Thermophysical Behavior of Aqueous Blends of Piperazine and Potassium Carbonate as Carbon Dioxide Capture Solvent

By

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14575

Dissertation submitted in partial fulfillment
of the requirement for the
Bachelor of Engineering (Hons)
(CHEMICAL)

SEPTEMBER 2014

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CERTIFICATION OF APPROVAL

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Approved by,

____

(BHAJAN LAL)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2014

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 acknowledgement, and that the original work contained herein have not been or done by unspecified sources or persons.

MUHAMMAD IQWAN BIN MAT KAMIL

ABSTRACT

This project concerns the thermophysical behavior of aqueous blends of Piperazine (PZ) and Potassium Carbonate as carbon dioxide, CO_2 capture solvent. The blends of amine solution has the potential to increase the rate of absorption of CO_2. The objectives of this project are: (1) to find out the physical properties of PZ to activate potassium carbonate solution in water; (2) to study the effect of temperature change on the physical properties of PZ, potassium carbonate and blends of PZ and potassium carbonate solutions; (3) to study the effect of concentration change on the physical properties of the blends of amines and (5) compare the result with conventional solvent. The scope of study of this project covers the refractive index surface tension for the physical properties of the chemicals solution and also the effect of temperature change and concentration change on the amines. Different set of concentration of PZ and potassium carbonate will be prepared for the blends solution. This experimental based project also will be conducted on the different set of temperatures. Each of potassium carbonate solution will be blended with five different set of percentage (wt%) of PZ and water during the experiment. This experiment will be conducted at different temperatures which are from 293.15K to 323.15K. The result of the experiment will be the refractive index and surface tension for each blends solution. When the data is obtained, further analysis and appropriate discussion will be explained.

ACKNOWLEDGEMENT

This project would not have been possible without the assistance and guidance of certain individuals and organization whose contributions have helped in its completion. I would like to express my deepest gratitude to the Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for giving me the chance to undertake this remarkable final year project.

Firstly, I would like to express my thanks and gratitude to the project supervisor, Dr Bhajan Lal for his precious input and aid all the way to the completion of this project, who was always willing to assist me, provided good support, patient and effective guidance have helped my project to completion. Besides, I would also like to take this opportunity to express my deepest thanks to Dr Asna Md Zain, the coordinator for this course who had given me guidance in completing this final year project report. Last but not least, my heartfelt gratitude goes to my family and friends for providing me continuous support throughout the duration of this project.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Environmental issues due to emissions of pollutants from combustion of fossil fuels have become global problems, including air toxics and greenhouse gases (GHG). Carbon dioxide (CO_2) which is among GHG is the largest contributor in regard of its amount present in the atmosphere which contributes to 60% of global warming effect. The concentration of CO_2 in the air has been increasing dramatically and also been pointed as the main cause of global warning. The growing industry such as coal-fired power plant gives a large impact on the emission of CO_2. The study on the absorption of CO_2 is well developed to ensure the reduction of CO_2 emissions. The removal of acid gas impurities (in particular CO_2 and hydrogen sulfide) from a gas stream is a significant operation in gas processing. The active nature of acidic gases, the gas stream may absorb them by a number of different chemical or physical absorbent. Generally, there are various technology used to absorb CO_2 such as chemical absorption, physical absorption, cryogenic method, membrane separation and biological fixation. Chemical absorption has been proved as the most effective method. The best option for capturing CO_2 is by using amine-based absorption. Traditionally, the primary and secondary amines such as monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) have been used industrially for the removal of CO_2 from natural gas and industrial gas stream. These amines have high CO_2 absorption capacity that make them as the attractive solvent for removal of acidic gases from the industrial gas streams.

Numerous investigators have explored the solubility and reaction rate of CO_2 in aqueous potassium carbonate (Benson et al., 1954, 1956; Tosh et al., 1959). Piperazine (PZ) which is one of the amine-based chemical can act as an activator for postassium carbonate solvent for the absorption of CO_2 process. The cyclic symmetric and diamine in a six-membered saturated ring characteristics of piperazine has been studied as a promoter or activator for amine systems such as MDEA/PZ and MEA/PZ blends to improve CO_2 mass transfer rates. Furthermore, the difference in surface tension and refractive index of piperazine in solution gives different solvent capacity and rate of CO_2 absorption. Piperazine has been studied as a solvent for absorption systems for the removal of CO_2 and is reported that it is more effective than the primary and secondary amines.

1.2 PROBLEM STATEMENT

Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at levels as high as 80% (Dortmund and Doshi, 1999).The highly corrosive property of CO_2 when mix with water and can cause corrosion on the pipelines and equipment unless it is partially removed. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity (Dortmund and Doshi, 1999).

Chemical absorption using amine is considered to be the most cost effective based on the current technologies. For example, conventional solvent such as aqueous solutions of monoethanolamine (MEA) is used as the CO_2 solvent. However, the cost of absorption using MEA is relatively high. The major reasons including:

(i) a high rate of degradation in the presence of oxygen
(ii) a high energy consumption for the regeneration of the solvent
(iii) a high rate of corrosion of the process equipment
(iv) a fast evaporation rate causing high solvent losses

All these problems translate into high capital and operating costs (Veawab et al, University of Regina). Thus, the operation cost can be reduced by using a better solvent for the absorption of CO_2 process. The solvents should have a higher CO_2 absorption capacity as well as faster CO_2 absorption rate. The solvent also should have a high degradation resistance and low corrosivity (Veawab et al, University of Regina).

The absorption of CO_2 from natural gas by potassium carbonate solvent has gained widespread acceptance. However, potassium carbonate has low heat of regeneration, but its reaction rate is slow compared to amines. The blending of amine such as piperazine can activate potassium carbonate and increases its rate of reaction. For the rate of absorption of CO_2, it is highly depending on the concentrations of piperazine and potassium carbonate. Thus, different surface tension and refractive index for both chemical solutions give different result in this project.

The surface tension and refractive index determine the concentration of the solution. They are important for the mass transfer rate modeling of absorption as these parameters influence the value of the liquid side mass transfer coefficient. In this project, we can see how the different in concentration of piperazine and potassium carbonate solvent shows different rate of absorption of carbon dioxide.

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objective of this project is to find out the physical properties of piperazine to activate potassium carbonate solution in water. The differences in surface tension and refractive index of piperazine amine show different effect towards activating potassium carbonate solution as absorber of CO_2. Thus, by studying the surface tension and refractive index of piperazine at certain temperature and pressure, the absorption process of CO_2 can be accelerated. Besides, other purpose of this project is to study the effect of temperatures change on the physical properties of PZ and potassium carbonate solution. Another purpose is to study the effect of concentration change on the physical properties of the aqueous blends of piperazine and potassium carbonate. The result obtains in this project will be compared with conventional solvent to study the differences in the physical properties of the blends amine. The rate of absorption of CO_2 increases when using the aqueous potassium carbonate promoted by secondary amine, piperazine.

Basically this study is an experiment based project. This project covers the physical properties of piperazine which are its surface tension and refractive index. Different set of weight percentages (wt %) of piperazine and potassium carbonate solution will be prepared during the experiment.

1.4 RELEVANCY OF PROJECT

Carbon Capture and Storage (CCS) has become a key technology in climate change mitigation programs worldwide. CCS includes the study of greenhouse gas emission reduction potential and cost of implementation. Impacts on human health and the environment have, however, received considerably less attention (Veltman et al, 2009). The results of the project can expose a great potential of blends of potassium carbonate and piperazine that might lead to a better approach for development of advanced technologies in carbon dioxide capture with minimum environmental effects and operational cost-saving.

1.5 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME

Abide by the suggested milestone, the project scope has been narrowed down to make it feasible and accomplished within 14 weeks.

