Hydrate Phase Equilibrium for Methane in Synthetic Seawater

by

Rian Farisha Bt Ajaz Ahmad Khan

Dissertation submitted in partial fulfilment
of the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Petroleum Engineering Programme
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BACHELOR OF ENGINEERING (Hons)

(PETROLEUM ENGINEERING)

Approved by,

____
(Dr Khalik Bin Mohamad Sabil)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2012

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.

RIAN FARISHA BINTI AJAZ AHMAD KHAN

ABSTRACT

This paper discuss on the experiment to determine the hydrate phase equilibrium for methane and synthetic seawater solution of different salinity. This will help to understand the phase equilibrium behaviour and effect on the phase equilibrium line using various concentrations of methane and synthetic seawater. Due to lack of experimental data for these system in open literature and also the problem caused by gas hydrate plugging in the production and transportation line had made it important to investigate on the hydrate phase equilibrium of these mixtures. In the present work, the isobaric three phase, hydrate, water rich liquid, and vapour equilibrium conditions are going to be studied and measured in order to identify the hydrate forming stable region. The experiment will be carried out in a low temperature range and high pressure condition. A full view of Hydreval equipment will be used to gather data on the methane hydrate formation using the synthetic seawater prepared with 28 000 ppm, 31 000 ppm and 35 000 ppm of salinity. The findings will give better insight for the design of industrial operations where it is desired to understand the behaviour of gas hydrate in order to avoid its formation.

ACKNOWLEDGEMENT

"To succeed you need to find something to hold on to, something to motivate you, something to inspire you."

– Tony Dorsett

First and foremost, I would like to express my deepest gratitude towards the Most Graceful, Allah SWT for giving me the opportunities to live in a peaceful life and most conducive environment and also being able to complete my final year project. I would also like to extend my gratitude to both of my parents whom continuously give support and encouragement on any decisions that I make and pray towards my success in life.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

1.1.1 Overview

Gas hydrates are crystalline compounds that are formed by physically stable interactions between water and relatively small gas molecules that occupy the cavities built by water molecules. Typical natural gas molecules that can contribute to hydrates formation include methane, ethane, propane and carbon dioxide.

The gas hydrate has an appearance similar to that of snow or ice and three different types of hydrate lattices may form when gas constituents come in contact with water – namely structure I, II, and H hydrates. Under a given suitable pressure and temperature, carbon dioxide ($CO_{2)}$ will form a structure I hydrate whereas methane (C_1) will enter both small and large cavities of structure I and structure II hydrates as well as the small and medium sized cavities of structure H hydrates.

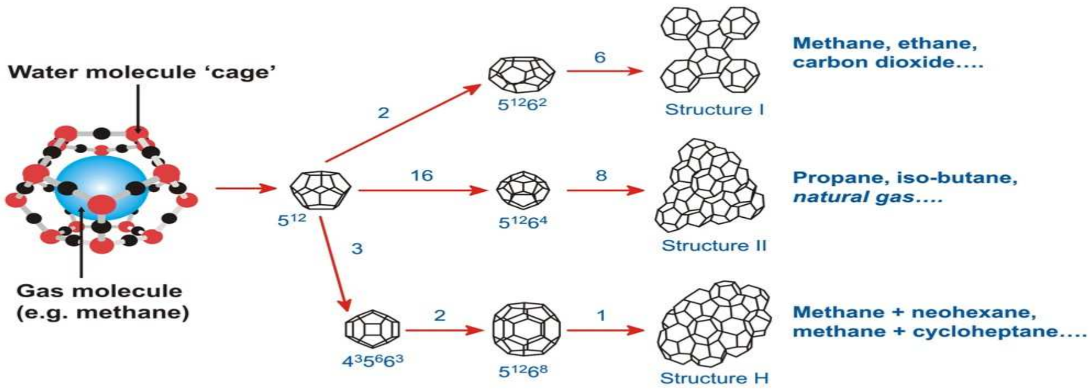

Figure 1: Gas hydrate structures

Naturally occurring gas hydrate can form in two discrete geological situations which are in marine shelf sediments [Kvenvolden, 1993; Kvenvolden and Lorenson, 2000] or on-shore polar region beneath permafrost. Hydrates can easily occur in these two types of settings because these are the settings where the pressure-temperature conditions are stable for hydrate formation [Lerche and Bagirov, 1998]. Gas hydrate can be detected seismically [Hornbach et.al, 2003] as well as using well logs data [Goldberg and Saito, 1998].

Four major aspects that contribute to gas hydrates formation are low temperature which is commonly less than 300K or 26.85 ° Celcius, high pressure existence more than 38 bar of hydrostatic pressure at 277K, non-polar guest molecule which is smaller than 0.9nm and lastly the presence of water.

Gas hydrates somehow gives advantage as an important resource for energy. Gas hydrate usually occurs in the pore spaces of sediments, and may form cements, nodes, veins, or layers. The quantity of natural gas in sedimentary gas hydrates greatly surpassing the resource of all other combustible fossil fuel. However, the utilization of gas hydrates as an unconventional energy resource still limited due to lack of economical method for massive gas hydrates production [Sloan et. al, 2007].

One of the setbacks of gas hydrates is that it has the great possibility to be forming during the production and transportation. These hydrate formation often can be found in the pipeline and could cause blocking or plugging in the pipeline or equipment. The hydrate formation blocking could lead to catastrophic consequences and disrupt production. Therefore, a means of inhibitor had to be introduced to control the formation of hydrate.

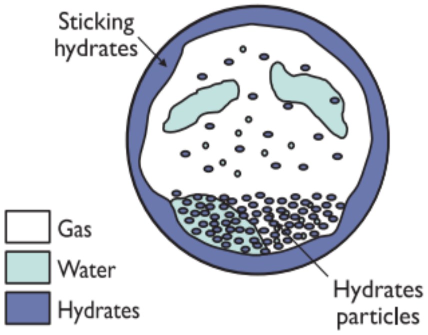

Figure 2: Gas hydrate blocking in transportation line

The study of phase equilibrium on gas hydrate has been started long after the first discovery in 1810 of chlorine hydrate by Sir Humphrey Davy [Sloan et. al, 2007]. Phase is a region of space throughout which all physical properties of a material essentially uniform or in homogenous. To achieve equilibrium on the phases, it is dependent on the pressure and temperature and a single substance may be separate into two or more distinct phases. Moreover, it is important to study this area as gas hydrate can change the stiffness of the sediments and helps to understand hazard to sea floor installations in deep water such as wells, pipelines and drilling platforms.

As for methane gas hydrate according to Figure 3 and 4 below, the three phases equilibrium line can be consisted of hydrate, water rich liquid and vapour (H-L_w-V) phase, ice, liquid water and hydrate (I- L_w-H) phase, ice, liquid water and vapour (I-L_w-V) and ice, hydrate and vapour (I-H-V) phase.

