Phase Equilibrium Measurement of Methane Hydrate with Hydrate Promoters

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12361

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

JANUARY 2012

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CERTIFICATION OF APPROVAL

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Petroleum Engineering Programme

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Approved by,

_____

(Dr. Khalik bin Mohamad Sabil)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2012

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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.

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MARLINA IYLIA BINTI MOHD JAMAL

ABSTRACT

In view of the fact that natural gas hydrate is getting more crucial in the oil and gas industry nowadays, either to prevent its formation or to enhance its formation, this project is about the study of three phase equilibria (H-L_w-V) for methane hydrate and performance of hydrate promoters towards methane hydrate formation. Therefore, the purpose of this project is also to analyse two types of hydrate promoters' ability in escalating methane hydrate formation. All of these phase equilibria measurement of hydrates will be done by using pure water. In this project, main focused will be given towards the study of phase behaviour for methane hydrate with the influence of two hydrate promoters, which are sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF). The phase equilibria for simple methane hydrate was execute as verification data that can be used as a reference to other hydrate phase equilibria which consist of methane and hydrate promoters. By study the phase equilibria of methane hydrate, the result is useful to overcome flow assurance problem in natural gas pipeline. The significant of knowing phase behaviour of methane hydrate with promoters is to be applied for practical applications that desire formation of hydrate such as in natural gas storage and natural gas transportation. The hydrate phase equilibrium will be measured by using Hydreval equipment.

ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Hydrate is a crystalline solid compound which contains water molecules and other guest molecules. The water molecules are referred as host molecules while guest molecules consist of nonpolar and low molecular weight gas molecules that stabilize the crystal. The presence of water can lead to hydrate formation since there is hydrogen bonding form between water molecules which act as cage that will entrap guest molecules. The structure and chemical bond of hydrate will be discussed further in Section 2.2. Gas hydrates also called as clathrates which the word clathrate is a Latin word, 'clathratus' that means a lattice. This is due to the structure of hydrates as the water molecules form cages around the guest molecules.

Hydrates were first discovered in the early 1800s by two scientists, Sir Humphrey Davy and Michael Faraday when they were experimenting with chlorine-water mixtures [1]. As the mixtures cooled, the scientists noticed a solid material forming at temperatures above the normal freezing point of water (0°C). Due to the finding, many other scientists studied these strange materials. They generally worked out with the process of hydrates formation by studying the structure of hydrates molecules which includes water molecules or also known as host molecules and other guest substances molecules. Besides, they had classified various molecules that could co-exist as hosts or lattice formers and guests at various conditions which each variety was stable. However, because natural occurrences were not known, the subject remained only as academic curiosity.

During 1930's, E.G. Hammerschmidt determined that hydrate was responsible for plugging natural gas pipelines, mainly those located in cold environments [1]. This was the second phase and beginning of the modern research era of hydrates as an industrial nuisance. Afterwards, Dr. Dendy Sloan started a small body of researchers led by him at the Colorado School of Mines. They investigated the physics of various clathrates including the construction of the first

predictive models of their formation. The main focus of this work was to develop chemical additives and other methods that can inhibit hydrate formation as to avoid plugging in the pipeline. Thus, this research still continues until the present.

Then, hydrate research entered the third phase in the late 1960's when solid natural gas or methane hydrate was observed as a naturally-occurring constituent of subsurface sediments in Messoyahka gas field of the Western Siberia basin. By mid 1970, the scientists speculate that any hydrate formation can exist when in conditions of low temperature and high pressure, anywhere in the world, not only in permafrost regions but also under deep oceans. However, hydrate can quickly dissociate or melting when removed from its natural environment. This the era where scientists start to broad the studies of natural gas hydrates globally.

There are many drilling projects done by major countries that hunting for naturally-occurring natural gas hydrates since hydrates are currently considered as a potential unconventional energy source. By 1999, the growing recognition of the size and extent of the global methane hydrate resource gave rise to a number of critical scientific and public policy issues. Thus, U.S. Congress offered legislation in 1999 that concluded in the signing into law of the Methane Hydrate Research and Development Act of 2000 [1]. This law is to overcome the environmental issues, emerging natural gas supply shortages and also to increase reliance on foreign energy.
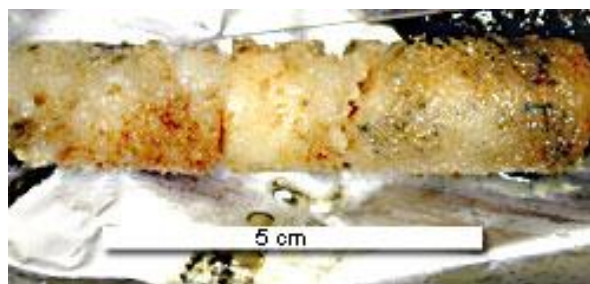
Figure 1.1: Core covered by hydrates from the Johnson Sealink cruise in the Gulf of Mexico in July 2001. *(Photo courtesy to Ian McDonald Texas A&M)*

1.2 PROBLEM STATEMENT

The importance of studying phase equilibrium of methane hydrate with promoters in pure water are as follows: (1) In oil and natural gas industries, gas hydrates are known as harmful materials since it can lead to "blockage problems" which cause serious operational and safety problems [10]. At certain condition; typically low temperature and high pressure condition, in the pipeline, presence of water contents will come into contact with oil or natural gas components which can lead to gas hydrate formation. Then, this gas hydrate will grow and entirely plugged the pipeline; usually occurred in production pipeline. Therefore, this research will be focused on identifying the methane hydrate phase equilibria in order to prevent hydrate formation in oil and natural gas pipelines and overcome the blockage problem. From the hydrate phase equilibrium data, hydrate formation condition and hydrate dissociation condition are known which can be applied to control the condition in gas pipeline; pressure and temperature, to avoid hydrate formation.

(2) Gas hydrates not only give negative effect in oil and natural gas industry but also provide benefit. Hydrate formation is important for natural gas storage and natural gas transportation. Natural gas storage in hydrates has been investigated because hydrates store large quantities in a unit volume of solid phase of natural gas (~180 Sm^3/m^3 of hydrate) [16, 20]. Gudmundsson and Parlaktuna [7] showed that the hydrate can be stored at -15 °C under atmospheric pressure for 15 days and retaining almost all of the gas in their experiment. They also showed a significant cost saving about 24% for the transportation of natural gas in the form of hydrates compared to liquefied natural gas [16, 20]. Due to this hydrate formation advantage, this is the reason of studying several potential hydrate promoters as to compare which promoters provide more increment in hydrate formation rate and also result in longer duration of hydrate phase formation. In addition, there are several studies which have been reported that hydrate formation rate show a significant increased with the addition of surfactant molecules [13, 15, 30].

1.3 OBJECTIVE

The purpose of this project is to study the three phase equilibria, hydrate-water liquid-vapour (H-L_w-V), of simple methane (CH_4) hydrate and mixture of methane hydrate with hydrate promoters in pure water. Hence, two hydrates promoters, which are sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF), are chosen in the study to measure their potentials in enhancing methane hydrate formation. The influence of both hydrate promoters in escalating the equilibrium boundary or phase boundary of methane hydrate is the main interest in this study.

1.4 SCOPE OF STUDY

This study will produce several results regarding phase equilibria of simple methane hydrate and mixture of methane hydrate with promoters in the presence of pure water. Furthermore, the comparison between two potential hydrate promoters in enhancing equilibrium boundary of methane hydrate can be determined. Since the main focus in this study is toward the hydrate promoters' potential in promoting hydrate formation, the study about hydrate phase equilibria with promoters is important and can be obtained by learning the behaviour of hydrates as well as the hydrate promoters' physical and chemical properties. The project is planned and feasible to be done in a period of at most 8 months. The approach that will be used is by using laboratory testing and knowledge about the experimental method and the function of equipment use will also need to be learnt.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 PHASE EQUILIBRIUM

In a general definition, a phase is a region of material or always referred as state of matter which all physical properties throughout it are essentially uniform [22]. Several physical properties of a material are referred to density, index of refraction, and chemical composition. For example, this study is about measurement of three phase equilibria which the three phases involved are vapor; V, liquid water; Lw and solid hydrate; H.

Then, phase boundaries is related to the changes in the organization of matter, such as a change from liquid to solid or from solid to vapor [22]. Usually many compositions will form a uniform single phase when in equilibrium, however, depending on the temperature and pressure even a single substance may separate into two or more distinct phases. Inside each phase, the properties are uniform but between the two phases properties differ. For example, in the system consists of water and gas which forms a two phase system. Most of the water is in the liquid phase where it is held by the mutual attraction of water molecules. Even at equilibrium, molecules are constantly in motion and sometimes a molecule in the liquid phase gains enough kinetic energy to break away from the liquid phase and enter the gas phase [22]. Similarly, every once in a while a vapor molecule collides with the liquid surface and condense into the liquid. When achieve equilibrium, condensation and vaporisation processes are exactly balance and there is no net change in the volume of either phase [22]. This condition is known as phase equilibrium condition.

A diagram showing the various phases of a system is called a phase diagram. Phase diagram can be divided into four categories which are single component phase diagram, binary phase diagram, ternary phase diagram and multicomponent phase diagram. Binary phase diagram consists of two components in the system such as phase diagram for methane and water, refer Figure 2.1. The axis values in phase

diagram are usually pressure (P) and temperature (T). The phase diagram usually shows the pressure and temperature conditions for stable phases. In addition, phase equilibrium condition of two phase or multiphase is represented by phase equilibrium line in the phase diagram. Phase diagrams are useful for material engineering and material applications. From the phase diagram, scientists and engineers understand the behaviour of a system for one component or compounds. Therefore, hydrate phase equilibria measurements are very useful in the field of hydrate research and study.

