ O
Ternary Blends	
5 % PC + 2% PZ + 93 % H ₂ O	10 % PC + 2% PZ + 88 % H ₂ O
5 % PC + 4% PZ + 91 % H ₂ O	10 % PC + 4% PZ + 86 % H ₂ O
5 % PC + 6% PZ + 89 % H ₂ O	10 % PC + 6% PZ + 84 % H ₂ O
5 % PC + 8% PZ + 87 % H ₂ O	10 % PC + 8% PZ + 82 % H ₂ O
5 % PC + 10% PZ + 85 % H ₂ O	10 % PC + 10% PZ + 80 % H ₂ O
15 % PC + 2% PZ + 83 % H ₂ O	20 % PC + 2% PZ + 78 % H ₂ O
15 % PC + 4% PZ + 81 % H ₂ O	20 % PC + 4% PZ + 76 % H ₂ O
15 % PC + 6% PZ + 79 % H ₂ O	20 % PC + 6% PZ + 74 % H ₂ O
15 % PC + 8% PZ + 77 % H ₂ O	20 % PC + 8% PZ + 72 % H ₂ O
15 % PC + 10% PZ + 75 % H ₂ O	20 % PC + 10% PZ + 70% H ₂ O
25 % PC + 2% PZ + 73 % H ₂ O	
25 % PC + 4% PZ + 71 % H ₂ O	
25 % PC + 6% PZ + 69 % H ₂ O	
25 % PC + 8% PZ + 67 % H ₂ O	
25 % PC + 10% PZ + 65 % H ₂ O	

* Percentages are the weight percentages

3.3 Physical Properties Measurement

Density

The density of different aqueous (PC+PZ) blends was measured using a digital densimeter (Mettler Toledo, DM 40) with an accuracy of $\pm 5 \times 10^{-5}$ g·cm⁻³. The apparatus was calibrated each time before and after the measurement in order to obtain accurate results. Standard water of Millipore quality was used in the calibration process.

Viscosity

A digital rolling ball microviscometer (Anton Par, model Lovis-2000M / ME) with an accuracy of up to 0.5 % was used to measure the viscosity of the aqueous (PC+PZ) blends. Before filling the sample in a suitable capillary, the capillary was properly washed with acetone, and air-dried to avoid any error in the reading. Before and after each experiment, the viscometer was carefully calibrated with Millipore water. For the measurement, the capillary was filled with the sample by the help of the syringe, kept inside the viscometer until the set temperature was achieved, and finally, the measurement was started.

3.4 Gantt Chart and Key Milestone

Table 9 Gantt chart and Key Milestone for FYP

Activities \ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Confirmation of Project	■	■																										
First meeting with supervisor		■																										
Preliminary project works		■	■	■	■																							
Submission of Proposal						●																						
Proposal Defence								■																				
Experimental Run									■	■	■	■	■	■														
Data extraction													■	■														
Submission of interim report														●														
Experimental Run																■	■	■	■									
Data extraction																■	■	■	■									

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	
Submission of Progress report																			●										
Experiment Run																					■	■	■						
Report writing																						■							
Pre-SEdEx																						●							
Submission of technical paper																										●			
Submission of final report																										●			
Oral Presentation																											●		
Submission of hardbound																												●	

● Suggested Milestone

■ Process

CHAPTER 4

RESULTS AND DISCUSSION

The physical properties such as density and viscosity of piperazine activates aqueous solution of potassium carbonate (PC+PZ) were experimentally measured for 25 various concentrations over a wide range of temperature.

4.1 Density

The measured densities of piperazine activated aqueous solution of potassium carbonate (PC+PZ) at the temperature range from (20 to 60) °C are shown below:

Table 10 Density of water

Temperature (°C)		Density (g/cm ³)			
		1	2	3	Avg
20	293.15	0.9981	0.9981	0.9981	0.9981
30	303.15	0.9957	0.9957	0.9957	0.9957
40	313.15	0.9923	0.9923	0.9923	0.9923
50	323.15	0.9882	0.9881	0.9882	0.9882
60	333.15	0.9829	0.9827	0.9832	0.9829

Figure 4 Plot of density of water against Temperature range (20-60°C)

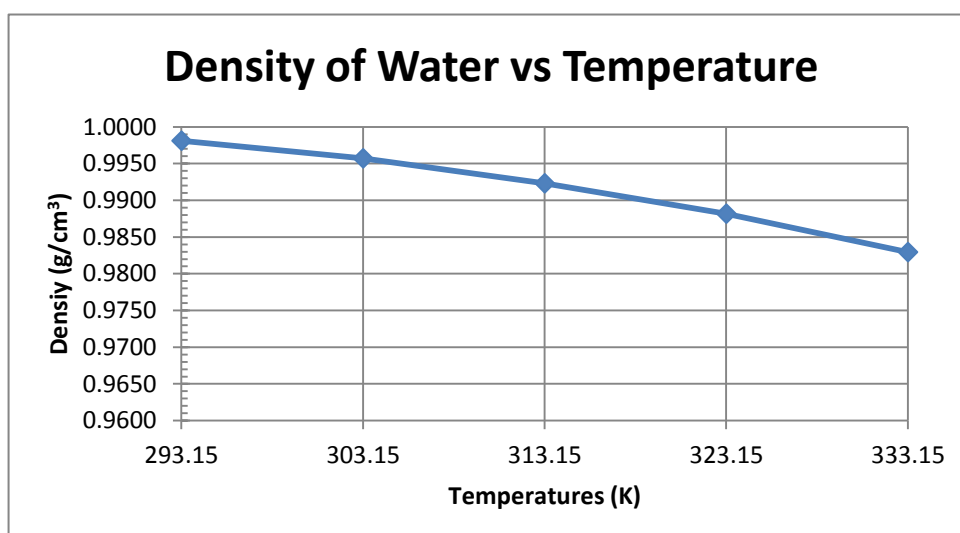


Table 11 Density of Potassium Carbonate

Temperature (°C)		Density (g/cm ³)					
		0% PC	5% PC	10% PC	15% PC	20% PC	25% PC
		100% H ₂ O	95% H ₂ O	90% H ₂ O	85% H ₂ O	80% H ₂ O	75% H ₂ O
20	293.15	0.9981	1.0411	1.0823	1.1207	1.1585	1.1967
30	303.15	0.9957	1.0385	1.0792	1.1176	1.1551	1.1930
40	313.15	0.9923	1.0349	1.0754	1.1131	1.1505	1.1885
50	323.15	0.9882	1.0308	1.0705	1.1087	1.1454	1.1834
60	333.15	0.9829	1.0246	1.0650	1.1027	1.1403	1.1777

Figure 5 Plot of Density of Potassium Carbonate against Temperature range (20-60°C)

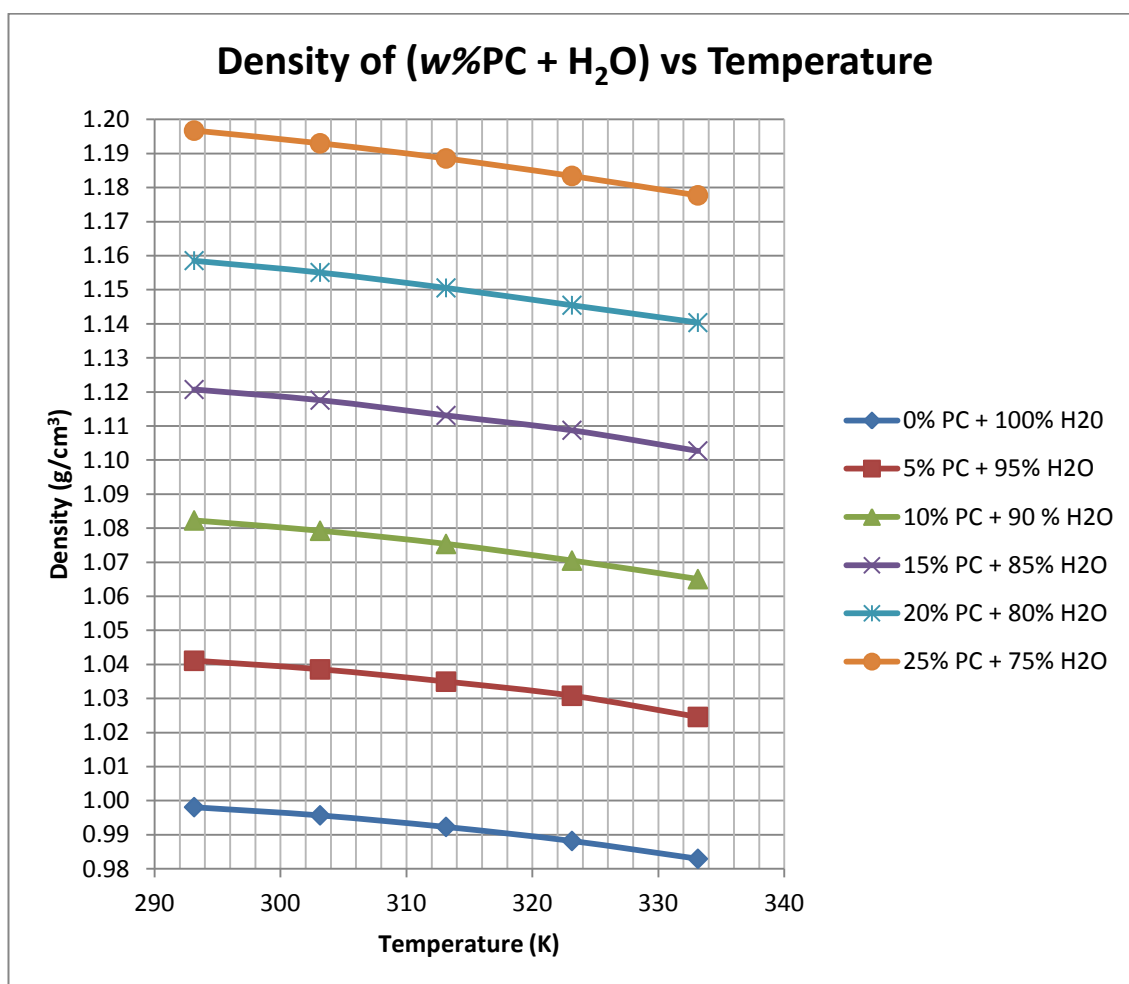


Table 12 Density of Piperazine

Temperature (°C)		Density (g/cm ³)					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		100% H ₂ O	98% H ₂ O	96% H ₂ O	94% H ₂ O	92% H ₂ O	90% H ₂ O
20	293.15	0.9981	0.9990	0.9999	1.0009	1.0020	1.0032
30	303.15	0.9957	0.9964	0.9973	0.9982	0.9992	1.0003
40	313.15	0.9923	0.9930	0.9938	0.9947	0.9956	0.9966
50	323.15	0.9882	0.9888	0.9896	0.9904	0.9912	0.9921
60	333.15	0.9829	0.9841	0.9848	0.9856	0.9864	0.9871