CHAPTER 2

LITERATURE REVIEW

Excessive carbon dioxide, which is caused by intensive human activities, is considered as one of the contributions to global warming that result in serious environmental problems. Most commercial processes for removal of bulk CO_2 from industrial gas streams involve the use of absorbents which are usually amine-based aqueous solutions, for example, monoethanolamine (MEA), diethanolamine (DEA) N-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). Recently, researchers have focused their attention to aqueous amino acid salts as the CO_2 absorbent because it is nontoxic, thermally stable, able to be regenerated, and commercially available. Piperazine has become the component for the CO_2 absorption.

2.1 TECHNOLOGY OPTIONS FOR CARBON DIOXIDE CAPTURE

There are many technologies developed for the separation and capture of CO_2 from gas stream. Basically, these technologies are based on different physical and chemical processes including absorption, adsorption, membranes, and cryogenics. The choice of suitable technology depends on the characteristics of the flue gas stream (Rao & Rubin, 2002). Figure below shows a wide range of technologies available for CO_2 separation and capture.

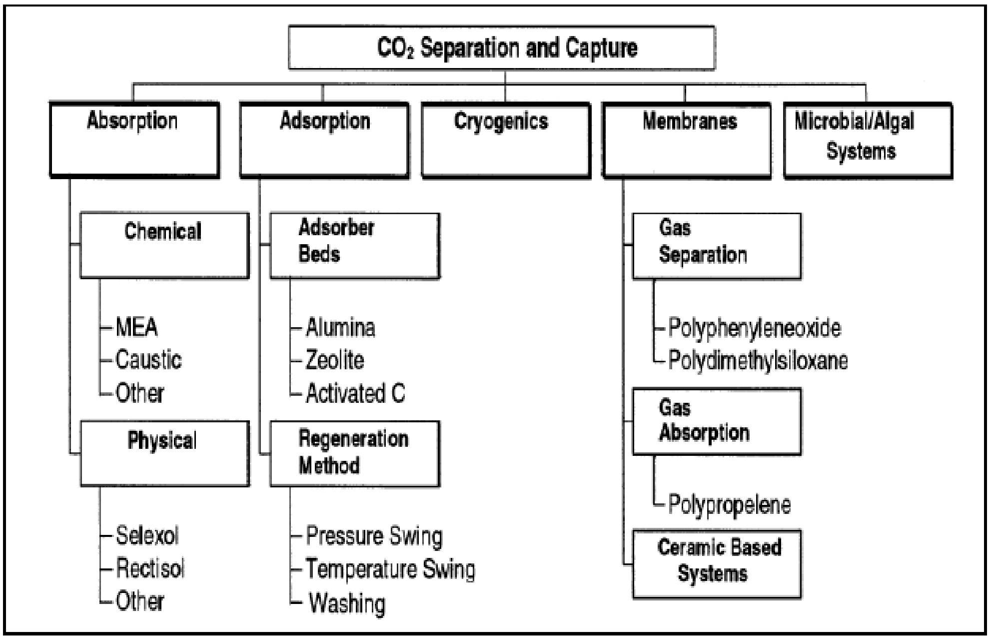


FIGURE 2.1 Technology options for CO_2 separation and capture. (Source: Rao & Rubin, 2002)

Chemical Sovent	Physical Solvent	Direct Conversion
MEA	Selexol	Iron Sponge
DEA	Rectisol	Stretforf
TEA	Purisol	Unisulf
MDEA	Spasolv	Takahax
DIPA/ SHELL ADIP	Propylene Carbonate	LO-CAT
DGA/ Fluor Econamine	Estasolven	Lacy-Keller
Proprietary Amine	Alkazid	Townsend
Benfield (Hot Carbonate)		Sulfint
Catacarb (Hot Carbonate)		
Giammarco-Vetrocoke (Hot Carbonate)		

Diamox		
Dravo/ Still		
Specialty Solvent	Distillation	Gas Penetrtion
Sulfinol	Ryan Holmes	Membrane
Amisol	Cryfrac	Molecular Sieve
Flexsorb LE 711		
Optisol		
Zinc Oxide		
Sulfa Check		
Slurrisweet		
Chemsweet		
Merox		

TABLE 2.1 Type of process used for CO_2 capture (Source: Dr Maurice Stewart (2005), Acid Gas Sweetening, Stewart Training Corporation)

2.2 AMINE-BASED ABSORPTION SYSTEM FOR CARBON DIOXIDE CAPTURE

Rochelle (2009) said that amine-based absorption and stripping systems have been studied for carbon dioxide capture from coal-fired power plants and have shown the most promise for effective carbon dioxide control. The examples of aqueous solutions of alkanolamines that have been used for the absorption of CO_2 process are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and methhydiethanolamine (MDEA). These alkanolamines have been competing with another class of acid gas treating solvents, the sterically hindered amines (Sartori et al, 1994).

Commonly, the primary amine monoethanolamine (MEA), the secondary amine diethanolamine (DEA), and the tertiary amine methyldiethanolamine (MDEA) are used as the solvents for removing CO_2.

These amines react rapidly with CO_2 to form carbamates. By the addition of a primary or secondary amine to a purely physical solvent such as water, the CO_2 absorption capacity and rate is enhanced manifold (Rinker, Ashour and Sandall, 2000).

However, the high heat of absorption relatively associated with the formation of carbamate ions caused the cost of regenerating primary and secondary amine is high. Thus, the amine blends such as potassium carbonate/piperazine and methyldiethanolamine/piperazine are being studied to apply in this process. The blend amines can increase the rate of absorption of CO_2. Astarita (1961) is very definite: “Aqueous primary amine solutions, such as monoethanolamine, have been shown to have fast reaction rates”. However, the concentration of the blend amines varies with the rate of absorption.

2.3 POTASSIUM CARBONATE SOLVENT FOR CARBON DIOXIDE ABSORPTION

Potassium carbonate is one of the options used in the absorption of carbon dioxide process. Although it has low heat of regeneration, but its rate of reaction is slow compared to amines. For the reason, piperazine is been pointed as the best way to activate the potassium carbonate solution. Plus, the blending of amines accelerates the absorption process (Bosch et al., 2001). The concentrations of amines and potassium carbonate are highly effect the heat of absorption of carbon dioxide.

2.4 PIPERAZINE AS AN ACTIVATOR FOR POTASSIUM CARBONATE SOLUTION

The cyclic diamine structure of piperazine causes the rapid formation of the carbamates. It can catalyzed proton extractions in the reaction mechanism. Besides, this special property of piperazine can theoretically absorbs two moles of carbon dioxide for every mole of amine. Based on the previous study, piperazize has been used as a promoter for amine systems such as MDEA/PZ or MEA/PZ blends to improve CO_2 mass transfer rates and it is reported that piperazine is more effective than the conventional activators. Moreover, the boiling point of piperazine is 146.5°C which is lower than MEA (170°C), indicating the possibility for higher volatility. Increasing the concentration of piperazine in solution allows for increased solvent capacity and faster CO_2 absorption rates. Thus, this proves that piperazine is an effective promoter in potassium carbonate. Previous research has indicated that piperazine is an effective promoter in methyldiethanolamine (MDEA) and MEA solutions (Bishnoi, 2000; Dang, 2001).

2.5 SOLVENT DEVELOPMENT

It is well known to contact carbon dioxide containing acidic gas mixtures with a liquid solvent to remove these acidic gases (Hong, 1980). Generally, there are two classes of solvents used in scrubbing process which are physical solvent that absorb the acidic gas physically and chemical solvent which chemically react with the acidic gas for removal of same. Furthermore, physical solvent provides low circulation rates and low regeneration energy for its recovery. While, for chemical solvent, it effectively operates on gaseous mixtures containing low concentrations of acidic gas.