The condition where liquid and vapor can both exist in equilibrium under certain temperature and pressure condition is similar to the condition where solid and vapor can coexist without any liquid present [22]. Solid and vapor phase equilibrium is represented as below equation:

$$s \Longleftrightarrow v$$
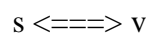
The double arrow indicates the conversions from solid to vapor which is sublimation process, and otherwise, from vapor to solid which is deposition process. These two processes occur at equal rates where there is no macroscopic change in the system [22]. The similar condition is also occurred in three phase equilibria; hydrate, liquid water and vapour (H-L_w-V), where there are four processes happen at equal rates. The four processes are sublimation process, dissociation process, vaporisation process and condensation process.
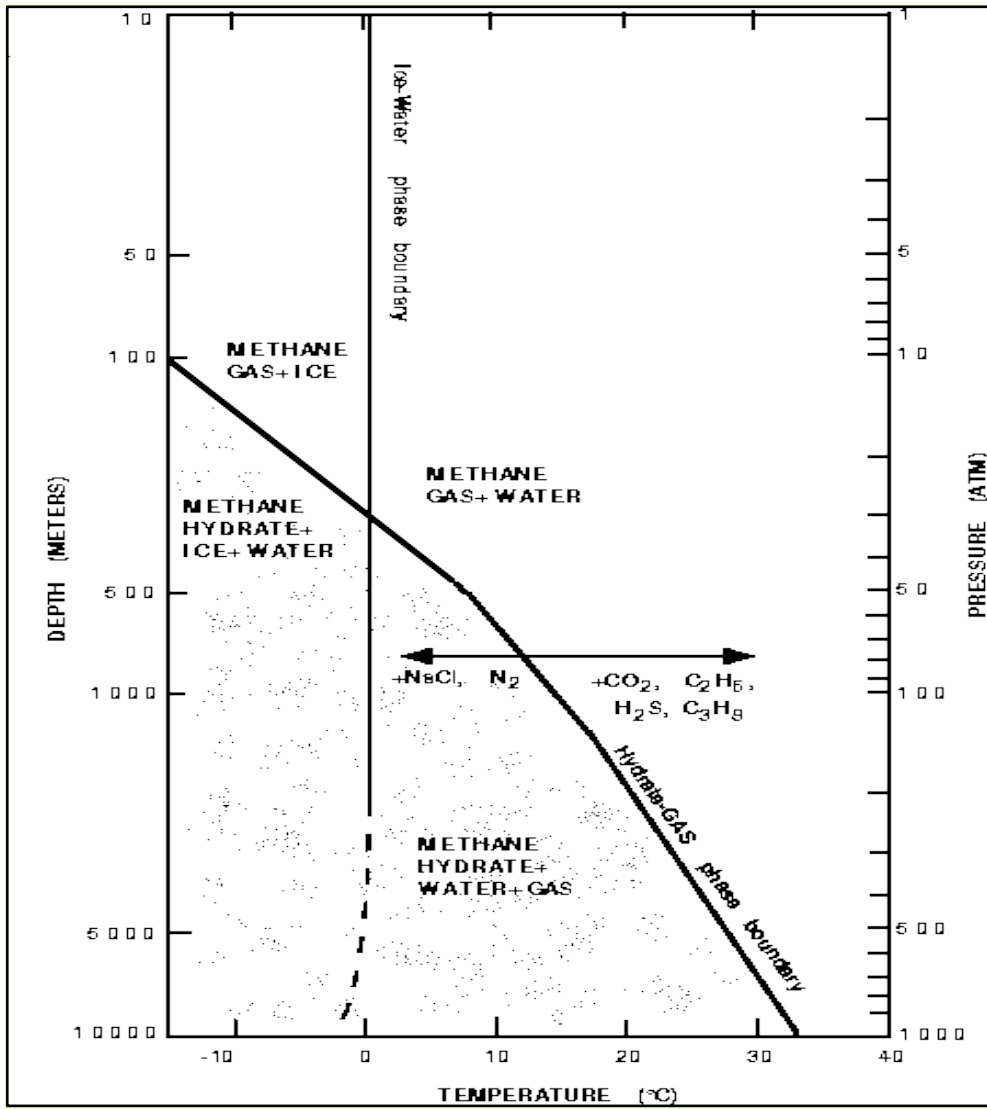
Figure 2.1: Phase diagram of methane and water, two components. *(Redrawn and Kvenvolden, 1993)*

2.2 GAS HYDRATE

Gas hydrates look similar to ice or pack of snow by physical appearance. However, hydrate's molecular structure and chemical properties are absolutely different from ice or snow. Natural gas hydrates are solids that form from a combination of water and one or more hydrocarbon or non-hydrocarbon gases. As mention earlier, water molecules are referred as host molecules while nonpolar and low molecular weight gas molecules indicate as guest molecules. Hydrate structure consists of the guest molecules that are "caged" within a crystal structure composed of host molecules which cause by hydrogen bonding between water molecules [1]. The inclusion of nonpolar gas molecules into the hydrate structure makes the structure stabilized. Therefore, hydrates can form at temperatures above the freezing point of liquid water which is 0°C (32°F) [19]. There are four main elements that influence hydrate formation which are temperature, pressure, water and hydrate guest molecules.
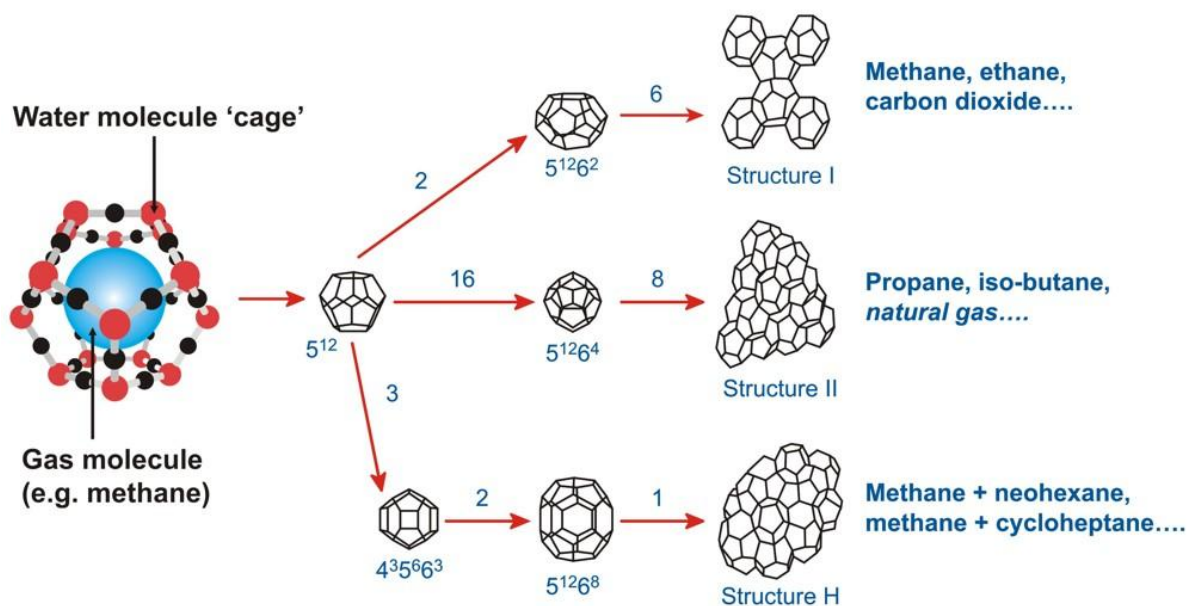
Figure 2.2: Hydrate structure I, II and H. *(Source from http://www.pet.hw.ac.uk/research/hydrate/hydrates_what.cfm)*

These are several natural gas that usually found in the hydrates formation which are methane, ethane, propane, iso-butane, butane, nitrogen, carbon dioxide, and hydrogen sulphide. Generally gas hydrates is typically dominated by methane. Each of this gas has different properties especially molecular sizes that will affect

structured of hydrate whether structure I (sI), structure II (sII), or structure H (sH). sI hydrates are the most commonly hydrate structure which encases small diameter molecules (0.40 - 0.55 nm) such as methane or ethane gas [1]. sII hydrates (0.60 – 0.70 nm) and sH hydrates (0.80 – 0.90 nm) accommodate larger guest molecules, typically propane or iso-butane for sII or combinations of methane gas and neohexane or cycloheptane for sH, but these both structures are less prevalent in nature [1].

