

**Experimental Investigation of Gas Hydrate Phase Boundary In The Presence Of  
Ethylene Glycol**

by

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**13794**

Dissertation submitted in partial fulfillment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Chemical)

MAY 2014

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# CERTIFICATION OF APPROVAL

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Approved by,

---

(Dr Bhajan Lal)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

**MAY 2014**

## CERTIFICATION OF ORIGINALITY

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

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FAIEQAH BINTI ZAINAL ABIDIN

## ABSTRACT

The gas hydrate-liquid water-vapor (H-L<sub>w</sub>-V) equilibrium conditions of multicomponent gases i.e. Synthetic Natural Gas A (SNG-A) and Synthetic Natural Gas B (SNG-B) in which both have high concentration of carbon dioxide, CO<sub>2</sub> i.e. approximately 69% are measured. In addition, the hydrate-phase equilibrium in the presence of thermodynamic inhibitor of ethylene glycol at 10 wt. % and 20 wt. % is also investigated at 30 to 60 bar range of pressure. Experimental results showed that the gas hydrate equilibrium conditions were shifted to the inhibition region in accordance with the increased ethylene glycol concentration. Comparison of experimental temperature suppression caused by the addition of ethylene glycol with the results predicted by commercially used gas hydrate software, CSMGem showed slight deviation. Further study on the modeling calculations of gas hydrate equilibrium conditions is recommended to get better predictions of gas hydrate equilibrium conditions.

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## **ABBREVIATIONS AND NOMENCLATURES**

CSMGem – Colorado School of Mines Gibbs Energy Minimization

H-L<sub>W</sub>-V – Hydrate-liquid water-vapor phase

MEG – Methyl ethylene glycol

SNG-A – Five components gas mixture

SNG-B – Seven components gas mixture

Wt. % – weight percent

# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND OF STUDY

Natural gas hydrates are crystalline solid composed of gas molecules and water. They exist at conditions of low temperature and high pressure. There are several types of gas hydrates structures. The formation of different types of natural gas hydrates structures depend on the guest molecules trapped inside the water cages.

In the oil and gas industry, the pipeline systems of natural gas are in conditions of thermodynamically favoring the formation of gas hydrates. This leads to the formation of gas hydrates inside the pipeline system and hinder the transport system of natural gas. Eventually, the formation of gas hydrates which are solid can plug the transmission lines and cause flow assurance failure. Concerns on production arise as it impacted significant economic risks in the gas and oil industry as the production is stopped and the dissociation of gas hydrates sometimes takes as long as months.

The petroleum industry would like to maintain their processes outside of the hydrate stability range. There are several methods of gas hydrate mitigation which are chemical, hydraulic, thermal and mechanical processes methods. Of all these, gas hydrate inhibitor has been widely implemented in industry to combat gas hydrate formation since the gas transmission lines unavoidably exist in gas hydrate temperature and pressure stability range.

Generally, there are two types of gas hydrates inhibitor; thermodynamic inhibitor and kinetic inhibitor. Thermodynamic inhibitor works by shifting the hydrate equilibrium curve to the hydrate stability region; by which it lowers the temperature and increases the pressure of hydrate stability formation. Several types of thermodynamic inhibitors are hydrogen bonding fluids like alcohols and glycols, and electrolyte solutions. Ethylene

glycol is a hydrogen bonding fluid and is widely used as thermodynamic hydrate inhibitor.

Also the content of gas molecules inside natural gas plays a role in the formation of gas hydrates. Different composition of gas can form different types of gas hydrates that can likely behave thermodynamically different. Extensive researches are done to study the effects of thermodynamic inhibitors towards gas hydrate stability temperature and pressure range in order to identify the optimal amount of thermodynamic gas hydrate inhibitor to avoid formation of gas hydrates.

## **1.2 PROBLEM STATEMENT**

Formation of gas hydrate in oil and gas pipelines results in flow assurance failure. Consequently, stoppages of costly production occur and thus raise concern on significant economic risks of oil and gas industry, and also on the safety thereof due to a pressure build up impacted from gas hydrate formation inside the pipelines.

Gas hydrates equilibrium curve hydrate-liquid water-vapor (H-L<sub>W</sub>-V) is much affected by the gas composition. Different gas composition yields different gas hydrate equilibrium curve H-L<sub>W</sub>-V. There are only few literatures that discussed on gas hydrate equilibrium curve of multicomponent gases especially with high concentration of CO<sub>2</sub>. This project is carried out in order to gather data of H-L<sub>W</sub>-V for multicomponent gases and those of high concentration of CO<sub>2</sub>.

The inhibition method using chemical as thermodynamic inhibitor shows prominent result in the industry. This method is efficient but limited by the large quantities of inhibitors implemented which is 60 wt%. Besides, the additives are difficult to recover from water. Hence, the effective range of concentration of ethylene glycol as inhibitors that can shift the equilibrium temperature of gas hydrate stability is determined.

### **1.3 OBJECTIVES**

1. To determine the efficiency of ethylene glycol by determining the gas hydrate equilibrium curve H-L<sub>w</sub>-V.
2. To compare experimental equilibrium curve of multicomponent gas hydrates of high CO<sub>2</sub> concentration with prediction results from commercially used gas hydrate software, CSMGem.

### **1.4 SCOPE OF STUDY**

The scope of study for this project revolves mainly on laboratory experiments in which the gas hydrate stability curve of two types of multicomponent gas that have high CO<sub>2</sub> composition are measured using the T-cycle step-heating method in the presence of ethylene glycol as thermodynamic inhibitor.

The effect of ethylene glycol on gas hydrate stability curve by means of temperature suppression was observed. The experiment to study the gas hydrates stability curve in the presence of ethylene glycol are be observed based on:

- I. Different weight percent of ethylene glycol
- II. Different pressure of gas injected
- III. Composition of gas injected
- IV. Shifting of the gas hydrate stability curve

Further simulation study using CSMGem gas hydrates software to predict the gas hydrate stability conditions is conducted. The experimental results are then compared with the data obtained from the simulation study.

### **1.5 RELEVANCY AND FEASIBILITY**

This project is a continuation study of different types of thermodynamic inhibitors such as methanol and electrolytes towards different types of gas in the lab. Thus, with the

availability of chemicals needed and apparatus and previously achievable experiment method, this project is feasible within the time frame of final year project.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 GAS HYDRATES

Natural gas hydrates are solid, non-stoichiometric compounds of small gas molecules and water (Sloan, 2003). Gas hydrates usually forms at conditions of low temperature and high pressure. The typical range of the temperature and pressure of gas hydrates formation are less than 300 K and more than 0.6 MPa respectively (Makogon & Cieslewicz, 1981; Sloan, 2003).

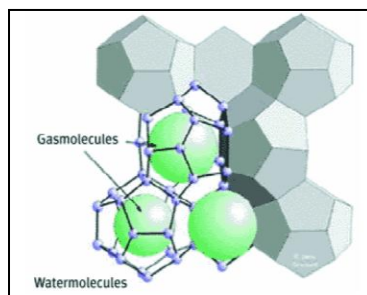


Figure 1: Crystalline solid of gas hydrate ("Dynamics of gas hydrates in polar environment," 2008)

As illustrated in Figure 1, the water molecules are usually termed as host cavities or cage while the gas molecules termed as guest molecules (Chatti, Delahaye, Fournaison, & Petitet, 2005; Koh et al., 2002; Sloan, 2003).

##### 2.1.1 Gas Hydrates Structures

(Koh et al., 2002; Sloan, 2003) state that gas hydrates can exist in several structures which are cubic structure I, cubic structure II and hexagonal structure H. Basically, the two most common naturally occurring gas hydrates are structure I and structure II (Koh et al., 2002).

The structure of the gas hydrates is determined by the size of the “guest” molecules and the composition of the gas mixture. Typical gas molecules that combined with water molecules to form gas hydrates are methane, ethane, propane, carbon dioxide

and hydrogen sulfide (Koh et al., 2002; Sloan, 2003). Figure 2 illustrates the three common hydrate unit crystal structures according to their respective guest molecules.

