Experimental Study of Salinity Effects on Interfacial Tension between Carbon Dioxide and Brine

by

Alya Sorfina binti Baharuddin

Supervisor: Dr Khalik M Sabil

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

SEPTEMBER 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Experimental Study of Salinity Effects on Interfacial Tension between Carbon Dioxide and Brine

by

Alya Sorfina binti Baharuddin

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

Approved by,

____
(Dr Khalik M Sabil)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2013

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

ALYA SORFINA BINTI BAHARUDDIN

ABSTRACT

Water-Alternating-Gas (WAG) process has been an increasing interest for Enhanced Oil Recovery (EOR) to improve sweep efficiency by injecting water and gas such as carbon dioxide (CO_2) alternately into oil reservoirs. Sequestration of CO_2 is a method with great potential for reducing greenhouse gases emissions. An experimental study was conducted to measure the interfacial tension (IFT) between CO_2 and brine of equal molar concentrations consisting of $MgCl_2$ and NaCl. The experiments were conducted at various pressures (500, 1000 and 2000 psi), temperatures (27, 71 and 100˚C) and brine salinities corresponding to molarities, m= 0.045, 0.1 and 0.5 of each salt, representing the conditions of CO_2 storage in deep saline aquifers. CO_2/brine IFT increases with salinity and temperature but decreases with pressure. The sum of the individual IFT increments due to each salt contained in the brine is the total increase of CO_2/brine IFT assuming an analogous behavior for other salts which indicates a strong additive effect on IFT when brine contains various salts. The IFT also increases due to cation valence. IFT 700 is used to measure the CO_2/brine IFT. It computes the drop shape image and computes the IFT from solving algorithm based on the Laplace equation.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful. The author would like to use this opportunity to thank several people for their help and support, as well as their contribution in time, effort, advice, and help in completing this project.

First and foremost, deepest appreciation to beloved supervisor Dr Khalik M Sabil for his whole-hearted supervision as well as his patience and guidance whilst allowing the author the room to work in her own way. His enthusiasm and dedication had inspired the authors to strive harder in the future. The author would like to express her sincerest gratitude to co-supervisors, Mr Babak Moradi and Dr Bhajan Lal for their excellent direction, invaluable feedback, constructive suggestions and detailed corrections, which played enormous role resulting in the completion of this project guidance

Token of appreciation also goes to the laboratory technologists, Mr Shahrul and Ms Shahidah Zakariya for their help and assistance in facilitating upon completing each part of the project. Last but not least, heartfelt gratitude to the author’s family and friends who have been giving endless courage and moral support to keep her constantly engaged in this project.

Thank you.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Major interfacial interactions which are interfacial tension, wettability, capillarity and interface mass transfer are really important in the distribution of fluid and porous media behavior [5, 12-13]. Successful of any CO_2 storage operations depends on the interfacial interactions between CO_2, brine and oil and/or gas reservoirs. In the area of EOR using chemicals and miscible gas solvents, petroleum engineers aims on the interfacial tension between fluid phases.

Carbon dioxide injection, either miscible or immiscible has been recognized as an efficient method to enhance oil recovery and to reduce CO_2 emissions. EOR processes often involve Water-Alternating-Gas (WAG) process as many oil reservoirs are underlain by an aquifer. The injection of CO_2 and water into an oil reservoir helps in mobilizing the oil and possibly increases the permeability.

CO_2 sequestration by subsurface storage is seen as a key mechanism for reducing the emission of greenhouse gases to the atmosphere. CO_2 has the greatest effect of the greenhouse gases, but taken together, methane (CH_4), chlorofluorocarbon, nitrous oxide (N_2O), ozone and black carbon currently have comparable effects on radiative forcing [2]. CO_2 can be captured from a variety of anthropogenic sources such as burning of fossil fuels, clearing of forests and manufacture of cement and stored in geological reservoir.

The study of CO_2/brine IFT is important as it governs fluid distribution in the porous media. In the case of CO_2-EOR process, the interfacial tension between oil and injected CO_2 will be decreased thus forming a low viscosity fluid that can be easily displaced and produced. Consequently, it improves the recovery efficiency of the reservoir. For CO_2

sequestration in deep saline aquifers, CO_2/brine IFT significantly improves the flow process and it controls the capillary-sealing efficiency. The decreasing of the IFT between CO_2 and brine will significantly reduce the sealing capacity of the caprock hence causes the injected CO_2 to migrate through the caprock into upper formations.

1.2 Problem Statement

Both CO_2-EOR injection and CO_2 sequestration into the subsurface involves CO_2 to come in contact with brine. Generally in real conditions, the brine of reservoirs is a mixture of different salts containing different anions whereas the cation is either monovalent or divalent ($MgCl_2$, Na_2SO_4, $NaHCO_3$ etc). Consequently, the effects of salt mixtures on CO_2/brine IFT need to be studied.

Researchers have been done on the effect of salinity of the interfacial tension between CO_2 and brine. However, only a few researches done on the effect of salt mixtures on the interfacial tension between CO_2 and brine. To discover the nature and extent of this study, the best way is to perform laboratory experiments.

1.3 Objectives

The study of interfacial properties between CO_2 and fluids present in oil reservoirs and deep saline aquifers is essential for a better understanding in both CO_2-enhanced oil recovery and CO_2 sequestration through geological carbon storage. The main objective of this study is to determine the effect of salinity (including both salt type and concentration) on IFT between CO_2 and brine over the range of conditions applicable to CO_2 storage in underground reservoirs. In short, the objectives that can also be put into account are:

a) To study the effect of salt concentration in mixtures on CO_2/brine IFT

The effect of salt concentration is really important because the salinity increases as depth increases in the subsurface. The increase of CO_2/brine IFT depends on the distribution of ions in the aqueous phase and its effect on the interfacial configuration.

b) To determine the effect of valence of cations in mixtures on CO_2/brine IFT

Reservoir brines usually contain different types of salts that have either monovalent or divalent cations such as NaCl that contains a cation of Na^+ and $CaCl_2$ that contains a cation of Ca^{2+}.

c) To analyze and justify the relationship of the effect of salt mixtures on CO_2/brine IFT under storage conditions

Since CO_2-EOR and CO_2 sequestration involves the injection of CO_2 into the subsurface, the conditions of the reservoirs or aquifers such as temperature and pressure is really important for this study.

1.4 Scope of Study

An experimental laboratory study was conducted to determine the effect of salt mixtures on interfacial tension (IFT) between CO_2 and brine consisting two types of salts which are sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). The experiments were repeated at different pressures, temperatures and salinities which represents the conditions during CO_2 storage in deep saline aquifers. There are three parts in this study which are:

1) Preparation of brine solutions

2) Density measurement
3) IFT measurement

1.5 The Relevancy of the Project

There are three reasons on why this project is relevant which are:

- Few studies conducted on topic
- High demand of CO_2 for EOR
- Concern on the emissions of greenhouse gases

Studies on the effect of salinity on interfacial tension between CO_2 and brine were performed by authors such as Chalbaud et al [5-6] and Aggelopoulos et al [14-15]. Nevertheless, only a few researches were conducted on the effect of salt mixtures on the interfacial tension between CO_2 and brine. CO_2 injection has shown positive results in increasing production rate thus improving the oil recovery. Consequently, the demand for CO_2 is increased especially for the future. The emissions of greenhouse gases causes the depletion of ozone that can contributes to global warming thus affecting the Earth's climate. The concern in reducing CO_2 emissions is really important. Therefore, this project is relevant to the study.

1.6 Feasibility of the Project

A project will not be achievable without its specified objectives and scope of studies which is to study the effects of salinity on interfacial tension between CO_2 and brine. This project is feasible as there are pre-existing researches related to the project. Moreover, this project is also possible within the time frame that has been suggested by the university. This semester, FYP students need to complete their project as they have been focusing on their project proposal last semester.