While, same as guest molecules, water has different properties that affect hydrate formation. Actually water has four different coordination numbers and this factor will affect the cages and cavities size that will entrap the guest molecules to form hydrate. The temperature and pressure are depends on the hydrate guest molecules where each guest will form hydrate at different condition as shown in Figure 2.3. For example, at 5 MPa and 15°C, only ethane and hydrogen sulfide form hydrate.
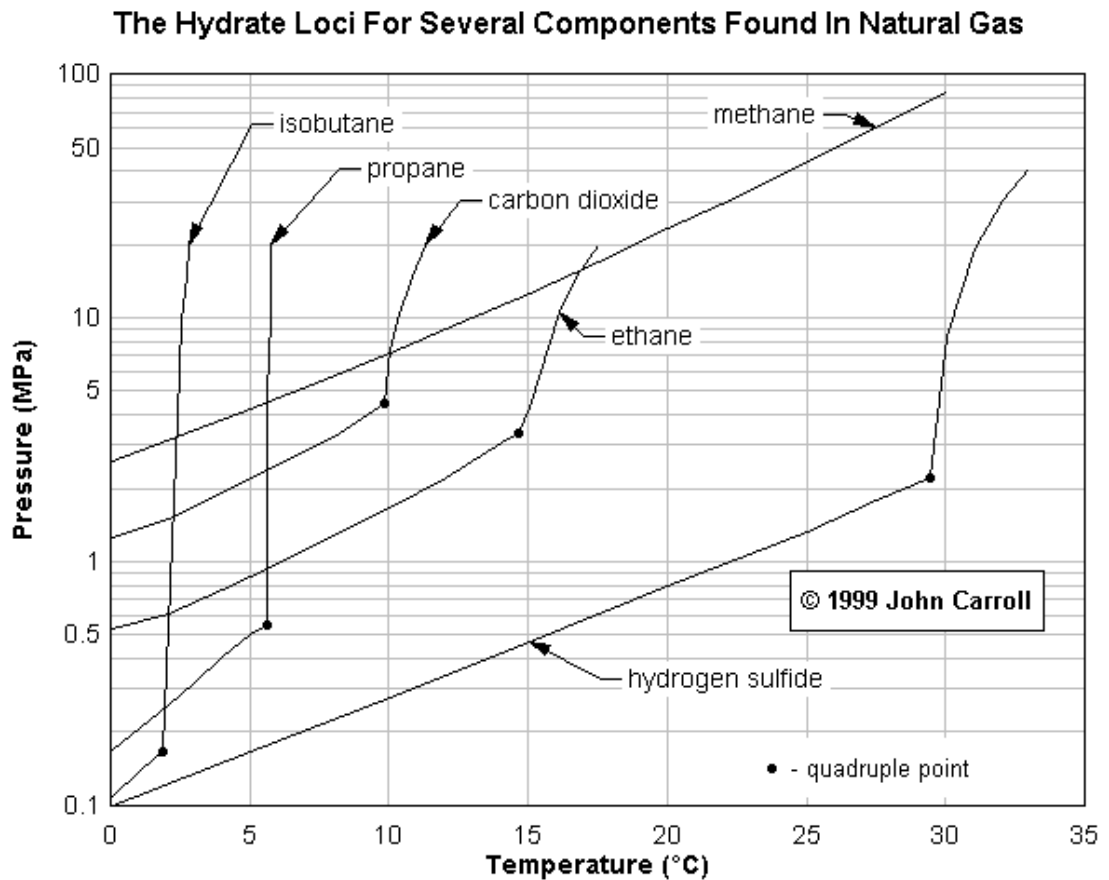
Figure 2.3: Hydrate phase diagram of several natural gas components. *(Source from http://www.telusplanet.net/public/jcarroll/HYDR.HTM)*

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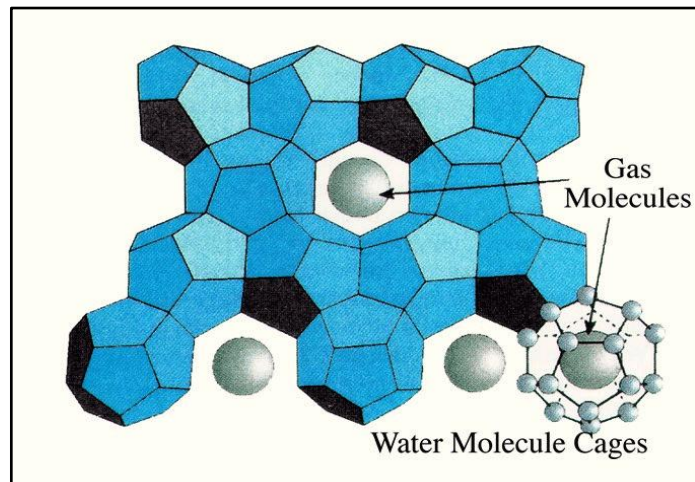
Figure 2.4: Cages that formed by water with gas molecules entrap within it. *(Source from http://dusk.geo.orst.edu/oceans/deep_currents.html)*

Although hydrate is a compound formed from water and gas but there are no chemical bond exists between the host and the guest as its bond together through weak Van Der Waals forces [1]. Van der Waals interactions between the trapped guest molecule and the surrounding water cage walls stabilize and support the individual polyhedra forming the hydrate lattice and restrict the translational motion of the guest molecule. Apart from above, unit cell of sI consists of 46 water molecules, forming two types of cages which are small and large. Unit cell of sII consists of 136 water molecules, forming also two types of cages; small and large. Unit cell of sH consists of 34 water molecules, forming three types of cages which are two small of different type and one huge.

2.3 HYDRATE PROMOTER

Other than the main four elements that influence hydrate formation which are temperature, pressure, water and composition of the gas mixture, the formation and dissociation of hydrates are also affected by the presence of different chemicals. There are some of chemicals that act as inhibitors, and some of other chemicals act as promoters. Hydrate formation with promoters for the function of natural gas storage and transport has been reported in some previous literature [8,25,27]. Without presence of hydrate promoters, practical applications of hydrate storage processes have been hindered by some problems, such as slow hydrate formation rate, limited amount of hydrate storage capacity, and the short duration of hydrate formation stability [19].

The reason of slow hydrate formation rate is there is volume of water that does not react with methane gas due to low solubility of methane gas in water [35]. Usually, only a thin film of hydrate is formed at the interface between water and methane gas. There are several approaches recommended by previous researchers in escalating solubility of gas in water where the methods can be divided into two; by mechanical methods and by chemical methods. The chemical method consists of hydrate promoters' application by using certain amount or concentration of thermodynamic or kinetic promoters. As a result, mass transfer between gas and liquid is enhanced and hydrate formation can be efficiently increased. One type of hydrate promoters is the surfactants which there are responsible for the rapid formation of hydrates under certain conditions [19].

The surfactant molecules give influence to hydrate formation process by escalating mass transfer and by reducing kinetic difficulties during hydrate formation [19]. Previously, several studies have been reported showing a significant increased in hydrate formation rate with the addition of surfactant molecules [13–15,30]. Zhong and Rogers [35] reported that the formation rates of gas hydrates in a static system can be escalated multiple times at above the critical micelle concentration (CMC) of water containing sodium dodecyl sulfate (SDS) or related surfactant. They found that the CMC of SDS for ethane and natural gas hydrate formation was approximately 242 ppm. Han et al. [11] investigated that the maximum gas hydrate formation for natural

gas achieved when the concentration of SDS was at 300 ppm in 90 wt % methane. Sun et al. [31] reported that the effect of a non-ionic surfactant on hydrate storage capacity is less pronounced compared to that of an anionic surfactant. Link et al. [17] determined that SDS is the best anionic surfactant for promoting methane hydrate formation. SDS has a potential to prevent hydrate particles from agglomerating and forming a rigid hydrate film in the liquid and gas interface that would hinder further hydrate formation.

Based on the present work, tetrahydrofuran (THF) which is cyclic ethers is used as a hydrate promoter that can greatly reduce the required hydrate formation pressure and enhance the corresponding kinetic rate [29]. Cyclic ethers have been generally known to form simple hydrates with water or mixed hydrates with low-molecular weight gases such as CO_2, CH_4 and N_2 [1]. In addition, THF forms structure II hydrate; sII, thus THF molecules only occupy the larger cages in the hydrate lattice. Zhang et al. [34] studied the gas hydrate formation of binary gas mixtures of H_2 and CH4 in the presence of 6 mol% tetrahydrofuran (THF). It resulted that the presence of THF in water drastically reduced the hydrate formation pressure of pure CH_4 and also the mixtures of H_2 and CH_4.

CHAPTER 3
METHODOLOGY

3.1 RESEARCH METHODOLOGY

3.1.1 Apparatus, Equipment and Materials

Apparatus and Equipment

Equipment that will be used for all planned experiment is Hydreval from Vinci Technologies, as shown in Figure 3.1. Hydreval is a based on motor driven PVT cell which is a comprehensive instrument designed to determine thermodynamic stability of hydrates in liquid phase and gas phase. The system allows three methods to detect hydrate formation which are increase of temperature, isobaric and increase of pressure, isothermal. The chamber is closed at one end of the piston and at the other end is cell head made of titanium alloy. The piston is equipped with a magnetic driven stirrer which provides homogenous agitation of fluid sample. In addition, all the parameters; pressure, cell-volume, and temperature can be regulated using a computerized visualisation. Table 1 below shows the main technical specifications of this equipment that need to be considered during planning and running the experiment. In addition, other apparatus utilized in this study is external pump which is used to pump gas and liquid into the sapphire cell.