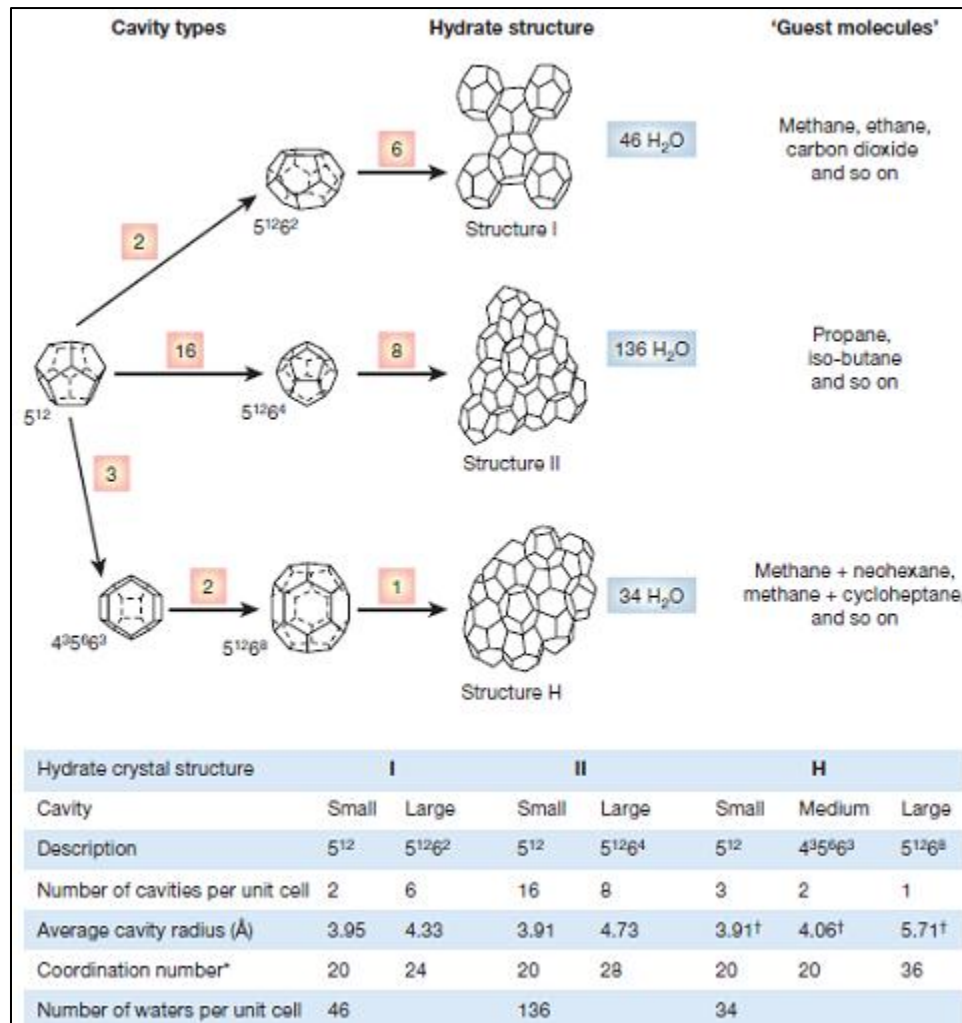


Figure 2: The three common hydrate unit crystal structure (Sloan, 2003)

Small guest molecules like methane, ethane and propane form structure I gas hydrates, whereas larger molecules like butane, iso-butane form structure II gas hydrates. Even larger molecules like iso-pentane and neohexane form structure H gas hydrates in the presence of a help gas like methane (Sloan, 1998). For mixtures of gases, the equilibrium hydrate structure is sensitive to the gas composition (Subramanian, Kini, Dec, & Sloan Jr, 2000). As mentioned in “Evidence of Structure II Hydrate Formation from Methane + Ethane Mixtures” by (Subramanian et al., 2000), a CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub> mixture

containing as little as 1% C<sub>3</sub>H<sub>8</sub>, is predicted to form structure II hydrate compared to pure CH<sub>4</sub> which forms structure I hydrate.

Usually in gas hydrate formation studies, macroscopic quantities like pressure, temperature and fluid phase compositions are measured whereas gas hydrate-phase properties such as structure type, cage occupancies, and guest composition, are predicted using models that are based on the theory of van der Waals and Platteeuw (1959). However, studies conducted by (Saito, Marshall, & Kobayashi, 1964) shows there have been instances where a model has been fit to and subsequently used to predict the wrong hydrate structure. Extensive researches to combat the shortcomings of the predictions found that Raman and NMR are two very powerful spectroscopic methods that can be used to obtain structural and compositional information about the solid hydrate phase (Subramanian et al., 2000).

### **2.1.2 Drawbacks of Gas Hydrates**

Early in 1934, Hammerschmidt discovered that natural gas hydrates are responsible for blocking gas pipelines (Koh et al., 2002; Wu, Wang, & Liu, 2007). In his own research article entitled Formation of Gas Hydrates in Natural Gas Transmission Lines, (Hammerschmidt, 1934) states that the presence of water vapor in natural gas has always been a source of trouble to the natural gas industry in the measurement and transportation of the gas. Due to the liquefaction and subsequent freezing of water within the system leads to the formation of solid matter which usually resembles ordinary snow in appearance. The movement of the gas through the pipelines tends to collect and compress the snow at low spots until the line may become entirely plugged. Figure 3 shows gas hydrates formation in pipelines.





Figure 3: Gas hydrates formation in pipelines ("Gas hydrates stability,")

Thermodynamic conditions favoring gas hydrate formation are often found in pipelines. Gas transmission pipelines usually operate at low temperature and high pressure. This phenomenon of gas pipeline plugging due to gas hydrates is a crucial encounterment in oil and gas industry since this problem leads to production stoppages which results to substantial economic risks. Not only that, the plugging of the pipelines raises concern on the safety hazards to personnel and damages of production equipment. Due to the pressure build up at the region before the gas hydrate formation, the pipelines can burst and blow off (Farzaneh-Gord, Rahbari, Bajelan, & Pilehvari, 2013; Koh et al., 2002; Sloan, 2003; Wu et al., 2007). Hence, this explains on the concern on safety hazards and damages of production equipment.

## 2.2 PHASE BEHAVIOR OF GAS HYDRATES FORMATION

Since the formation of gas hydrates is known to cause plugging of pipelines in oil and gas industry, extensive researches on gas hydrate are done. Prevention of hydrate formation has become an important matter (Wu et al., 2007). In order to study the thermodynamic effect of the inhibitors towards gas hydrate system, the phase behavior of gas hydrates formation need to be understood.

The crystalline structure of solid gas hydrate crystals has a strong dependence on gas composition, pressure and temperature (Makogon & Cieslewicz, 1981). Different

guest molecules have different range of phase behavior but mostly around the same range of low temperature below 300 K and high pressure of range more than 0.6 MPa. The size of the lattice cavities greatly influences the phase diagrams of hydrates and the predicted thermodynamically stable structure (Lundgaard & Mollerup, 1992).

To understand the phase behavior and stability of gas hydrates in the large range of temperature and pressure, and the phase equilibrium of hydrate systems with inhibitors, an accurate thermodynamic model is needed.

### **2.2.1 Multicomponent gas hydrates with high concentration of CO<sub>2</sub>**

Presence of high concentrations of CO<sub>2</sub> and H<sub>2</sub>S along with other components is often found in natural gas, often referred as sour gas; thereby limiting the accurate functioning of several of the available phase behavior models. The major limitation for their inaccuracy can be attributed to the complexity involving CO<sub>2</sub> and H<sub>2</sub>S in hydrate systems (Mekala & Sangwai, 2014).

Carbon dioxide and hydrogen sulfide are very soluble in water and thermodynamically form clathrates individually or in combination with natural gas at relatively higher temperatures and lower pressures when compared to those that have lower concentration of CO<sub>2</sub> and or H<sub>2</sub>S. Therefore, sour gas readily forms hydrates and stays stable at such higher temperatures and lower pressures. These conditions are mostly prevalent in most important commercial oil and gas transmission lines from production facilities and hence cause plugging, corroding the pipelines and causing other flow assurance related issues as mentioned previously (Mekala & Sangwai, 2014).