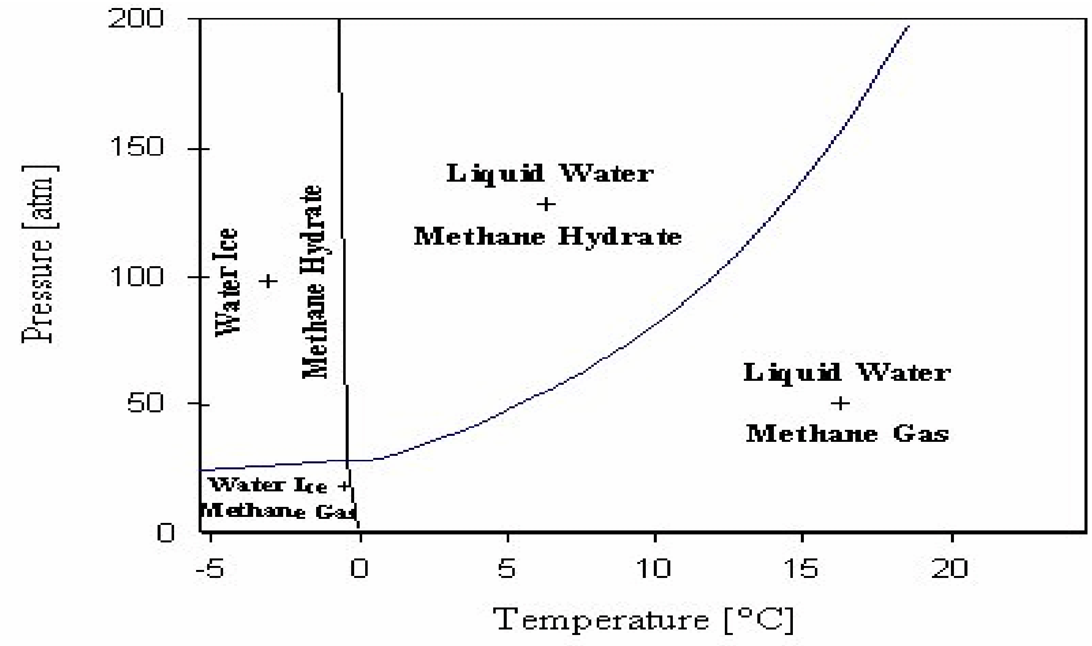

Figure 3: Phase diagram of methane hydrate in pure water

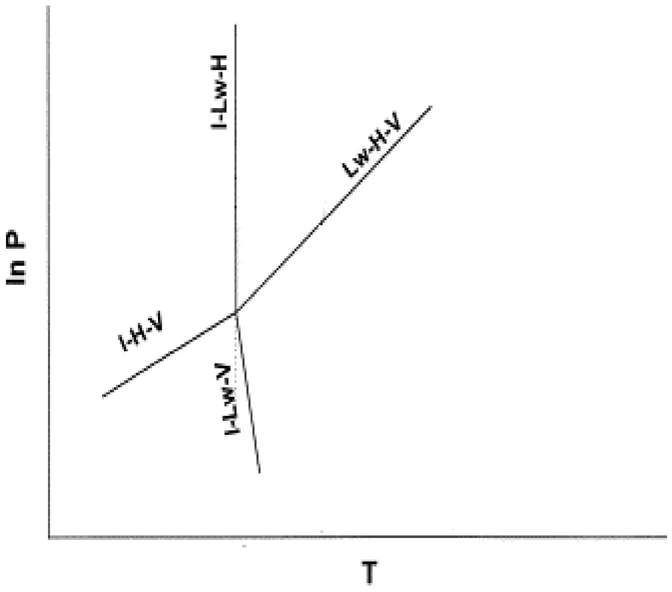

Figure 4: Example of Pressure-Temperature phase diagram for methane + water system

In petroleum production, formation water or brine solution is naturally produced together with petroleum reservoir fluids. This formation water contains dissolved salt and it will affect the solubility of hydrocarbon and water. On average, brine or sea water has a salinity of 3.5% or 35 g/L. The most common components that dissolved in formation water are sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4) and other minor constituents [Millero F.J , 1996].

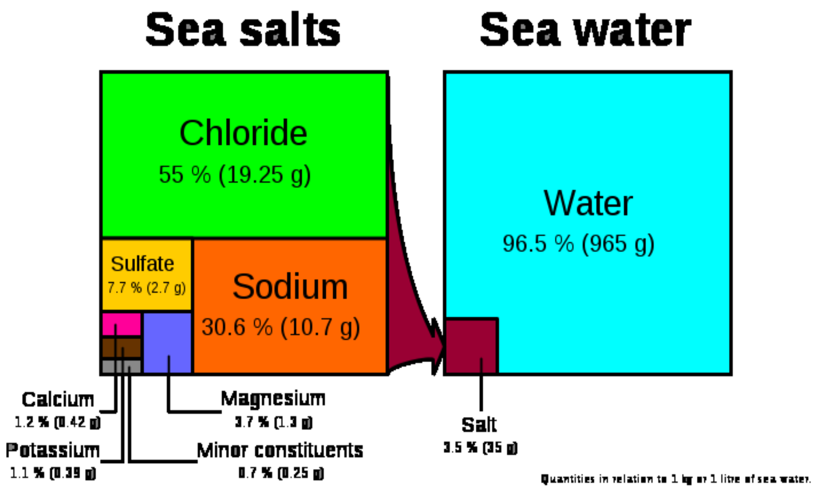

Figure 3: Common composition of sea water (35 000 ppm)

1.2 Problem Statement

1.2.1 Problem Identification

Vast amount of natural gas composed of mainly methane and other hydrocarbons have been known to exist in the marine sediments of ocean floor and permafrost zone in a hydrate state. Alongside with another hydrocarbons produce, carbon dioxide is also formed naturally in this region and becoming a major concern for the potential impact of rising greenhouse gas levels in the atmosphere. When carbon dioxide came in contact with seawater or brines, and its injection into natural gas hydrate deposits will result in the dissociation of methane hydrates.

Furthermore, hydrate formation will tend to plug in the flow lines during production and transportation which will lead to much greater risk. Removal actions need to be taken by introducing heat or dissolving the hydrate by chemical means. Removal of the methane hydrate formed must be carefully controlled because of the potential for the hydrate to undergo a phase transition from the solid hydrate to release water and gaseous methane at a high rate as the pressure is reduced [Max M.D, 2003]. The rapid release of methane gas in a closed system can result in a rapid increase in pressure thus creating greater risks. Therefore, an understanding or study of hydrate phase equilibrium considering methane becomes necessary in order to overcome these problems.

Moreover, lack of experimental data availability due to hydrate phase equilibrium in the open literature had been one of the contributing grounds to pursue this research. This information on hydrate phase behaviour is vital to the oil and gas industry.

1.2.2 Significant of the Project

Based on the problem identification, the isobaric three phase, hydrate, water rich liquid, and vapour equilibrium conditions are going to be studied and measured in order to identify the hydrate forming stable region. Moreover, an approach is also made to measure hydrate phase equilibrium conditions at various compositions of methane in the system and using different brine salinity.

1.3 Objective

To experimentally determined the three phase equilibrium (H-L_w-V) of methane and synthetic seawater solution.

- Sub-objective

  To understand the phase equilibrium behaviour and effect on the phase equilibrium line using various salinity of synthetic seawater.

1.3.1 Scope of Study

This study will be concentrating on the experimental setup, experiment works and analysis of the phase behaviour using various parameters such as methane concentrations or electrolytes solution salinity of the hydrate formations in order to develop the hydrate phase equilibrium. Any effect on the phase equilibrium line by using different concentration will be recorded and analyzed.

1.4 Relevancy of the Project

By executing this experimental work and then documented it, reservoir engineer and production engineer will be having additional and adequate resources and references when they encountered with a situation involving the existence of hydrates especially forming from methane in their well or transportation line. Moreover, this project will be as a base of understanding in any hydrate behaviour possibilities and can be a guideline in decision making afterwards.

1.5 Feasibility of the Project

In University Technology Petronas, all the equipments, chemicals and guidance are readily available. Therefore, with proper planning and efficient work load distribution, this project has met the time frame which is 4 months for accomplishment including the experimental work and documentation process.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrate Formation and Dissociation

Hydrate formation and dissociation is the most essential concern in hydrates study. Hydrates formation and dissociation process are clearer if being dealt in a laboratory system. Experimental procedures were conducted and the pressure and temperature profile were observed to relate to hydrate formation and dissociation. Hydrate formation varies on different pressure and temperature and this can be determined from the hydrate phase behaviour line. An alternative hydrate formation and dissociation experiment is shown in the pressure and temperature trace of Figure 5 by implementing isochoric (constant volume) and the temperature is change during this experiment.