Table 1: Main technical specifications of Hydreval equipment

Item	Type / model / specification
Volume capacity	Maximum volume capacity: ~ 80 cc
Operating pressure	Maximum: 200 Bar ~ 3000 psi
Operating Temperature	Option cooling system down to -60°C up to 175°C
Cell material	Titanium / sapphire
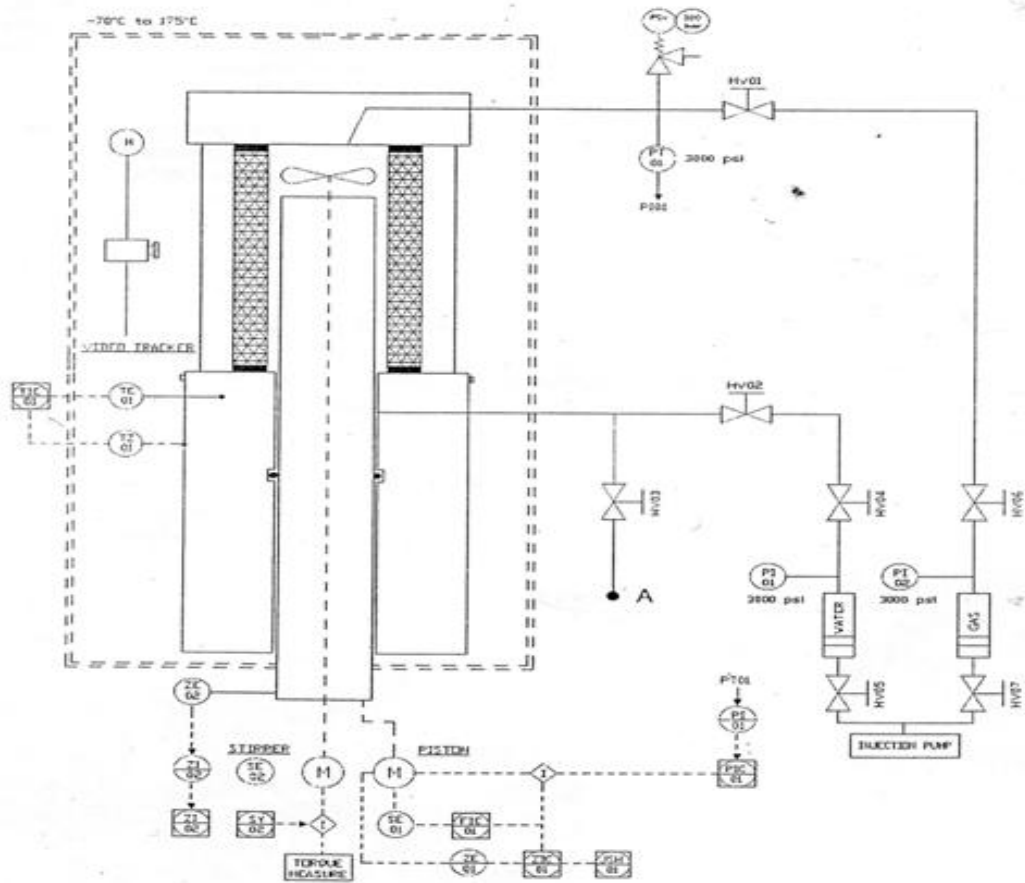
Figure 3.1: Schematic diagram of the experimental apparatus. (adapted from Hydreval Operation and Maintenance Manual, n.d)

Figure 3.2: Hydreval equipment

Figure 3.3: External pump

Figure 3.4: Gas inlet
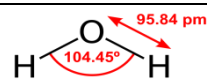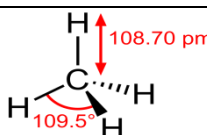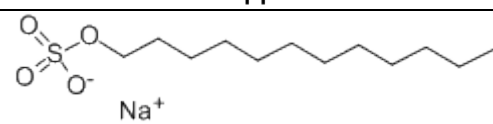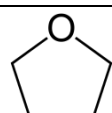
Figure 3.5: Liquid accumulator

Materials

The chemicals used in this work are distilled water (H_2O), methane (CH_4), sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF). All chemicals and their information are tabulated in Table 2. Methane gas, SDS and THF were used without any further purification. Methane (CH_4) was supplied by MOX-Linde Gases Sdn. Bhd. While pure (distilled) water is prepared in the UTP laboratory. The chemical that will be used as hydrate promoters are sodium dodecyl sulfate (SDS) and tetrahydrofuran (THF) which obtained from Avantis Laboratory Supply. Due to the usage of promoters at different concentrations, in term of weigh percentage (wt%), and part per million (ppm), the promoters were diluted with distilled water.

Table 2: Information of chemicals used in this work.

Component	Purity (%)	Phase	Chemical Structure
H_2O	Distilled	Liquid	
CH_4	99.90	Gas	
SDS	> 95.0	Solid	
THF	> 99.0	Liquid	

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3.1.2 Methodology

Flow chart below, Figure 4.1, shows the sequence of experiments that will be conduct to meet the objective of this project. First of all, verification test or control experiment of phase equilibria measurement for simple methane hydrate by using pure water need to be conducted since the results is used as reference for phase equilibria data of other hydrate mixture. After that, the project proceeds by performing several experiments of phase equilibria measurement for mixture methane hydrate with promoters. There are two experiments will be carried out for THF that are at two selected concentrations of THF; 5 wt% and 7 wt %. Similar to SDS, the experiments carry out using SDS will be at two different concentrations which are 300 ppm and 600 ppm. Every experiment which involved hydrate promoters were conducted at same experimental pressure.
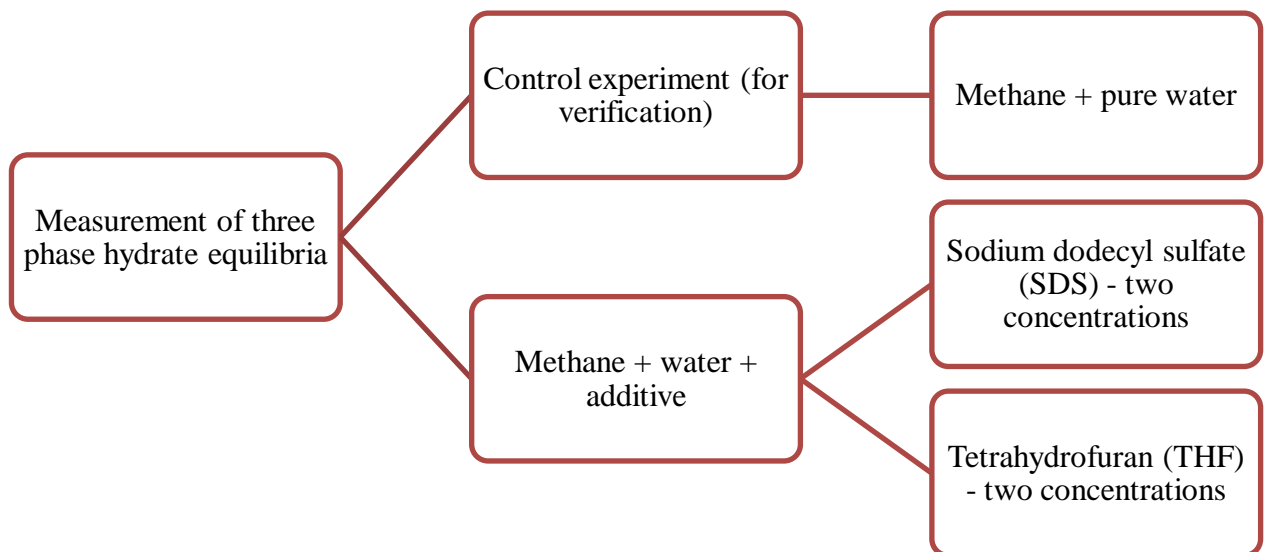
Figure 3.6: Experimental work flow chart

3.1.3 Sample Preparation

Primarily, stock solution of high concentration solution was prepared first. At 600 ppm concentration, 0.6 grams SDS was dissolved in 999.4 ml of distilled. For SDS, there are two concentrations that will be used in this study which are at 600 ppm and 300 ppm. Then, 600 ppm SDS stock solution was diluted with distilled water to produce 300 ppm concentration. Equation below is used to calculate volume of 600 ppm SDS solution required to be used for producing 300 ppm SDS solution concentration.

$$M_1V_1=M_2V_2 \qquad (1)$$

Where, M_1 is the concentration of stock solution and M_2 is the concentration of desired solution. In the meantime, V_1 is the volume of stock solution that will be used to produce desired concentration solution with V_2 volume. Then, the prepared solution that will be used in the test is filled into the liquid accumulator which this liquid will later be transferred into the sapphire cell by using the external pump. Thus, THF solution also prepared using the similar preparation method and calculation.

3.1.4 Measurement of Hydrate Equilibrium Point

The equilibria points of hydrate formation (H-Lw-V) were measured using isochoric method. The sapphire cell was then washed using distilled water and then vacuumed alternately for two rounds. 30 ml of promoter solution at desired concentration was injected into sapphire cell by using external pump. Then, the temperature was cooled down to 2-3 $^{\circ}$C above hydrate equilibrium. Afterwards, the cell was flushed with methane gas to ensure it was air free. While flushing, the stirrer was switched off to prevent solubility of methane in the aqueous solution. The methane gas was then supplied into the cell until the desired pressure is achieved.

After the temperature and pressure of the system remained constant, the stirrer was switched on at 504 rpm speed and the temperature was set to slowly decrease at rate 0.5°C per hour for obtaining the hydrate formation. This speed; 504 rpm is chosen as the stirrer speed due to the sufficiency of the stirring rate to remove the clathrate hydrate from gas-liquid interface. The hydrate formation in the vessel was detected by visual observation and every data was recorded for each reduced temperature. The temperature was then increased slowly to observe hydrate dissociation. As a result, a pressure-temperature diagram was obtained for each experiment conducted.