CHAPTER 2

LITERATURE REVIEW

2.1 Storage of Carbon Dioxide in Geologic Formations

The effect of industrial revolution has shown as the concentrations of the most important greenhouse gases which are CO_2, methane (CH_4) and nitrous oxide (N_2O) all have risen substantially from their preindustrial-age levels, with the rise starting in the late 1800s [2]. Emissions of CO_2 are approximately $24X10^9$ tonnes/yr (24 Gt/yr), or approximately 6.5 Gt/yr of carbon that prove the current emissions exceed the capacity of the natural systems to absorb them. CO_2 contributes the largest to global warming than other greenhouses gases emissions [4].

The challenge of stabilizing CO_2 concentrations will require more-efficient use of energy and development of a variety of new technologies. There is only one way that could meet this challenge which is the carbon dioxide capture and storage (CCS) that would otherwise be emitted to the atmosphere [2]. The general idea of CCS is to capture CO_2 from large point sources such as fossil fuel power plants, fuel processing and other industrial plants, compress it and then inject it into a suitable underground storage site [8]. Several potential geological reservoirs can be used to store captured CO_2 from power and large industrial plants which include depleted and disused oil and gas fields, deep saline aquifers and deep unminable coal seams [4].

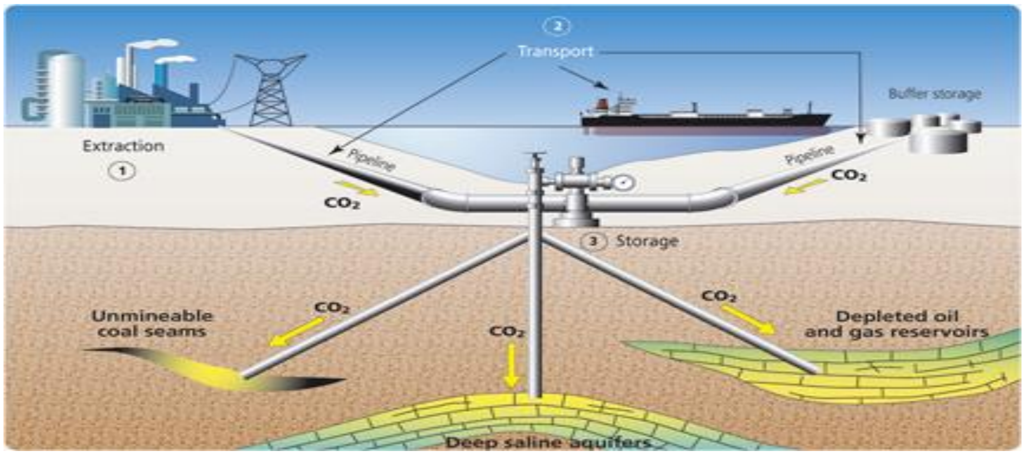


Figure 1 Geological CO_2 Storage

Deep saline aquifers have the largest storage capacity and widest distribution, are ubiquitous in sedimentary basins and can be used immediately for CO_2 storage [11] but oil reservoirs are the most likely to be used preferentially initially because of the positive economic potential for increased oil production through CO_2 or acid gas based EOR schemes [10]. However there are certain barriers of geological storage which are [4]:

- The high costs of capturing, processing and transporting anthropogenic CO_2
- Incomplete understanding of reservoir processes and storage methods
- Monitoring, verification and environmental safety of CO_2 storage
- Lack of functioning emission trading system and storage regulations; and
- Commercial/organizational conflicts between CO_2 storage and production in EOR or natural gas recovery

2.1 Enhanced Oil Recovery

Substantial quantities of oil will normally remain in the reservoir at depletion if only the primary production processes are utilized [16]. As better technology and understanding of reservoir behavior have been developed and the search for even more successful production processes is continually being pursued, capability to improve recovery has grown seriously. Since all recovery improvement measures are costly, economics are extremely significant.

EOR which stands for enhance oil recovery can be defined as the effort to increase ultimate production of oil and gas from a reservoir. The development of technology and better understanding on reservoir behavior have made it possible to improve recovery operations and further studies are currently being pursued to search for better productive alternatives. Enhanced oil recovery refers to any reservoir process to change the existing rock/oil/brine interactions in the reservoir. Here is an incomplete list [17]:

a. Water injection
b. Thermal recovery: in situ combustion – forward: dry, wet, Toe-to-Heel Air Injection (THAI), and CAPRI (i.e., variation of THAI with a catalyst for in situ upgrading); reverse, high-pressure air injection; steam soak and cyclic huff-and-puff steam flood; SAGD, VAPEX (solvent gas VAPor Extraction), Expanding Solvent VAPEX (ES-VAPEX) or ES-SAGD; Steam and Gas Push (SAGP); hot water drive; electromagnetic
c. Miscible flooding: CO_2, nitrogen, flue gas, hydrocarbon, solvent
d. Chemical flooding: polymer, deep-formation profile control using gels, surfactant, alkaline, emulsion, foam and their combinations
e. Microbial

However, only CO_2 injection will be focused as this project studies the effect of salinity on interfacial tension between CO_2 and brine containing $MgCl2_2$ and NaCl.

2.2 Gas Injection

Gas injection is a widely used secondary recovery method for oil production. The main purposes of gas injection are [16]:

a) To prevent depletion of the main source of reservoir energy in gas cap drive reservoirs

b) To create a gas cap drive to replace a less efficient recovery mechanism (such as solution drive), and
c) To prevent oil movement into the gas cap of strong water drive or combination drive reservoirs.

CO_2 has been used to enhance oil recovery for over fifty years [3]. An incremental recovery being as high as 22% of original oil in place has been shown through both experimental and field data. CO_2 is observed to be an excellent solvent for miscible CO_2 floods. The advantages of using CO_2 as a solvent in miscible floods are [12, 18]:

- It promotes swelling
- It reduces oil viscosity
- It increases oil density
- It is soluble in water
- It can vaporize and extract portions of the oil
- It achieves miscibility at pressures of only 100 to 300 bar
- It reduces water density
- It reduces the difference between oil and water density, and then reduce the change for gravity segregation
- It reduces the surface tension of oil and water, and result in a more effective displacement

CO_2 becomes mutually soluble with the crude oil when CO_2 is injected into an oil reservoir. As CO_2 dissolves in the oil it swells the oil and reduces its viscosity thus helps in improving the efficiency of the displacement process. Although other similar miscible solvents can be used to push the oil from underground reservoirs, it does not make economic sense to do so regardless of their effectiveness. Other than that, CO_2 is a naturally occurring source that can be extracted in large quantities and most of human activities produce CO_2, which could also become a source as it can be captured inexpensively.