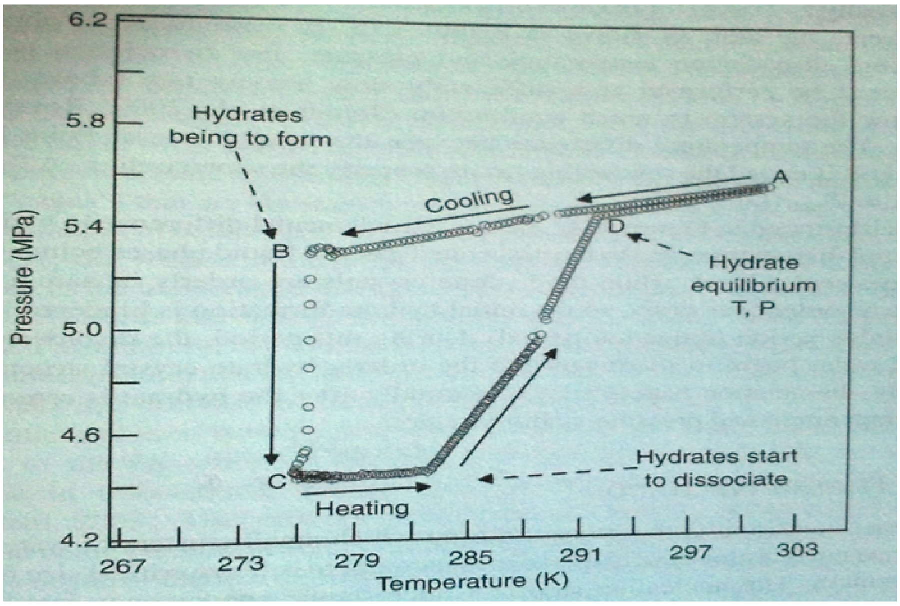

Figure 4: Temperature and pressure trace for formation of simple methane hydrates [Sloan et. al, 2007]

As the temperature is lowered, the pressure decreases, the metastability of the system prevents hydrate forming at point D but instead, the pressure continues to decrease until hydrate formation occur at point B. (A to B is the induction period). Then, the pressure drops rapidly until point C this line from B to C is called catastrophic growth. The system is heated from point C in Figure 3 so that pressure increase along the dissociation line to point D. Finally at point D, the hydrates are completely dissociated and the hydrate equilibrium condition is given by this point [Sloan et. al, 2007].

Hydrates must be performed at a sufficiently slow heating rate at about 0.12K/h to allow the system to reach equilibrium in order to avoid obtaining an erroneous dissociation temperature and pressure [Tohidi et al., 2000; Rovetto et al., 2006]. An appropriate value of cooling rate is also needed for the hydrate formation to reach point B.

2.2 Effect of Hydrate Phase Transition during Deep Water Drilling

When drilling in oil- and gas-bearing formations submerged in deep water, the reservoir gas may flow into the well bore and form gas hydrates owing to the low temperatures and high pressures found during deep water drilling. The gas hydrates may then flow upward with drilling mud or other discharged fluids. As they rise, the pressure in the annulus decreases and the hydrates dissociate into gas and water. The rapid gas expansion ejects fluid from the well, reducing the pressure further, which leads to more hydrate dissociation and further fluid ejection. The resulting violent expulsion of the phase transition of fluid from the annulus is one potential cause or contributor to what is referred to as a kick [Wang Z. and Sun B. 2009].

2.3 Gas Hydrate Importance to the Energy Industry and Society

Gas hydrates of interest primarily for 3 different reasons either positively or negatively:

- *Gas hydrates are a potential energy resource*

  Considering the planet as a whole, the quantity of natural gas in sedimentary gas hydrates greatly exceeds the conventional natural gas resources [Kvenvolden, 1993]. Numerous studies had been carried out discussing on the energy resource potential of gas hydrates and estimated amount of natural gas contained in the world's gas hydrate accumulations is enormous, but is speculative and ranges over three orders of magnitude, from about 2,800 to 8,000,000 trillion cubic meters of gas [Collet, 2004].

  However, utilization of gas hydrates as an energy resource has been largely inhibited by the lack of economical methods for massive production for most hydrate accumulation, especially marine shelf hydrate. A variety of different mechanism have been proposed for economically developing gas hydrates as an unconventional gas source such as an analytical modelling of gas recovery from in situ hydrates dissociation [Goel et. al, 2001] or conducting a comparative assessment of natural gas hydrate production models [Sawyer et. al, 2000].

- *The role of gas hydrate in past and future climate change*

  Gas hydrates are also of interest because of their potential role in climate change. Gas hydrates in continental shelf sediments can become unstable either as a result of warming bottom water, or as a result of pressure drop due to a reduction in sea level. If these marine gas hydrates begin to rapidly disassociate into gas and water, then the methane trapped in the gas hydrates can be released to the atmosphere.

  Methane is a greenhouse gas and it is many times more effective as a greenhouse gas than carbon dioxide. Therefore, if methane flux in atmosphere is sufficient enough in quantity, it can cause a global warming problem. This process is believed to have influenced past climate changes

[Henriet, 1998; Hesselbo et.al, 2000] and may enhance current global episode.

- *Flow Assurance Problem*

As discussed earlier, gas hydrates can spontaneously form in petroleum production equipment and pipelines associated with deep-water petroleum production and onshore petroleum production. This reason is an area of interest for gas hydrates studies as unwanted hydrates can clog equipment, thus preventing the optimum production of hydrocarbons.

Figure 5: Formation of gas hydrates plugging in the pipeline

Various researches had been conducted and continuously to prevent hydrate formation in petroleum production and transportation equipment. Paez used the approach of low dosage inhibitor, kinetics inhibitor and anti agglomerant to prevent hydrate from forming [Paez, 2001]. In his work, he also provide guidelines for field remediation in keeping operating pressure and temperature out of hydrate formation region by making system adjustments such as applying heat, using insulated pipelines or adding chemical compounds (thermodynamic inhibitor) that change the behaviour of the new mixture. Yousif and Dunayevsky work uses other option included radial heat tracing, pipe warm-up and hot water circulation through coiled tubing to overcome this operational hazard [Yousif and Dunayevsky, 1997].

2.4 Seawater

Seawater is a complex solution containing a wide variety of organic and inorganic chemicals. The seawater is divided into few classes based on how much dissolved salt is in the water or the concentration of salt in the water. The concentration of water is expressed in parts per million (ppm) [Bergman J.,2001]:

- Fresh water – less than 1 000 ppm
- Slightly saline water – from 1 000 ppm to 3 000 ppm
- Moderately saline water – from 3 000 ppm to 10 000 ppm
- Highly saline water – from 10 000 ppm to 35 000 ppm

Ocean water where most of the petroleum production are has a salinity in the range of 28 000 ppm to 35 000 ppm. Figure 7 below shows the salinity versus depth profile for ocean water. The profile projected the generalized salinity-depth profile for the South Atlantic Ocean [Bergman J., 2001].

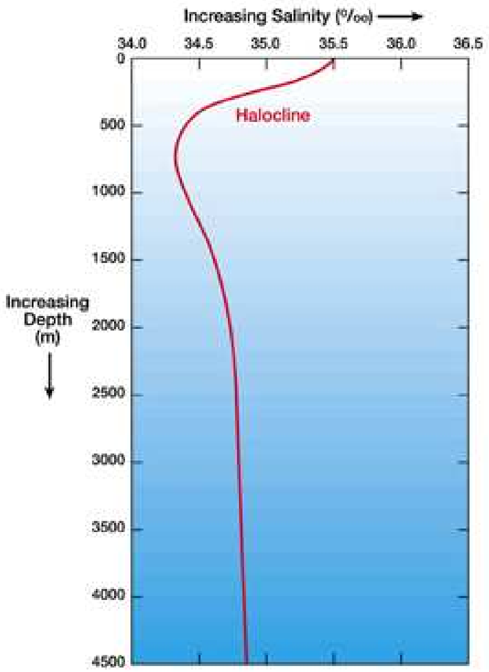

Figure 6: Salinity - depth profile

In this profile, salinity at the surface is high and then salinity decreases until at depth of about 1,000 meters. Salinity then increases again slightly with increasing depth. Halocline is a layer of water where salinity rapidly changes with depth.

A standard seawater with a salinity of 35 000 ppm has a freezing point of 1.9°C (3.4° F), which is lower than freshwater. This freezing point depression is a result of the presence of ions in the water which tends to make the water more stable in its liquid form than as a solid [Farley R. H., 2005].

2.5 PVT Cell

Based on previous studies that had been done, PVT Cell is the most common equipment that been used to studied on the phase behaviour measurement.