3.2 PROJECT ACTIVITIES

3.2.1 Key milestone

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┌─────────────────────────────────────────────────────────────────┐
│      Do research regarding project title and project objective    │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│      - Understanding the fundamental theories and concepts        │
│      - Performing a literature review on the topic                │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Identify the experimental procedures, equipments used, chemicals  │
│ used and changing parameters that will be test in the experiment  │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│      - Preparing for the extended proposal report                 │
│      - Performing literature review                               │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│   - Training using the equipment and familiarize with it function │
│   - Prepare for proposal defense                                  │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Perform verification test for obtaining control data (methane     │
│ hydrates with pure water)                                         │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Perform real phase equilibrium test of hydrate - methane with     │
│ pure water (varies at different esperimental temperature and      │
│ pressure)                                                         │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Perform phase equilibrium test of hydrate with two additives -    │
│ methane + water + each additive                                   │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Discuss the findings from the results obtained and make a         │
│ conclusion out of the study, determine if the objective has been  │
│ met                                                               │
└─────────────────────────────────────────────────────────────────┘
                                ▼
┌─────────────────────────────────────────────────────────────────┐
│ Compilation of all research findings, literature reviews,         │
│ experimental works and outcomes into a final report               │
│ (dissertation). Also prepare for oral presentation.               │
└─────────────────────────────────────────────────────────────────┘
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3.2.2 Gantt chart

| Project Activities	FYP 1							FYP 2						
	1-2	3-4	5-6	7-8	9-10	11-12	13-14	1-2	3-4	5-6	7-8	9-10	11-12	13-14
-Study and research on the topic -Study on hydrate phase equilibrium -Study on hydrates promoter	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
-Attend equipment training -Understand the experiment methodology process -Prepare chemicals that will be used (order from supplier if not available)					▓	▓	▓	▓						
-Plan for the experimental flow - Determine the pressure and temperature set value - Conduct the verification test using pure methane with pure water							▓	▓	▓					
- Run the experiment of methane hydrate with presence of promoter (SDS) - Run the experiment of methane hydrate with presence of promoter (THF)											▓	▓		
-Prepare for extended proposal report -Prepare for oral proposal defense -Work on interim report		▓	▓	▓	▓	▓	▓							
-Prepare for progress report -Prepare poster and technical paper - Prepare for viva -Work on dissertation										▓	▓	▓	▓	▓

CHAPTER 4
RESULT AND DISCUSSION

4.1 RESULTS AND DISCUSSIONS

Equilibrium Measurement of Pure Methane Hydrate

For verification experiment, pure methane was used together with pure water and the tests were conduct at four different experimental pressures and experimental temperatures. The starting experimental pressure and temperature were listed in the Table 3 below. Figure 4.1 shows temperature and pressure trace result from one of the test that had been carried out using pure methane. From pressure and temperature trace, hydrate formation and dissociation can be identified. Previously mention that all of the experiments in this study were conducted at constant volume condition and the temperature was set as the changing variable; neither methane gas nor water is added to the system during the experiment.

Table 3: Experimental pressure and temperature value for equilibrium measurement of pure methane hydrate.

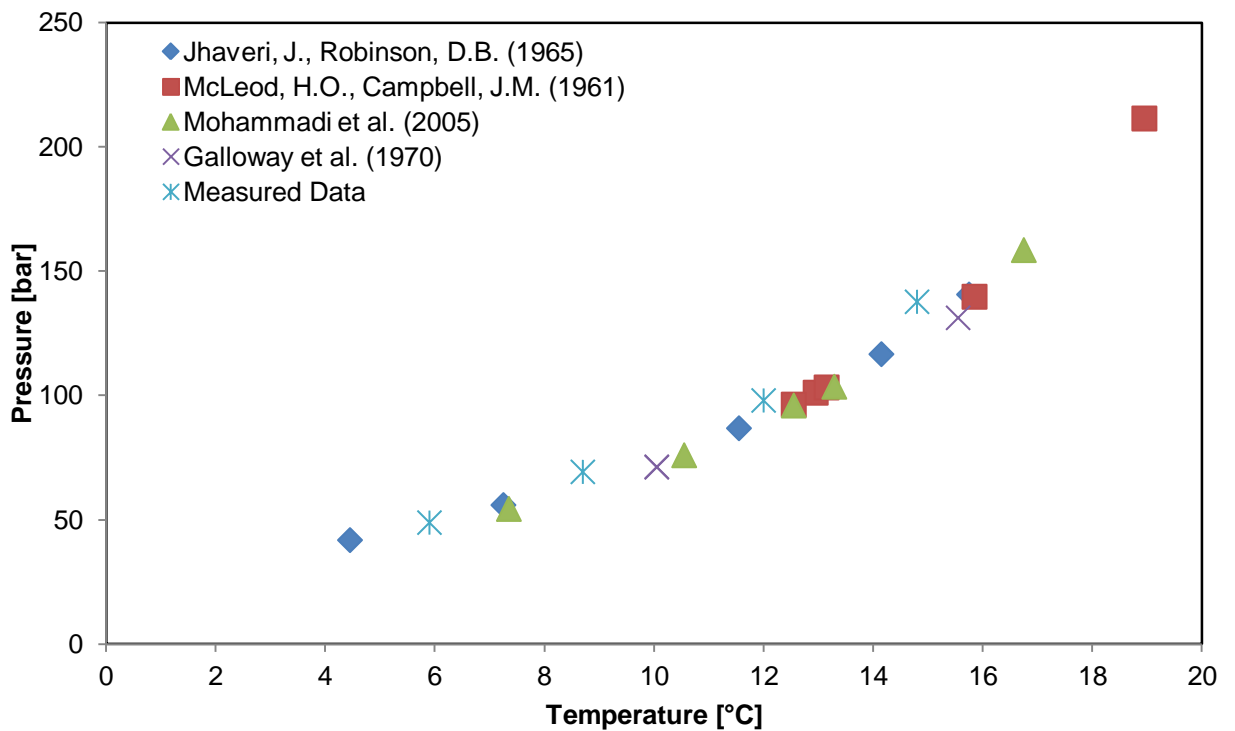| Experimental Pressure (bar)	Experimental Temperature (^{o}C)
138.9	16
100	14
70	12
50	8
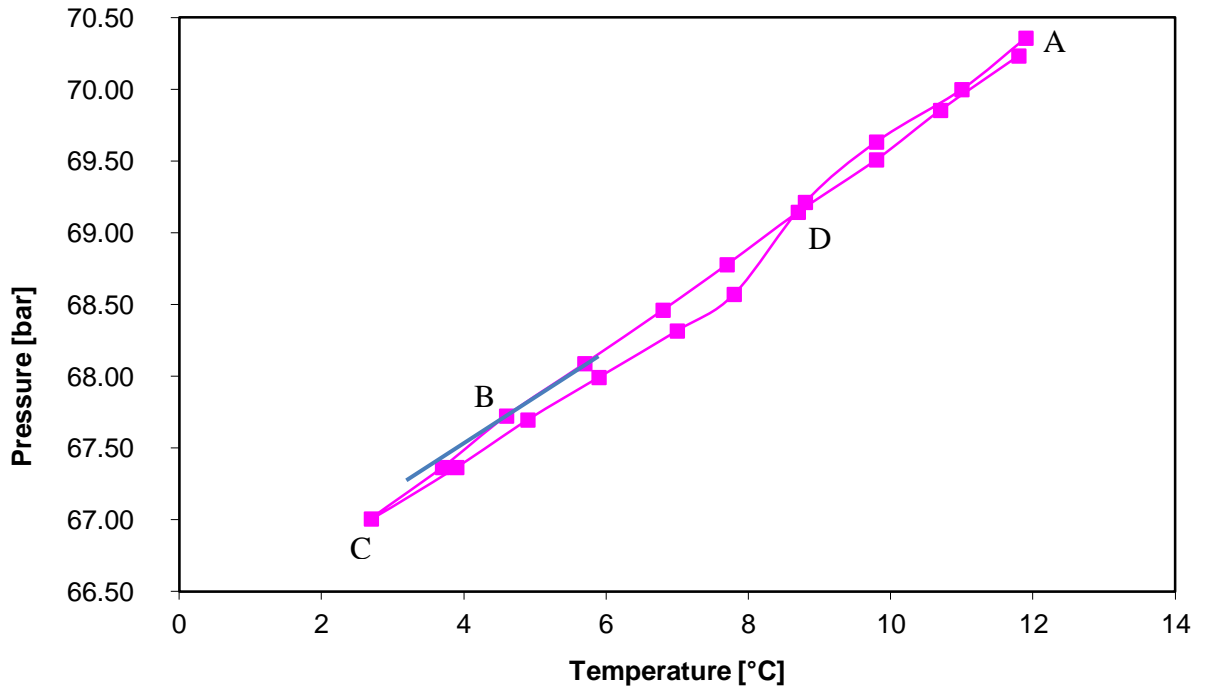
Figure 4.1: Pressure and temperature trace of pure methane with pure water at experimental pressure, 70 bar.