Figure 6 Plot of Density of Piperazine against Temperature range (20-60°C)

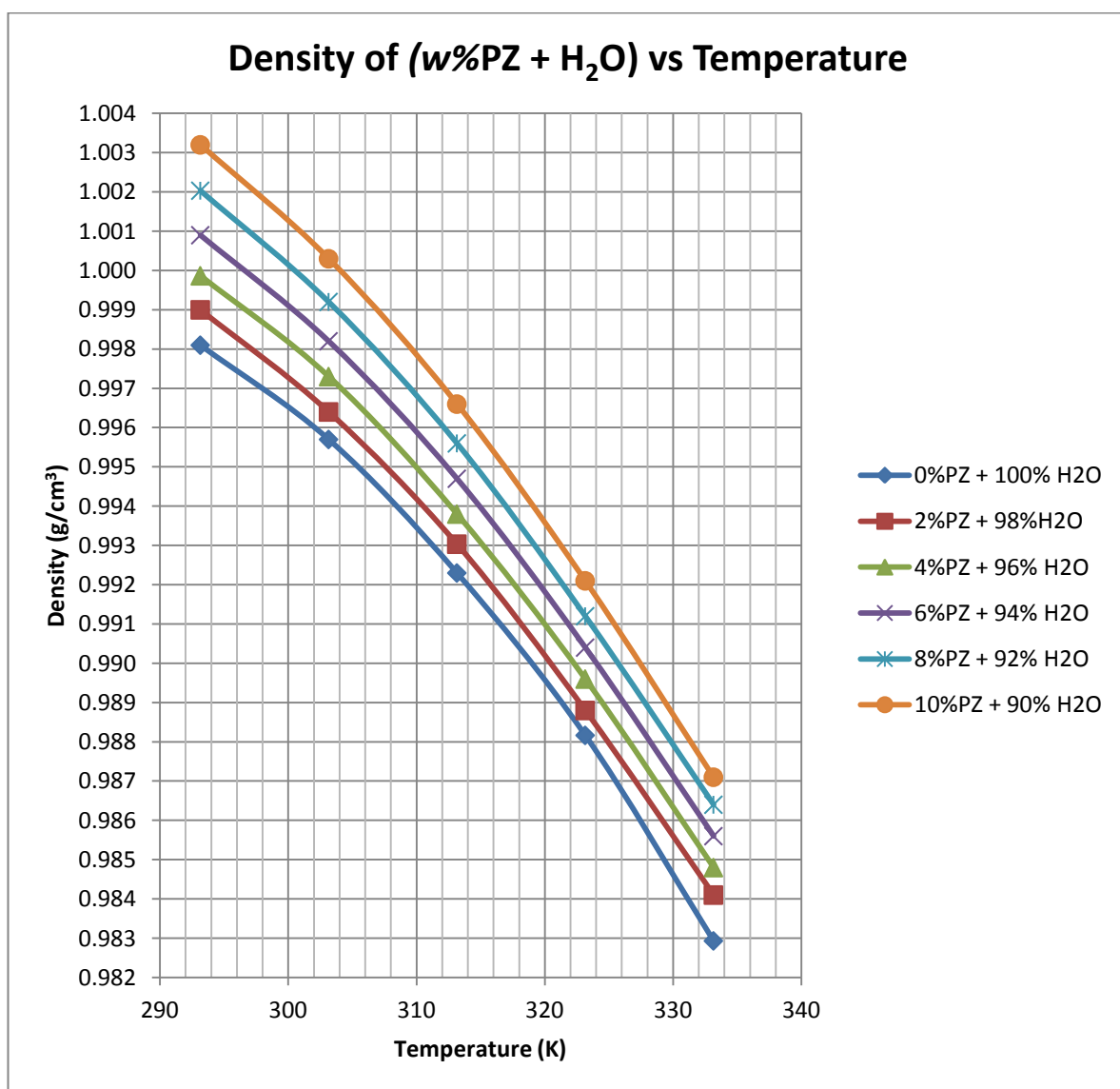


Table 13 Density of 5wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Density (g/cm ³)					
		5% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		95% H ₂ O	93% H ₂ O	91% H ₂ O	89% H ₂ O	87% H ₂ O	85% H ₂ O
20	293.15	1.0411	1.0410	1.0424	1.0433	1.0424	1.0447
30	303.15	1.0385	1.0379	1.0392	1.0400	1.0391	1.0415
40	313.15	1.0349	1.0342	1.0354	1.0362	1.0352	1.0379
50	323.15	1.0308	1.0299	1.0309	1.0317	1.0306	1.0333
60	333.15	1.0246	1.0241	1.0249	1.0262	1.0252	1.0278

Figure 7 Plot of Density of 5wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

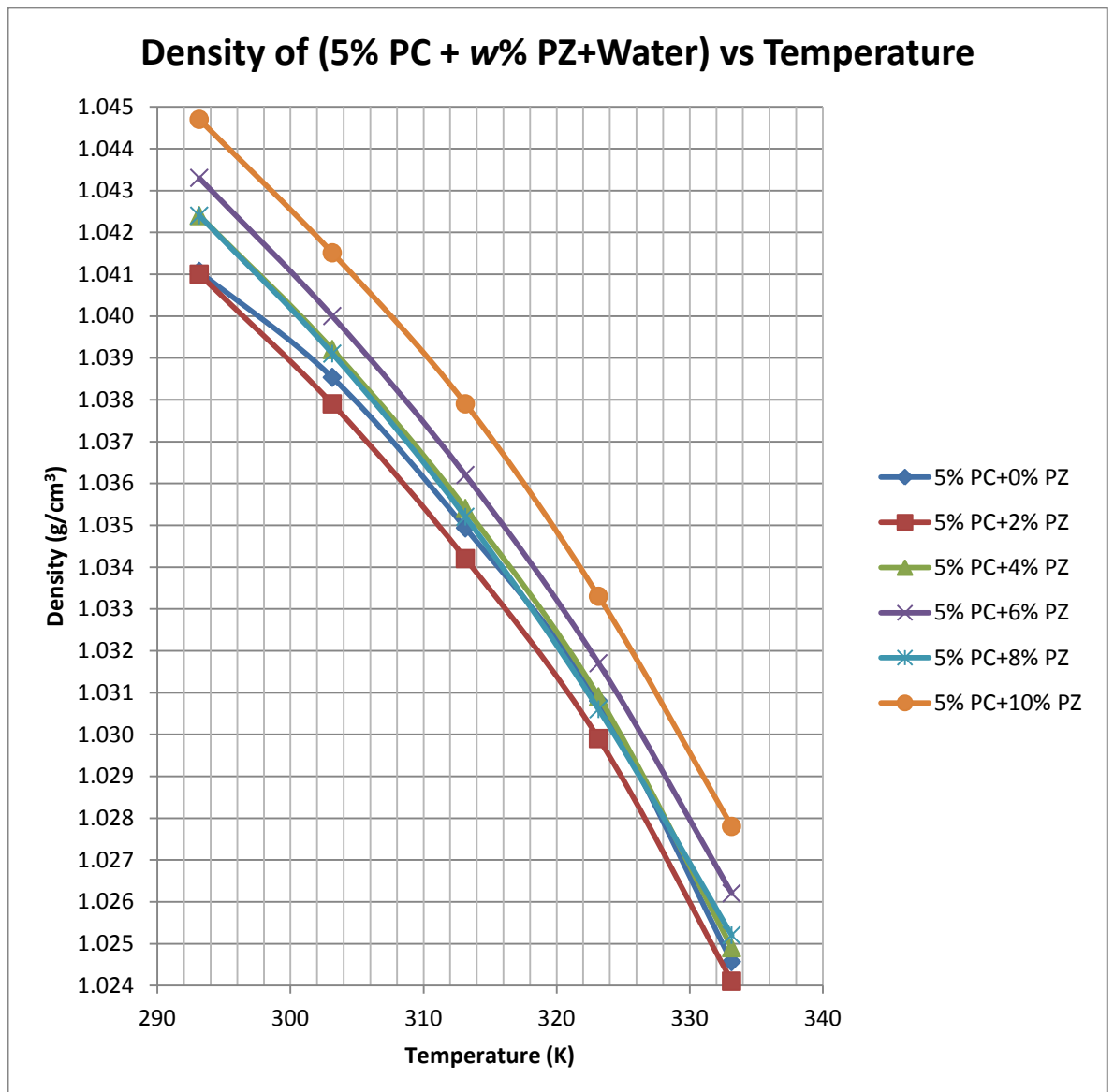


Table 14 Density of 10wt% Potassium Carbonate + w% Piperazine

Temperature (°C)		Density (g/cm ³)					
		10% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		90% H ₂ O	88% H ₂ O	86% H ₂ O	84% H ₂ O	82% H ₂ O	80% H ₂ O
20	293.15	1.0823	1.0822	1.0827	1.0838	1.0854	1.0853
30	303.15	1.0792	1.0786	1.0790	1.0801	1.0816	1.0813
40	313.15	1.0754	1.0745	1.0748	1.0761	1.0772	1.0770
50	323.15	1.0705	1.0700	1.0702	1.0714	1.0724	1.0722
60	333.15	1.0650	1.0645	1.0646	1.0659	1.0669	1.0668

Figure 8 Plot of Density of 10wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