Predictions of formation and dissociation conditions for these hydrates are necessary in applications for preventing such hazards, primarily due to the blockages of pipelines. Phase equilibrium of gas hydrates are therefore necessary for developing mitigation techniques to resolve the gas hydrates flow assurance failure in oil and gas transmission pipelines.

## 2.3 INHIBITION OF GAS HYDRATES

Considering the significant economic risks in the oil and gas industry and concerns on safety hazards towards personnel on site due to pressure build up at the region before the gas hydrate formation that can lead to pipe blast and damages of production equipment, extensive researches to mitigate gas hydrate occurrence is done.

Generally, there are four main processes investigated to combat hydrate formation and ensure regular flow inside gas transmission pipelines. They are chemical, hydraulic, thermal and mechanical processes (Chatti et al., 2005; Li et al., 2011).

The chemical method, which can be used either to prevent or remove plugs, consists in injecting additives in the pipe that act differently on hydrate agglomeration according to whether the inhibitors are thermodynamics, kinetic or dispersant. Thermodynamic inhibitors work by shifting the equilibrium temperature in order to enable gas hydrate crystallization at different temperature and pressure than the pipelines thermodynamic conditions. New generations of inhibitors i.e. kinetic and dispersant, work in ways of slowing down gas hydrate crystal growth and prevent hydrate agglomeration respectively.

Secondly, the hydraulic removal method is based on the dissociation of the gas hydrate plug by depressurization. This method is suitable given the porous structure of the gas pipelines plugs. It is not suitable for liquid hydrocarbons, since pressurization induces its vaporization.

Thirdly, the thermal method consists in delivering locally a heat flow towards the plug through the pipe wall in order to raise the system temperature above the hydrate formation point. This method is only applicable for external pipelines and not for subsea equipment.

Last but not least, a mechanical method, such as pipeline pigging can be used to prevent hydrate plugs. Pipeline pigs are inserted into the pipe and travel throughout the pipeline driven by product flow. These projectiles then remove the obstacles or deposits they encounter.

Despite all these processes, pipeline blockages caused by gas hydrate remains a concern in the oil and gas industry. Since the flow assurance management is critical to successful and economic operation of oil and gas production system (Mokhatab, Wilkens, & Leontaritis, 2007), ongoing research is still being conducted in this field. The selection of an optimal method involves taking into account the type of products (gas, liquid hydrocarbon or crude oil) transported. Sometimes several processes can be combined to destroy plugs more efficiently, for instance, chemical inhibitors can be used in conjunction with a mechanical removal method. Thus, in order to find the optimal method for specific cases, all inhibition methods need to be tested. From the result of the tests, the highest and promising method in consideration to several factors such as economic and feasibility of the approach is taken as the inhibition method.

### **2.3.1 Ethylene Glycol – Thermodynamic Inhibitor**

According to (Li et al., 2011), under many circumstances, from the four methods of gas hydrates inhibition, injecting inhibitors are the only feasible choice. Chemicals that lie under the category of thermodynamic inhibitors are alcohols, glycols, or inorganic salts. These thermodynamic inhibitors are one kind of inhibitor studied widely. For many years, in industrial practice in order to prevent hydrate related risks, injection of thermodynamic hydrate inhibitors has been implemented at the well head commonly methanol or mono-ethylene glycol (Cha et al., 2013).

These additives thermodynamically destabilize the gas hydrates and effectively shift the hydrate equilibrium phase boundaries to the temperature and pressure conditions that are unfavorable for gas hydrate formation in pipelines. Specifically, the inhibitors have a significant effect on water and consequently reduce the activities of water to the lower values. Generally, the thermodynamic inhibitors having strong electrostatic charges or bonding to water molecules through hydrogen bonds have the function of inhibition (Li et al., 2011).

Ethylene glycol is also known as mono ethylene glycol (MEG) or 1-2, ethanediol ("Draft Assessment for ethylene glycol," 2013). According to (Hemmingsen, Burgass, Pedersen, Kinnari, & Sørensen, 2011), ethylene glycol is less volatile and less soluble in

liquid hydrocarbons compared to methanol; the other frequently used thermodynamic hydrate inhibitor. Therefore, less ethylene glycol is lost to the hydrocarbons phases than methanol. Ethylene glycol also offers the advantages of which it can be effectively reclaimed, regenerated and recycled for continuous injection. Generally, ethylene glycol is over-preferred compared to the other heavier glycols i.e. diethylene glycol (DEG) and triethylene glycol (TEG) since on a weight basis, ethylene glycol is more efficient and has a lower impact on the viscosity of the water phase compared to the heavier glycols.

As discussed by (Cha et al., 2013) in their work on thermodynamic and kinetic hydrate inhibition performance of aqueous ethylene glycol solutions for natural gas, two hydroxyl groups of ethylene glycol as shown in Figure 4, form hydrogen bonds with multiple water molecules and keep water molecules from forming gas hydrate cages.

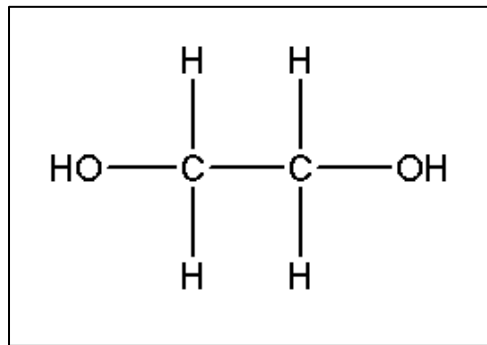


Figure 4: Ethylene glycol formula

As the concentration of the ethylene glycol is increased, the chemical potential of aqueous phase decreases result in shifting of hydrate equilibrium curve conditions to lower temperature and higher pressure.

Figure 5 depicts the ternary gas hydrate equilibrium conditions in the presence of typical thermodynamic inhibitors i.e. methanol and electrolytes. In the presence of methanol and electrolytes the gas hydrate equilibrium conditions is shifted to the left i.e. to lower temperatures. As the concentrations of the inhibitors are increased, the temperatures continue to decrease and the pressures ascend. And the gas hydrate equilibrium conditions moves further from the pipelines equilibrium condition.

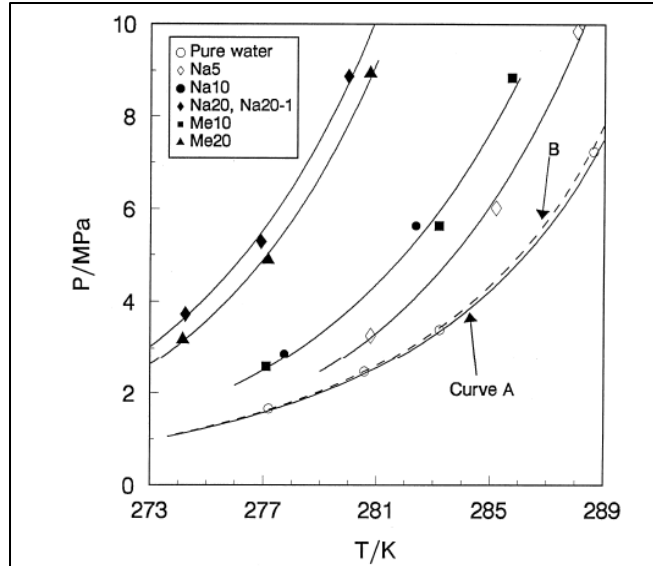


Figure 5: Ternary gas mixtures hydrate equilibrium conditions (Bishnoi & Dholabhai, 1999)

According to (Chatti et al., 2005), type of products transmitted in the pipelines affect the selection of optimal gas hydrate inhibition method. Hence, different types of gas i.e. multicomponent gas, binary or ternary mixture of gas result in different equilibrium conditions in both the absence and presence of inhibitors. As presented in Figure 5 and Figure 6 for ternary gas mixtures and natural gas mixtures respectively, both gases are tested with different type of thermodynamic inhibitors and their equilibrium conditions differ accordingly to their components of gas.