As the cell temperature is lowered, the pressure also decreased. This is due to gas contraction as well as increment of gas solubility upon cooling process at constant pressure. Point D from Figure 4.1 is the hydrate equilibrium point where the equilibrium pressure obtained is 69.14 bar and the equilibrium temperature is at 8.8°C. However, at this point, hydrate does not form because of metastability. Thus, the system pressure continues to decrease linearly with temperature for several hours until point B without obtain any hydrate formation and this distance from A to B is called as induction period.

At point B, hydrates begin to form. The pressure drop should be steep at region B to C as it is the hydrate growth period. During this period, sudden pressure drop occur since a lot of gas molecules trap into host molecules and form hydrates. Hydrate dissociation begins when the cell was heated from point C where temperature increased back, thus the system pressure also increased. At first the pressure decreased slowly and then rapidly along steep dissociation line; from point C to D. Lastly, at point D the hydrates are completely dissociated. The temperature and pressure where the hydrate phase totally disappears is taken as the phase
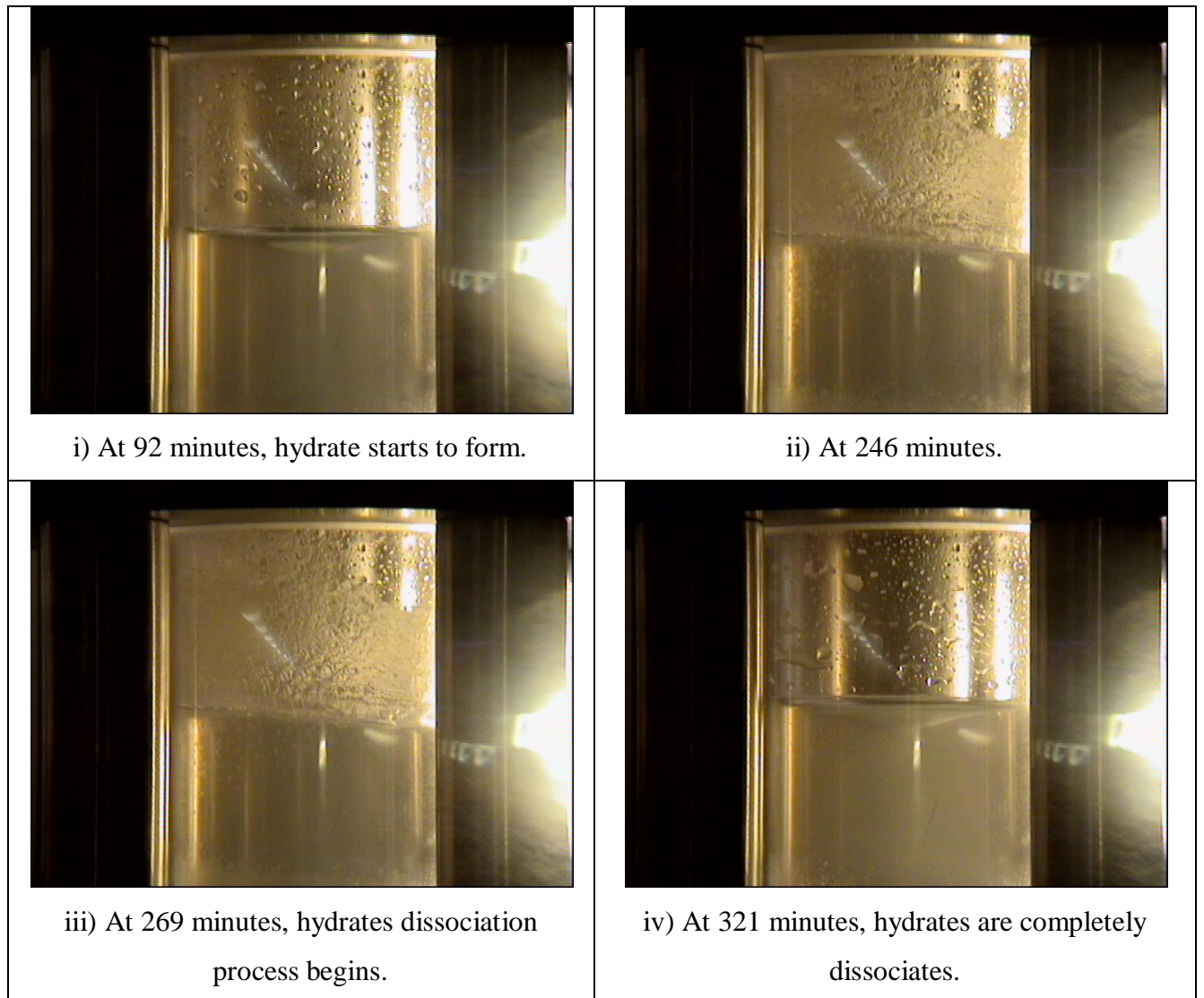
23

equilibrium temperature and phase equilibrium pressure. Therefore, point D was the hydrate equilibrium condition. This was also confirmed by the picture of the cell recorded by Hydreval every one minute.

As a result from the four equilibrium measurement tests, methane hydrate phase equilibrium line is attained and comparison is made with the data from several previous literatures. As shown in Figure 4.2, the H-L$_w$-V data indicate that the verification experiment concurred with several previous literatures review. Hence, the methodology used and the experiment conducted using Hydreval equipment is valid to be used in this study and the result attained can also be compared to other hydrate research study.

Figure 4.2: Three phase hydrate equilibria diagram of pure methane with water.

i) At 92 minutes, hydrate starts to form.	ii) At 246 minutes.
iii) At 269 minutes, hydrates dissociation process begins.	iv) At 321 minutes, hydrates are completely dissociates.

Figure 4.3: Hydrate formation at equilibrium pressure 69.14 bar.

*Methane Hydrate with Promoters (Hydrate Formation Thermodynamic)*

Methane hydrate equilibrium measurement experiments with both hydrate promoters were conducted at same experimental pressure for every experiment which was 137.56 bar. This pressure was selected due to observe the performance of both promoters at high pressure condition. The hydrate formation thermodynamic is considered by plotting pressure versus temperature or also known as pressure and temperature trace diagram as shown in Figure 4.4, Figure 4.5, Figure 4.7 and Figure 4.8.

Figure 4.4 and Figure 4.5 show pressure and temperature trace diagram at different concentration of sodium dodecyl sulfate (SDS); 300 ppm and 600 ppm respectively. The sudden drop of pressure after induction time was obviously recorded. Several researchers understand that the major function expected from methane hydrate promoting agent is to improve the solubility of the hydrate forming gas in water [17]. They observed that above critical micelle concentration (CMC) of SDS which is an anionic surfactant, the solubility of methane increases while at surfactant concentration below or around CMC, the gas solubility remains similar to that of pure water.

From this study, SDS performance were observed and the results were plotted in Figure 4.6, which display the effect of different SDS concentrations towards methane hydrate equilibrium temperature at same experimental pressure, 138.9 bar. CMC of a surfactant solution generally defined as the concentration of surfactant above which micelles are spontaneously formed [35]. The surface tension between water and methane gas are decreases as the surfactant concentration increase up to the CMC. Then, the surface tension reduction is not significant above CMC concentration. Lower surface tension between water and methane gas indicates that the solubility of methane gas in the water higher, thus promotes the methane hydrate formation. CMC of a surfactant solution depends on temperature, pressure and nature of the hydrate forming gas.

Based on Figure 4.6, by adding 300 ppm of SDS concentration, the equilibrium temperature is slightly increased, approximately 3°C increment,