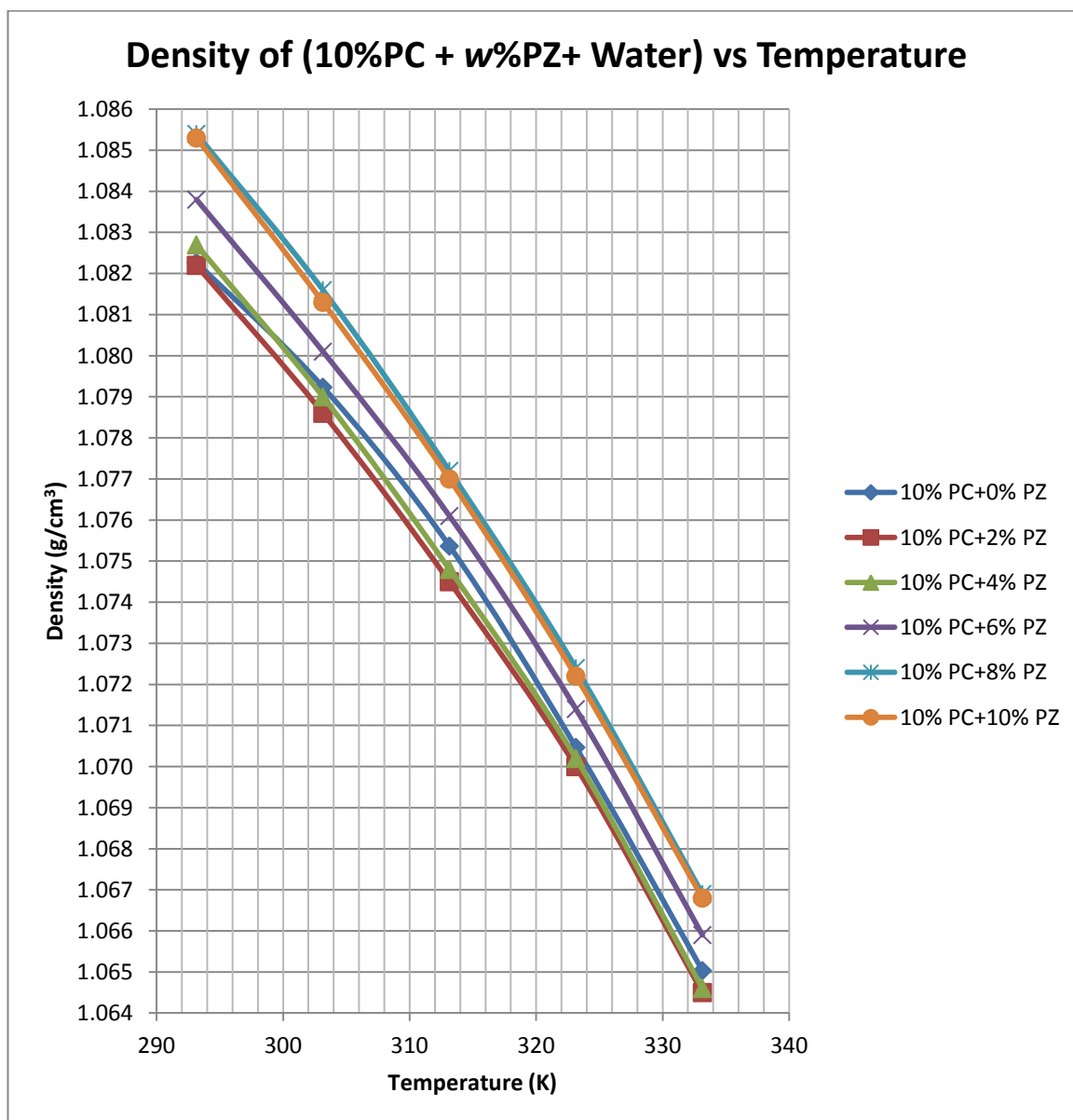


Table 15 Density of 15wt% Potassium Carbonate + w% Piperazine

Temperature (°C)		Density (g/cm ³)					
		15% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		85% H ₂ O	83% H ₂ O	81% H ₂ O	79% H ₂ O	79% H ₂ O	77% H ₂ O
20	293.15	1.1207	1.1214	1.1213	1.1222	1.1234	1.1245
30	303.15	1.1176	1.1174	1.1173	1.1181	1.1189	1.1198
40	313.15	1.1131	1.1130	1.1130	1.1137	1.1142	1.1149
50	323.15	1.1087	1.1082	1.1082	1.1090	1.1096	1.1098
60	333.15	1.1027	1.1028	1.1040	1.1049	1.1050	1.1051

Figure 9 Plot of Density of 15wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

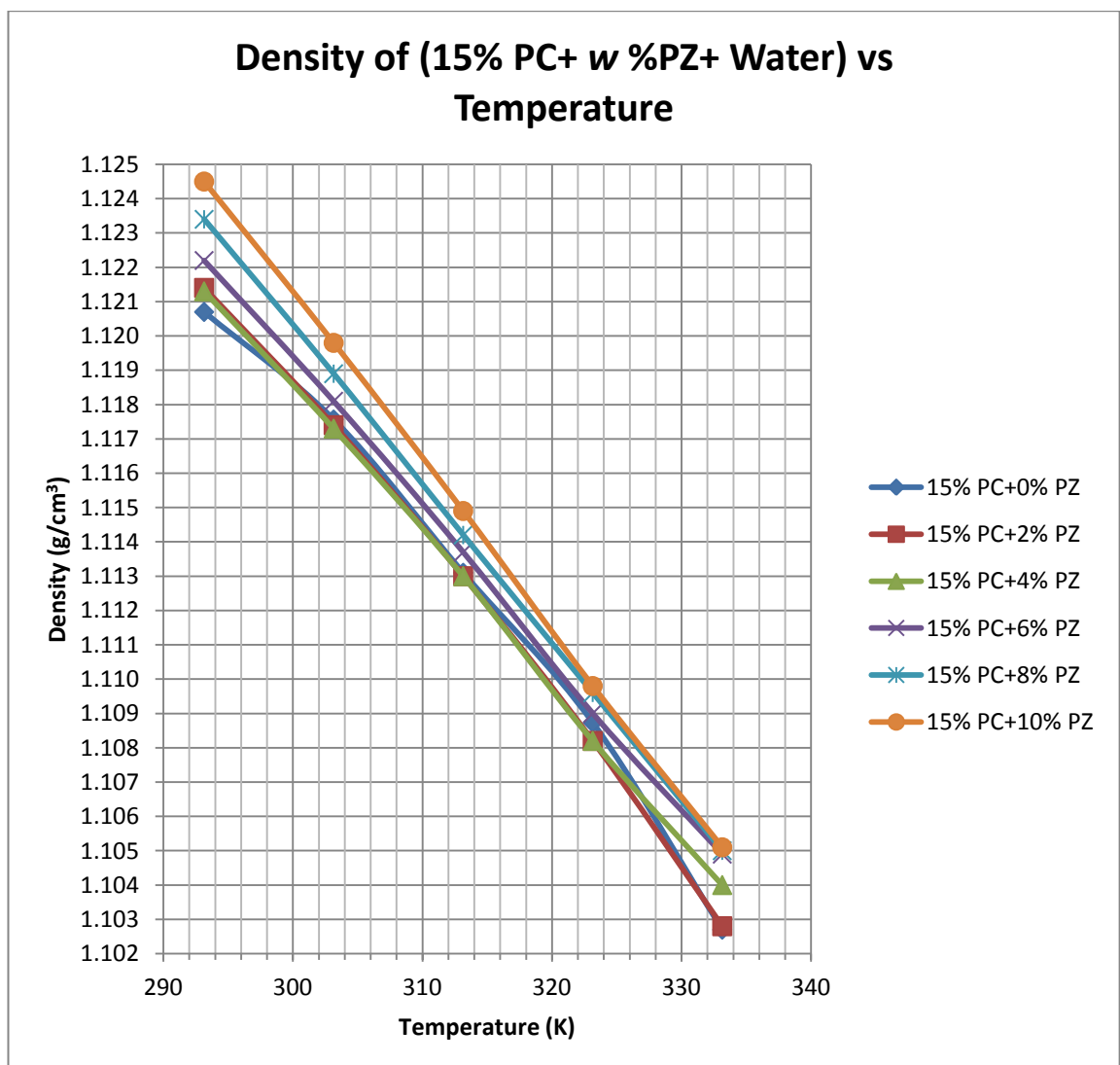


Table 16 Density of 20wt% Potassium Carbonate + w% Piperazine

Temperature (°C)		Density (g/cm ³)					
		20% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		80% H ₂ O	78% H ₂ O	76% H ₂ O	74% H ₂ O	72% H ₂ O	70% H ₂ O
20	293.15	1.1580	1.1598	1.1608	1.1616	1.1628	1.1636
30	303.15	1.1551	1.1553	1.1563	1.1570	1.1579	1.1585
40	313.15	1.1510	1.1505	1.1515	1.1519	1.1526	1.1529
50	323.15	1.1459	1.1454	1.1463	1.1464	1.1471	1.1472
60	333.15	1.1401	1.1400	1.1408	1.1410	1.1415	1.1415

Figure 10 Plot of Density of 20wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