2.5.1 Definition

Solvent can be defined as substances that can physically dissolve other substances; specifically they are inorganic and organic liquids able to dissolve other gaseous, liquid or solid substances (Scheithauer, 2000). The solvent that does not undergoes chemical change qualified for a suitable solvent. As Scheithauer (2000) mentioned that the components of the solution may be recovered in their original form by physical separation processes, such as distillation, crystallization, sublimation, evaporation and adsorption.

2.5.2 Physical analysis

The physical properties of solvents are essential for the liquid-film mass transfer coefficient and are important for mass transfer modeling of absorbers and regenerators. Physical properties that are being analyzed in this study are as follows:

(a) Refractive index (RI)

Refractive index is basically the ratio of the velocity of light in air to the velocity of light in the medium being measured: $n_D = [V_{air}]/V_{liquid}$. It is used to measure of how light is refracted when it pass through another medium. The purity of a liquid can be determined through refractive index. Refractive index can be used to identify an unknown liquid compound, or it can be used as a means of measuring the purity of a liquid compound by comparing it to a literature values (Chem 211: Refractrometry).

(b) Surface Tension

Surface tension, $\boldsymbol{\sigma}$ is defined as the force exerted in the plane of the surface per unit length. The boundary between a liquid phase and a gas phase can be considered a third phase with properties distinct from those of the liquid gas (Poling, Prausnitz and O’Connel, 2000). There are unequal forces acting upon the molecules on the macroscopic surface layer. Thus, the tension produces upon the surface layer tends to contract to the smallest area compatible with the mass of material, continer restraints, and etxternal forces, e.g. gravity.

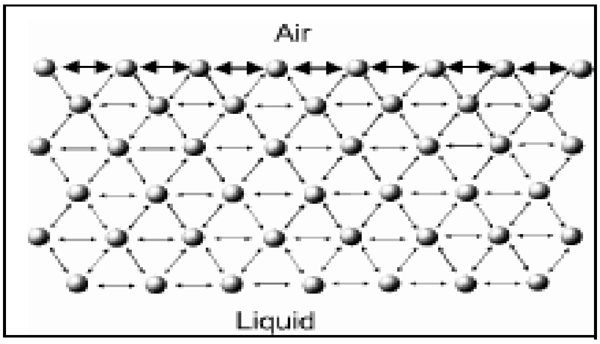


FIGURE 2.2 Molecules behavior on the surface of a liquid
(Source: KSV Instruments Ltd.)

Surface tension decreases with temperature as cohesive forces decrease with an increase of molecular thermal activity. The common units for surface tension are dynes/cm or mN/m.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 RESEACRH METHODOLOGY

The research on this project was done in order to generate feasible plan for the project. Massive amount of research papers, journals and articles were analyzed to get a better understanding on the absorption process of carbon dioxide by potassium carbonate solution promoted by piperazine. From this way, the finding of advantages and disadvantages from this project can be generated. Also, from the research, a suitable experimental procedure can be generated.

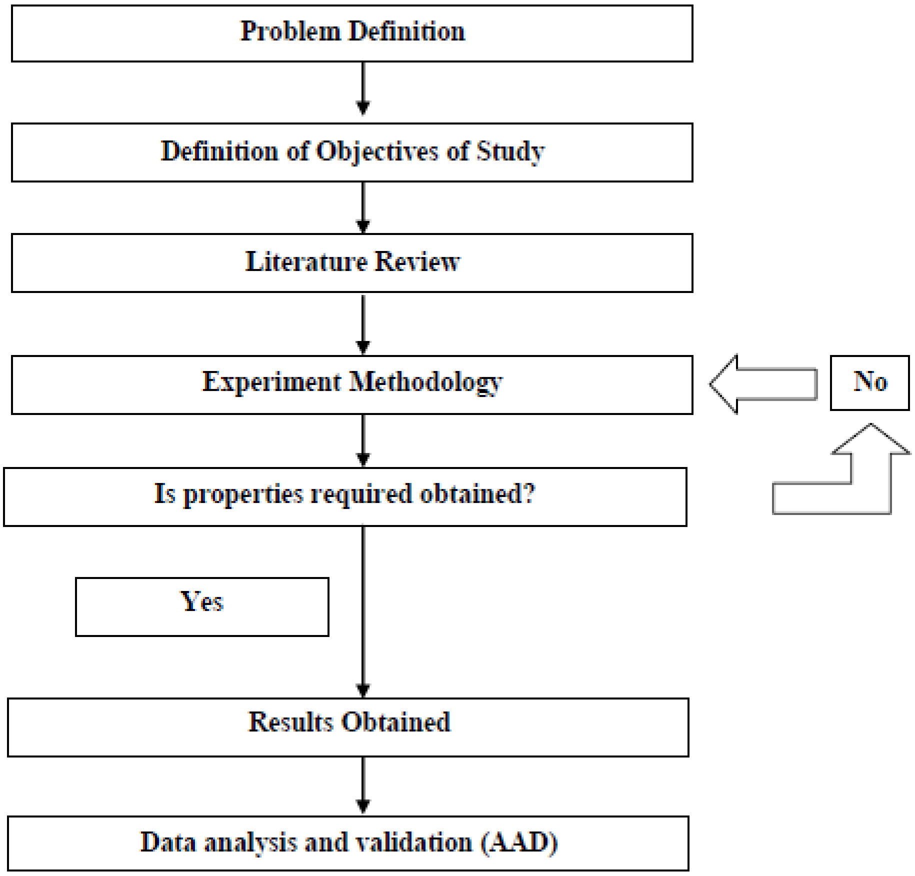


FIGURE 3.1 Research Methodology

3.1.1 Materials

3.1.1.1 Chemicals

Piperazine with stated purity of 99.9% (GC, area %) and potassium carbonate will be used without any purification. The measurements for each sample will be performed in duplicate and the average values are reported.

3.1.2 Experimental Work

3.1.1.2 Refractive index measurement

The refractive indices of the samples which varying concentration of potassium carbonate (5%, 15%, 15%, 20% and 25%) and piperazine (2%, 4%, 6%, 8% and 10%) are determined using a programmable digital refractometer. The refractive indices are measured at 293.15K to 323.15K

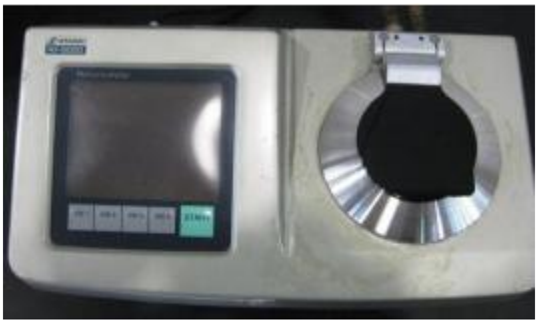


FIGURE 3.2 Digital Refractometer (RX-5000,alpha, Atago)

3.1.1.3 Surface tension measurement

The surface tension of varying concentration of potassium carbonate (5%, 15%, 15%, 20% and 25%) and piperazine (2%, 4%, 6%, 8% and 10%) are determined using

Interfacial Tension Meter (IFT 700, Vinci Technologies) at 293.15 K.