compared to the equilibrium temperature of pure methane. This proved that SDS only gave a small effect in terms of thermodynamic hydrate which involved methane hydrate formation and dissociation as it shift the equilibrium temperature slightly higher. From previous study, SDS which is an anionic surfactant shows more significant effect in kinetic hydrate by escalating hydrate formation rate and also hydrate storage capacity [13,14,35].
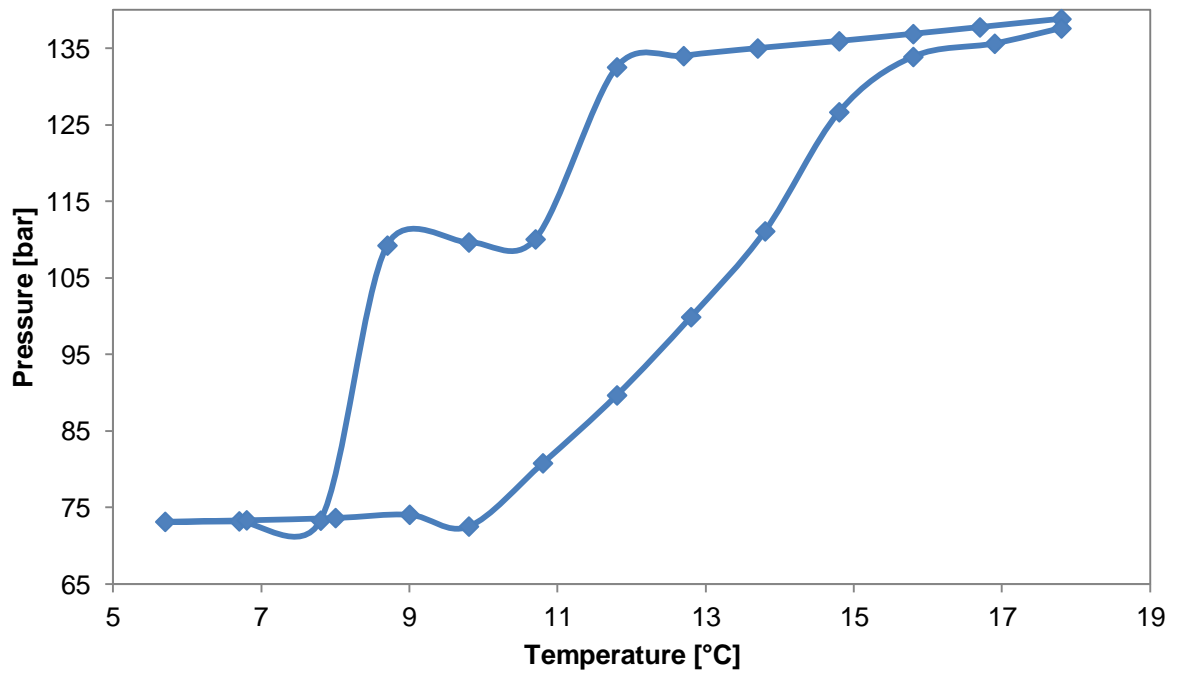
Figure 4.4: Pressure and temperature trace of methane with SDS at 300 ppm concentration.
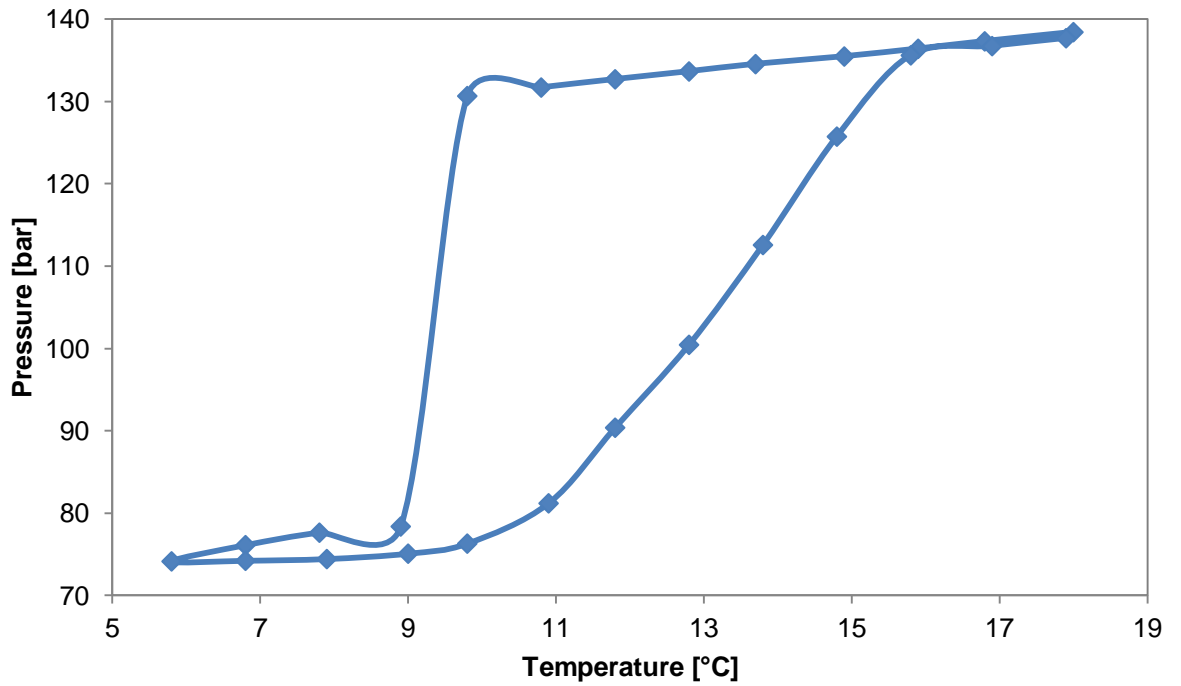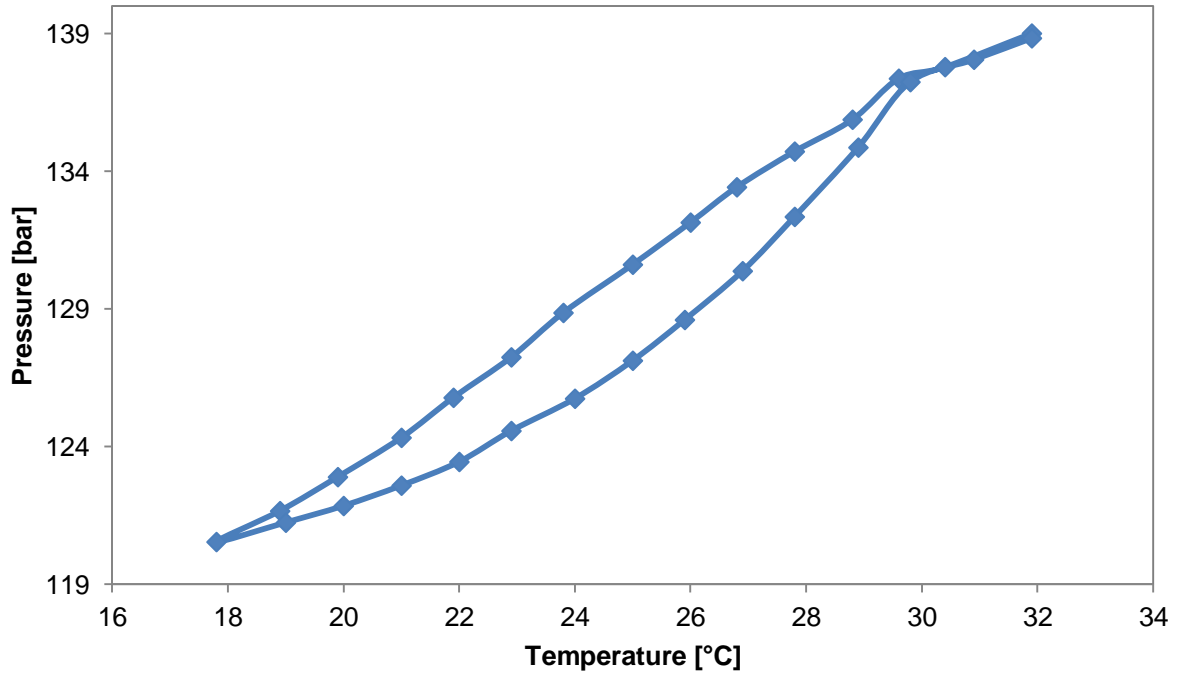
Figure 4.5: Pressure and temperature trace of methane with SDS at 600 ppm concentration.
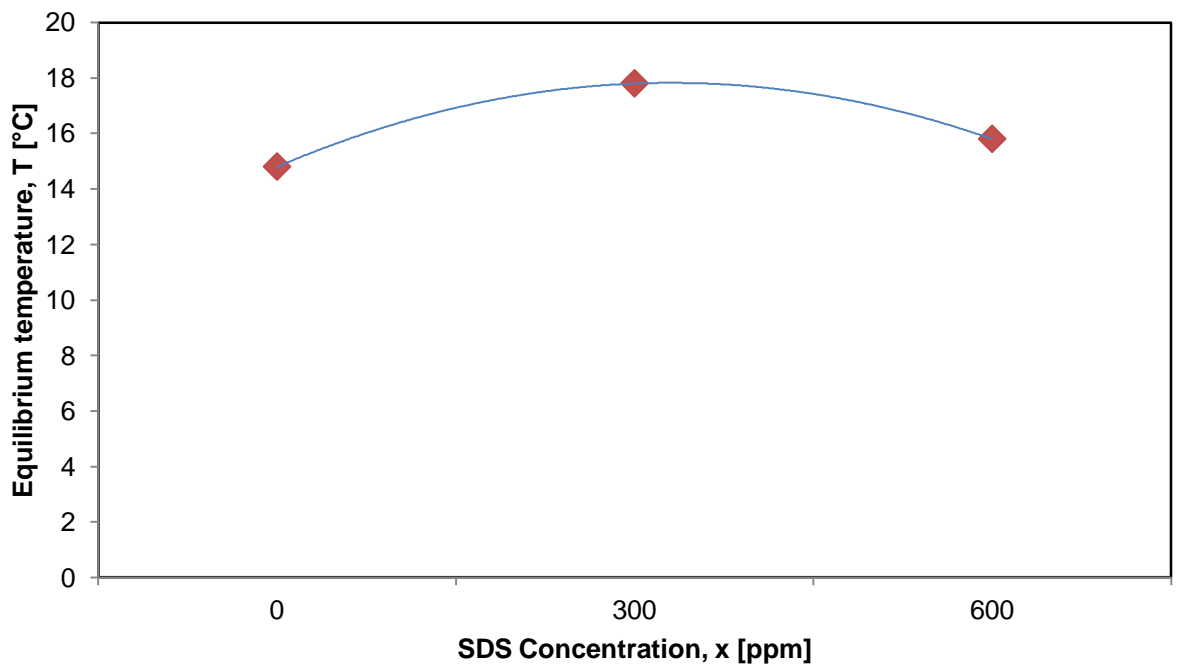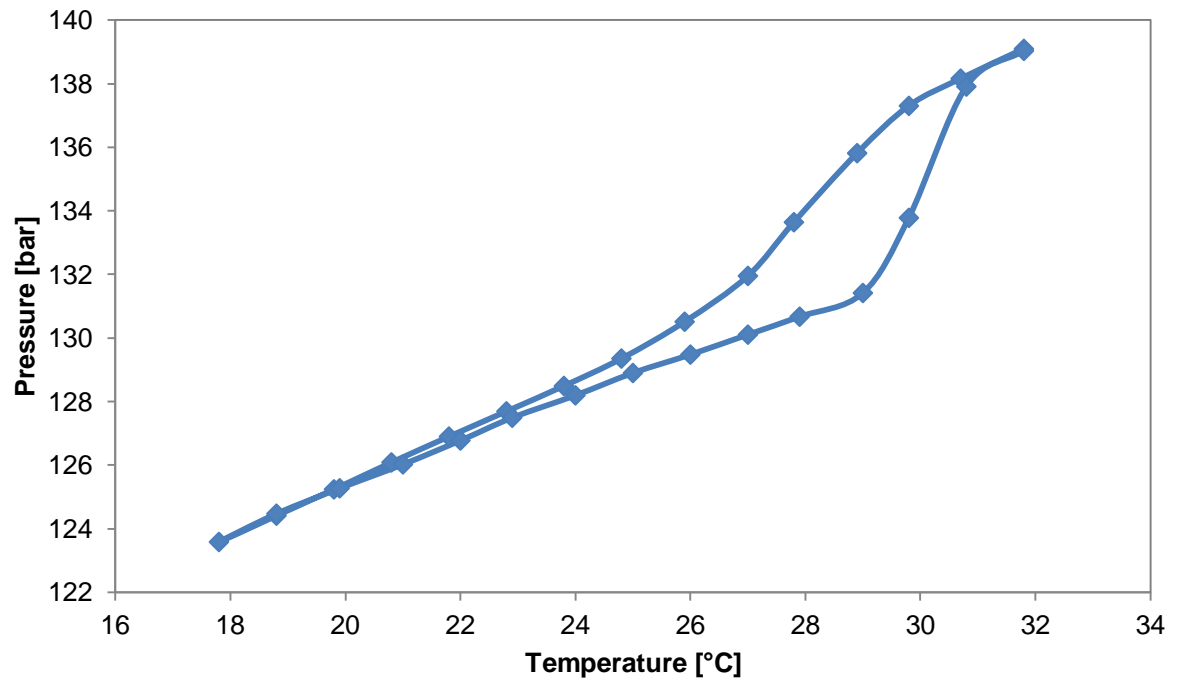