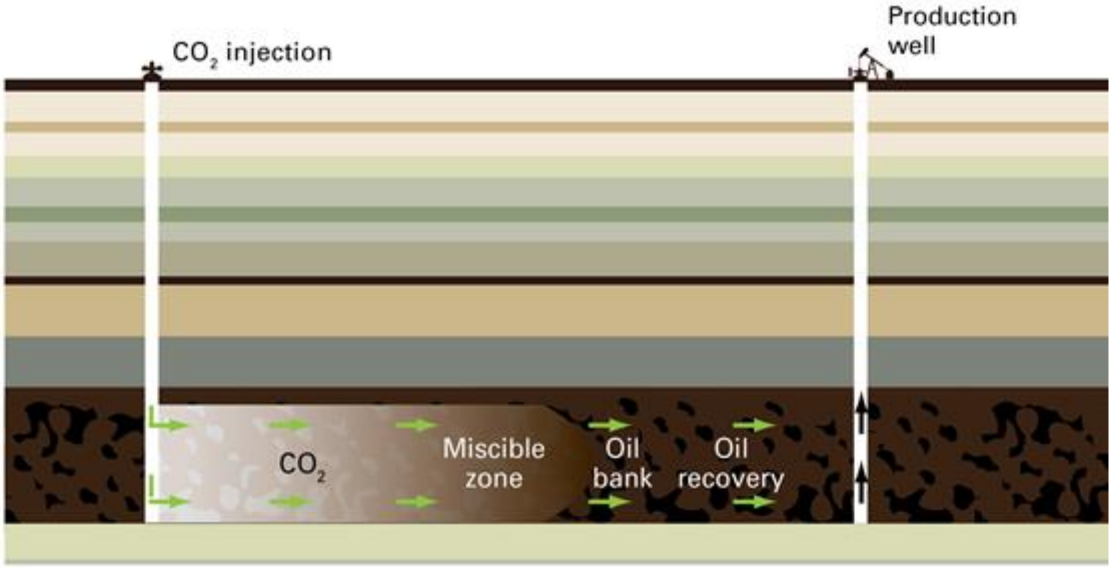


Figure 2 CO_2 Injection

The first commercial CO_2 injection occurred in Scurry Country, Texas in 1972 which is also known as SACROC (Scurry Area Canyon Reef Operators Committee) Unit [2]. Chevron which is the operator recovered CO_2 from natural gas processing plants in the southern part of the basin and transported the gas 220 miles for injection at SACROC.

2.3 Interfacial Tension

Interfacial tension is defined as the tension that exists at the interface of the two fluid phases due to the imbalance between the molecular attractive and repulsive forces [19]. The concept of capillary pressure is often being related with the interfacial tension to study the distribution of fluids in crude oil reservoirs. IFT also determines the fluid phase relative permeabilities which explain the flow behavior of hydrocarbon fluids in porous reservoir rocks.

Two main interfacial interactions which are interfacial tension and rock wettability are important in this study because [6, 15]:

a) they control the capillary-sealing efficiency with respect to CO_2 of the caprock,
b) a low permeable medium usually imbibed with water and

c) they control the transport properties (relative permeabilities and residual saturations) of the water (or brine) and CO_2 phases in the reservoir rock

The effectiveness of CO_2 sequestration in deep saline aquifers and different types of hydrocarbon reservoirs is largely governed by the fluid-fluid and fluid-rock interfacial interactions among which interfacial tension is of central importance [5, 14] that in this project is between CO_2, brine and reservoir minerals. The CO_2 migration within the geological formation as well as its storage efficiency is, mainly, governed by the interactions of fluid and rock properties, the heterogeneity and other topographical and geological features of the porous formation [14-15].

In miscible gas injection processes, improved oil recovery relies greatly on the interactions between the displacing gas and displaced oil to create near-zero interfacial tension between the fluid phases [19]. Miscibility means zero interfacial tension between the fluid phases. Thus low interfacial tension between the fluid phases is desired for reduced capillary pressure and residual oil saturations and is the main goal of any chemical and miscible gas injection enhanced oil recovery process.

Chalbaud et al (2008) has reported on the CO_2/brine IFT [6] and stated that the interfacial tension highly influences the flow process and on the other hand it controls the capillary-sealing efficiency. This is particularly important in CO_2 storage

$$P_c^{th} = P_{CO_2} - P_{brine} = \frac{2\,\gamma_{b,CO_2} COS\,\theta}{R}$$

where P_c^{th} is the threshold capillary pressure in the saturated brine caprock, which characterizes the ability of a porous medium saturated with a wetting phase (brine) to flow of a non-wetting phase (CO_2); R is the largest connected pore throat in the caprock and θ is the contact angle.

In 2011, Aggelopoulos, Robin and Vizika stated that the IFT increase due to cation valence is associated with the stronger repulsion of the cations from the interface as their valence increase and result in at least the double for solutions containing divalent cations than the one corresponding to monovalent cations, at storage conditions [14-15]. The IFT increase is more than twice for $CaCl_2$ than that for NaCl at a given molality of the aqueous phase, reflecting the effect of different cation valence between the two salts.

The total IFT increase, due to brine (NaCl + $CaCl_2$) salinity is the sum of the individual IFT increments arising individually from each salt [14]. This indicates a strong additive effect on IFT when the brine is a mixture of these two salts. We can obtain the total increase of CO_2/brine IFT as the sum of the individual IFT increments due to each salt contained in the brine assuming an analogous behavior for other salts such as KCl, $MgCl_2$ etc.

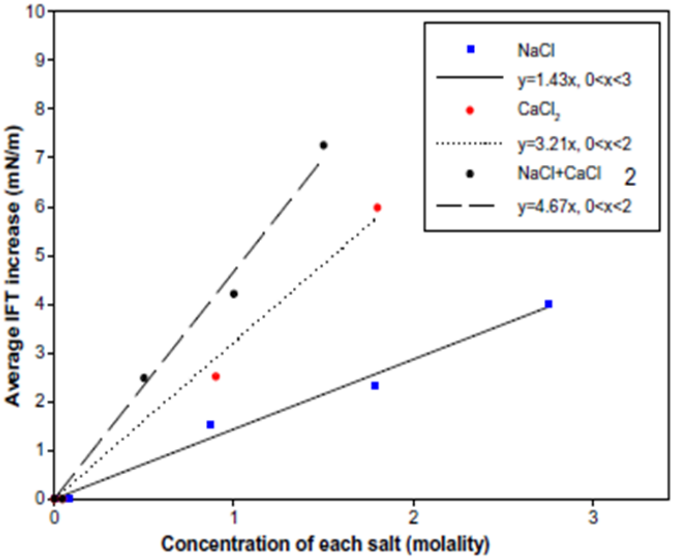


Figure 3 Comparison between IFT increase of CO_2/NaCl solution, $CO_2/CaCl_2$ solution and CO_2/(NaCl + $CaCl_2$) brine as a function of each salt's molality

The effect on IFT increases in the following sequence [5-7]:

$Cs^+ < Rb^+ < NH_4^+ < K^+ < Na^+ < Li^+ < Ca^{2+}\ Mg^{2+}$

The presence of salts in brine increases the interfacial tension compared to the pure water case at the same pressure and temperature [5-6]. Several authors [5,7-14] reported that measured γ_{b,CO_2} strongly decreases with increasing reservoir pressure. The effect of reservoir temperature seems to be smaller, γ_{b,CO_2} increases with increasing temperature. This behavior is observed until the γ_{b,CO_2} reached a plateau. Once it reaches the plateau, its value does not depend on the pressure neither on the temperature [6, 14-15].

For a similar range of temperatures and pressures, several authors have already reported the presence of plateau in the IFT value in the case of pure water-CO_2 system [6]. Nevertheless, the value of the γ_{b,CO_2} at the plateau does depend on the salt concentration. The γ_{b,CO_2} increases linearly with molal salt concentration [6-11, 13-15] and this increase is not negligible for concentrations over 30 000ppm of NaCl [5]. The water salinity of saline aquifers increases with depth [11, 15].

The temperature and salinity effects on IFT working against pressure effects are also intuitive when considering that CO_2 solubility in brine increases with pressure [14] and decreases with increasing temperature and salinity [9, 11-12]. Deeper, higher pressure formations that have a more uniform porosity character will likely provide more storage capacity for CO_2 based on the maximum obtainable saturation and effective CO_2 maximum relative permeability.

The relative decrease in the brine-to-CO_2 viscosity ratio, caused by the increase in CO_2 viscosity with little effect on the viscosity of the brine due to pressure increase, is of similar magnitude to the decrease in IFT [10]. Therefore, CO_2/brine IFT, CO_2 solubility and viscosity ratio have similar dependencies on pressure, temperature and water salinity.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

To determine the effect of salinity on interfacial tension between carbon dioxide and brine, the best way is to perform laboratory experiments which duplicate as close as possible to the actual conditions.