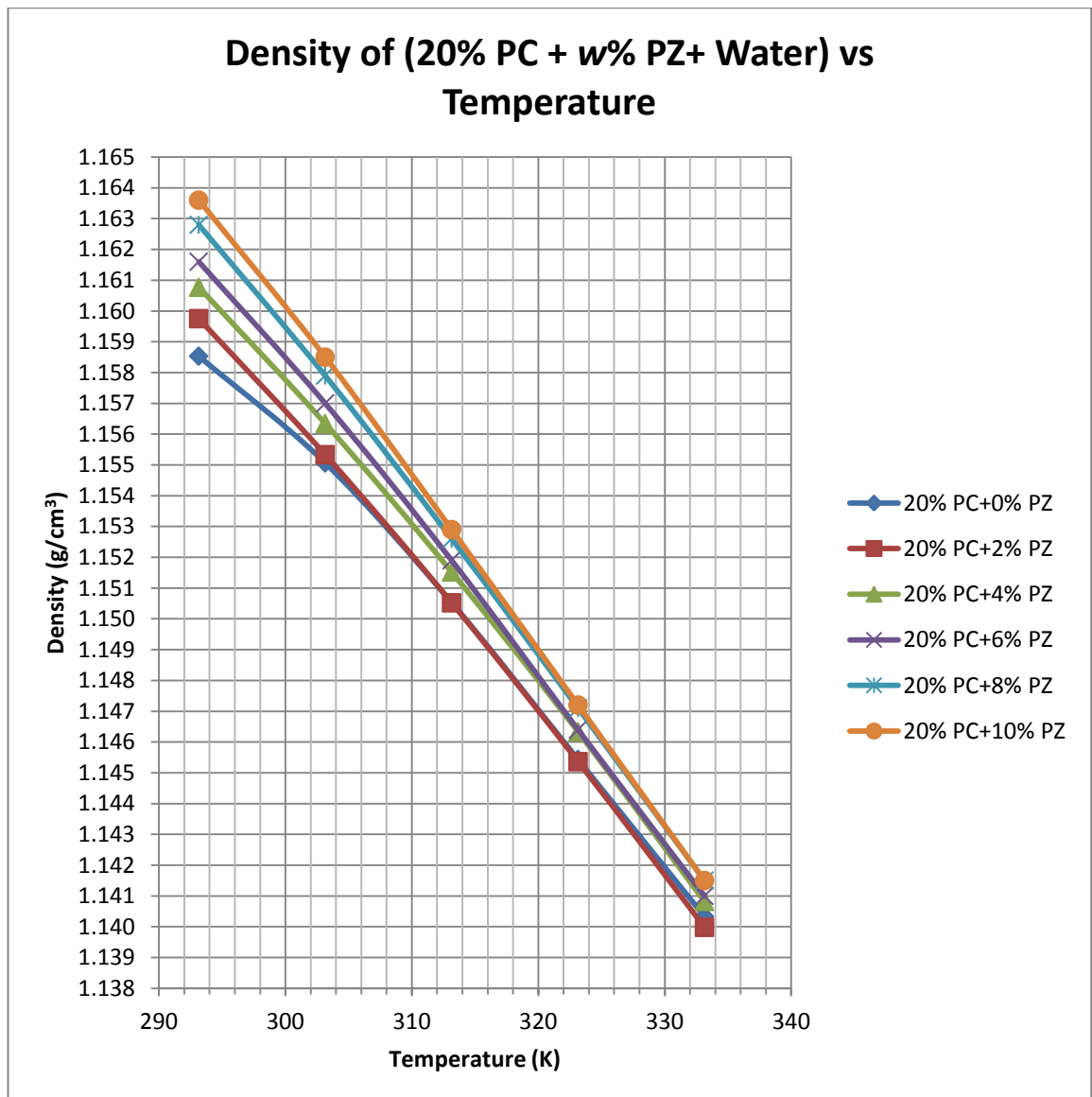
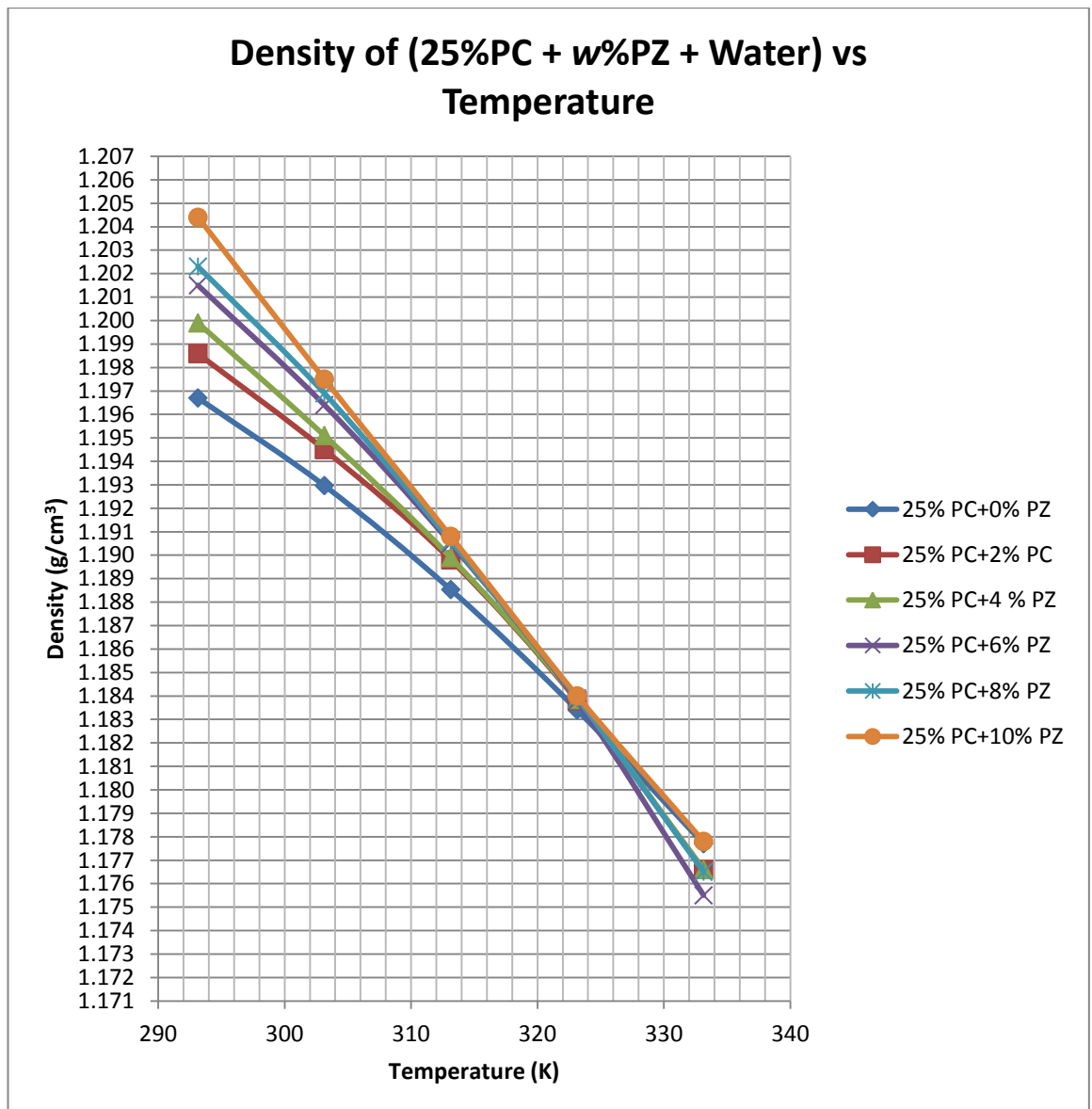


Table 17 Density of 25wt% Potassium Carbonate + w% Piperazine

Temperature (°C)		Density (g/cm ³)					
		25% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		75% H ₂ O	73% H ₂ O	71% H ₂ O	69% H ₂ O	67% H ₂ O	65% H ₂ O
20	293.15	1.1967	1.1986	1.1999	1.2015	1.2023	1.2044
30	303.15	1.1930	1.1945	1.1951	1.1964	1.1969	1.1975
40	313.15	1.1885	1.1898	1.1899	1.1905	1.1906	1.1908
50	323.15	1.1834	1.1838	1.1839	1.1838	1.1839	1.1840
60	333.15	1.1777	1.1766	1.1766	1.1755	1.1765	1.1778

Figure 11 Plot of Density of 20wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)



The graphs plotted in figures from 6 till 11 indicates that with an increase of temperature, the density decreases. However, there is an increase in densities with an increase of the piperazine concentration in each composition of potassium carbonate.

4.1.1 Comparison with literature value

To establish the accuracy of density meter used, the experimental data obtained for piperazine activated methyl-diethanolamine (MDEA) has been compared with the reported value by Subham Paul and Bishnupada Mandal.

The composition taken from the literature review is:

21 wt% MDEA+9% PZ+70% H₂O

Temperature (°C)		Density (g/cm ³)					Difference = Lit Value – Average Value
		Lit Value	Run 1	Run 2	Run 3	Average	
20	293.15	1.0253	1.0332	1.0332	1.0336	1.0333	0.0078
30	303.15	1.0203	1.0286	1.0286	1.0290	1.0287	0.0083
40	313.15	1.0154	1.0235	1.0235	1.0239	1.0236	0.0081
50	323.15	1.0100	1.0179	1.0179	1.0183	1.0180	0.0079
60	333.15	1.0038	1.0118	1.0118	1.0122	1.0119	0.0081

Table 18: Comparison values between the literature values and the experimental values.

*The literature value is sourced from *Journal Chemical Engineering, Data 2006, 51, 2242-2245*. Authors Paul S. and Mandal B.

$$\text{Average Absolute Deviation, AAD} = \frac{1}{N} \sum_{i=1}^N \frac{|\rho_{\text{exp},i} - \rho_{\text{calc},i}|}{\rho_{\text{exp},i}} = 0.008 \%$$

Thus, the density data obtained in this study are in good agreement with data of Subham Paul and Bishnupada Mandal.