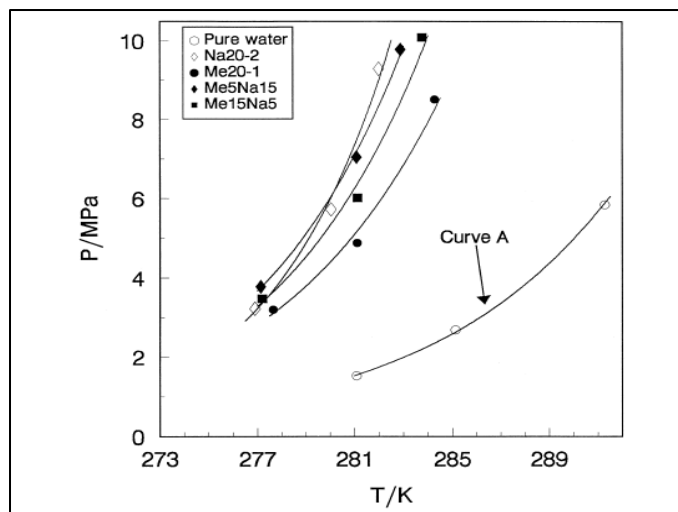


Figure 6: Natural gas mixtures hydrate equilibrium conditions (Bishnoi & Dholabhai, 1999)

Ethylene glycol is one of the thermodynamic inhibitor for gas hydrate formation that has been extensively studied on. There are several literatures that publish and discuss on the effective concentration of ethylene glycol in shifting the thermodynamic equilibrium to lower region so as gas hydrate would not form at the equilibrium condition of the oil and gas pipelines.

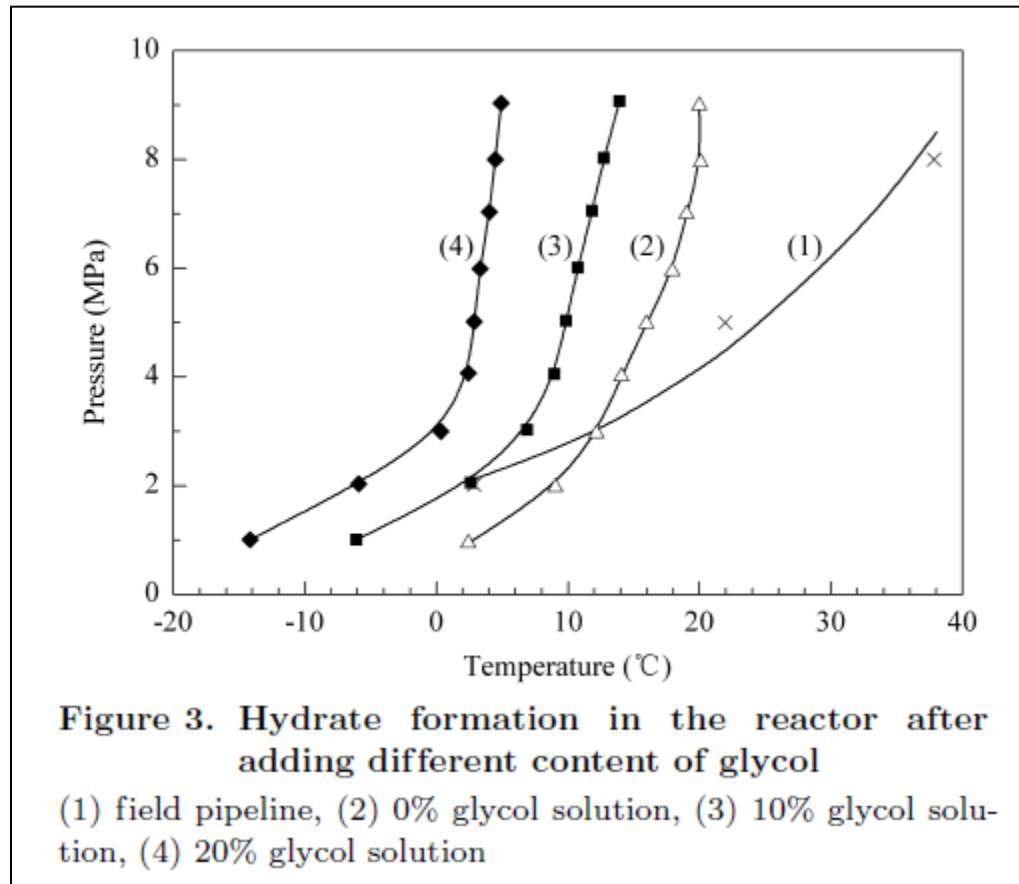


Figure 7: Gas hydrate equilibrium conditions in the presence of ethylene glycol (Wu et al., 2007)

Figure 7 shows the experimental results from literature by (Wu et al., 2007). The plots of pressure against temperature in the presence of different concentration of ethylene glycol are depicted. As expected, the thermodynamic equilibrium condition is shifted to the left in the presence of ethylene glycol. From the experiment conducted by (Wu et al., 2007) using natural gas, introduction of 10 wt% of ethylene glycol is enough to shift the equilibrium condition of natural gas hydrate from the pipeline equilibrium condition.

The concern when using thermodynamic inhibitor as a mean of gas hydrate mitigation method is that the thermodynamic inhibitors especially alcohols and glycols are limited by the large quantity of additives implemented which is 60 wt%. Moreover, they are difficult to recover from water (Chatti et al., 2005). This will contribute to economic costs since the inhibitors need to be continuously supplied (Li et al., 2011). Hence, an effective and optimal concentration needs to be determined so that the mitigation process is not only feasible but also economical in practice.



# CHAPTER 3

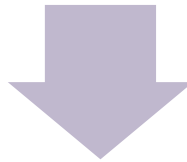
## METHODOLOGY

### 3.1 RESEARCH METHODOLOGY

In order to carry out this project, a sequence of research methodology is planned to ensure the project runs well and accordingly. The flow chart below denotes the research methodology planned for this project conduction.

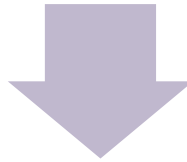
#### **Experimental Study**

- To conduct preliminary experiment works i.e. preparing solutions of various concentration of ethylene glycol
- To conduct experiment to study phase behavior of SNG-A and SNG-B multicomponent gases in the presence of different concentration of ethylene glycol



#### **Simulation Study**

- To predict gas hydrate equilibrium conditions of multicomponent gases; SNG-A and SNG-B in the presence of specified ethylene glycol concentrations i.e. 10 and 20 wt. % using CSMGem software



#### **Data Collection, Results and Discussion**

- To collect data of SNG-A and SNG-B gas hydrates equilibrium conditions at different weight percent of ethylene glycol
- To plot the data of temperatures and pressures into Pressure vs Temperature graph
- To analyze the hydrate equilibrium curve of different conditions (i.e. different weight percent of ethylene glycol) by comparing the experimental results with results from commercially used gas hydrate software, CSMGem

### 3.2 MATERIALS

This project emphasizes on studying the equilibrium conditions for hydrate formation of multicomponent gases that especially have high concentration of CO<sub>2</sub>, in the presence of ethylene glycol. There are two types of multicomponent gas that are studied in this project, namely SNG-A and SNG-B with each has five and seven different components respectively. The different components of SNG-A and SNG-B multicomponent gases are tabulated in the table below.

Table 1: Chemicals used in this project

Gas	Components / Quantity	Supplier
SNG-A	Propane Ethane Nitrogen Methane Carbon Dioxide	Air Products Singapore Pte. Ltd.
SNG-B	Butane Iso-butane Propane Ethane Nitrogen Methane Carbon dioxide	Air Products Singapore Pte. Ltd.
Ethylene glycol	10 wt%	Merck
	20 wt%	
De-ionized water	25 cc $\approx$ 1.388 mol H <sub>2</sub> O	-

Ethylene glycol alone is specifically selected as thermodynamic inhibitor to be studied towards these two multicomponent gas hydrates stability with two different weight percent i.e. 10 and 20 wt%.