A mixture of **NaCl and $MgCl_2$** were tested.

The interfacial tension will be measured at three temperatures which are **27, 71 and 100˚C** over pressures of **500, 1000 and 2000 psi**, brine salinities corresponding to molarities **m= 0.045, 0.1 and 0.5** of each salt representative of storage conditions.

The experiments for this study are divided into three parts which are:

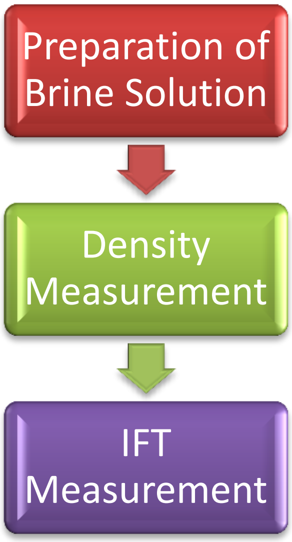


Figure 4 Workflow of the Study

3.1.1 Preparation of Brine Solution

Brine is a mixture of two salts at equal molal concentrations in water. Preparation of brine is required in this study for both density and IFT measurement.

- Density measurement : 100 ml of solution is needed
- IFT measurement : 300 ml of solution is needed

A total of 9 solutions which differentiates concentration of brine were prepared to achieve the objectives of this study. The solutions are:

i. NaCl (m=0.045)
ii. $MgCl_2$ (m=0.045)
iii. NaCl + $MgCl_2$ (m=0.045)
iv. NaCl (m=0.1)
v. $MgCl_2$ (m=0.1)
vi. NaCl + $MgCl_2$ (m=0.1)
vii. NaCl (m=0.5)
viii. $MgCl_2$ (m=0.5)
ix. NaCl + $MgCl_2$ (m=0.5)

The experiment of density and IFT measurement were first tested on a salt solution alone before tested for mixtures of brine.

Procedures:

1) Weigh an amount of NaCl and 500 ml of distilled water to get the molality of 0.045.
2) Mix the salt and distilled water in a 1 litre clean beaker for at least 30 minutes.
3) Repeat with $MgCl_{2.}$

500 ml solution for each molality was prepared for density and IFT measurements. The amount of salts needed to prepare these solutions is listed in the table below:

Table 1 Amount of Salts Needed for Density and IFT Measurement

Sample	Molalities	Amount of salts needed (grams)	
		NaCl	$MgCl_2$
Single	0.045	1.05192	3.6592
	0.1	2.3376	8.132
	0.5	11.688	40.66
Mixture	0.045	0.52596	1.8296
	0.1	1.1688	4.066
	0.5	5.844	20.33
Total		22.6163	78.6768

Electronic Balance was used to weigh the salts. The standard operational procedure for this equipment is as in Appendix 1.

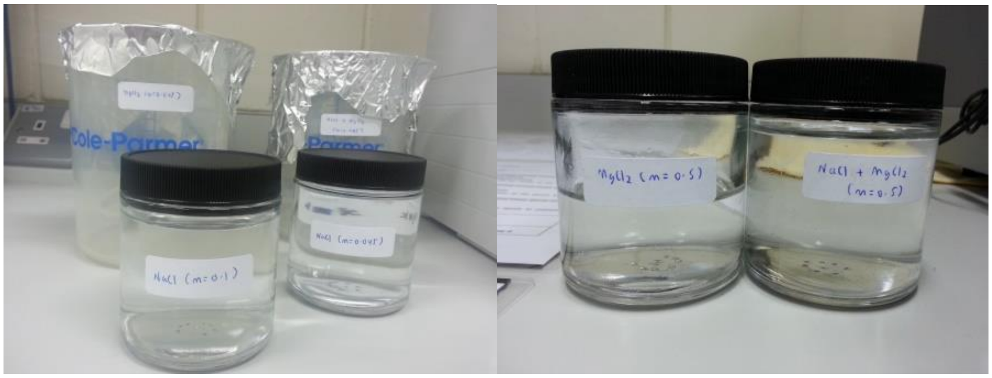


Figure 5 Samples of Brine

3.1.2 Density Measurement

Density meter is required to determine the densities of the solutions. The density ρ is defined as mass divided by volume:

$\rho = \frac{m}{V}$, where m is mass and V is volume.

The unit of density is kg/m^3 or g/cm^3. 1 g/cm^3 = 1000 kg/m^3.

Mass is independent from external conditions like buoyancy in air or gravity. It agrees with weight in vacuum. True density of liquids and gases is measured with the oscillating U-tube method. The densities of liquids and gases are highly temperature-dependent. Therefore density measurement always requires an accurate temperature measurement or control. Typically, density decreases with increasing temperature as the individual molecules require more space due to their thermal motion.

Note: Water is quite a unique liquid. The density maximum is reached at a temperature of 3,98 °C with $\rho = 0.999972$ g/cm^3.

Figure 6 External Measuring Cell DMA HP and DMA 4500 M

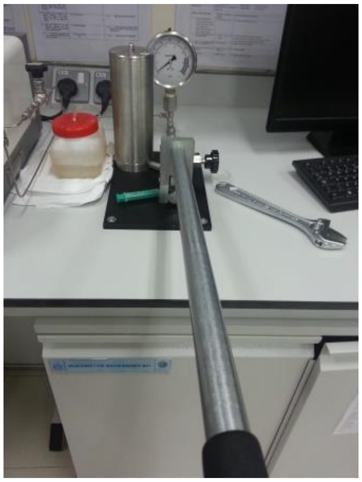


Figure 7 Pump Used to Increase Pressure

The External Measuring Cell DMA HP and DMA 4500 M are used in this project. The External Measuring Cell DMA HP measures density and specific gravity at sample pressures up to 700 bar (10 000 psi) and temperatures up to 200 °C (392 °F). It is connected to a DMA 4100 M, DMA 4500 M, DMA 5000 M or DSA 5000 M to control DMA HP and read out the measurement data.

The advantages of using The External Measuring Cell DMA HP and DMA 4500 M:

1) Can be tested at high pressures and high temperatures
    - No-hassle measurement at high pressures and/or high temperatures
    - Only 2 mL sample required

2) Density measurement under extreme conditions

    - DMA HP is controlled by an integrated Peltier thermostat for measurements of samples under extreme conditions
    - Using the DMA 4500 M as the control and evaluation unit, samples with high viscosity and/or high melting point or softening range such as bitumen, pitch or concentrated polymer solutions can be measured

- Due to the very broad range of measuring conditions, e.g. pressures up to 700 bar (10 000 psi) and temperatures up to 200 °C (392 °F), DMA HP is very well suited for studying the behavior of liquids and gases

The standard operating procedure for this equipment is as in Appendix 2.

3.1.3 Interfacial Tension (IFT) Measurement

Pendant drop method is used in this experimental study. Interfacial tension and surface tension can be measured by using this method even at elevated temperatures and pressures. The shape of a drop is determined by its radii of curvature, R_1 and R_2. In the case of a spherical drop, these are equal. The connection between interfacial pressure (the pressure across the interface) and these radii of curvature is called the Young-Laplace equation [20]:

$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Where,

ΔP = Interfacial pressure difference
γ = Interfacial tension
R_1, R_2 = Surface's radii of curvature

In a column of fluid of density ρ and height h,
$\Delta P = \rho g h$

and g is the acceleration due to gravity, ($9.8 m/s^2$).

The Young-Laplace equation shows the pressure is quite high in a small drop among other things (e.g., radius of 5 microns). The weight of a pendant drop can be measured by using Tate's Law:

$W = 2 \pi r \gamma$

Where,

W = Weight of drop
R = Radius of wetted tip
γ = surface tension

Basically a pendant drop or standing bubble or drop (Drop Fluid) may be generated in a second immiscible fluid (Pressure Fluid). The drop shape image is computed, and then the interfacial tension is computed from solving algorithm of the Laplace equation.