4.2 Viscosity

The measured viscosities of piperazine activated aqueous solution of potassium carbonate (PC+PZ) at the temperature range from (20 to 60) °C are shown below:

Table 19 Viscosity of water

Temperature (°C)		Viscosity (mPa/s)			
		1	2	3	Avg
20	293.15	1.002	1.001	1.003	1.002
30	303.15	0.798	0.798	0.798	0.798
40	313.15	0.653	0.653	0.653	0.653
50	323.15	0.547	0.547	0.548	0.547
60	333.15	0.467	0.467	0.468	0.467

Figure 12 Plot of viscosity of water against Temperature range (20-60°C)

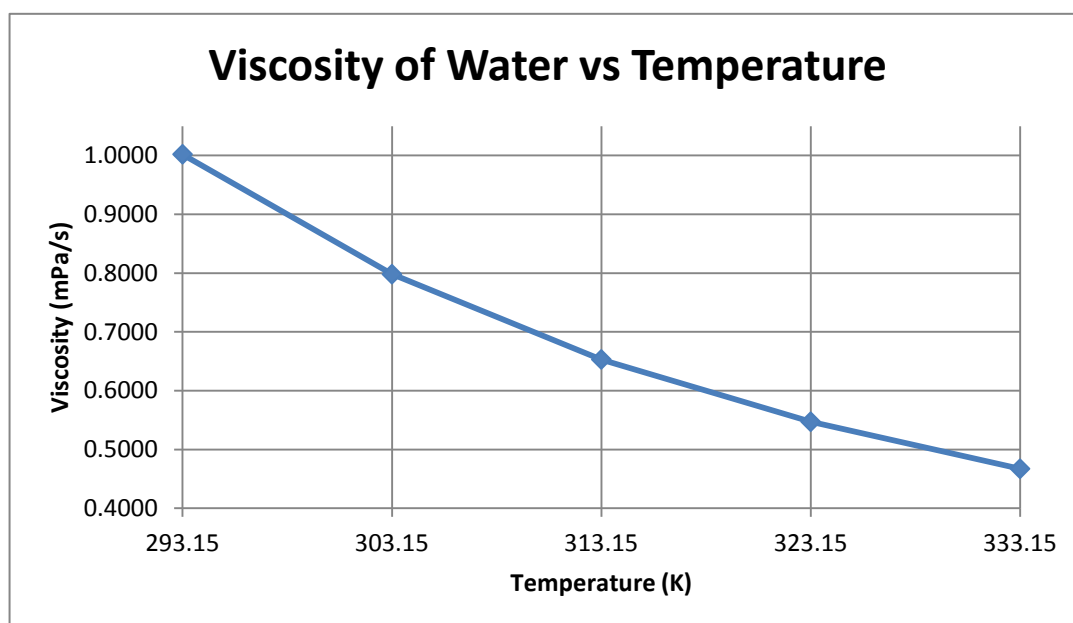


Table20 Viscosity of Potassium Carbonate

Temperature (°C)		Viscosity (mPa/s)					
		0% PC	5% PC	10% PC	15% PC	20% PC	25% PC
		100% H ₂ O	95% H ₂ O	90% H ₂ O	85% H ₂ O	80% H ₂ O	75% H ₂ O
20	293.15	1.002	1.0067	1.1158	1.3031	1.5055	1.7267
30	303.15	0.798	0.8099	0.9023	1.0555	1.2183	1.3952
40	313.15	0.653	0.6697	0.7481	0.8763	1.0134	1.1556
50	323.15	0.547	0.5662	0.6334	0.7421	0.8570	0.9773
60	333.15	0.467	0.4890	0.5489	0.6401	0.7377	0.8405

Figure 13 Plot of viscosity of potassium carbonate against Temperature range (20-60°C)

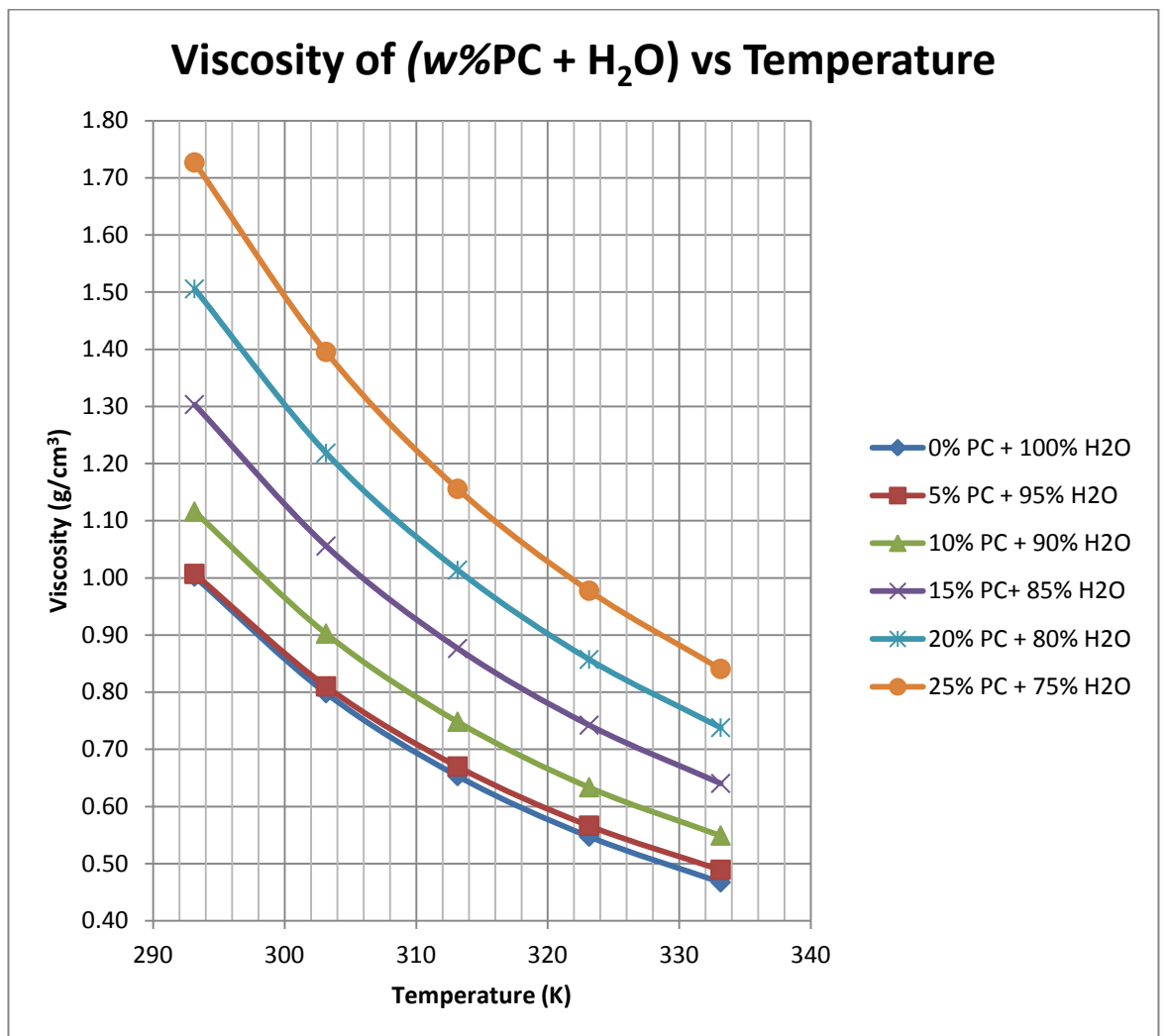


Table 21 Viscosity of Piperazine

Temperature (°C)		Viscosity (mPa/s)					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		100% H2O	98% H2O	96% H2O	94% H2O	92% H2O	90% H2O
20	293.15	1.0020	1.0038	1.1128	1.1975	1.3386	1.5090
30	303.15	0.7980	0.7938	0.8724	0.9311	1.0318	1.1487
40	313.15	0.6530	0.6480	0.7071	0.7496	0.8231	0.9072
50	323.15	0.5470	0.5434	0.5886	0.6199	0.6795	0.7474
60	333.15	0.4670	0.4655	0.5010	0.5247	0.5770	0.6236

Figure 14 Plot of viscosity of piperazine against Temperature range (20-60°C)