FIGURE 3.3 Interfacial Tension Meter (IFT 700, Vinci Technologies)

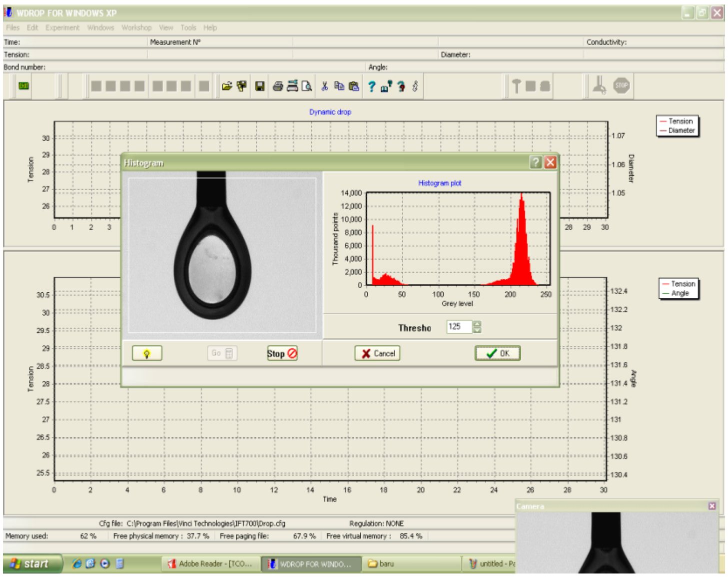
A drop of liquid needs to be formed with suitable needle size (1.0 – 1.5 mm). The camera that is setup in the IFT meter will capture the image of the droplet and send the data to the computer. The software WDROP will be used to calculate the surface tension. The settings of the software are as follows:

1. The tension meter needs to be calibrated each time forming a new drop. The settings that need to be calibrated are Focus, Histogram, Vertical Setup and Optical Calibration with tube.

Cfg file: C:\Program Files\Vinci Technologies\IFT700\Drop.cfg Regulation: NONE

Memory used: 64 % Free physical memory : 36.0 % Free paging file: 67.1 % Free virtual memory : 85.4 %

FIGURE 3.4 Adjusting the Focus

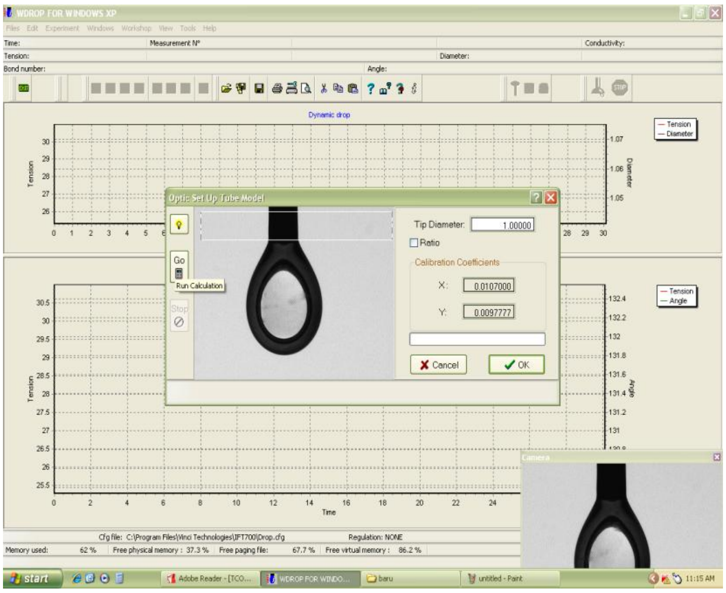


Threshold 125

Cfg file: C:\Program Files\Vinci Technologies\IFT700\Drop.cfg Regulation: NONE

Memory used: 62 % Free physical memory : 37.7 % Free paging file: 67.9 % Free virtual memory : 85.4 %

FIGURE 3.5 Adjusting the Histogram



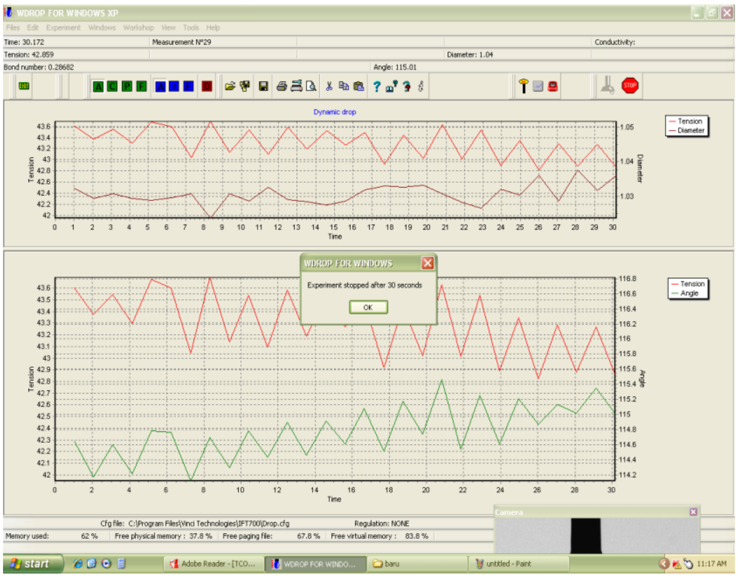
Time:
Measurement N°
Conductivity:
Tension:
Diameter:
Bond number:
Angle:

Tip Diameter: 1.00000
☐ Ratio
X: 0.0107000
Y: 0.0097777

Cfg file: C:\Program Files\Vinci Technologies\IFT700\Drop.cfg
Regulation: NONE
Memory used: 62 %
Free physical memory : 37.3 %
Free paging file: 67.7 %
Free virtual memory : 86.2 %

FIGURE 3.6 Adjusting the Optical Calibration

2. The data will be obtained after running the test for 30 seconds



Time: 30.172
Measurement N°29
Conductivity:
Tension: 42.859
Diameter: 1.04
Bond number: 0.28682
Angle: 115.01

Experiment stopped after 30 seconds

Cfg file: C:\Program Files\Vinci Technologies\IFT700\Drop.cfg
Regulation: NONE
Memory used: 62 %
Free physical memory : 37.8 %
Free paging file: 67.8 %
Free virtual memory : 83.8 %

FIGURE 3.7 The calculation run for 30 seconds

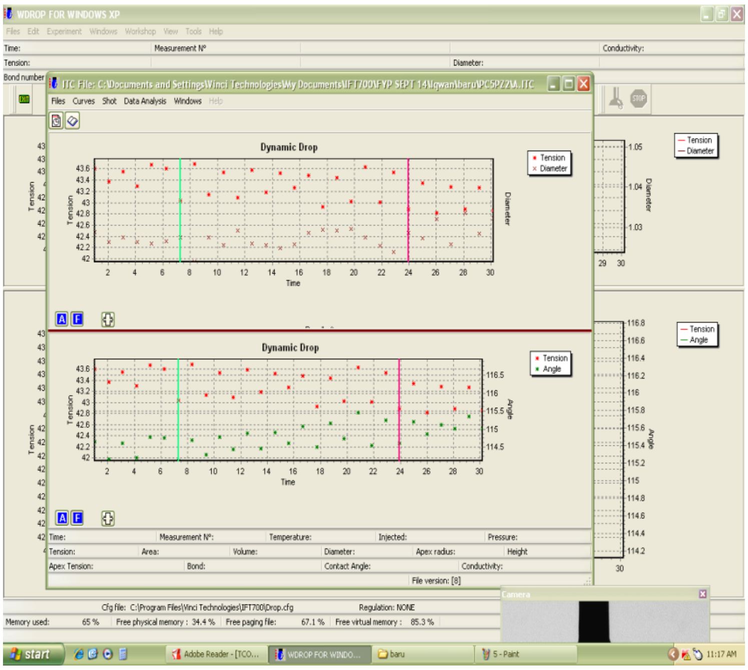
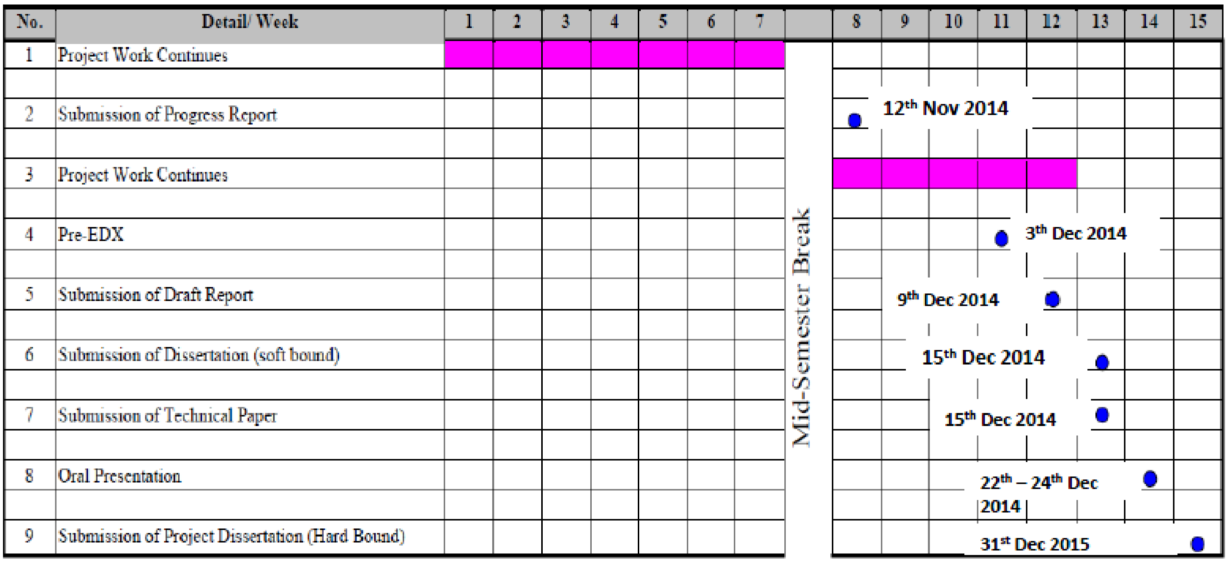