Bulk Fluid:
Refers to the fluid where the droplet is released.
Example: Water droplet released in the atmosphere. Air is the bulk fluid.

Drop Fluid:
Refers to nature of the fluid of the droplet.
Example: Water droplet released in the atmosphere. Water is the drop fluid.

IFT 700

The equipment that will be used in this experiment is **IFT 700**. It is designed to determine the interfacial tension and contact angle, but also to observe heat and mass transfer phenomena. The experiment can be operated at high pressure (up to 69 MPa, 10 000 psi) and high temperature (up to 200˚C). The apparatus allows for the determination at reservoir conditions of interfacial tension between liquid-gas and liquid-liquid interfaces using pendant drop method as well as the contact angle between liquid and solid interfaces using sessile drop method.

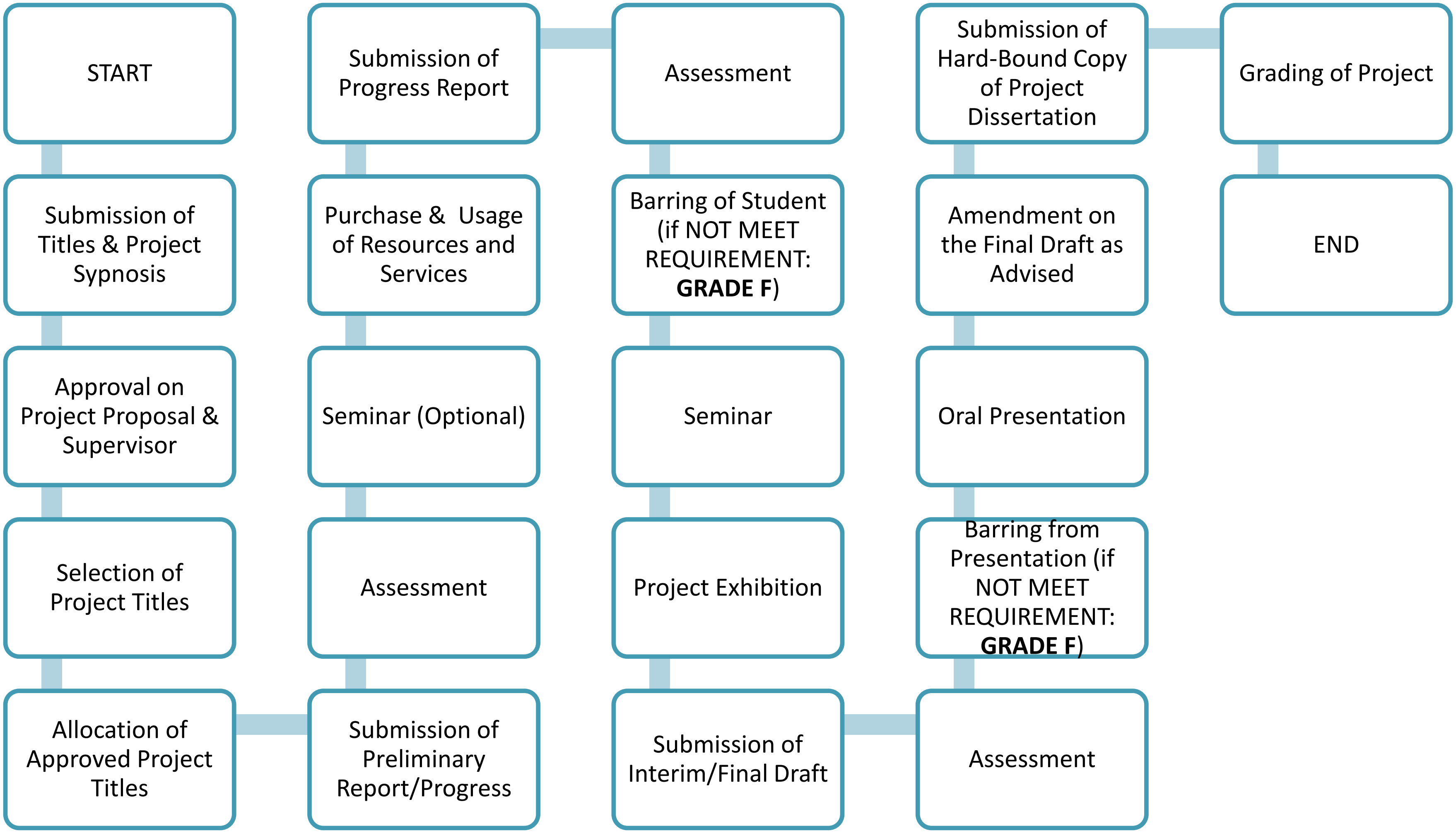
A liquid drop is created and put in contact with gas or solid in a cell at reservoir conditions. A camera connected to a computer records the shape of the liquid drop to derive the interfacial and contact angle properties. The Drop Analysis System software allows the fast calculation of surface and interfacial tension of pendant drop and contact angles of sessile drops.

Figure 8 IFT 700

The advantages of using IFT 700 are:

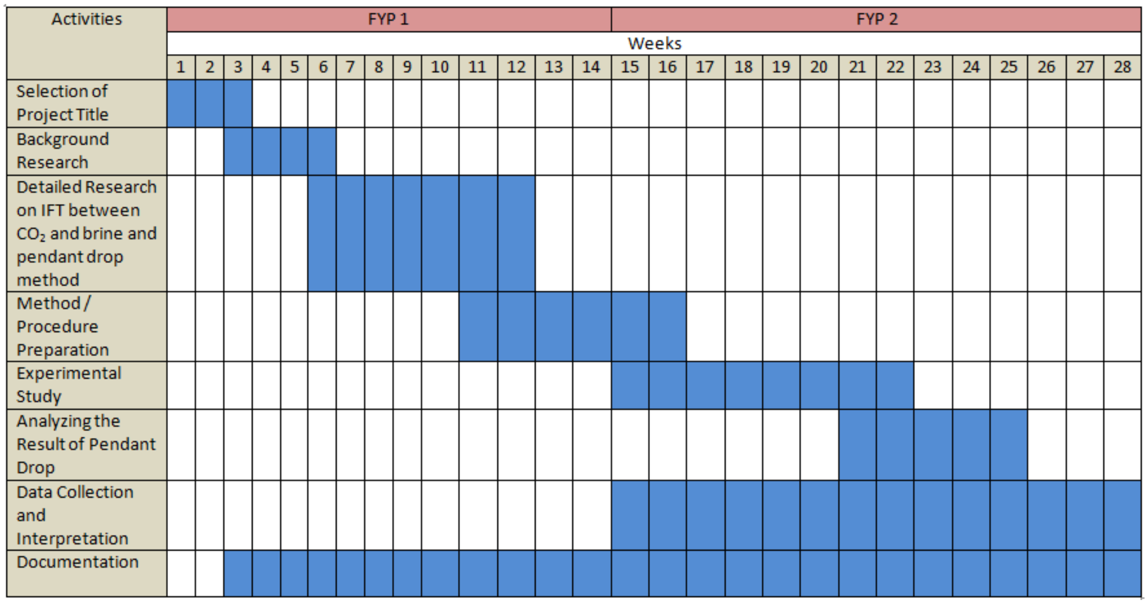
a) Easy to use
b) Provided with an advanced drop analysis software
c) Has a very good stability of the drop

