

**Investigation of 1-butyl-3-methylimidazolium Chloride (BMIM-Cl) as Hydrate  
Inhibitor**

by

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13913

Dissertation submitted in partial fulfillment of the requirements for the  
Bachelor of Engineering (Hons)  
(Petroleum)  
JANUARY 2014

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## **CERTIFICATION OF APPROVAL**

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Approved by,

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(A.P. Dr Ismail bin Saad)

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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(SITI FATIMAH ILI BINTI OMAR)

## **ABSTRACT**

Methane hydrate has been discussed as one of the unconventional reservoir, expected to be commercialized in 15 years' time [1]. There are a few methods in extracting the gas from hydrates, but there seem to be few drawbacks from each of them. This study is about the production of methane gas from methane hydrates by dissociation of hydrate using the hydrate inhibitor. The hydrate inhibitor that is used in this study is an ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIM-Cl). This study utilized high pressure hydrate studies system (HYDREVAL) to examine the thermodynamic equilibrium of methane hydrate and evaluate the performance of BMIM-Cl. Using the Hydrevale, the P-T graph, pressure versus temperature is produced. Due to limitation and restriction, the results obtained are insignificant. The result show that BMIM-Cl insignificantly shifts the equilibrium curve of methane hydrate from high to low temperature and obtain the new equilibrium curve away from the methane hydrate stability curve. The temperature difference is calculated, and it can be seen that BMIM-Cl is not effective at low pressure. In conclusion, BMIM-Cl has a high potential to be explored more as hydrate inhibitor.

## **ACKNOWLEDGEMENT**

Alhamdulillah, all praises to Allah SWT The Almighty, for the blessings, health and strength He had given me throughout the semesters for completing this Final Year Project.

First and foremost, I would like to express my highest gratitude to my supervisor, Madam Mazuin Jasamai for her continuous support, motivation, advices, constructive comments and guidance on this project. She also always reminds me not to give up despite of the obstacles and challenges I faced throughout the year. I would never forget her kindness in every aspect she has shown. Not to forget, I would like to thank my supervisor, Dr. Ismail for his support during the project execution.

Special thanks to my hydrates colleagues, Ms Syazwani Abdullah, Mr Zulqarnain Hatta and Mr Wan Imran Syahmi for their ideas and thoughts from the beginning of the research phase until the lab sessions and completion of this project.

I would also like to thank the lab technicians in Block 15 (Petroleum Engineering Department), Mr Faiz and Mr Iswadi for teaching and advising me on how to handle the equipment in the labs and their willingness to standby outside their working hours to allow us to conduct the experiment in the lab.

Not to forget to my parents, family and friends for being very supportive and motivative upon the completion of my project.

Last but not least, thank you to Universiti Teknologi PETRONAS for the opportunity and providing great facilities for me to work on for this project. I hope that the experience and knowledge that I gained from this project will be a valuable stepping stone for my future career development, insyaAllah.

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## **ABBREVIATIONS AND NOMENCLATURES**

BMIM-Cl	1-butyl-3-methylimidazolium chloride
CH <sub>4</sub>	Methane
EMIM-Cl	1-ethyl-3-methylimidazolium chloride
EMIM-Br	1-ethyl-3-methylimidazolium bromide
HP $\mu$ DSC	High pressure micro differential scanning calometry
HYDREVAL	Hydrate study system
H <sub>2</sub> O	Water
MeOH	Methanol
MPa	Mega pascal
Psig	pound per square inch (gauge)
SAGD	Steam assisted gravity drainage
SAFT	Statistical associating fluid theory
UTP	Universiti Technology PETRONAS
Wt%	Weight percent

# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 BACKGROUND STUDY**

Hydrates are discovered by researchers in three stages. The first stage is on 1810, where researchers discovered a compound consists of gas and water, and the curiosity leads the study on this new compound. Second stage is during the year of 1930s, where gas hydrates is considered a problem. The high pressure and low temperature condition caused the hydrates to form. The last phase of discovery is when the hydrates are known to be present in two different environment [2].