FIGURE 3.8 Results for the surface tension

3.2 KEY MILESTONE AND GANTT CHART



No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	🟪	🟪	🟪	🟪	🟪	🟪	🟪	Mid-Semester Break								
2	Submission of Progress Report									●	12th Nov 2014						
3	Project Work Continues									🟪	🟪	🟪	🟪	🟪			
4	Pre-EDX												●	3th Dec 2014			
5	Submission of Draft Report										9th Dec 2014			●			
6	Submission of Dissertation (soft bound)											15th Dec 2014			●		
7	Submission of Technical Paper												15th Dec 2014		●		
8	Oral Presentation												22th – 24th Dec 2014			●	
9	Submission of Project Dissertation (Hard Bound)												31st Dec 2015				●

● Suggested milestone

🟪 Process

FIGURE 3.9 Gantt chart

CHAPTER 4

RESULT AND DISCUSSION

There are two parts of experimental work to be completed within the time frame given which are measuring refractive index and surface tension of aqueous blends of Piperazine and Potassium carbonate. The aqueous (potassium carbonate + water), (piperazine + water) and (potassium carbonate + piperazine + water) solutions were prepared gravimetrically using an analytical balance (Mettler Toledo model AS120S).

4.1 REFRACTIVE INDEX

The refractive indices varying concentration of potassium carbonate, K_2CO_3 (5%, 15%, 15%, 20% and 25%) and piperazine, PZ (2%, 4%, 6%, 8% and 10%) were determined using programmable digital refractometer (RX-5000 alpha, Atago) at temperatures (293.15 to 323.15) K with a temperature control accuracy of ± 0.05ºC.

Result:

The results obtained are as follows:

Concentration (wt%)		Temperature		Refractive Index (n_D)
K_2CO_3	H_2O	C	K	
5	95	20	293.15	1.34120
		25	298.15	1.34060
		30	303.15	1.33992
		40	313.15	1.33855
		50	323.15	1.33685
		20	293.15	1.34866
		25	298.15	1.34799

10	90	30	303.15	1.34727
		40	313.15	1.34600
		50	323.15	1.34427
15	85	20	293.15	1.35646
		25	298.15	1.35572
		30	303.15	1.35496
		40	313.15	1.35356
		50	323.15	1.35186
20	80	20	293.15	1.36495
		25	298.15	1.36405
		30	303.15	1.36321
		40	313.15	1.36190
		50	323.15	1.36018
25	75	20	293.15	1.37152
		25	298.15	1.37071
		30	303.15	1.36989
		40	313.15	1.36860
		50	323.15	1.36668

TABLE 4.1 Data of refractive indices for K_2CO_3 + water

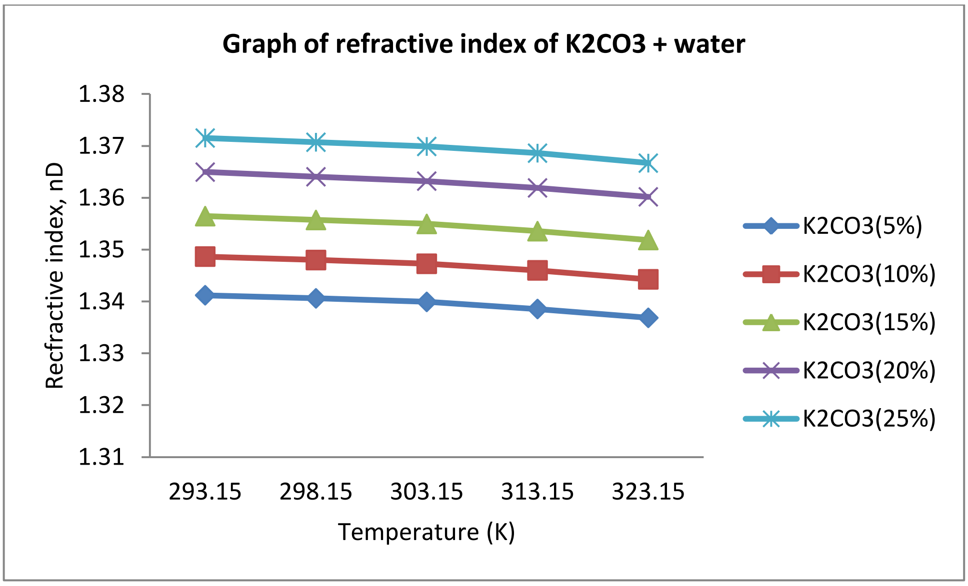


FIGURE 4.1 Graph of refractive index of K_2CO_3 + water

Concentration (wt%)		Temperature		Refractive Index (n_D)
PZ	H_2O	C	K	
2	98	20	293.15	1.33670
		25	298.15	1.33583
		30	303.15	1.33526
		40	313.15	1.33392
		50	323.15	1.33241
4	96	20	293.15	1.33982
		25	298.15	1.33949
		30	303.15	1.33884
		40	313.15	1.33742
		50	323.15	1.33588
6	94	20	293.15	1.34254
		25	298.15	1.34250
		30	303.15	1.34176
		40	313.15	1.34046
		50	323.15	1.33880
8	92	20	293.15	1.34715
		25	298.15	1.34615
		30	303.15	1.34543
		40	313.15	1.34383
		50	323.15	1.34230
10	90	20	293.15	1.35126
		25	298.15	1.35073
		30	303.15	1.35005
		40	313.15	1.34862
		50	323.15	1.34754