3.2 Final Year Project Flow Process



3.3 Gantt Chart

Table 2 Gantt Chart



Activities	FYP 1														FYP 2													
	Weeks																											
	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
Selection of Project Title	■	■	■																									
Background Research			■	■	■	■																						
Detailed Research on IFT between CO_2 and brine and pendant drop method						■	■	■	■	■	■	■																
Method / Procedure Preparation											■	■	■	■	■	■												
Experimental Study															■	■	■	■	■	■	■	■						
Analyzing the Result of Pendant Drop																					■	■	■	■	■			
Data Collection and Interpretation															■	■	■	■	■	■	■	■	■	■	■	■	■	■
Documentation			■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■

3.4 Key Milestones

Table 3 Key Milestones

Milestone	Week
Early Research Development • Research Background • Scope of study	**9**
Middle Research Development • Detailed research • Developing the theory • Data gathering • Testing the theory • Experimental Study	**19**
Final Research Development ▪ Analyzing the result of pendant drop ▪ Finalizing the results ▪ Completing the documentation	**26**

3.5 Tools (eg. Equipment, hardware, etc.) Required

1. Analar grade salts

Component	Purity	Supplier	Phase
Sodium Chloride, NaCl	>0.99	Avantis	Solid
Magnesium Chloride, $MgCl_2$	>0.99	Avantis	Solid

2. Electronic balance
3. Distilled water
4. 1000 ml glass beaker
5. Small bottle
6. Spatula
7. Carbon dioxide with purity >0.995
8. Density meter
9. IFT 700

Figure 9 Electronic Balance

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Data Gathering and Analysis

4.1.1 Density Measurement

To carry out the IFT measurement test, density of each solution is needed. Tables below show the densities of solutions for each molality.

Density values for solutions with molality of 0.045:

Table 4 Density values for solutions with molality of 0.045

Temperature (°C)	**Pressure (psi)**	**Density (g/cm^3)**		
		NaCl	**$MgCl_2$**	**NaCl + $MgCl_2$**
27	500	1.000235	1.002097	1.001803
	1000	1.002585	1.004018	1.003803
	2000	1.006575	1.008400	1.008193
71	500	0.982670	0.984810	0.982083
	1000	0.985430	0.986763	0.984900
	2000	0.989430	0.990947	0.988300
100	500	1.188280	1.190453	1.186697
	1000	1.191180	1.192913	1.189855
	2000	1.196280	1.198073	1.196410

Density values for solutions with molality of 0.1:

Table 5 Density values for solutions with molality of 0.1

Temperature (°C)	**Pressure (psi)**	**Density (g/cm^3)**		
		NaCl	**$MgCl_2$**	**NaCl + $MgCl_2$**
27	500	1.002145	1.005465	1.003623
	1000	1.004380	1.007445	1.004760
	2000	1.008320	1.011470	1.009290
71	500	0.983380	0.988210	0.986750
	1000	0.985490	0.990325	0.988820
	2000	0.989760	0.994275	0.992920
100	500	1.188565	1.194840	1.193010
	1000	1.191390	1.197165	1.195440
	2000	1.197740	1.202250	1.200490

Density values for solutions with molality of 0.5:

Table 6 Density values for solutions with molality of 0.5

Temperature (°C)	**Pressure (psi)**	**Density (g/cm^3)**		
		NaCl	**$MgCl_2$**	**NaCl + $MgCl_2$**
27	500	1.016730	1.025830	1.020595
	1000	1.018460	1.028095	1.022615
	2000	1.022465	1.032055	1.026530
71	500	0.998540	1.009027	1.003070
	1000	1.000605	1.011300	1.005060
	2000	1.004445	1.015215	1.009055
100	500	1.207025	1.220903	1.212913
	1000	1.209395	1.223770	1.215940
	2000	1.214490	1.228515	1.220705

Density values for CO_2:

Table 7 Density values for CO_2

Temperature (°C)	**Pressure (psi)**		
	500	1000	2000
27	0.075385	0.69364	0.85268
71	0.059717	0.13954	0.43676
100	0.05328	0.11762	0.29485

Based on the results on the table above, it can be clearly seen that as the molality increases, the density is also increased. This confirms that the density increases as the salinity increases due to the addition of salts in the distilled water. When salt is added to water, the salt for example NaCl, will dissolves into ions which are Na^+ and Cl^-. The volume increases by only a small factor but the mass increases by a large factor. There are basically two reasons:

1. NaCl is much denser than distilled water, mainly because its ions have more mass than they oxygen and hydrogen atoms in the water molecules.
2. The ions of NaCl attract and attach with the water molecules so that the volume of salt water is not as high as the water volume plus the salt volume.

4.2 Results and Discussion

4.2.1 Effect of Pressure and Temperature on CO_2/Brine IFT

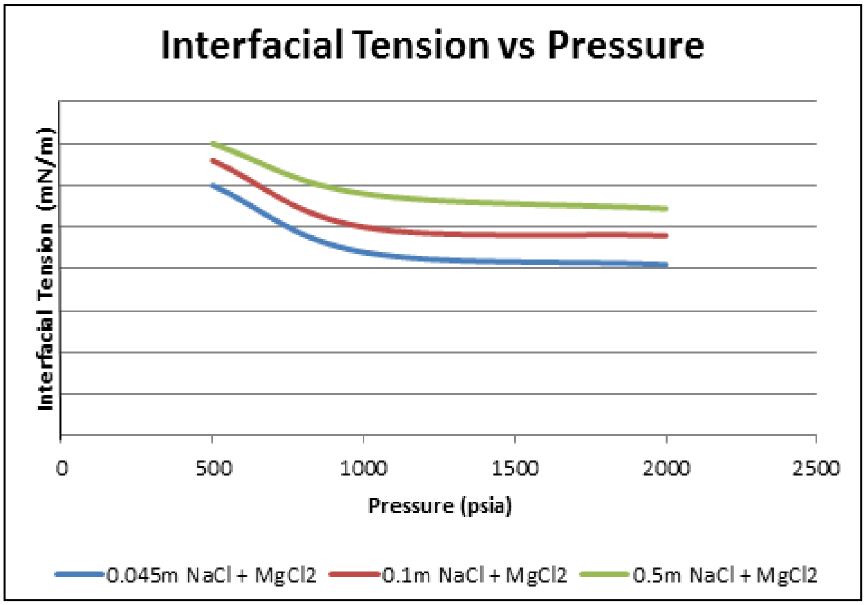


Figure 10 Interfacial Tension vs Pressure

From Figure 10, under constant temperature, IFT measurements are observed to be decreasing as the pressure increases. This is due to the solubility of CO_2 in brine increases as pressure increases [14]. The decreasing of IFT is steeper at lower pressures while the rate of IFT decreases at higher pressures declines and gradually vanishes. At high pressures, a plateau value of IFT is reached for all brine concentrations [6].

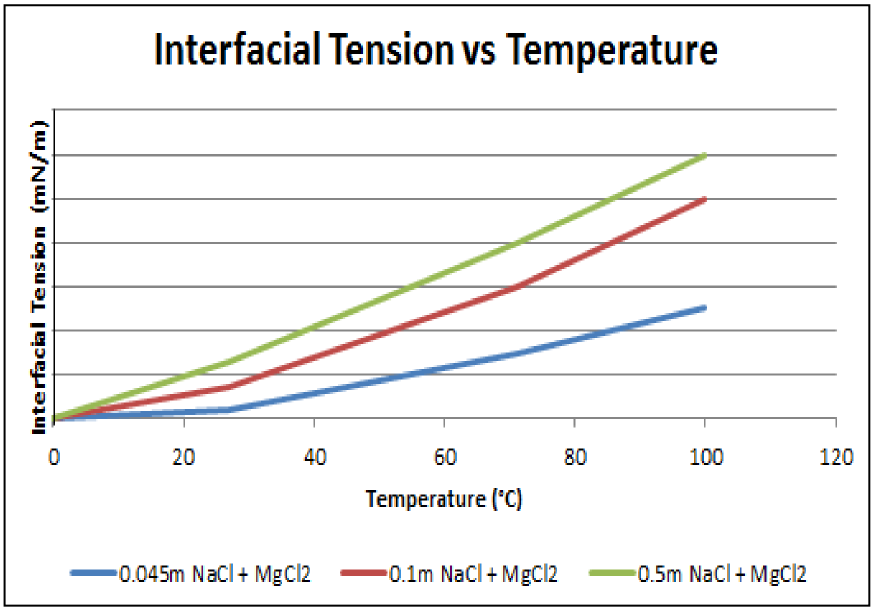


Figure 11 Interfacial Tension vs Temperature

Under constant pressure, figure above shows that IFT between CO_2 and brine increases as temperature increases. From researches, it was explained that there is almost no IFT increase for temperatures ranging from 71 to 100°C which might be caused of low salinities [14-15]. Researchers however still cannot conclude a clear relationship between IFT increase and temperature.