### **3.3 EXPERIMENTAL EQUIPMENT**

The experimental equipment, hydrate cell as shown in the figure is composed of several parts. They are high-pressure equilibrium cell, constant temperature air bath, pressure increase system, temperature and pressure test system and data acquisition system. The main part of the experimental setup is the high pressure equilibrium cell with a 60 cm<sup>3</sup> fixed internal volume and maximum operating pressure of 20 MPa. This equilibrium cell is made of sapphire equipped with double sight glasses for visual confirmation of hydrate formation and disappearance. The equilibrium cell temperature is immersed in a thermostatic where temperature of the thermostatic bath is controlled by circulating ethanol by means of thermostat and through flow cooler. A platinum temperature probe inserted in the cell interior is used to measure the temperature of the system. The pressure is measured by pressure transducer. A data acquisition system is used for recording the system pressure and temperature throughout the experiments.

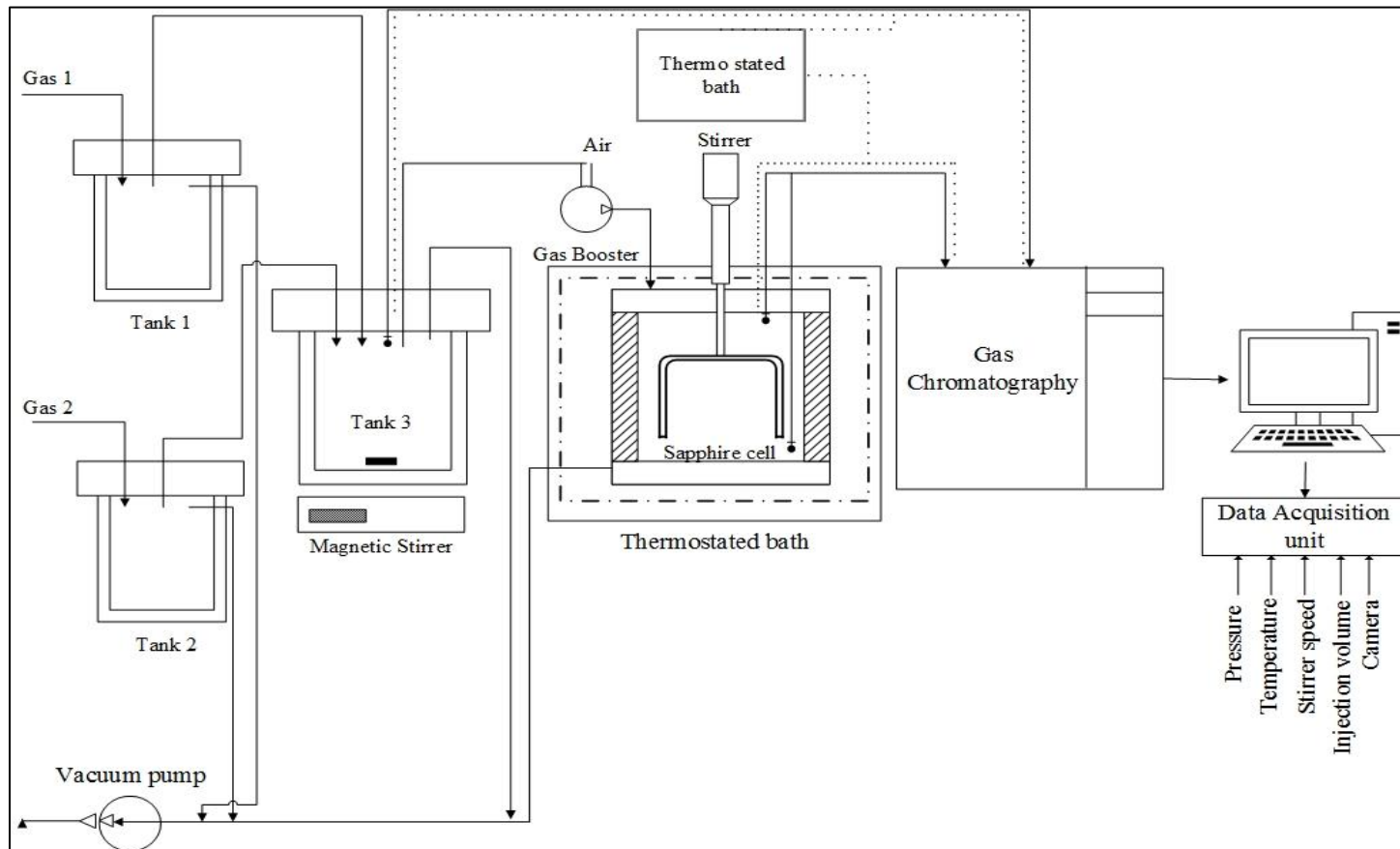


Figure 8: Typical schematic diagram of the hydrate equilibrium cell

### 3.4 EXPERIMENTAL PROCEDURES

1. The gas hydrate equilibrium cell is well-cleaned and then evacuated with vacuum pump.
2. Prepared aqueous solutions containing the known concentrations of inhibitor (ethylene glycol) is introduced into the cell.
3. The pressure of the cell is increased to the desired pressure, initially 30 bar, by introducing the gas (SNG-A or SNG-B).
4. Following the isochoric-search method (Tohidi, Burgass, Danesh, ØStergaard, & Todd, 2000), the temperature is slowly decreased at a rate of 0.5 K/min until hydrate formation in the cell is detected by pressure drop and confirmed by visual observation.
5. The temperature is later increased in steps at slow rate of 0.2 K/ min.
6. After complete decomposition of existing gas hydrate in the cell, the point at which the slope of pressure-temperature plot changes sharply is considered as the hydrate dissociation point.
7. The temperature and pressure of the equilibrium cell are recorded using the data acquisition unit every 5 s.
8. The experiment is then repeated by increasing the pressure to 40, 50 and 60 bar consecutively.

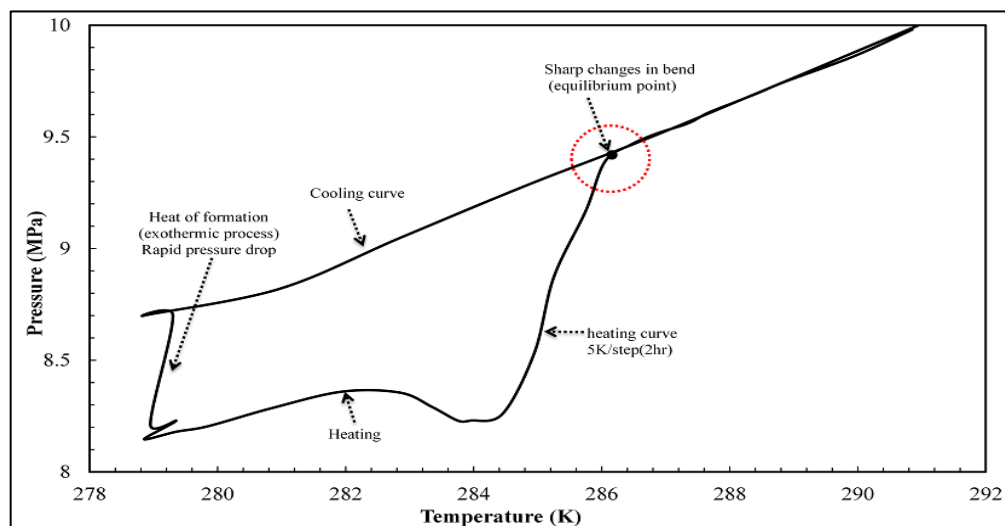


Figure 9: Achieving gas hydrate equilibrium point through isochoric method

### 3.5 SIMULATION STUDY

From the dissociation points obtained through experimental work, simulation study using CSMGem, software-generated models is conducted to get predictions of gas hydrate equilibrium temperatures at the same pressure range and to assess the applicability of the current model.

### 3.6 COMPARISON OF EXPERIMENTAL AND PREDICTIONS DATA

#### 3.6.1 Average Absolute Deviation ( $AAD^T$ )

Comparison between experimental data and prediction data of both G5 and G7 gas hydrates equilibrium in different aqueous phase conditions are done by calculating the errors between both of the values at specified pressure ranges. Average Absolute Deviation ( $AAD^T$ ) for each aqueous phase conditions is then calculated and tabulated.