2.2.1 Overview of PVT Cell

PVT cell which is basically a hollow stainless steel cylinder about 600 cm3 capacity, has provided a window for visual observation of the bubble pressure so the process of differential release consisting of gas extraction can be done by keeping the constant bubble size.

PVT cell is able to withstand high pressure and temperature which is up to 10000 psi and 350° F. Based on Figure 1 below, PVT cells main component consist of equilibrium cell with Plexiglass windows, a magnetic stirrer, and suitable connection for charging and discharging materials. The presence of hydrate was detected visually from the window of equilibrium cell [Dholabhai P.D, 1993].

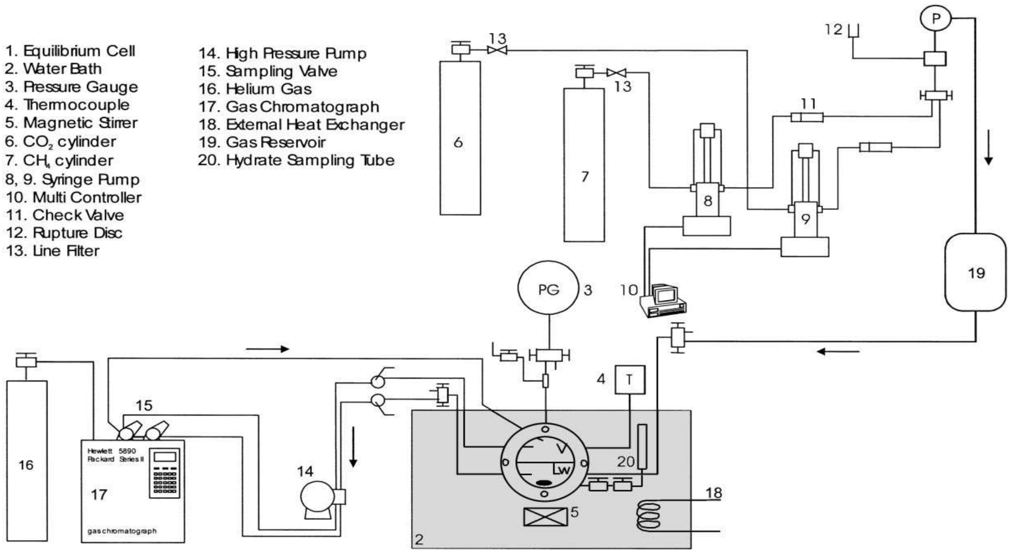

Figure 7 : Schematic diagram of PVT Cell [Dholabhai P.D, 1994].

2.6 Hydreval Equipment

However in the laboratory, the equipment that can be used to measure the phase equilibrium is Hydreval due to its similarity in characteristic to PVT Cell. The Hydreval is a complete instrument designed to determine experimentally thermodynamic stability of hydrates into melted oil and gases phase. It is based on a motor driven PVT cell which can be use in different configurations to perform the required test. The chamber is enclosed at one end by the piston of embedded pump and the other by a dedicated cell head made from titanium alloy. The piston is equipped with a magnetic driven stirrer for homogenous agitation of the fluid sample. Hydreval has a volume capacity of 80 cc and can be operated until 200 bar or 3000 psi and temperature range of -20^{O}C to 150^{O}C. All parameters such as volume control, pressure and temperature can be monitored from the software system installed for easy visualization. An external pump is used to insert the gas and liquid from the accumulator to the sapphire cell. [Hydreval Opman]

Figure 8: Hydreval equipment

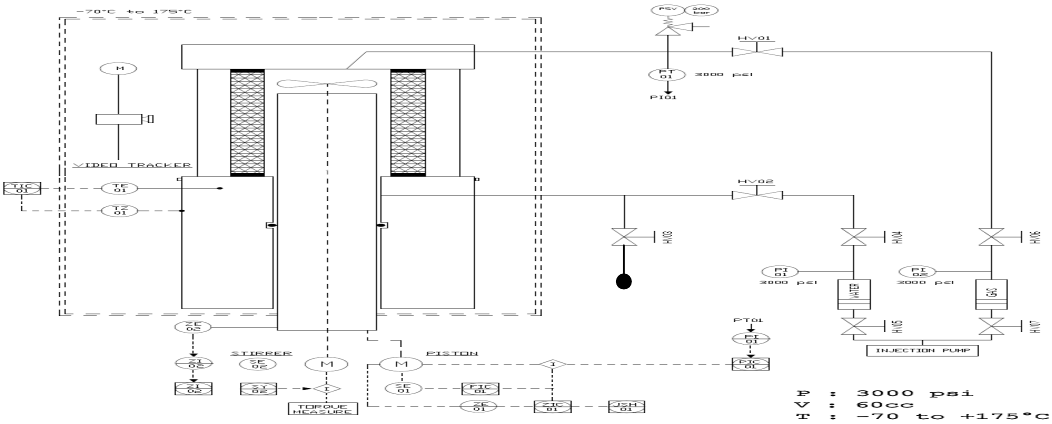

Figure 10: General schematic diagram of Hydreval

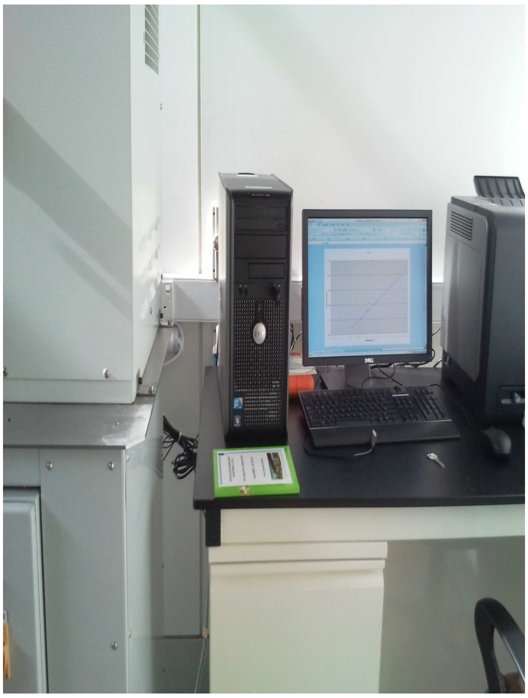

Figure 11: Data collection system

Figure 12: Liquid accumulator

Figure 13: External pump

Figure 14: Gas inlet

2.7 Research Findings

2.7.1 Methane and water system research

Until now, there are only few studies had been carried out that concentrating on the hydrate equilibrium methane and synthetic seawater system. Ohgaki et. al had conducted a study for high pressure phase equilibrium on the methane hydrate system. They investigated the three phase coexistence curve of methane hydrate, saturated water and saturated fluid of methane in the temperature range from 305 to 321 K and pressure range from 98 MPa to 500 MPa. However, they also pursue their studies by using a Raman microprobe spectrometer to investigate the intramolecular vibration of the gas molecule and the intermolecular vibration of water both in hydrate crystal and coexisting phase which is not applied in this work [Ohgaki et. al, 1999]. In other work, Zadjia Atik had governed an experiment for methane hydrate in seawater by applying low pressure. The pressure range used in his experiment is ranging from 3.42 to 22.5 MPa. The three phase of hydrate-liquid-gas was determined using an isochoric method. From this experiment, they also generated an equation for predicting the three phase of hydrate formation [Atik Z. et al, 2010].

As mention earlier, ionic solids in seawater solution can inhibit the formation of hydrate. Maekawa, in his work had measured the hydrate for methane and mixture of methane and ethane, in both pure water and 3 wt% NaCl for pressure from about 3 to 12 MPa. His data show that the hydrate formation temperature was reduced by about 1° C for brine with this concentration [Maekawa, 2001]. Measurement of the hydrate formation for a natural gas mixture in pure water and in solutions of various ionic salts had been conducted by Mei et. al for pressures from about 0.6 to 2.5 MPa. They observed on how the temperature changes with different concentrations o the ionic salts [Mei et. al, 1998]. Pankaj D. Dholabhai had measured the hydrate equilibrium conditions in aqueous electrolyte solutions containing NaCl, KCl, and $CaCl_2$ with mixtures of methane and carbon dioxide. In this research, it is reported that the electrolytes had caused an inhibition effect towards the hydrate formation. At a given pressure, the equilibrium temperature is lower for higher ionic strength which clearly indicates the inhibiting effect. [Dholabai P.D, 1994].