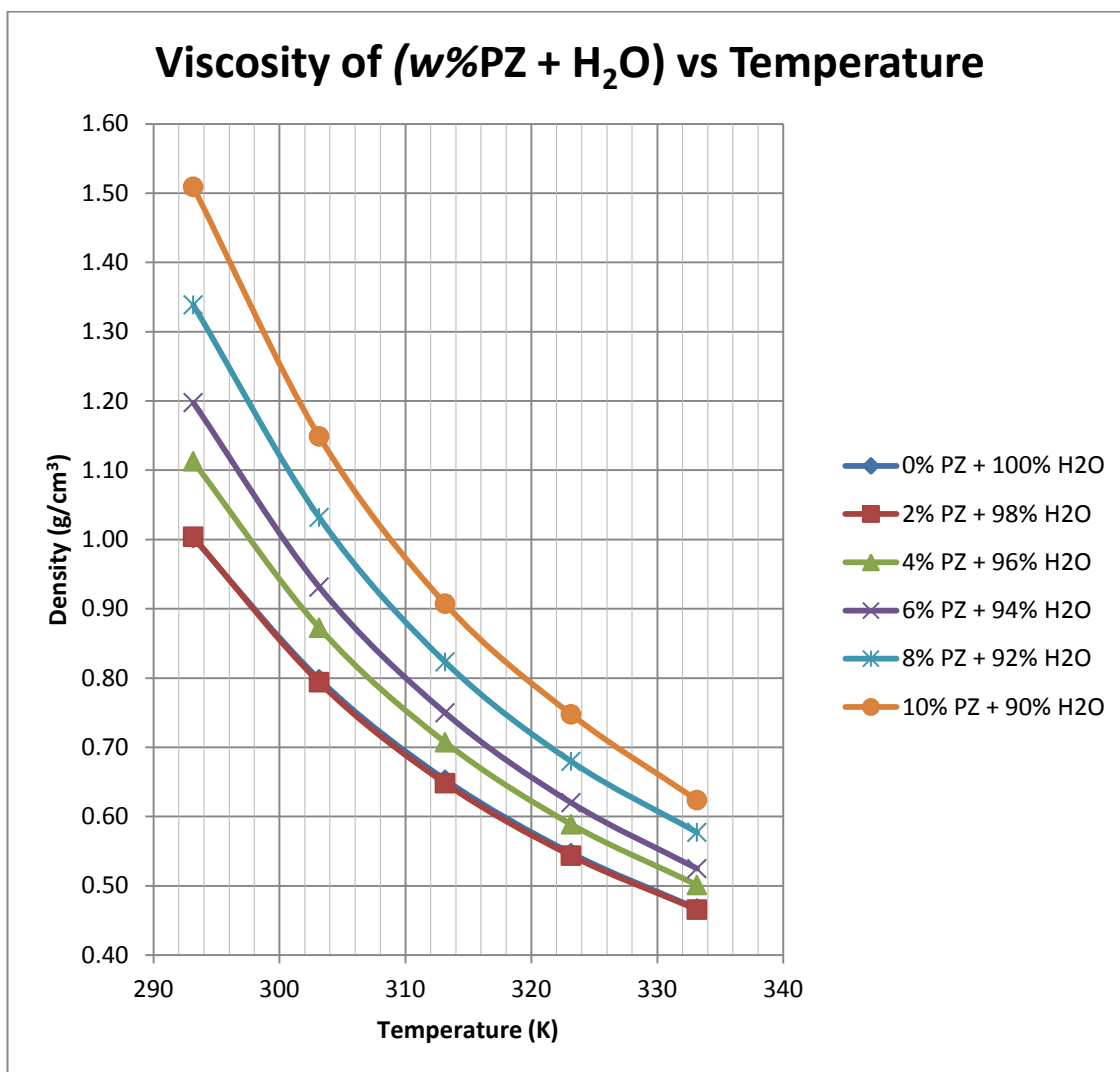


Table 22 Viscosity of 5wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Viscosity (mPa/s)					
		5% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		95% H2O	93% H2O	91% H2O	89% H2O	87% H2O	85% H2O
20	293.15	1.0067	1.1141	1.1984	1.3759	1.5408	1.7077
30	303.15	0.8099	0.8893	0.9483	1.0804	1.1639	1.3131
40	313.15	0.6697	0.7293	0.7735	0.8748	0.9358	1.0457
50	323.15	0.5662	0.6131	0.6463	0.7257	0.7722	0.8538
60	333.15	0.4890	0.5260	0.5509	0.6146	0.6558	0.7141

Figure 15 Plot of Viscosity of 5wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

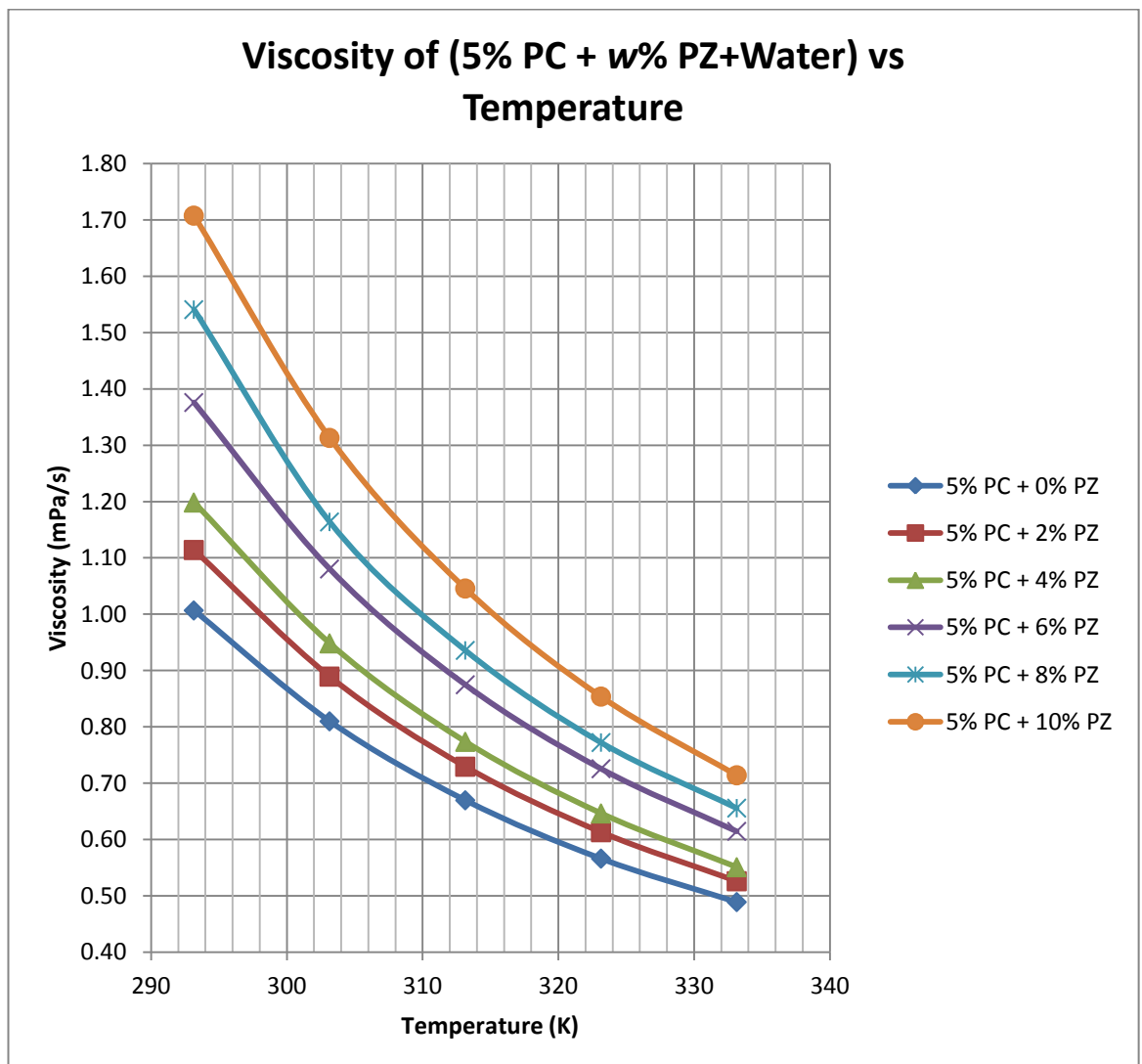


Table 23 Viscosity of 10wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Viscosity (mPa/s)					
		10% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		90% H2O	88% H2O	86% H2O	84% H2O	82% H2O	80% H2O
20	293.15	1.1158	1.2255	1.3602	1.4923	1.6898	1.9217
30	303.15	0.9023	0.9837	1.0818	1.1771	1.2812	1.4839
40	313.15	0.7481	0.8100	0.8844	0.9375	1.0255	1.1841
50	323.15	0.6334	0.6826	0.7399	0.7939	0.8557	0.9694
60	333.15	0.5489	0.5861	0.6310	0.6724	0.7007	0.8117

Figure 16 Plot of Viscosity of 10wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

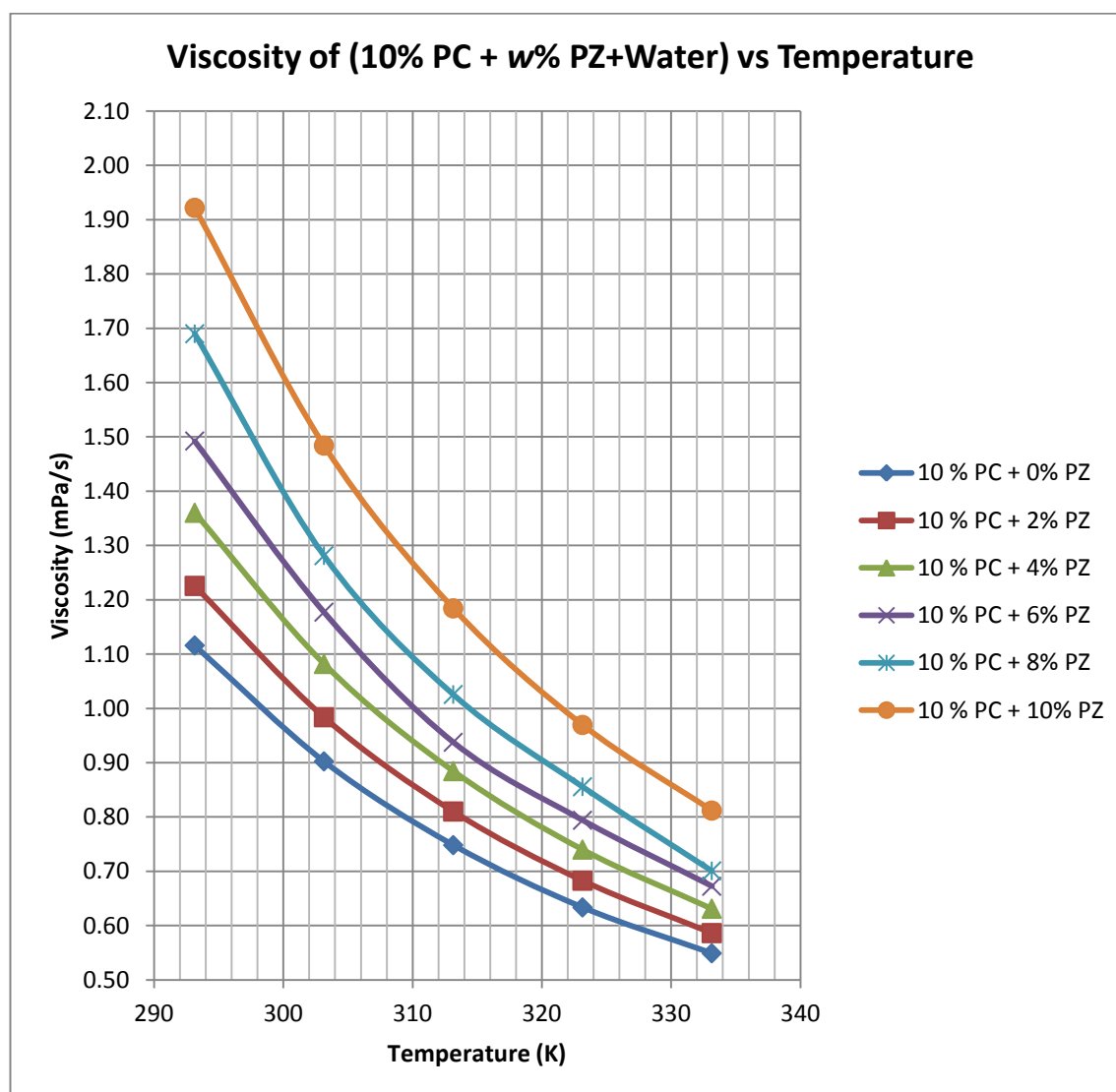


Table 24 Viscosity of 15wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Viscosity (mPa/s)					
		15% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		85% H2O	83% H2O	81% H2O	79% H2O	79% H2O	77% H2O
20	293.15	1.3031	1.4559	1.5445	1.7534	1.8554	1.9564
30	303.15	1.0555	1.1803	1.2310	1.3843	1.4535	1.5350
40	313.15	0.8763	0.9702	1.0076	1.1248	1.1589	1.2086
50	323.15	0.7421	0.8156	0.8435	0.9350	0.9630	1.0154
60	333.15	0.6401	0.6977	0.7192	0.7927	0.8264	0.8525