4.2.2 Effect of Salt Concentration on CO_2/Brine IFT

Based on the graphs on interfacial tension versus temperature and pressure (Figures 10 and 11), it can be clearly seen that the IFT measurements increase as the salinity increases at all temperatures. For higher pressures, where plateau of IFT has been reached, the increase of IFT is almost the same for all temperatures [14].

4.2.3 Effect of Cation Valence on CO_2/Brine IFT

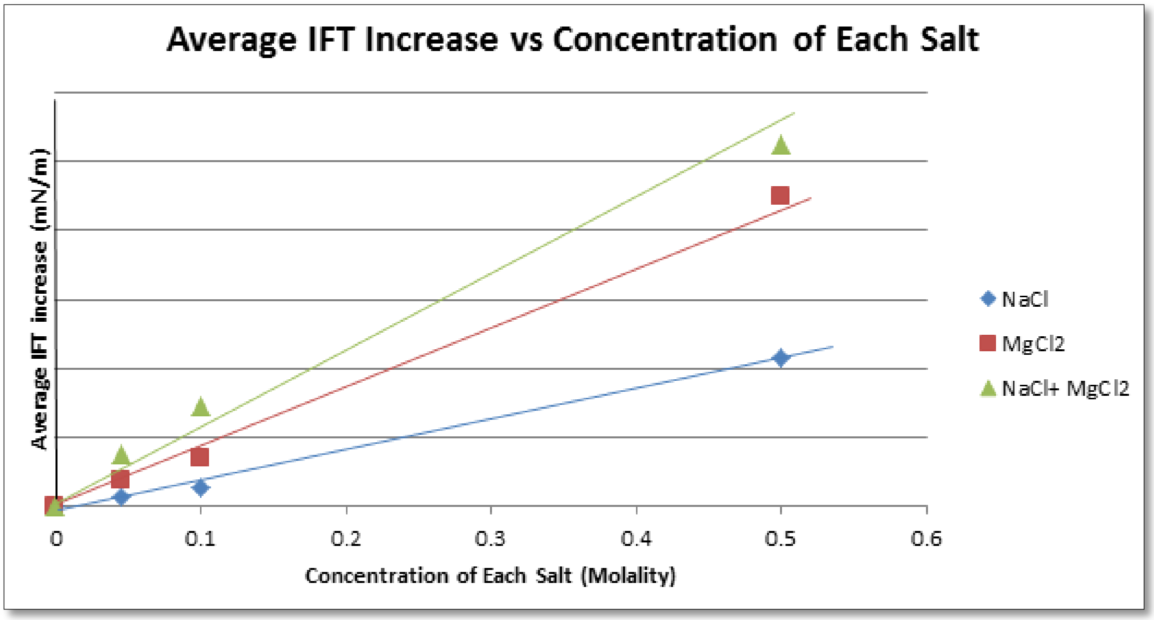


Figure 12 Average IFT Increase vs Concentration

It is known that $MgCl_2$ has a higher cation valence of +2 than NaCl which has a cation valence of +1. By comparing the average IFT increase of $MgCl_2$ and NaCl from the above graph, it can be seen that the slope for $CO_2/MgCl_2$ solution is more than twice of CO_2/NaCl system. This IFT increase is due to the stronger repulsion of the divalent cations Mg^{2+} from the interface and their higher hydration as compared to the monovalent cation Na^+ [15]. In other words, the IFT increase for solutions containing divalent cations ($MgCl_2$) is at least twice that of solutions containing monovalent cations (NaCl), at a given molality.

4.2.4 Additive Effect of Different Salts on CO_2/Brine IFT

In real systems, reservoir brine is composed of different salts such as KCl and $CaCl_2$. Therefore, it is a curiosity whether the IFT increase due to brine salinity is additive.

Figure 12 shows that the average IFT increase for NaCl + $MgCl_2$ is much higher than the ones for NaCl and $MgCl_2$. It can be concluded that the average IFT increase for NaCl + $MgCl_2$ is the sum of the corresponding ones of CO_2/NaCl solution and CO_2/$MgCl_2$ solution. This indicates a strong additive effect on IFT when the brine is a mixture of two salts. Thus, the total IFT increase is the sum of the individual IFT increments caused by each salt [14].

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The measurements of interfacial tension between carbon dioxide and brine in this study cover the range of temperatures of 27˚C to 100˚C, pressures up to 2000 psi and different salinities of when CO_2 is injected in deep geological subsurface. Lab testing based on reservoir conditions are necessary as this project involves the injection of CO_2 into the subsurface. The outcome of this study is extremely important to CO_2 storage in deep saline aquifers as it allows the exact determination of IFT values for each aquifer just by analyzing the chemical composition of the brine and determining the effect of concentration of each salt present in it.

The brine used in this study is a mixture of equal molalities of NaCl + $MgCl_2$ which both coexisting in deep saline aquifers. The presence of different cations that is either monovalent or divalent, Mg^{2+}, Ca^{2+}, Na^+ and K^+, usually can be found in carbonate reservoirs. The effect of valence of cations is vital in this study as different valence of cations gives dissimilar results. In this study, aqueous solutions containing chloride anions are focused as the brine in deep saline aquifers or reservoirs is almost entirely comprised from salts containing the anion Cl^-. Therefore, $MgCl_2$ and NaCl salts are used in this study.

Density meter is used to measure the density of the mixtures and also CO_2. The IFT measurements are conducted by using the IFT 700 for the pendant drop case. Based on researches that have been done on IFT between CO_2 and brine, the IFT decreases with increasing reservoir pressure but increases with increasing temperature. The IFT also increases linearly with molal salt concentration. At a molality, the IFT increase for solutions containing divalent cations ($MgCl_2$) is at least twice than solutions containing monovalent cations (NaCl). Other than that, the total IFT increase due to brine (NaCl + $MgCl_2$) salinity is the sum of the individual IFT increments due to each salt contained in the brine.

5.2 Recommendations

The IFT between CO_2 and brine can also be predicted by using empirical correlations of the traditional Parachor method. The Parachor method has been widely used to predict IFT. IFT prediction is important for modeling many secondary and tertiary oil recovery processes. This method is used because of its simplicity and it also can calculate in the low and high IFT regions. However, additional IFT experimental data at higher pressures is needed in order to know if the correlation proposed in this study could be used for higher reservoir depths.

More studies need to be conducted to explain the relationship between IFT of CO_2 and brine and temperature as the IFT values remain unaltered in the temperature range from T=27°C to 71°C. Further researches also need to be done for a wider range of brines varying not only in concentration but also in composition for both anions and cations. This is because in actual conditions, the reservoir brine is a mixture of different salts containing different anions and cations either monovalent or divalent such as $CaCl_2$, Na_2SO_4 and KCl. More salts need to be added in a mixture for further exploration in this study.