Seong-Pil Kang et al stated in his research that the addition of inhibitors such as electrolytes, alcohol, and polymers will weakened the water molecules in linking the hydrogen bonds. These inhibitors will lower the fugacity of water and thus means it requires much lower temperature and higher pressure to form hydrates [Kang et. al, 1998].

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

3.1.1 Flow Chart

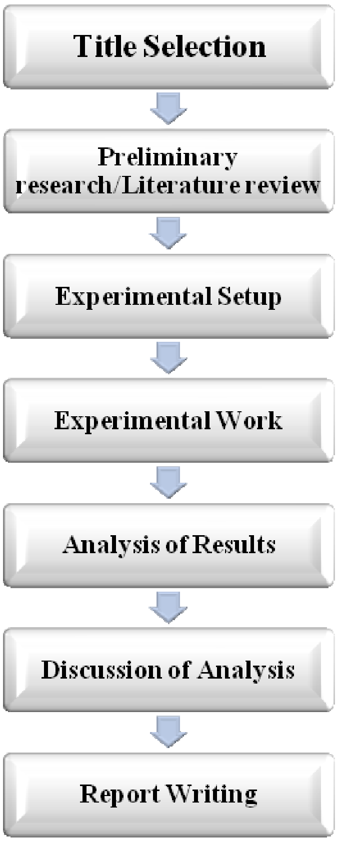

Figure 15: Research project work flow

Title Selection: After a thorough and further discussion with supervisor, it has been decided to conduct a research based on the phase equilibrium for hydrate formation for methane and synthetic seawater system focusing on the synthetic seawater salinity effect.

Preliminary Research/ Literature Review: A study has been done to get a clear and concise understanding on the basic properties of hydrates, hydrates formation and to obtain an initial overview on the expected findings from this research project.

Experimental Setup: This research will be conducted in a laboratory using Hydreval equipment for measuring the phase behaviour while visually monitoring the hydrate formation.

Experimental Work: In this project, methane composition and synthetic seawater salinity will be the manipulating factor to study their effect on the hydrate equilibrium measurement. Several assumptions have been identified to facilitate on this experiment.

Analysis of Result: The expected result is to obtain a three phase equilibrium data of synthetic seawater water solution, methane hydrate, and vapour. A comprehensive observation will be closely monitored for synthetic seawater which has been discussed earlier have an inhibiting effect towards the hydrates temperature or pressure.

3.1.2 Experimental Setup

Apparatus

The main component of the apparatus (Hydreval) will consists of a stainless steel sapphire equilibrium cell with a window for visual observation, magnetic stirrer, and a suitable connection for charging or discharging materials.

The apparatus is operated based on these equilibrium principles:

- *Vigorous agitation is necessary for complete water transformation.*

  Agitation is important in conducting the experimentation to provide surface renewal and exposure of liquid water to the hydrate former. As more interfaces can be break, hydrate will be easily formed. Another reason for such agitation is to prevent water occlusion. Moreover, agitation in the form of flow fluctuations or bubbling gas through water is necessary to initiate hydrate formation, in order to decrease the metastability [Hammerschmidt, 1934].

- *Hydrate dissociation is used to measure hydrate equilibrium point*

  Carson and Katz work had provided a reason for accounting hydrate dissociation for equilibrium point. Their work had considered the metastability of the hydrate phase.

- *A rapid decrease in pressure or an increase in temperature indicates hydrate formation in a constant volume apparatus.*

  From previous work, it is concluded that when encapsulated in the hydrate, pressure will decrease. As the hydrate starts to dissociate, the pressure slope is also decreasing versus the temperature trace. From this observation, intersection point of heating and cooling isochors can be measured to obtain hydrate phase equilibrium point.

Preparation of synthetic seawater solution

Synthetic seawater solution is prepared using sea salt with different salinity with specified weighted amount to be used throughout the research project. Appropriate quantity of sea salt constituents will be weighed and added to a weighed quantity of water. The mixture will be stirred at room temperature to dissolve the electrolytes. Synthetic seawater were prepared for 35 000 ppm and 28 000 ppm salinity for this purpose of work. Initially, the solution was prepared by weighing an appropriate amount of salt mixture in a beaker and topping it up with fresh water to 1000g (refer to Table 1, Table 2 and Table 3).

Figure 16: Salts used in this work

Figure 17: Mixture of brine solution

Synthetic Seawater Recipe

Standard artificial seawater with a salinity of 35 000 ppm [Millero F., 1996]		Actual composition used in this work, g/kg
Salt	g/kg	
NaCl	23.98	24.052
$MgCl_2$	5.029	5.129
Na_2SO_4	4.01	4.0354
$CaCl_2$	1.14	1.1543
KCl	0.699	0.699
$NaHCO_3$	0.172	-
KBr	0.100	-
$B(OH)_3$	0.0254	-
$SrCl_2$	0.0143	-
NaF	0.0029	0.0029

Table 1: Synthetic seawater recipe for 35 000 ppm

Artificial seawater composition for 31 000 ppm	
Salt	g/kg
NaCl	21.357
$MgCl_2$	4.54
Na_2SO_4	3.574
$CaCl_2$	1.055
KCl	0.539

Table 2: Synthetic seawater recipe for 31 000 ppm

Artificial seawater composition for 28 000 ppm	
Salt	g/kg
NaCl	20.989
$MgCl_2$	3.52
Na_2SO_4	2.066
$CaCl_2$	1.067
KCl	0.50

Table 3: Synthetic seawater recipe for 28 000

Measurement of Hydrate Equilibrium Points

The methane hydrate equilibrium points were measured using isochoric method. Before charging a solution, the cell was rinsed with deionized and distilled water to wash out electrolytes from the previous experiment. Then, the sapphire cell must be vacuumed to control the experiment. Synthetic seawater solution of desired concentration of 30 cc will be charged into the sapphire cell, and the vapour phase of the cell of 50 cc will be purged with methane. The solution will be allowed to cool to the required temperature as initial setting point. Once the temperature can be obtain, the expected pressure will be monitored. Subsequently, the stirrer was set to 600 rpm for agitation to form hydrate. The temperature was lowered to allow hydrate formation and the formation of hydrates also will be observed. Then, the temperature was increased to allow the hydrate dissociation until the T-graph is intersected. If the pressure and temperature remain constant for an adequate time, the readings of constant pressure and temperature will be taken as the equilibrium conditions. The experiment then will be repeated using various concentrations of seawater salinity.

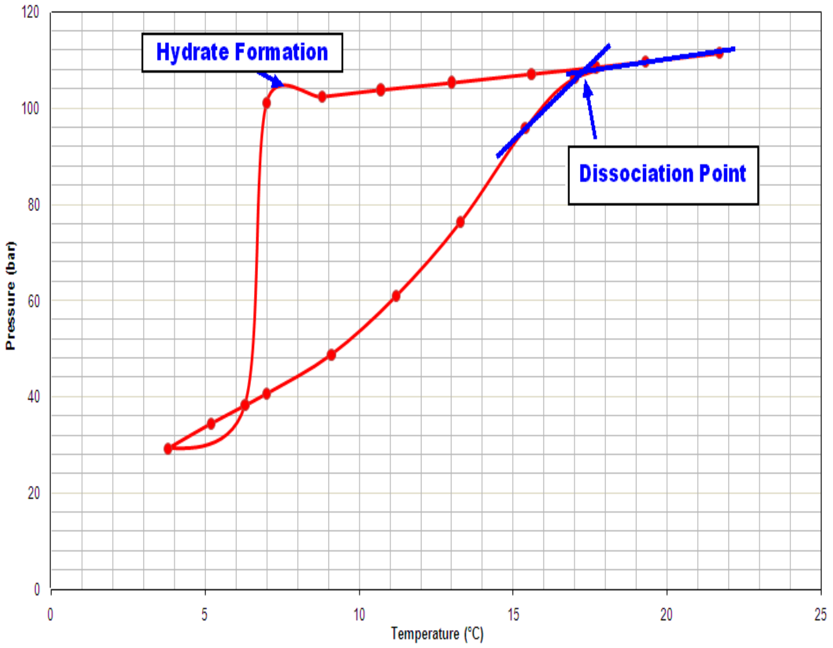

Figure 18: T-graph of hydrate equilibrium line

3.2 Key Milestone for Final Year Project

Detail	Week
Selection of Title	FYP 1
Literature Review and Research Findings	FYP 1
Training on Equipment Handling	FYP 1
Verification of Equipment - Test on pure CH_4 hydrate	Week 2-3
Experiment and Analysis on Effect of CH_4 on the Phase Behaviour	Week 3-4
Experiment and Analysis on Effect of Brine Salinity on the Phase Behaviour	Week 5-7