Figure 17 Plot of Viscosity of 15wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

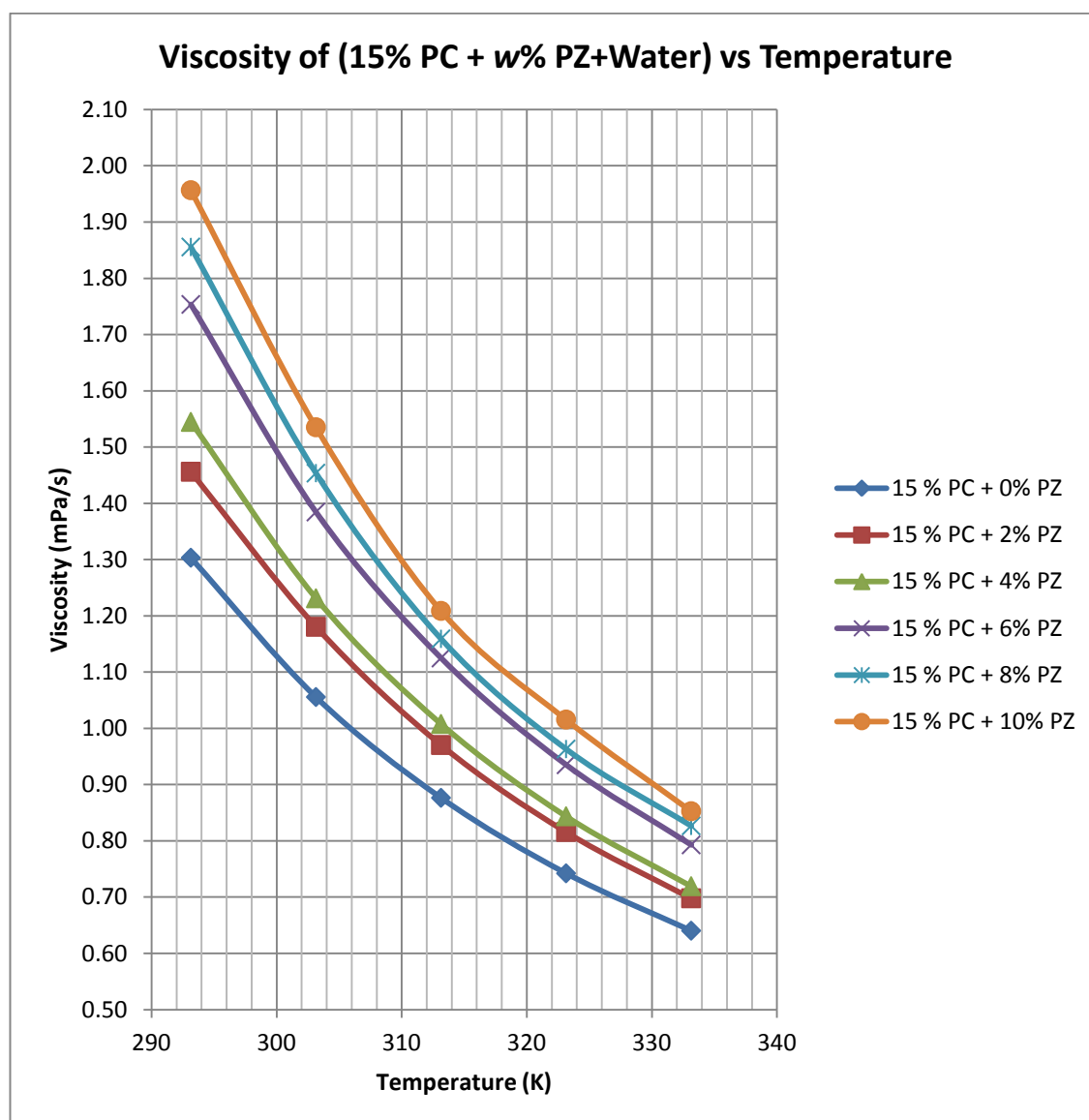


Table 25 Viscosity of 20wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Viscosity (g/cm ³)					
		20% PC					
		0% PZ 80% H ₂ O	2% PZ 78% H ₂ O	4% PZ 76% H ₂ O	6% PZ 74% H ₂ O	8% PZ 72% H ₂ O	10% PZ 70% H ₂ O
20	293.15	1.5055	1.5008	1.7190	1.7888	1.8541	1.9956
30	303.15	1.2183	1.2072	1.3703	1.4125	1.4565	1.5865
40	313.15	1.0134	0.9959	1.1213	1.1316	1.1500	1.2364
50	323.15	0.8570	0.8392	0.9381	0.9451	0.9648	1.0120
60	333.15	0.7377	0.7201	0.7992	0.8005	0.8094	0.8699

Figure 18 Plot of Viscosity of 20wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)

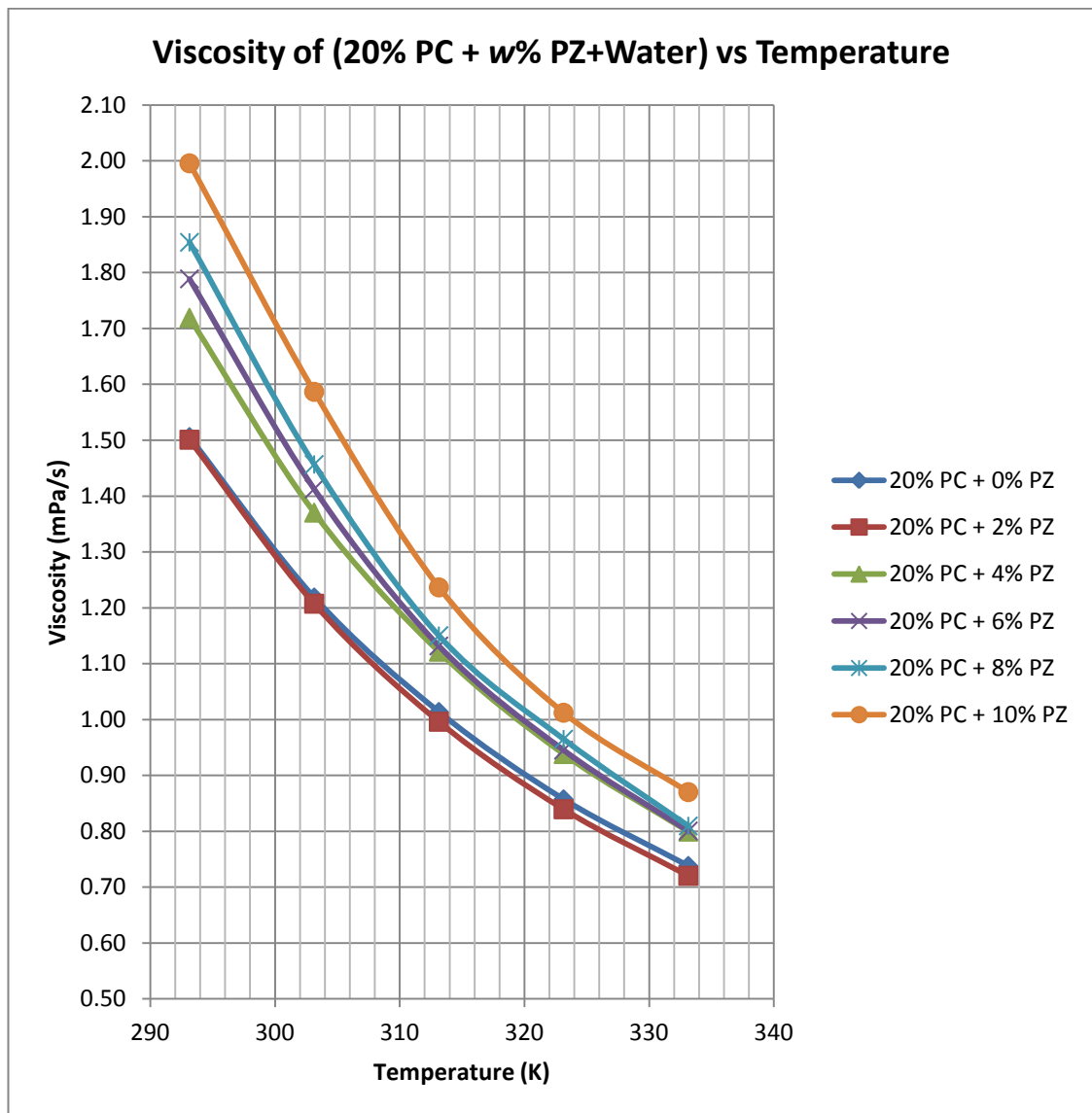
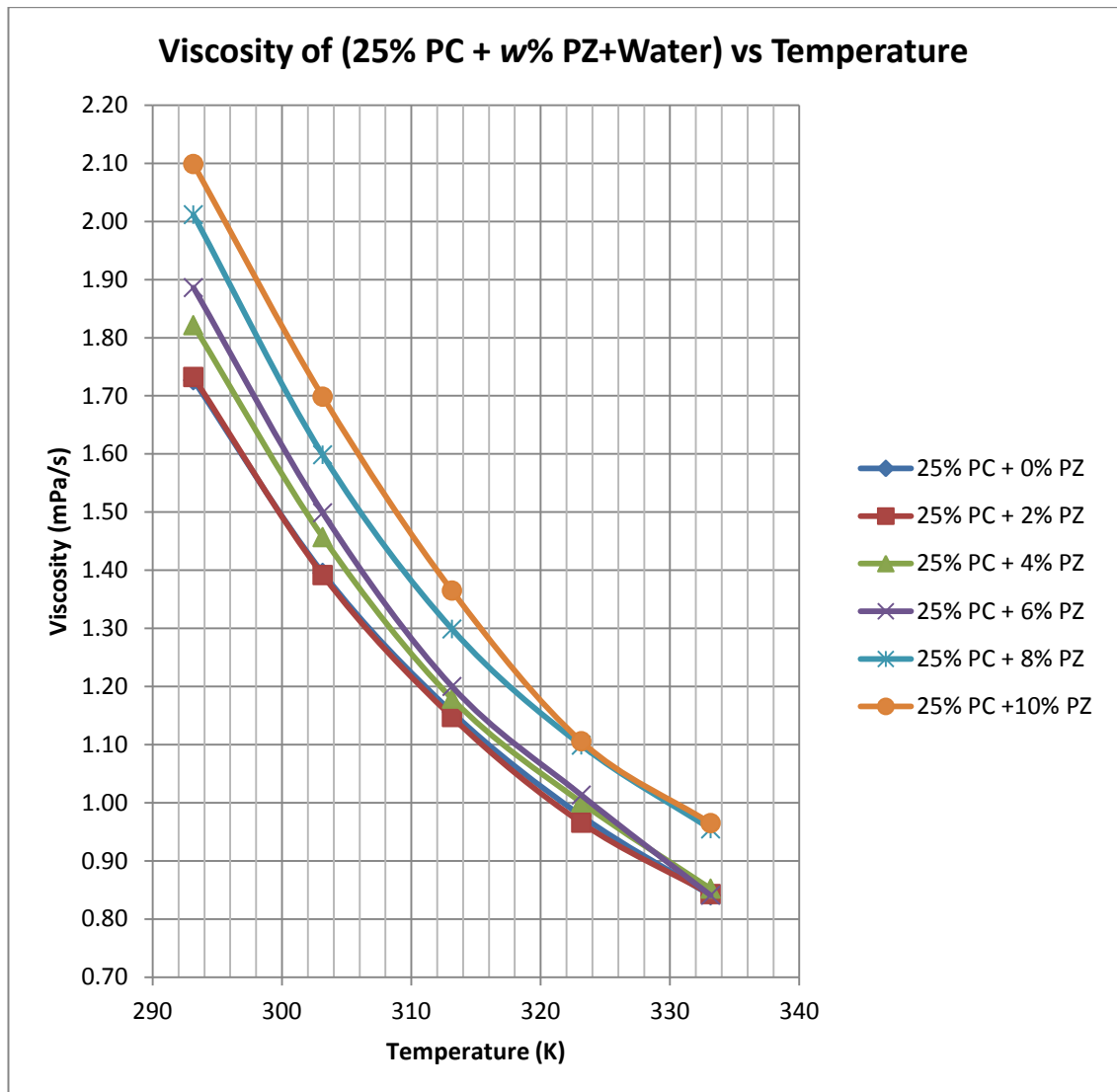