Figure 4.6: Performance of different SDS concentrations towards methane hydrate equilibrium temperature at constant pressure, 137.56 bar.

Hydrate equilibrium data for the ternary system of methane, tetrahydrofuran (THF) and water with 5 wt% and 7 wt% of THF in the aqueous solution are shown graphically and compared in Figure 4.9 with the binary system of methane and pure water. Similarly, the performance of THF in methane hydrate also showed the promotion of hydrate formation. However, compared to SDS, THF resulted a remarkable increase of equilibrium temperature than in the pure methane hydrate. From Figure 4.9, the equilibrium temperature increased from 14.8°C to 30.4°C at 5wt%, which is about 15.6°C increment.

The three phase equilibrium line (H-L$_w$-V) of single gas component system such as methane with presence of a soluble promoter; THF, is dependent on the pressure or temperature and concentration of the promoter in the hydrate forming systems. As represented in Figure 4.9, the addition of small amount of THF into water did give significant effect towards hydrate-water liquid-vapour (H-L$_w$-V) equilibria line by expands the hydrate stability region to higher temperature at same pressure. In contrary with general hydrate formation condition; hydrate forms at low temperature and high pressure, the increment of equilibrium temperature indicates that hydrate can be form at higher temperature. This observation confirms that the presence of tetrahydrofuran in the system increased the stability of the hydrate phase. However, take into account that the promotion effect of THF can shifts to inhibition effect at certain THF concentrations. This effect occurs due to the formation of hydrogen bond between O atom in THF molecule with water molecule as the THF concentration increase.

Figure 4.7: Pressure and temperature trace of methane with THF at 5 wt% concentration.

Figure 4.8: Pressure and temperature trace of methane with THF at 7 wt% concentration.
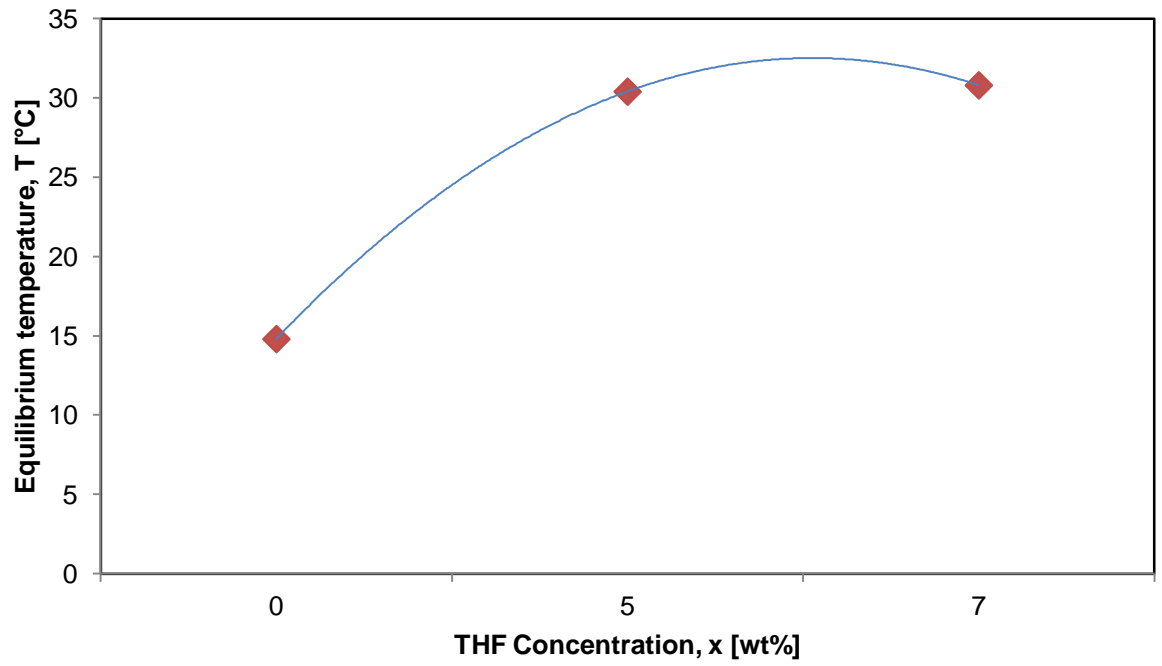
Figure 4.9: Performance of different THF concentrations towards methane hydrate equilibrium temperature at constant pressure, 137.56 bar.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The purpose of this project was to obtain phase equilibrium data on simple methane hydrate and comparison of methane hydrate equilibrium condition with difference type of promoters in the presence of pure water. The major focussed of this study is to analyze the influence of hydrate promoters towards the hydrate equilibrium boundary and also in sustaining the hydrate stability region. There are two promoters that are used in this project which are tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS), thus, comparison of each promoter's capability can be determined.

The effect of two different concentrations sodium dodecyl sulfate (SDS) towards methane hydrate three phase equilibira (H-L_w-V) were observed at same pressure, 138.9 bar. The results of two different SDS concentrations; 300 ppm and 600 ppm were compared with pure methane. According to the results obtained, by adding 300 ppm of SDS concentration, the equilibrium temperature is slightly increased, approximately 3°C increment than the equilibrium temperature of pure methane. Therefore, it is verified that SDS only showed a small effect in terms of methane hydrate formation and dissociation thermodynamically. Furthermore, based on the previous study regarding surfactant hydrate promoters, most of the finding resulted that anionic surfactant did increased the rate of hydrate formation and also improve hydrate storage capacity [13,14,35]. Thus, SDS which is an anionic surfactant shows more significant effect in kinetic hydrate formation by escalating hydrate formation rate and also increase hydrate storage capacity.

The three phase equilibria (H-L_w-V) of methane hydrate was largely shifted to higher temperature conditions by the addition of tetrahydrofuran (THF). Based on the results, the increment of equilibrium temperature is about 15.6^{o}C with the introduction of THF in the aqueous solution by only 5wt% concentration. Hence, THF was confirmed to act as a hydrate promoter and able to extend the stability

region of clathrate hydrates. Moreover, it was observed that the promoting effect of tetrahydrofuran is concentration dependent.

5.2 RECOMMENDATION

Continuous and further researches about hydrate phase equilibrium are required in order to develop deep understanding of the subject matter. More experimental work by testing more different concentration of hydrate promoters can be conducted to generate more reliable result and to find the most optimum concentration for the promoter used in escalating methane hydrate formation rate. Further research about mixture of methane hydrate phase equilibrium with promoters is required as a continuous to this project since this project only covered the thermodynamic effect of promoters towards methane hydrate formation. In addition, several other promoters also can be analyze in the future study as to make comparison which promoters are more potential in escalating rate of hydrate formation and also sustain more longer hydrate formation duration. Different type of surfactants including anionic and non-ionic can be analyzed in promoting hydrate formation. Furthermore, modelling work on methane hydrate with promoters can also be a part of study in the future. The result from the simulation can be compared with the experimental result, so that more information can be obtained and better understanding on the study is attained. The aim of future work is to provide more information that can be used for practical application. New findings are extremely crucial in leading the project to a success.

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