Given below are the formulas to calculate the errors and  $AAD^T$ :

$$Error = \left| \frac{T_{prediction} - T_{experimental}}{T_{prediction}} \right|$$

$$AAD^T = \frac{1}{np} \left| \frac{T_{prediction} - T_{experimental}}{T_{prediction}} \right|$$

Where;  $T_{prediction}$  = Temperature from CSMGem prediction

$T_{experimental}$  = Temperature from experimental work

$np$  = number of points

#### 3.6.2 Suppression Temperature Caused by the Presence of Ethylene Glycol

To investigate the inhibition effect caused by the addition of ethylene glycol, the experimental and predictions temperature suppression from the normal gas hydrate equilibrium conditions to the different concentrations of ethylene glycol are calculated. The values are then compared and analyzed.

### 3.7 PROJECT ACTIVITIES, GANTT-CHART AND KEY MILESTONES

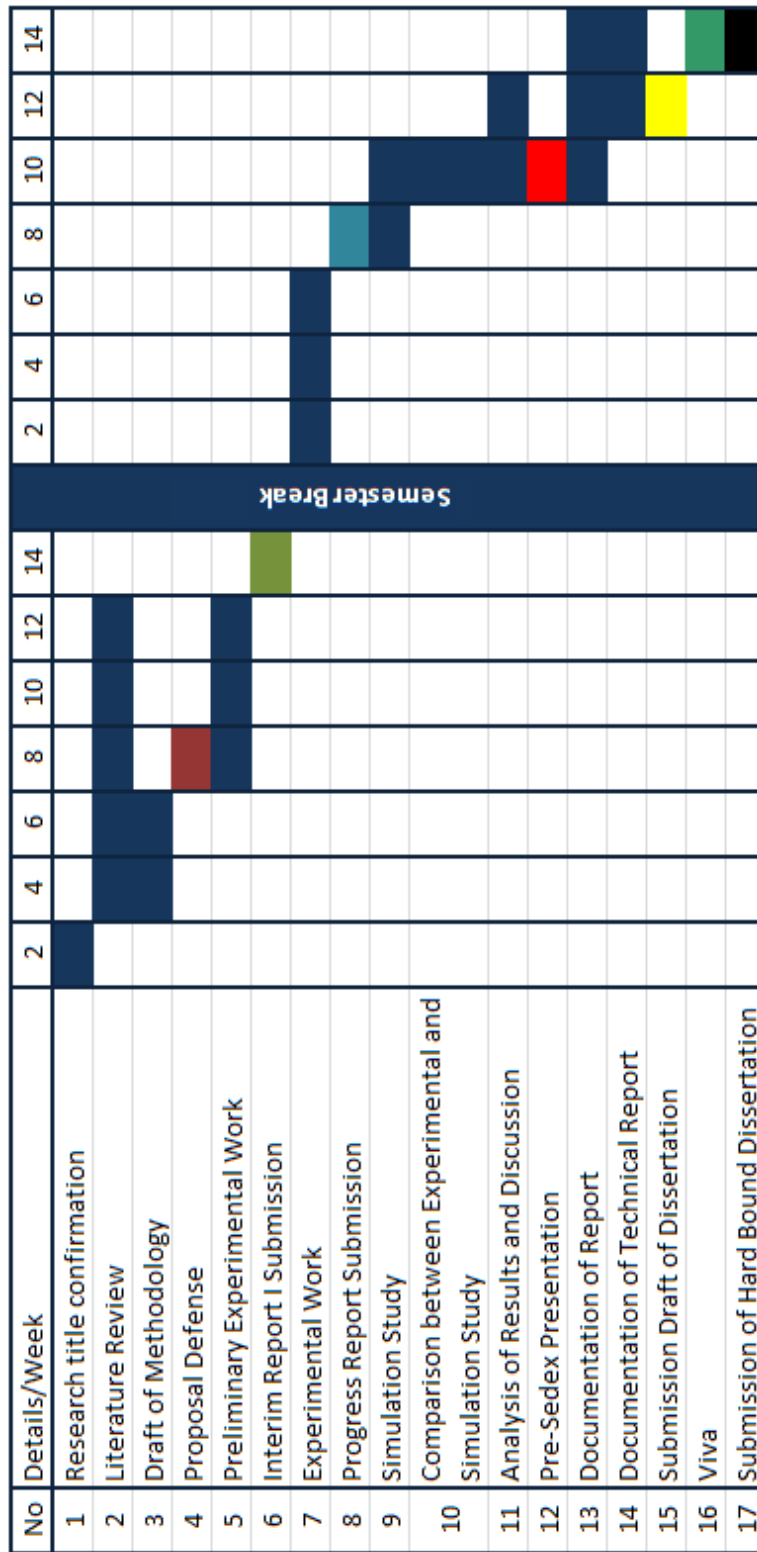


Figure 10: Gantt-Chart and Key Milestones

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 RESULTS AND DISCUSSION

The objective of this project is to gather multicomponent gas hydrate equilibrium H-L<sub>w</sub>-V curve (i.e. SNG-A and SNG-B) in the presence of ethylene glycol as thermodynamic inhibitor in a range of gas hydrate formations pressures.

Several sets of experiments are conducted based on methodology mentioned in the previous chapter. Data of gas hydrate equilibrium points shown in Figure 9 previously are collected to form a plot of pressure (bar) against temperature (°C) and shown in Figure 11 and 12. Figures 11 and 12 show the gas hydrate phase equilibrium for multicomponent gases in the presence of ethylene glycol; SNG-A and SNG-B respectively. For comparison, the figures also include the multicomponent gas hydrate; SNG-A and SNG-B equilibrium conditions without any inhibitor and predictions from CSMGem.

As observed in Figure 11 and 12, in the presence of ethylene glycol, the gas hydrates equilibrium conditions shifted to the gas hydrates stability region; i.e. to the left. The gas hydrates equilibrium conditions in the presence of higher weight percent of ethylene glycol (i.e. 20) are shifted more to the left than in the presence of 10 wt. % ethylene glycol. The higher the inhibitor content, the higher the temperature drop. At the same temperature, the hydrate formation pressure ascends with the inhibitor content.