TABLE 4.2 Data of refractive indices for PZ + water

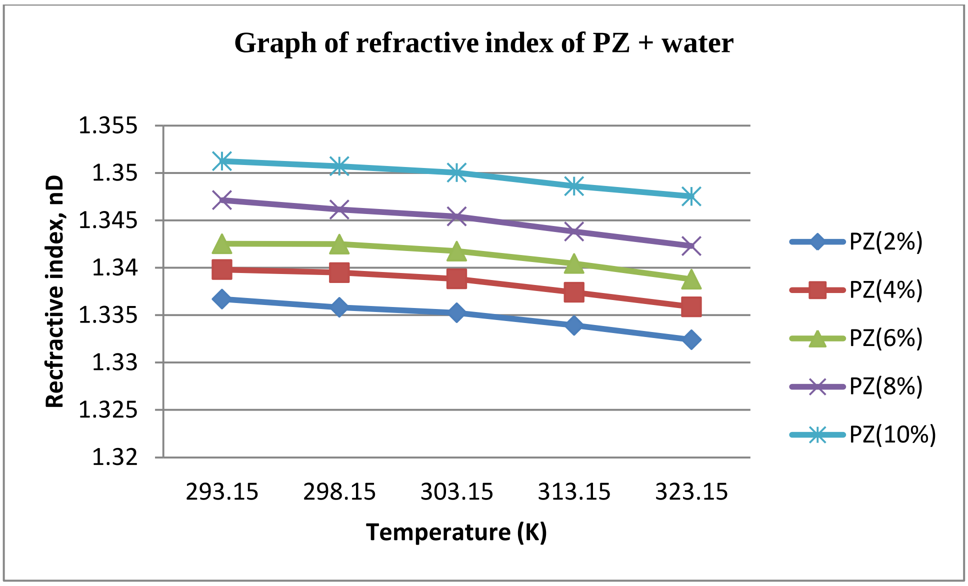


FIGURE 4.2 Graph of refractive index of PZ + water

Concentration (wt%)			Refractive Index (n_D)
K_2CO_3	PZ	H_2O	**(T = 20°C/293.15K)**
5	2	93	1.34316
	4	91	1.34784
	6	89	1.35106
	8	87	1.35374
	10	85	1.35816
10	2	88	1.35186
	4	86	1.35518
	6	84	1.35863
	8	82	1.36536
	10	80	1.36543
15	2	83	1.35899
	4	81	1.36219
	6	79	1.36471
	8	77	1.36781
	10	75	1.37199
	2	78	1.36525
	4	76	1.36842

20	6	74	1.37195
	8	72	1.36996
	10	70	1.37197
25	2	73	1.37062
	4	71	1.37489
	6	69	1.37477
	8	67	1.37707
	10	65	1.37765

TABLE 4.3 Data of refractive indices for blends of K_2CO_3 *and* PZ at T=20°C/293.15K

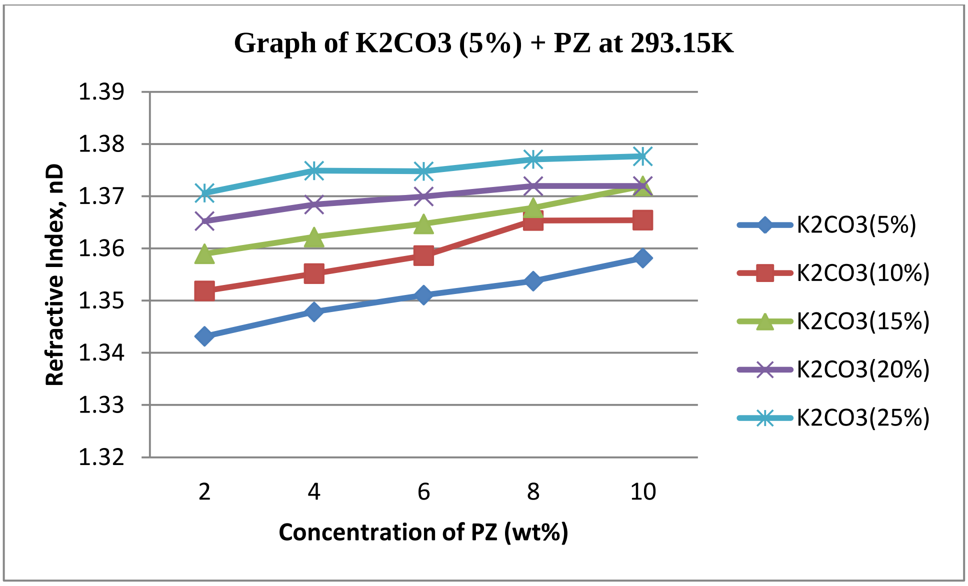


FIGURE 4.3 Graph of K_2CO_3 (5%) + PZ at 293.15K

Concentration (wt%)			Refractive Index (n_D)
K_2CO_3	PZ	H_2O	**(T = 25°C/298.15K)**
5	2	93	1.34374
	4	91	1.34755
	6	89	1.35060
	8	87	1.35351
	10	85	1.35832
	2	88	1.35179

10	4	86	1.35451
	6	84	1.35864
	8	82	1.36434
	10	80	1.36568
15	2	83	1.35800
	4	81	1.36232
	6	79	1.36462
	8	77	1.36852
	10	75	1.36937
20	2	78	1.36500
	4	76	1.36764
	6	74	1.36984
	8	72	1.37083
	10	70	1.37246
25	2	73	1.36977
	4	71	1.37379
	6	69	1.37401
	8	67	1.37703
	10	65	1.37805

TABLE 4.4 Data of refractive indices for blends of K_2CO_3 *and* PZ at T=25°C/298.15K

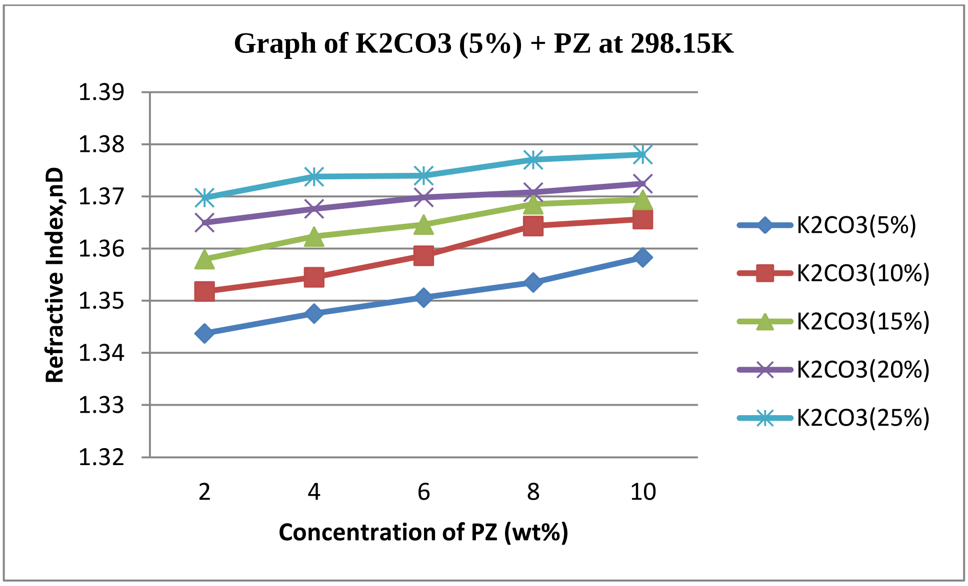


FIGURE 4.4 Graph of K_2CO_3 (5%) + PZ at 298.15K

Concentration (wt%)			Refractive Index (n_D)
K_2CO_3	PZ	H_2O	**(T = 30°C/303.15K)**
5	2	93	1.34311
	4	91	1.34688
	6	89	1.34993
	8	87	1.35298
	10	85	1.35756
10	2	88	1.35110
	4	86	1.35377
	6	84	1.35792
	8	82	1.36374
	10	80	1.36494
15	2	83	1.35726
	4	81	1.36156
	6	79	1.36386
	8	77	1.36775
	10	75	1.36843
20	2	78	1.36423
	4	76	1.36689
	6	74	1.37008
	8	72	1.36923
	10	70	1.37164
25	2	73	1.36899
	4	71	1.37325
	6	69	1.37309
	8	67	1.37719
	10	65	1.37626

TABLE 4.5 Data of refractive indices for blends of K_2CO_3 and PZ at T=30°C/303.15K