Table 4: Key milestone

3.3 Gantt Chart and Project Activities

Activity	FYP 1				FYP 2			
	Sept	Oct	Nov	Dec	Feb	Mar	Apr	May
Title Awarded	🟨							
Research findings on Hydrate Phase Equilibrium for CH_4 + Brine solution		🟨	🟨					
Prepare the experiment - Training on equipment handling				🟨				
Verification of equipment for CH_4 hydrate				🟨				
Brine solution preparation using sea salts				🟨	🟨			
Experiment and analysis on effect of brine salinity on the phase behaviour					🟨	🟨		
Data analysis							🟨	🟨
Report Completion							🟨	🟨
Technical Paper Writing							🟨	🟨

Table 5: Gantt chart

3.4 Tools, Equipments and Materials

The chemicals and materials needed in this experiment for the phase equilibrium study are:

- Sea salt for 35 000 ppm, 31 000 ppm and 28 000 ppm –
    - Sodium chloride
    - Magnesium chloride
    - Sodium sulphate
    - Calcium chloride
    - Potassium chloride
    - Sodium fluoride

- Methane supplied from MOX-LINDE GASES Sdn. Bhd with a certified purity of 99.99% was used.

Meanwhile, the tools and equipment required for the experiment are:

- External Pump
- Phase Equilibrium Measurement (Hydreval)

However, in future when the research started to be conducted, there might be other materials or equipments needed to complete this research and will be added to equip with the current one.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Phase Behaviour in the Hydrate Forming Region

First of all, an experiment of methane hydrate formation with pure water was conducted to verify and compare the data from this work and data reported by other literatures available. The data obtained for comparison in this work are given in Table 6 and plotted in Figure 19 below. As seen from this figures, the new data match those of Robinson et.al, McLeod et.al, Mohammadi et.al, and Galloway et.al.

Pressure (bar)	Temperature (°C)
135.55	14.8
97.05	11.8
68.07	8.6
50.62	6.6

Table 6: Measured data in this work

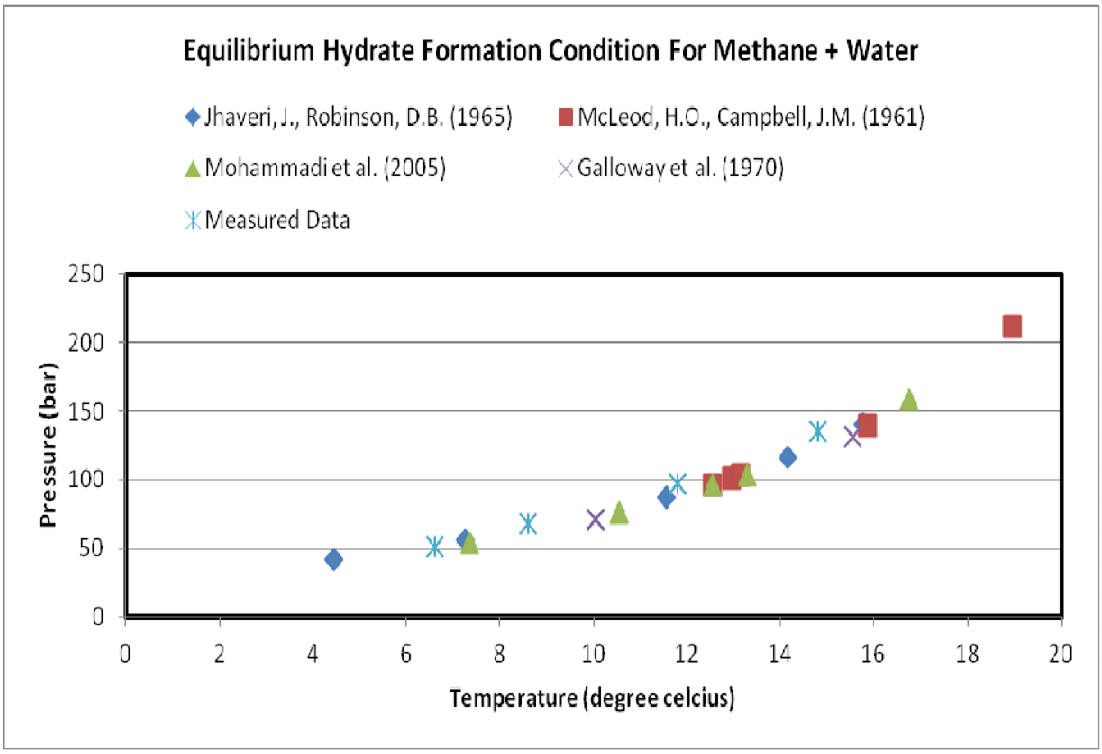

Figure 19: Equilibrium hydrate formation condition for methane + water

The phase equilibrium data for methane hydrate of hydrate-liquid water-vapour line for 35 000 ppm of synthetic seawater solution is plotted and shown in Figure 20. Hydrate equilibrium data for methane and seawater that had been measured earlier from Zadjia Atik are also included in this figure for comparison purpose with 35 000 ppm of synthetic seawater. As can be seen from the figure below, the data trend seemed to be agreeable with the compared literature. From the figure, it can be conclude that the method used to conduct this research is quite accurate.

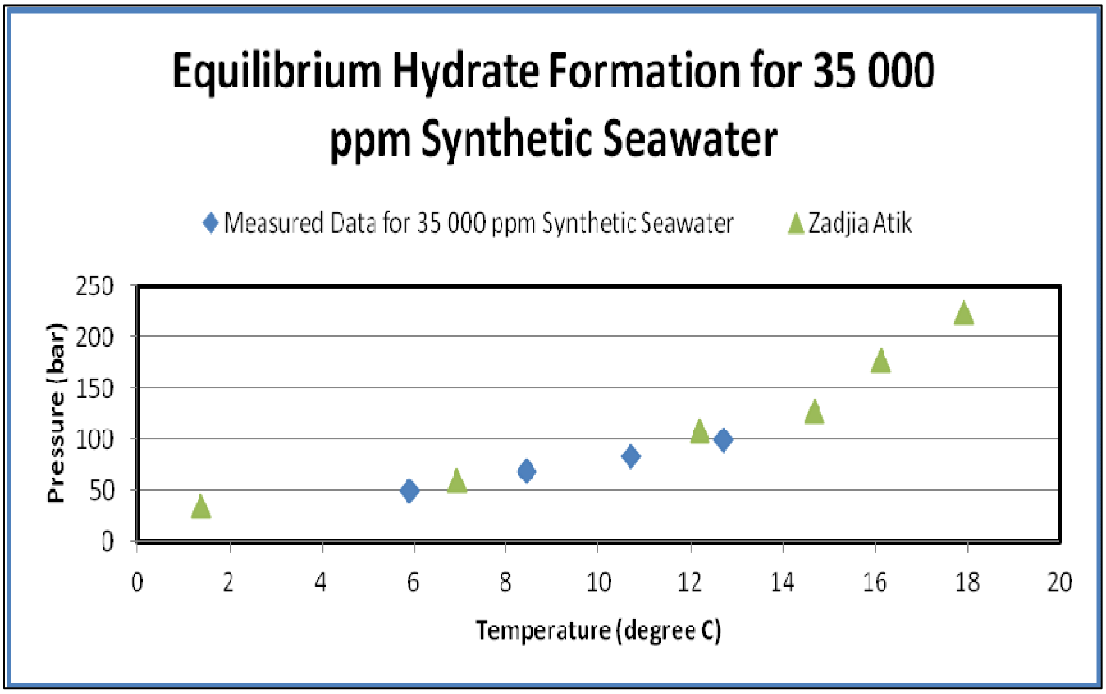

Figure 20: Equilibrium hydrate formation for 35 000 ppm synthetic seawater compared to Zadjia Atik (2010)