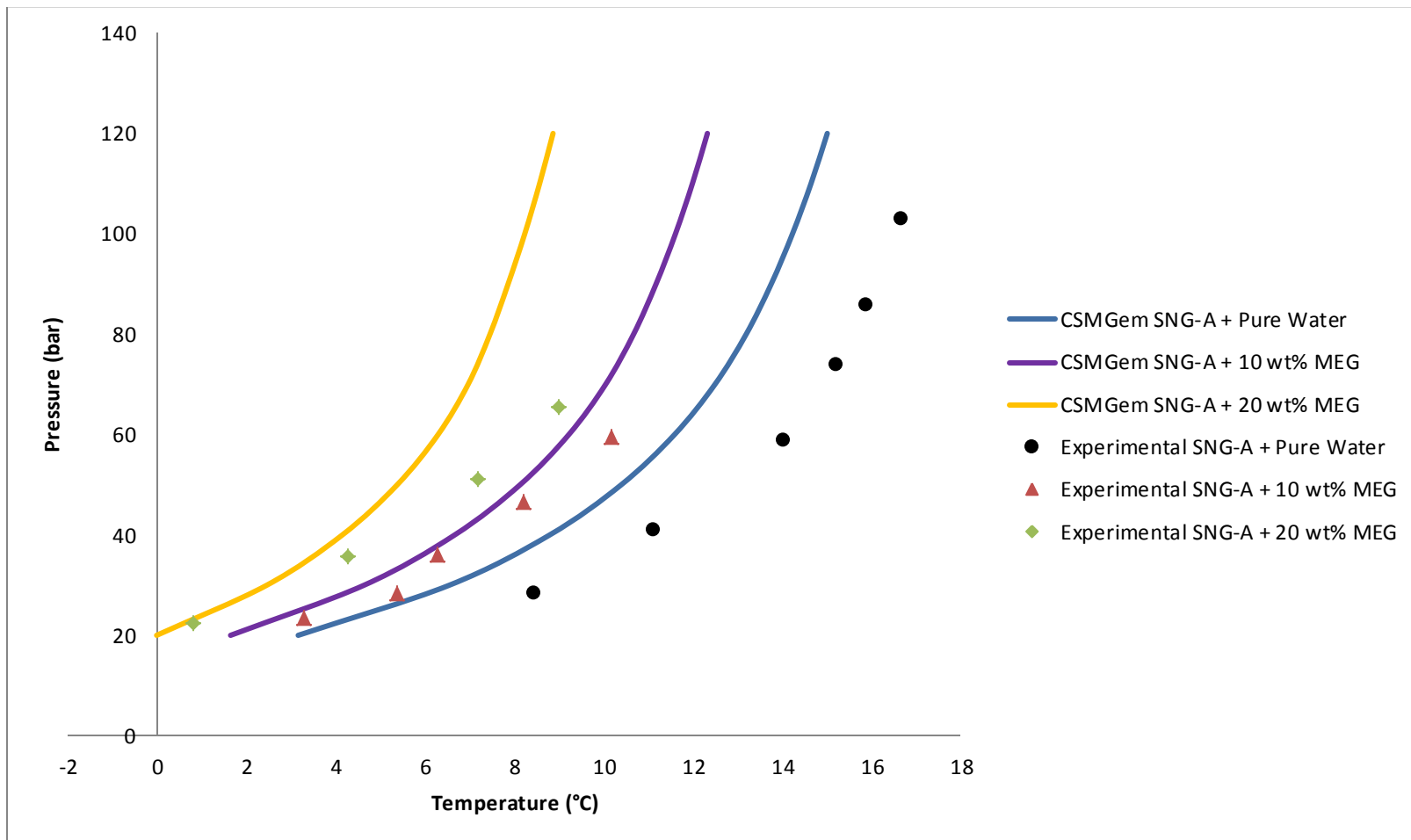


Figure 11: SNG-A hydrate equilibrium curve in the presence of methyl ethylene glycol (MEG)

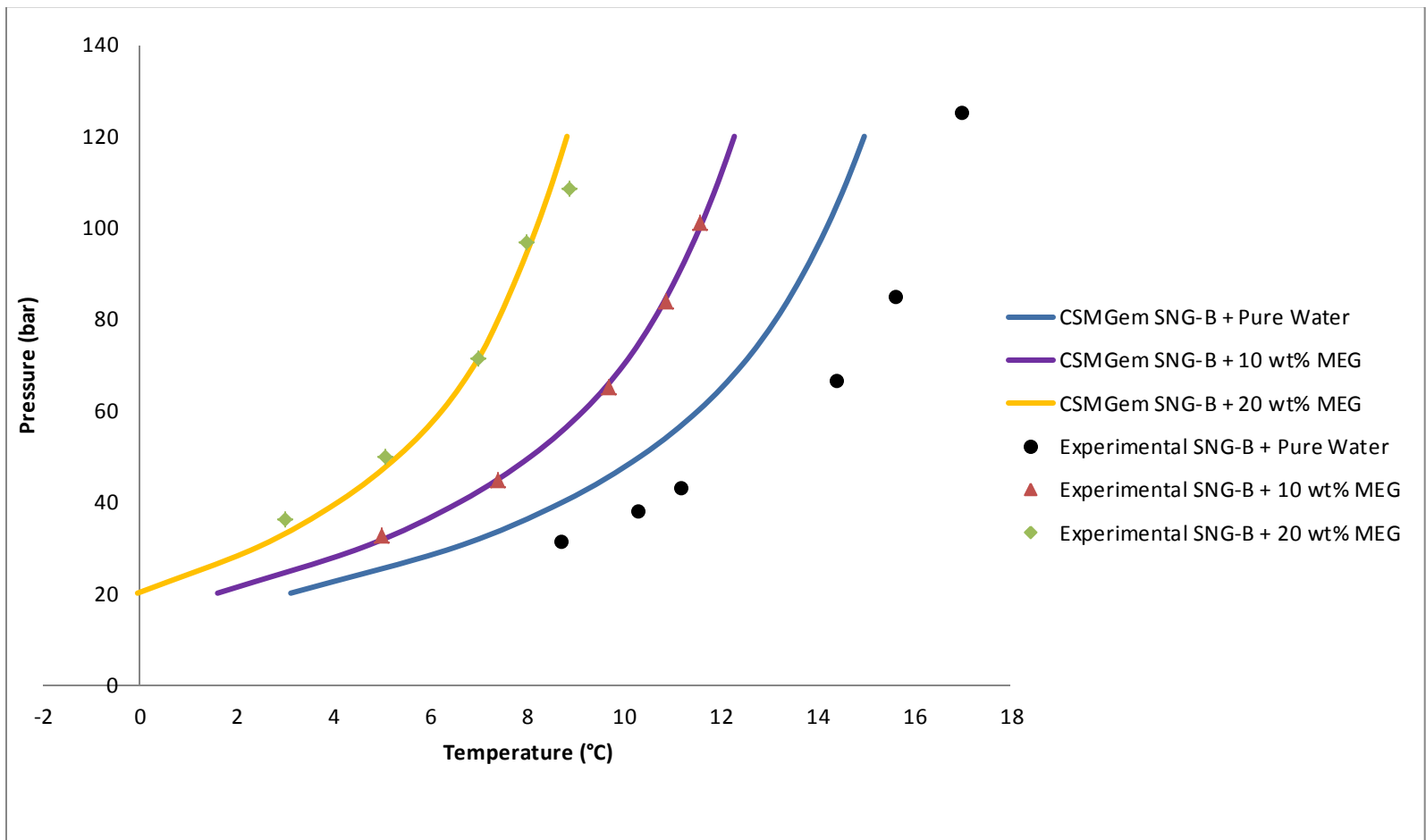


Figure 12: SNG-B hydrate equilibrium curve in the presence of methyl ethylene glycol (MEG)

#### **4.1.1 Synthetic Natural Gas-A (SNG-A) hydrate equilibrium conditions**

Figure 11 shows the plot of SNG-A hydrate equilibrium curve in the presence of ethylene glycol. Comparing the inhibition effect of ethylene glycol at different concentrations experimentally, suppression temperature from the normal multicomponent gas hydrates to the different concentrations of ethylene glycol are calculated and tabulated in Table 2. For SNG-A, an addition of ethylene glycol at 10 wt. % to the system causes temperature suppression of about 3°C. The addition of ethylene glycol at 20 wt. % to the system increased the temperature suppression to about 5°C.

It should be noted that for SNG-A, there are some discrepancies of inhibition effect between the measured values and the predictions from CSMGem. These are attributed by the components of SNG-A; which contains hydrocarbon; C1, C2 and C3. Usually these hydrocarbons only form structure I hydrate. However, the software generated modeling calculated all the formations of gas hydrates including structure I and structure II. Hence, this explains the discrepancies between the values of the experimental and the predictions.

#### **4.1.2 Synthetic Natural Gas-B (SNG-B) hydrate equilibrium conditions**

Figure 12 shows the plot of SNG-B hydrate equilibrium curve in the presence of ethylene glycol. Comparing the inhibition effect of ethylene glycol at different concentrations experimentally, an addition of 10 wt. % of ethylene glycol to the system causes temperature suppression of about 4°C. The addition of 20 wt. % of ethylene glycol to the system increased the temperature suppression to about 6°C.

The predictions from CSMGem are found to be reasonably agreed with the experimental values for SNG-B multicomponent gas. SNG-B contains hydrocarbons of C1, C2, C3 and C4. Addition of C4 and heavier components changes the crystal structure of formed hydrate from cubic structure I to cubic structure II in order to accommodate larger hydrocarbon molecules. Thus, the CSMGem modeling calculated and predicted well for SNG-B gas.