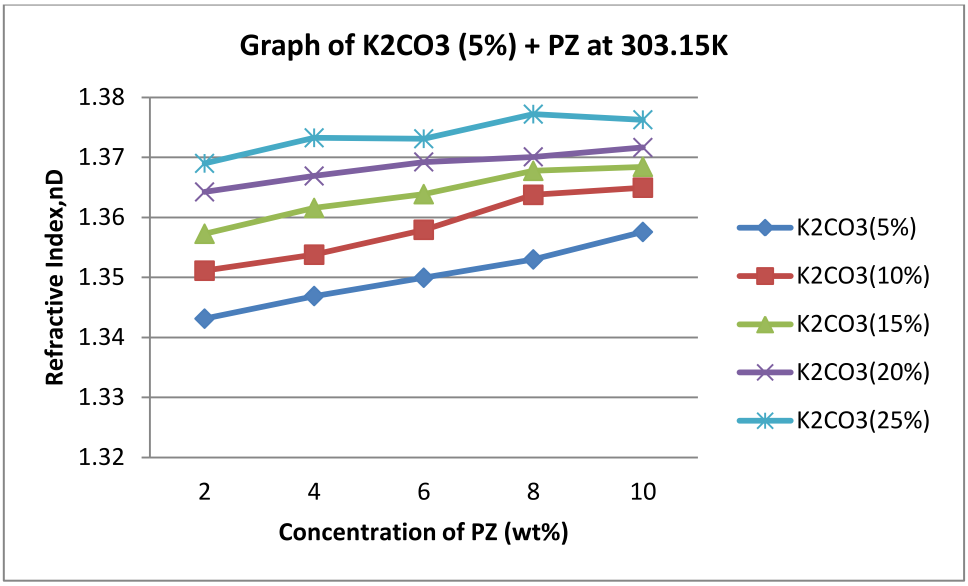


FIGURE 4.5 Graph of K_2CO_3 (5%) + PZ at 303.15K

Concentration (wt%)			Refractive Index (n_D)
K_2CO_3	PZ	H_2O	**(T = 40°C/313.15K)**
5	2	93	1.34177
	4	91	1.34538
	6	89	1.34871
	8	87	1.35143
	10	85	1.35646
10	2	88	1.34953
	4	86	1.35247
	6	84	1.35627
	8	82	1.36229
	10	80	1.36321
15	2	83	1.35576
	4	81	1.35993
	6	79	1.36248
	8	77	1.36603
	10	75	1.36671
	2	78	1.36255
	4	76	1.36545

20	6	74	1.36817
	8	72	1.36799
	10	70	1.36999
25	2	73	1.36758
	4	71	1.37157
	6	69	1.37187
	8	67	1.37542
	10	65	1.37514

TABLE 4.6 Data of refractive indices for blends of K_2CO_3 and PZ at T=40°C/313.15K

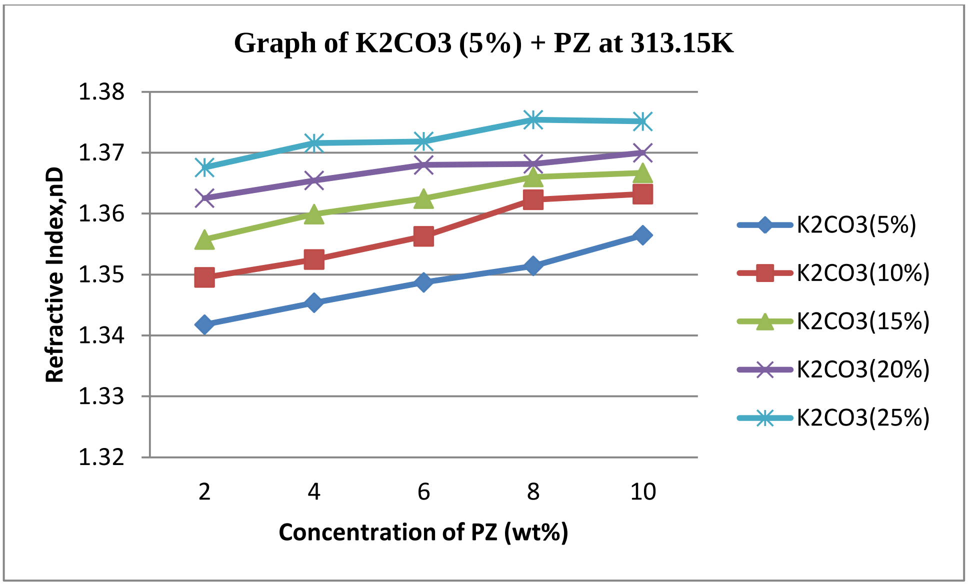


FIGURE 4.6 Graph of K_2CO_3 (5%) + PZ at 313.15K

Concentration (wt%)			Refractive Index (n_D)
K_2CO_3	PZ	H_2O	**(T = 50°C/323.15K)**
5	2	93	1.34019
	4	91	1.34368
	6	89	1.34689
	8	87	1.34974
	10	85	1.35464
	2	88	1.34751

10	4	86	1.35077
	6	84	1.35427
	8	82	1.36091
	10	80	1.36075
15	2	83	1.35465
	4	81	1.35743
	6	79	1.36111
	8	77	1.36365
	10	75	1.36500
20	2	78	1.36031
	4	76	1.36458
	6	74	1.36584
	8	72	1.36646
	10	70	1.36743
25	2	73	1.36628
	4	71	1.36913
	6	69	1.37032
	8	67	1.37350
	10	65	1.37336

TABLE 4.7 Data of refractive indices for blends of K_2CO_3 *and* PZ at T=50°C/323.15K

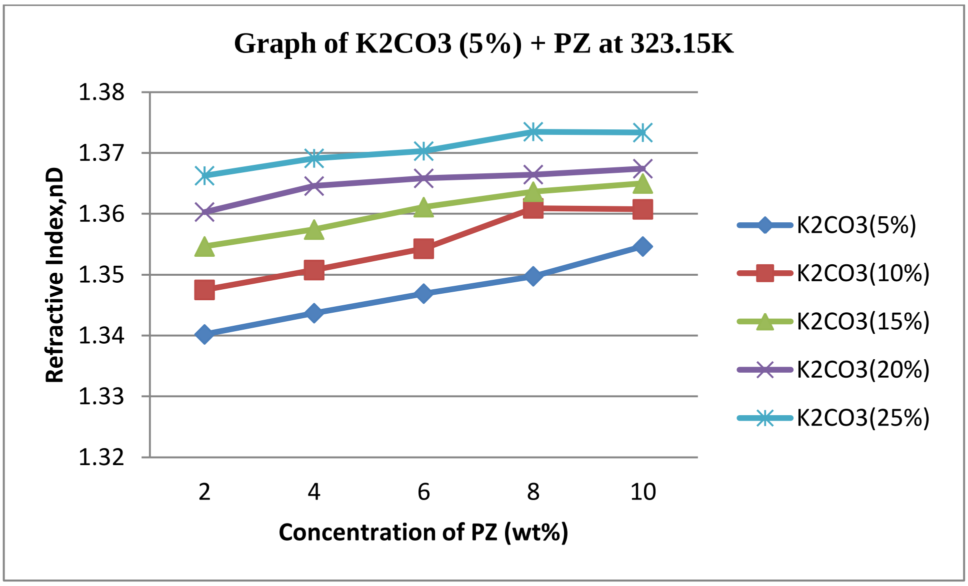


FIGURE 4.7 Graph of K_2CO_3 (5%) + PZ at 323.15K

The graph plotted shows that with an increase in temperature, the refractive indices value decrease and with an increase in concentration of amines, the refractive indices value increases.

4.2 SURFACE TENSION

The surface tension varying concentration of potassium carbonate, K_2CO_3 (5%, 10%, 15%, 20% and 25%) and piperazine, PZ (2%, 4%, 6%, 8% and 10%) were determined using Interfacial tension meter (IFT 700, Vinci Technologies) at temperatures (293.15) K with a temperature control accuracy of ± 0.05ºC.