REFERENCES

1. Christensen, J. R., Stenby, E. H. and Skauge, A. (2001). Review of WAG Field Experience. *SPE 71203.*
2. Jr., F. M. O. (2004). Distinguished Author Series: Storage of carbon dioxide in geologic formations. *SPE 88842.*
3. Worden, R. H. and Smith, L. K. (2004). Geological sequestration of CO_2 in the subsurface: lessons from CO_2 injection enhanced oil recovery projects in oil fields. In S. J. Baines and R. H. Worden (Eds.), *Geological Storage of Carbon Dioxide* (pp. 211-224). Geological Society, London: Special Publications, 233.
4. Gale, J. (2004). Why do we need to consider geological storage of CO_2? In S. J. Baines and R. H. Worden (Eds.), *Geological Storage of Carbon Dioxide* (pp. 7-15). Geological Society, London: Special Publications, 233.
5. Chalbaud, C., Robin, M. and Egermann, P. (2006). Interfacial tension data and correlations of brine/CO_2 systems under reservoir. *SPE 102918.*
6. Chalbaud, C., Robin, M., Lombard, J-M., Martin, F., Egermann, P., and Bertin, H. (2008). Interfacial tension measurements and wettability evaluation for geological CO_2 storage. *Advances in Water Resources, 32,* 98-109.
7. Li, X., Boek, E. S., Maitland, G. C., and Trusler, J. P. M. (2012). Interfacial tension of (brines + CO_2): $CaCl_2$(aq), $MgCl_2$(aq), and Na_2SO_4(aq) at temperatures between (343 and 423) K, pressures between (2 and 50) MPa, and molalities of (0.5 to 5) $mol.kg^{-1}$. *Journal of Chemical & Engineering Data, 57,* 1369-1375.
8. Li, X., Boek, E., Maitland, G. C., and Trusler, J. P. M. (2012). Interfacial tension of (brines + CO_2): (0.864 NaCl + 0.136 KCl) at temperatures between (298 and 448) K, pressures between (2 and 50) MPa, and total molalities of (1 to 5) $mol.kg^{-1}$. *Journal of Chemical & Engineering Data, 57,* 1078-1088.
9. Bennion, B. and Bachu, S. (2006). The impact of interfacial tension and pore-size distribution/capillary pressure character on CO_2 relative permeability at reservoir conditions in CO_2-brine systems. *SPE 99325.*
10. Bennion, D. B. and Bachu, S. (2006) Dependence on temperature, pressure and salinity of the ift and relative permeability displacement characteristics of CO_2 injected in deep saline aquifers. *SPE 102138.*
11. Bennion, D.B. and Bachu, S. (2008) A correlation of the interfacial tension between supercritical phase CO_2 and equilibrium brines as a function of salinity, temperature and pressure. *SPE 114479.*
12. Yang, D. and Gu, Y. (2004). Interfacial interactions of crude oil-brine-CO_2 systems under reservoir conditions. *SPE 90198.*

13. Lun, Z., Fan, H., Wang, H., Luo, M., Pan, W. and Wang, R. (2012). Interfacial tensions between reservoir brine and CO_2 at high pressures for different salinity. *Energy Fuels, 26,* 3958-3962.
14. Aggelopoulos, C. A., Robin, M. and Vizika, O. (2011). Interfacial tension between CO_2 and brine (NaCl +$CaCl_2$) at elevated pressures and temperatures: the additive effect of different salts. *Advances in Water Resources*, *34,* 505-511.
15. Aggelopoulos, C. A., Robin, M., Perfetti, E. and Vizika, O. (2010). CO_2/$CaCl_2$ solution interfacial tensions under CO_2 geological storage conditions: influence of cation valence on interfacial tension. *Advances in Water Resources, 33,* 691-697.
16. *Introduction to oil and gas production* (5th ed.). (1996). Washington, D.C.: American Petroleum Institute.
17. Sheng, J. J. (2011). *Modern chemical enhanced oil recovery theory and practice*. Oxford, UK: Elsevier Inc.
18. Mathiassen, O. M. (2003). *CO_2 injection gas for enhanced oil recovery and estimation of the potential on the Norwegian continental shelf*. Norwegian University of Science and Technology.
19. Mittal, K. L. (2008). *Contact Angle, Wettability and Adhesion.* BRILL
20. Woodward, R. P. Surface tension measurements using the drop shape method. PhD, Portsmouth, VA.
21. del Rio, O. I. and Neumann, A. W. (1997). Axisymmetric drop shape analysis: computational method for the measurement of interfacial properties from the shape and dimensions of pendant and sessile drops. *Journal of Colloid and Interface Science, 196,* 136-147.
22. Hebach, A., Oberhof, A., Dahmen, N., Kogel, A., Ederer, H. and Dinjus, E. (2002). Interfacial tension at elevated pressures – measurements and correlations in the water + carbon dioxide system. *Journal of Chemical & Engineering Data, 47,* 1540-1546.
23. Andrei, M., De Simoni, M., Delbianco, A. and Cazzani, P. (n. d.). Enhanced oil recovery with CO_2 capture and sequestration. Retrieved from http://www.worldenergy.org/documents/congresspapers/231.pdf
24. Li, Z., Dong, M., Li, S. and Huang, S. (2006). CO_2 sequestration in depleted oil and gas reservoirs – caprock characterization and storage capacity. *Energy Conversion and Management, 47,* 1372-1382.

APPENDICES

Appendix 1: Electronic Balance Standard Operating Procedure

BEFORE OPERATION

1. Make sure the machine is in good condition.
2. Safety first.

HOW TO OPERATE

1. Switch on the power supply.
2. Calibrate the equipment first
3. Clean the beaker and spatula before adding other chemicals.

AFTER OPERATION

1. Always make sure that the equipment column is clean and switched off after the experiment is completed.
2. Housekeeping.

There are potential accidents or hazards that can occur while handling this equipment such as electrical shock through wire connection and chemical reaction to exposed skin. Therefore, safety measures need to be taken for instance by using dry hand to switch on or off the power and wear proper gloves and respirators while measuring the weight of chemicals.

Appendix 2 : The External Measuring Cell DMA HP and DMA 4500 M Standard Operating Procedure

To Start Up DMA 4500:

1. Connect the power inlet of the DMA HP to the main first using the power cord. To switch the instrument on, use the power switch at the rear. The green LED on the front side of the DMA HP indicates that the power is on.
2. Then, switch on the DMA 4500 M.
3. Wait for at least 15 minutes for the temperature to stabilize.

After turning on the power, the instruments need approximately 15 minutes for temperature equilibration and internal temperature adjustments. During this time, “temp” is displayed.

Filling & Measuring Procedure:

1. Connect the syringe to the sample inlet adapter
2. Push the plunger of the syringe slowly and continuously until some sample emerges about 1 inch from the sample outlet adapter.
3. Leave the syringe in the filling position during the measurement.
4. Tap <Start> and wait until the measurement is finished. The progress bar shows the progress of the measurement with a growing red bar and the message “Measuring”. When the measurement is finished, the progress bar turns green, the message “Finished” is displayed and a beep sound is heard. The condition output field shows the message “valid”. The result values are frozen.
5. The display can be unfrozen by tapping <Monitor>. The result values are saved in the data memory and can be viewed or deleted.
6. Clean with solvent and dry the instrument. Measure the next sample. Acetone is recommended as the cleaning solvent.

Caution: Do not use syringe that contain lubricants. The lubricants can dissolve into your sample and lead to systematic measuring error.

Note: If the reading value is not accurate, perform density check and air/water check are recommended.

To Shut Down DMA 4500:

1. To switch the instrument off, turn off the DMA 4500M first. Then turn off DMA HP.

Potential accidents or hazards such as electrical shock and chemical spillage can occur while handling this equipment. Therefore, precautions need to be taken before using this equipment for instance to use while hand is in dry condition, wear protective clothing including gloves and goggles, rolled up sleeves and wear covered shoes and lab coat.