### 4.1.3 Tabulation of AAD<sup>T</sup> and Temperature Suppression for both SNG-A and SNG-B

As a whole, the gas hydrates equilibrium conditions for both multicomponent gases; SNG-A and SNG-B shifted to the inhibition region in the presence of ethylene glycol, in accordance with the increased inhibitor concentration. The average absolute deviation (AAD<sup>T</sup>) of predicted SNG-A and SNG-B gas hydrates equilibrium conditions in the presence of ethylene glycol evaluated using CSMGem software from experimental values and temperature suppression of SNG-A and SNG-B gas hydrates formation at specified ethylene glycol concentrations for experimental study,  $\Delta T_a$  and simulation study,  $\Delta T_b$  are tabulated in Table 2.

Table 2: Average Absolute Deviation (AAD<sup>T</sup>) of Predicted SNG-A and SNG-B hydrates equilibrium curves in the Presence of Ethylene Glycol Evaluated Using CSMGem Software from Experimental Values

Gas	Aqueous phase	No. data points	Temperature range (°C)	AAD <sup>T</sup> (°C)	$\Delta T_a$ (°C)	$\Delta T_b$ (°C)
SNG-A	Pure water	6	8 - 17	2.319	-	-
	10 wt% MEG	5	5 - 10	0.766	3.2 – 4.1	1.5 – 4.9
	20 wt% MEG	4	0.8 - 9	1.290	5.4 – 6.6	3.2 – 5.4
SNG-B	Pure water	6	10 - 17	2.021	-	-
	10 wt% MEG	5	5 - 12	0.069	3.8 – 4.7	1.4 – 2.4
	20 wt% MEG	5	3 - 9	0.233	6.6 – 8.0	4.3 – 6.2

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION AND RECOMMENDATION

The prime objective of this project is to determine the equilibrium H-L<sub>w</sub>-V curve of multicomponent gas hydrates (i.e. SNG-A and SNG-B) which have high content of CO<sub>2</sub> approximately 69%; in the presence of thermodynamic inhibitor i.e. ethylene glycol over a selected range of pressures. The experiments are conducted using isochoric equilibrium step-heating techniques in order to achieve optimum result.

It is found that in the presence of ethylene glycol, the gas hydrate equilibrium curves shift to the left, to the lower temperature and higher pressure region. To quantitatively investigate how the gas hydrate inhibition is affected by the presence of ethylene glycol, temperature suppression caused by the addition of ethylene glycol were measured experimentally and compared with the predictions from CSMGem software.

Further research is necessary to evaluate gas hydrate equilibrium curves of different types of multicomponent gas especially with high concentration of CO<sub>2</sub> and to obtain a modified prediction model.

## REFERENCES

- Bishnoi, P. R., & Dholabhai, P. D. (1999). Equilibrium conditions for hydrate formation for a ternary mixture of methane, propane and carbon dioxide, and a natural gas mixture in the presence of electrolytes and methanol. *Fluid Phase Equilibria*, 158–160(0), 821-827. doi: [http://dx.doi.org/10.1016/S0378-3812\(99\)00103-X](http://dx.doi.org/10.1016/S0378-3812(99)00103-X)
- Cha, M., Shin, K., Kim, J., Chang, D., Seo, Y., Lee, H., & Kang, S.-P. (2013). Thermodynamic and kinetic hydrate inhibition performance of aqueous ethylene glycol solutions for natural gas. *Chemical Engineering Science*, 99(0), 184-190. doi: <http://dx.doi.org/10.1016/j.ces.2013.05.060>
- Chatti, I., Delahaye, A., Fournaison, L., & Petitet, J.-P. (2005). Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. *Energy Conversion and Management*, 46(9–10), 1333-1343. doi: <http://dx.doi.org/10.1016/j.enconman.2004.06.032>
- Draft Assessment for ethylene glycol. (2013, 19-04-2013). from <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=24240347-1&offset=6>
- Dynamics of gas hydrates in polar environment. (2008). 2008, from <http://archive.noc.ac.uk/IPY/background.html>
- Farzaneh-Gord, M., Rahbari, H. R., Bajelan, M., & Pilehvari, L. (2013). Investigation of hydrate formation in natural gas flow through underground transmission pipeline. *Journal of Natural Gas Science and Engineering*, 15(0), 27-37. doi: <http://dx.doi.org/10.1016/j.jngse.2013.09.001>
- Gas hydrates stability. from <http://www.chem.ntnu.no/nonequilibrium-thermodynamics/index522b.html?page=17&project=1>
- Hammerschmidt, E. G. (1934). Formation of Gas Hydrates in Natural Gas Transmission Lines. *Industrial & Engineering Chemistry*, 26(8), 851-855. doi: 10.1021/ie50296a010
- Hemmingsen, P. V., Burgass, R., Pedersen, K. S., Kinnari, K., & Sørensen, H. (2011). Hydrate temperature depression of MEG solutions at concentrations up to 60&#xa0;wt%. Experimental data and simulation results. *Fluid Phase Equilibria*, 307(2), 175-179. doi: <http://dx.doi.org/10.1016/j.fluid.2011.05.010>

- Koh, C. A., Westacott, R. E., Zhang, W., Hirachand, K., Creek, J. L., & Soper, A. K. (2002). Mechanisms of gas hydrate formation and inhibition. *Fluid Phase Equilibria*, 194–197(0), 143-151. doi: [http://dx.doi.org/10.1016/S0378-3812\(01\)00660-4](http://dx.doi.org/10.1016/S0378-3812(01)00660-4)
- Li, X.-S., Liu, Y.-J., Zeng, Z.-Y., Chen, Z.-Y., Li, G., & Wu, H.-J. (2011). Equilibrium Hydrate Formation Conditions for the Mixtures of Methane + Ionic Liquids + Water. *Chemical Engineering Data*, 56, 119-123.
- Lundgaard, L., & Mollerup, J. (1992). Calculation of Phase Diagrams of Gas Hydrates. *Fluid Phase Equilibria*, 76, 141-149.
- Makogon, I. U. r. F., & Cieslewicz, W. (1981). *Hydrates of natural gas*: PennWell Books Tulsa, Oklahoma.
- Mekala, P., & Sangwai, J. S. (2014). Prediction of phase equilibrium of clathrate hydrates of multicomponent natural gases containing CO<sub>2</sub> and H<sub>2</sub>S. *Journal of Petroleum Science and Engineering*, 116(0), 81-89. doi: <http://dx.doi.org/10.1016/j.petrol.2014.02.018>
- Mokhatab, S., Wilkens, R. J., & Leontaritis, K. J. (2007). A review of strategies for solving gas-hydrate problems in subsea pipelines. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 29(1), 39-45.
- Properties of Organic Compounds and Other Covalent Substances. (2010). Retrieved 16-12-2010, from <http://chempaths.chemeddl.org/services/chempaths/?q=book/General%20Chemistry%20Textbook/Properties%20of%20Organic%20Compounds%20and%20Other%20Covalent%20Substances/1368/c>
- Saito, S., Marshall, D. R., & Kobayashi, R. (1964). Hydrates at high pressures: Part II. Application of statistical mechanics to the study of the hydrates of methane, argon, and nitrogen. *AIChE Journal*, 10(5), 734-740. doi: 10.1002/aic.690100530
- Sloan, E. D. (2003). Fundamental principles and applications of natural gas hydrates. *Nature*, 426(6964), 353-363.
- Subramanian, S., Kini, R. A., Dec, S. F., & Sloan Jr, E. D. (2000). Evidence of structure II hydrate formation from methane+ethane mixtures. *Chemical Engineering Science*, 55(11), 1981-1999. doi: [http://dx.doi.org/10.1016/S0009-2509\(99\)00389-9](http://dx.doi.org/10.1016/S0009-2509(99)00389-9)

- Tohidi, B., Burgass, R. W., Danesh, A., ØStergaard, K. K., & Todd, A. C. (2000). Improving the Accuracy of Gas Hydrate Dissociation Point Measurements. *Annals of the New York Academy of Sciences*, 912(1), 924-931. doi: 10.1111/j.1749-6632.2000.tb06846.x
- Wu, M., Wang, S., & Liu, H. (2007). A Study on Inhibitors for the Prevention of Hydrate Formation in Gas Transmission Pipeline *Journal of Natural Gas Chemistry*, 16(0), 81-85.