Result:

The results obtained are as follows:

Concentration (wt%)			Surface tension (mN/m)
K_2CO_3	PZ	H_2O	
5	2	93	42.86
	4	91	51.5
	6	89	53.76
	8	87	54.31
	10	85	55.01
10	2	88	43.02
	4	86	53.2
	6	84	54.22
	8	82	58.51
	10	80	59.66
15	2	83	43.36
	4	81	53.7

	6	79	58.18
	8	77	58.71
	10	75	63.18
20	2	78	45.7
	4	76	55.39
	6	74	58.23
	8	72	59.13
	10	70	64.21
25	2	73	48.7
	4	71	56.51
	6	69	59.05
	8	67	65.73
	10	65	67.13

TABLE 4.8 Data of surface tension for blends of K_2CO_3 and PZ

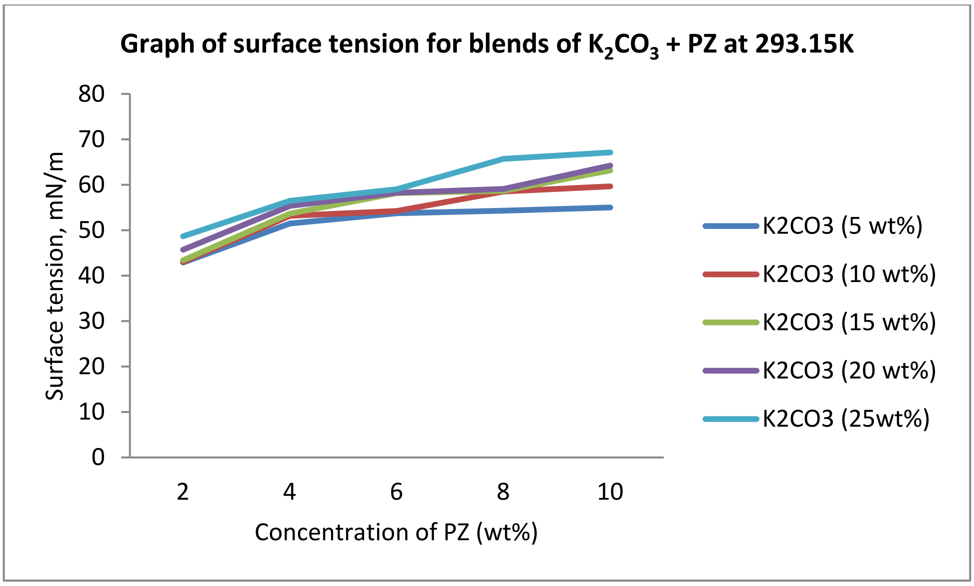


FIGURE 4.8 Graph of surface tension for blends of K_2CO_3 and PZ

The surface tension of aqueous solution of K_2CO_3 and PZ are plotted versus temperature in Figures 4.8 and 4.9. The graph showed that with an increase in temperature, the surface tension values decrease.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The study on the physical properties of piperazine to activate potassium carbonate solution in water is very important for the absorption of carbon dioxide. The growing industries nowadays affect in the increasing emission of carbon dioxide. The usage of aqueous primary amine solution, such as monoethanolamine (MEA) and secondary amine, such as diethanolamine (DEA) show good effect in the absorption of carbon dioxide process. However, piperazine is the most effective promoter potassium carbonate solution in order to increase the rate of absorption of carbon dioxide.

Piperazine is an effective additive to increase the absorption rate of carbon dioxide. Its low heat of absorption associated with aqueous potassium carbonate could potentially reduce energy costs associated with carbon dioxide removal. As for the result, the higher the concentration of blends of Piperazine and Potassium Carbonate and the lower the temperature, the higher the value of refractive index and surface tension. For the recommendation, a thermodynamic model will be necessary to encompass the expanded solvent concentrations and conditions. Besides, the solubility of carbon dioxide shall be compared with the solubility model values.

REFERENCES

1. Cullinane, J.T., Rochelle, G.T. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. Chemical Engineering Science 2004, 59, 3619 - 3630.

2. Cullinane, J.T., Rochelle, G.T. Kinetics of carbon dioxide absorption into aqueous potassium carbonate and piperazine. Ind. Eng. Chem. Res. 2006, 45, 2531 - 2545.

3. Samanta, A., Bandyopadhyay, S.S. Density and viscosity of aqueous solutions of piperazine and (2 – amino – 2 – methyl – 1 – piperazine) from 298 to 333K. J. Chem. Eng. Data 2006, 51, 467 – 470.

4. Murshid, G., Shariff, A.M., Keong, L.K., Bustam, M.A. Physical properties of aqueous solutions of piperazine and (2 – amino – 2 – methyl – 1 – propanol + piperazine) from (298.15 to 333.15) K. J. Chem. Eng. Data 2011, 51, 2660 – 2663.

5. Freeman, S. A., Dugas, R., Wagener, D. H. V., Nguyen, T., Rochelle, G. T. Carbon dioxide capture with concentrated, aqueous piperazine. International Journal of Greenhouse Gas Control 4 (2010), 119 – 124.

6. A. Halpern and J.Reeves, Experimental Physical Chemistry, 1988, Scott and Foresman.

7. Automatic Digital Refractomete RX-5000a-Plus, Atago Co. Ltd, <http://www.atago.net/english/product_rx.php> retrieved on 5th November 2009.

8. David Dortmundt & Kishore Doshi. (1999). Recent Developments in CO2 Removal Membrane Technology.

9. Kohl, A. L.;Nielsen, R. B. (1997). Gas purification, 5th ed.; Gulf Publishing Co.: Houston, TX.

10. Rao, A.B and S. Rubin (2002). “A Technical, Economic and Environmental Assessment of Amine-based Carbon Capture Technology for Power Plant Greenhouse Gas Control”. Environmental Science & Technology, 36 (20), 4467-4475.

11. Ayyaz Muhammad, Mohamed I. Abdul Mutalib, Thanabalan Murugesan, Amir Shafeeq, Density and Excess Properties of Aqueous N-Methyldiethanolamine Solutions from (298.15 to 338.15) K, Journal of Chemical & Engineering Data 2008 53 (9), 2217-2221.

12. Bruce E. Poling, John M.Prausnitz, and John P. O’Connell, 2000, The properties of gases and liquids, Fitfth edition, McGraw Hill.

13. Davis, M. L. and Cornwell, D. A. (1991). Introduction to Environmental Engineering. 2nd Edition, McGraw-Hill Inc.

14. Rubin, E. S. (2001). Introduction to Engineering and the Environment, 1st ed; McGraw-Hill: New York.

15. Scribd, Analytical Chemistry, http://www.scribd.com/doc/13500772/Analytical-Chemistry, retrieved on 2nd November 2009.

16. Veltman, K., Singh, B., Hertwich E., (2009). “Human and Environmental Impact Assessment of Postcombustion CO2 Capture Focusing on Emissions from Amine-Based Scrubbing Solvents to Air”, *Environmental Science and Technology*, Norwegian University pf Science and Technology.

17. Wypych George, 2001, Handbook of Solvents, ChemTec Publishing, William Andrew Publishing.

18. Adisorn Aroonwilas and Amornvadee Veawab. (2006). Characterization and Comparison of the CO2 Absorption Performance into Single and Blended

Alkanoamines in a Packed Column, Faculty of Engineering, University of Regina, Regina, Saskatchewan, Canada.

19. Bishoi, S.; Rochelle, G.T. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. Chem. Eng. Sci. 2000, 55, 5531-5543.

20. Geankoplis, C. J. Transport Processes and Separation Process Principles, 4th ed.; Prectice-Hall, Inc.: Englewood Cliffs, NJ, 2003.