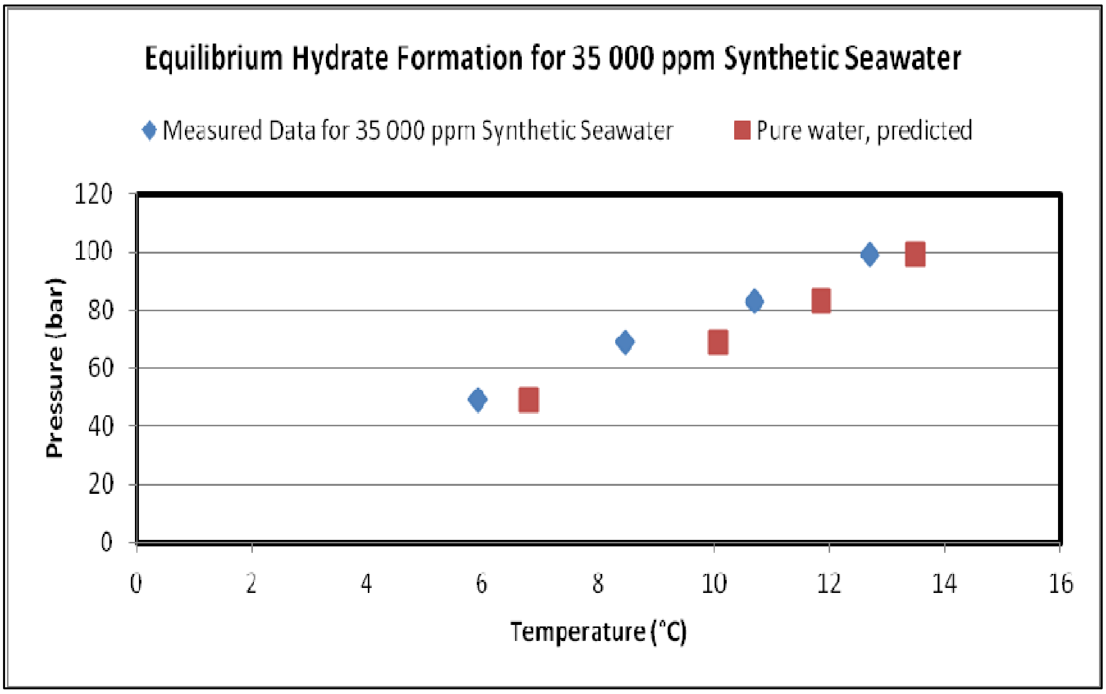

Figure 21: Equilibrium hydrate formation for 35 000 ppm synthetic seawater compared to predicted pure water with methane using vdWP hydrate equation of state

Pressure (bar)	Temperature (°C)
49.255	5.9
68.689	8.5
82.831	10.7
98.862	12.7

Table 7: Measured data for hydrate phase equilibrium of 35 000 ppm salinity

Pressure (bar)	Temperature (°C) without brine solution {calculated}
49.255	6.79
68.6897	10.06
82.83	11.84
98.862	13.48

Table 8: Predicted data for hydrate phase equilibrium using vdWP hydrate equation of state

The phase equilibrium data for 35 000 ppm of seawater then be compared with phase equilibrium data for methane and pure water prediction using van der Waals and Platteuw (vdWP) hydrate equation of state method. In Figure 21, it is clear that the line for the synthetic seawater have been shifted upward and left, showing there is some inhibition effect towards the hydrate formation. From this figure, it can be shown that at a given pressure, the equilibrium temperature is lower for synthetic seawater with ionic salts rather than pure water. Based on the figure, the salinity has shown significant thermodynamic effects towards the hydrate formation.

4.2 Effect of Synthetic Seawater Salinity towards the Hydrate Phase Region

Another set of experiments had been conducted to study the effect of synthetic seawater salinity towards the hydrate phase region measurement. The salinity used in this sets are 28 000 ppm and 31 000 ppm by considering the acceptable seawater salinity range in the deep sea. The initial pressure was set to 100 bar and the temperature was tested in the range of 18 ° Celsius to 3 ° Celsius in the sapphire cell.

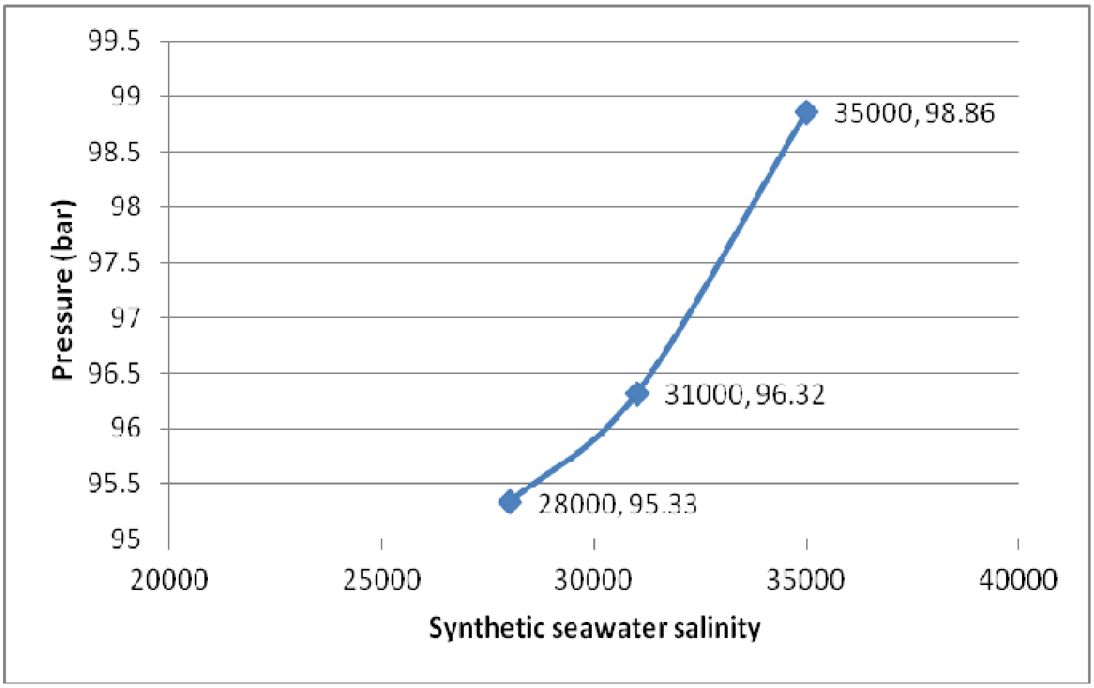

Figure 22: Pressure diagram for equilibrium hydrate condition for different seawater salinity

As shown in Figure 22, the difference in ionic strength in terms of salinity varies the pressure needed for hydrate equilibrium. As the salinity increases, the pressure for hydrate equilibrium becomes higher. This can be due to the ionic strength which inhibits the hydrate formation thus, requires more pressure to forming hydrate. The salts inhibit by ionizes in the solution and interacts with the dipoles of water molecules with much stronger Coulumbic bond than either the hydrogen bond. The stronger bonds of water with greater salt ions concentrations will inhibit hydrate formation hence explained the higher pressure needed to form hydrate.