Table 26 Viscosity of 25wt% Potassium Carbonate + w%Piperazine

Temperature (°C)		Viscosity (g/cm ³)					
		25% PC					
		0% PZ	2% PZ	4% PZ	6% PZ	8% PZ	10% PZ
		75% H ₂ O	73% H ₂ O	71% H ₂ O	69% H ₂ O	67% H ₂ O	65% H ₂ O
20	293.15	1.7267	1.7322	1.8214	1.8860	2.0115	2.0986
30	303.15	1.3952	1.3915	1.4568	1.4986	1.5984	1.6984
40	313.15	1.1556	1.1473	1.1790	1.1998	1.2987	1.3648
50	323.15	0.9773	0.9655	1.0005	1.0130	1.0987	1.1056
60	333.15	0.8405	0.8427	0.8521	0.8406	0.9546	0.9648

Figure 19 Plot of Viscosity of 25wt% Potassium Carbonate + w% Piperazine against Temperature range (20-60°C)



4.2.1 Comparison with literature value

To establish the accuracy of viscometer used, the experimental data obtained for piperazine activated methyl-diethanolamine (MDEA) has been compared with the reported value by Subham Paul and Bishnupada Mandal.

The composition taken from the literature review is:

21 wt% MDEA+9% PZ+70% H₂O

Temperature (°C)		Viscosity (mPa/s)					Difference = Lit Value - Average
		Lit Value	Run 1	Run 2	Run 3	Average	
20	293.15	4.8140	3.9419	4.0092	4.0078	3.9863	0.1719
30	303.15	3.4520	2.7593	2.8049	2.8079	2.7907	0.1916
40	313.15	2.5200	2.2585	2.0679	2.0685	2.1316	0.1541
50	323.15	1.8990	1.5512	1.5731	1.5829	1.5691	0.1737
60	333.15	1.3890	1.2409	1.2406	1.2509	1.2441	0.1043

Table 27: Comparison values between the literature values and the experimental values.

*The literature value is sourced from *Journal Chemical Engineering, Data 2006, 51, 2242-2245*. Authors Paul S. and Mandal B.

$$\text{Average Absolute Deviation, AAD} = \frac{1}{N} \sum_{i=1}^N \frac{|\eta_{\text{expt},i} - \eta_{\text{calc},i}|}{\eta_{\text{expt},i}} = 0.07 \%$$

Thus, the viscosity data obtained in this study are in good agreement with data of Subham Paul and Bishnupada Mandal.

The measured values of the density of the aqueous blends of (PC+PZ) at various temperatures from 298.15 to 333.15 K are presented in Table 12 till Table 16. It was found that with increasing mass fraction of potassium carbonate and piperazine in the blend, the density increased; however, the density decreased with increasing temperature. This could be due to the wider spaces between the blend molecules at higher temperatures. This density trend is similar to that previously reported work.

The data for the viscosity of different concentrations of aqueous (PC+PZ) blends in the temperature range of 298.15 to 333.15 K are listed in Table 21 and 25. After analysis of results, it was noticed that the viscosity decreased with increasing temperature. This could be due to a decrease in the internal resistance of the molecules with increasing temperature, which allows the solution molecules to flow easily, thereby reducing the viscosity. However, with increasing concentration of potassium carbonate and piperazine in the aqueous solutions, the viscosity tended to increase. The higher concentrated solutions had a higher viscosity than the lower ones, which may be due to the increased molecular resistance in the more concentrated solutions.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The physical properties of piperazine activated aqueous solution of potassium carbonate which is density and viscosity were measured at a wide range of temperature (20 to 80) °C. Density and viscosity tend to decrease with increasing temperature. The comparison between experimental and literature data were done in order to measure the accuracy and validate the equipment and methods used in this projects. The smaller the AAD value calculated, the accurate the data measured from the experimental work.

5.2 Recommendation

1. To further conduct the CO₂ solubility test with the piperazine activated aqueous solution of potassium carbonate.
2. To study the feasibility of having the blend PC/PZ as the CO₂ removal agent in the gas processing plant.

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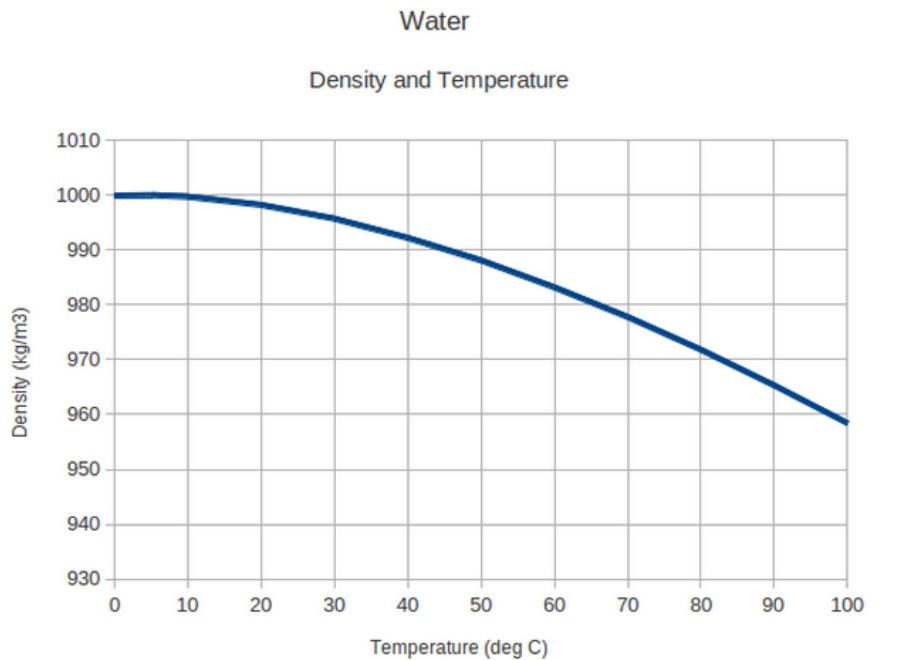
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APPENDICES

Appendix 1 Reference of Density and Specific Weight of Water at 0 - 100°C

Temperature - t - (°C)	Density - ρ - (kg/m ³)	Specific Weight - γ - (kN/m ³)
0	999.8	9.806
4	1000	9.807
10	999.7	9.804
20	998.2	9.789
30	995.7	9.765
40	992.2	9.731
50	988.1	9.690
60	983.2	9.642
70	977.8	9.589
80	971.8	9.530
90	965.3	9.467
100	958.4	9.399

Appendix 2 Graph of Density of Water vs Temperature



The Engineering ToolBox
www.EngineeringToolBox.com

Appendix 3 Reference of Dynamic and Kinematic Viscosity vs Temperature

Temperature - t - (°C)	<u>Dynamic Viscosity</u> - μ - (Pa s, N s/m ²) x 10 ⁻³	<u>Kinematic Viscosity</u> - ν - (m ² /s) x 10 ⁻⁶
0	1.787	1.787
5	1.519	1.519
10	1.307	1.307
20	1.002	1.004
30	0.798	0.801
40	0.653	0.658
50	0.547	0.553
60	0.467	0.475
70	0.404	0.413
80	0.355	0.365
90	0.315	0.326
100	0.282	0.29