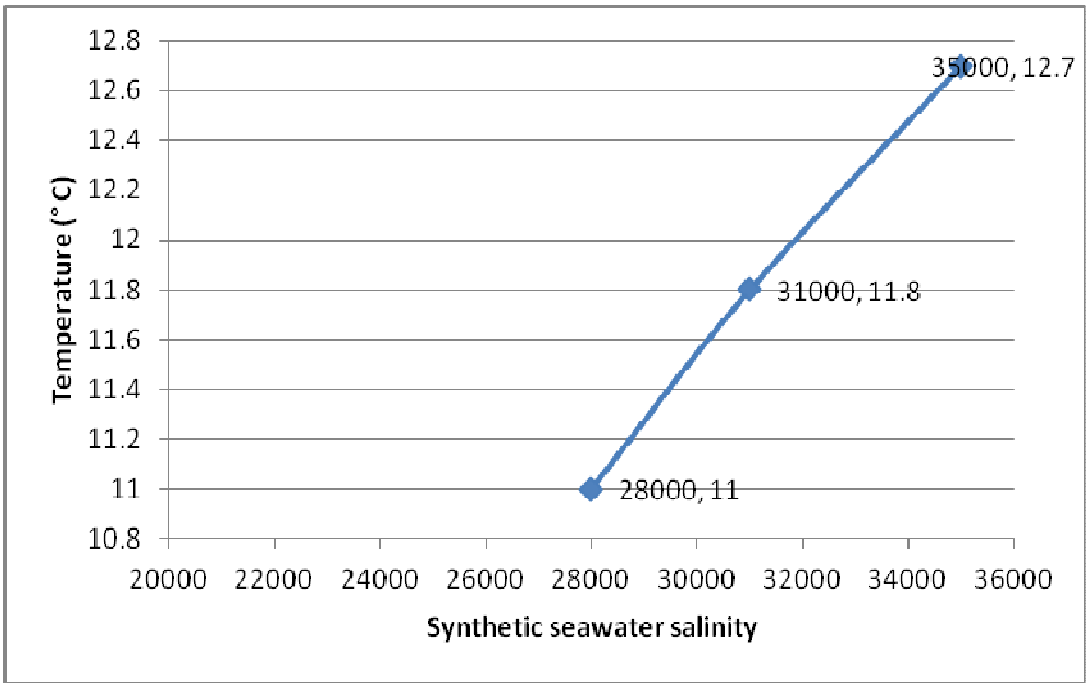

Figure 23: Temperature diagram for equilibrium hydrate condition for different seawater salinity

Referring to the figure above, it is shown that the temperature is increasing with different salinity of synthetic seawater. However, the offset is not far different from each other and with increasing salinity, higher pressure is needed to forming hydrate and the temperature is lower than forming hydrate with pure water. This factor is important so that the formation of hydrate can be controlled from plugging the transportation line with the given pressure and temperature.

Figure 24: Hydrate formation at 100 bar

Figure 25: Hydrate dissociation

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Two series of experiment had been conducted to obtain equilibrium line of the methane hydrate in synthetic seawater with different salinity and to identify the effect of salinity towards the hydrate equilibrium line. The data was measured from 50 bar to 100 bar and the cell was heated until 18 degree Celsius before the temperature was then decrease. In this experiment, it can be concluded that the ionics presence in the seawater have been able to slightly increase the pressure needed and decrease the temperature for three phase hydrate equilibrium. Moreover, the salinity gives such effect that the higher the concentration of the synthetic seawater, the higher pressure needed for equilibrium. This is also to show that seawater have significant inhibition effect towards hydrate formation. To summarize, this project is very reasonable to pursue and has a wide prospect especially in petrochemical engineering as it provides a means of reference to further study about hydrates formation and its behaviour. This research will also explore on methane hydrates and provides new perspective for the replacement of methane by carbon dioxide in the hydrate state, by determining the phase equilibrium using these two components. In future, this work can be expanded to be tested in isothermal parameter and broadened by adding promoters to see the effect of hydrate behaviour.

It is recommended to construct this study using the real seawater sample taken from Malaysian water. It is more efficient to investigate the hydrate formation with the normal amount of ionic salts contains in Malaysian seawater rather than using synthetic seawater that is prepared in the laboratory. This study can also be expanded using various seawater salinity to have clearer view on the effect of salinity in hydrate formation. Moreover, by combining certain ratio of the synthetic seawater with formation water will give a better insight towards understanding the gas hydrate behaviour. During conducting this experiment, there are also a few errors that can be avoid next in the future and it is advisable to use the lowest cooling rate possible to get more accurate results.

REFERENCES

Kvenvolden, K.A., *Gas hydrates as a potential energy resource – a review of their methane content*, The Future of Energy Gases.; 1993, p.555-561

Kvenvolden, K.A., Lorenson T. D., *The global occurrence of natural gas hydrate*, AGU Monograph, 2000, p. 55.

Lerche, I., E. Bagirov, *Guide to gas hydrate stability in various geological settings: Marine and Petroleum Geology,* 1998 *v.15*

Hornbach, M. J., W. S. Holbrook, A. R. Gorman, K. L. Hackwith, D. Lizarralde, I. Pecher, *Direct seismic detection of methane hydrate on the Blake Ridge: Geophysics*, 2003, v. 68, p. 92-100.

Goldberg D., Saito S., *Detection of gas hydrate using downhole logs*, The Geological Society, 1998, p.129-132.

Sloan, E.D.; Koh C.A. *Clathrate Hydrates of Natural Gases.* 3rd ed.; CRC Press 2007

Millero F.J *Chemical Oceanography.*2nd ed.; CRC Press 1996

Max M. D., *Natural Gas Hydrate in Oceanic and Permafrost Environment,* 1st ed.; Kluwer Academic Publishers 2003

Tohidi, B., Burgass, R.W., Danesh, K.K, Todd *Proc. Gas Hydrates: Challenges for the Future,* 2000

Wang Z., Sun B., *Annular multiphase flow behaviour during deep water drilling and the effect of hydrate phase transition*, 2009, Petroleum Science, vol. 6

Collet T. S., *Gas Hydrates as a Future Energy Resource,* Geotimes, 2004.

Goel, N., Wiggins M., Shah S., *Analytical modelling of gas recovery from in situ hydrates dissociation*, Journal of Petroleum Science and Engineering, 2001, v.29 (2).

Henriet J. P., *The Geological Society, London*, 1998, Special Publications.

Hesselbo S. P., Grocke D. R., Jenkyns H. C., Bjerrum J., Farrimond P., Morgans Bell H. S., Green O. R., *Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event*, Nature, 2000, v. 406.

Paez J. E., *Problems in Gas Hydrates: Practical Guidelines for Field Remediation*, SPE Paper 69424-MS, 2001, SPE.

Yousif, M.H., Dunayevsky, V.A., *Hydrate Plug Remediation: Options and Applications for Deep Water Drilling Operations*, SPE Paper 37624-MS, 1997, SPE.

Bergman J., *Salinity – Dissolved Salts, Measuring Salinity*, The Earth Scientist, August 2001. Retrieved from
http://www.windows2universe.org/earth/Water/dissolved_salts.html

Bergman J., *Salinity – Dissolved Salts, Measuring Salinity*, The Earth Scientist, August 2001. Retrieved from
http://www.windows2universe.org/earth/Water/salinity_depth.html

Farley R. H., *What is Seawater?*, vol. 5, 2005
Retrieved from reefkeeping.com/issues/2005-11/rhf/index.php

Sawyer W. C., Franz J., Yost A., *Comparative Assessment of Natural Gas Hydrate Production Models*, SPE Paper 62513, 2000, SPE.

Rovetto, L.R., Strobel, T.A., Koh, C.A, Sloan E.D., *Fluid Phase Equilib.* 2006, 84,247.

Hydreval Operation & Maintenance Manual, Vinci Technologies France

Nakano S., Moritoki M., Ohgaki K., *J. Chem. Eng. Data* 1999, 44, 254-257

Atik Z., Windmeir C., Oellrich L. R., *J. Chem. Eng. Data* 2010, 55, 804-807

Maekawa T., *Geochemical Journal*, 2001, vol.35, pp. 59-66

Mei D-H., Liao J., Yang J-T., Min T., *J. Chem. Eng. Data*, 1998, *43* (2), pp 178–182

Dholabhai P. D.; Bishnoi P. R. *J. Chem. Eng. Data* 1994, 39, 191-194.

Kang S.P.; Chun M.K et al.; *Fluid Phase Equilibria 147* 1998, 229-238

Hammerschmidt, E. G., *Ind. Eng. Chem.*, 1943, 26, 851.