Gas clathrate hydrates or often called gas hydrates, are the crystalline compounds which formed when water is in contact with hydrate guest under certain temperature and pressure [2]. What is meant by guest hydrates are the small molecule which are trapped in the water crystal lattice. These molecules are usually light hydrocarbons (e.g. methane), carbon dioxide and hydrogen sulfide. Water consists of one oxygen atom and two hydrogen atoms, which one of the hydrogen atoms can form another (i.e. secondary) bond with other molecule and the bond is said to have a tenth of the strength of the main covalent bonds holding the water together [2]. However, the bond between the host (i.e. water) and guest is not the factor of hydrates stability but due to the van der Waals forces of attraction between the guest molecules and water.



Figure 1 : Guest hydrates (green molecule) trapped in the caged-like structure of gas hydrates [3].

These gas hydrates can be found all over the world. Over the years, the formation of hydrates in pipelines is considered as a problem in flow assurance. However, the natural deposited gas hydrates were found in ocean and permafrost environment and is seen as new unconventional reservoir [2].

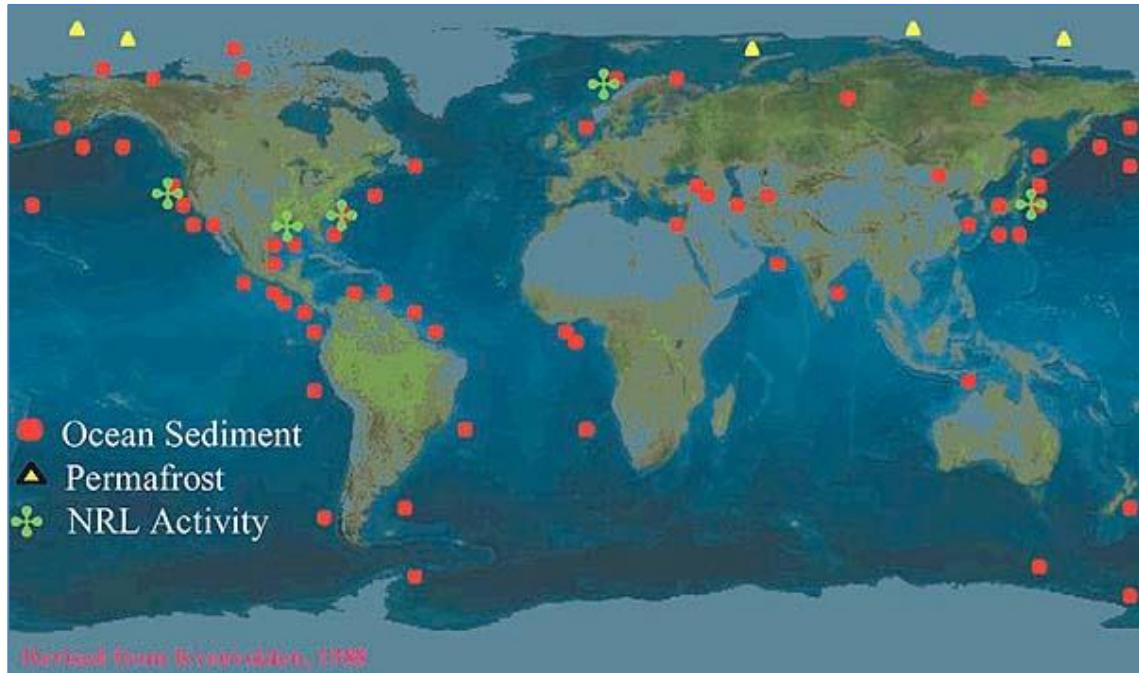


Figure 2 : Methane hydrates distribution all over the world [4].

The natural occurring hydrates exist in two main environment, permafrost and ocean where the conditions are suitable, low temperature and high pressure for the hydrates stability [5]. Of course, the hydrate guest and the water need to present in order to form gas hydrates. To be specific, hydrates will form at certain pressure and temperature which lies on the hydrate equilibrium line and it will maintain stable in hydrate form as long as the conditions are in the hydrate stability zone. In order for the hydrates to be dissociated, the conditions (i.e. the temperature or the pressure) must be in the hydrate free zone. In other words, less hydrate stability zone will produce more gas in the hydrates.

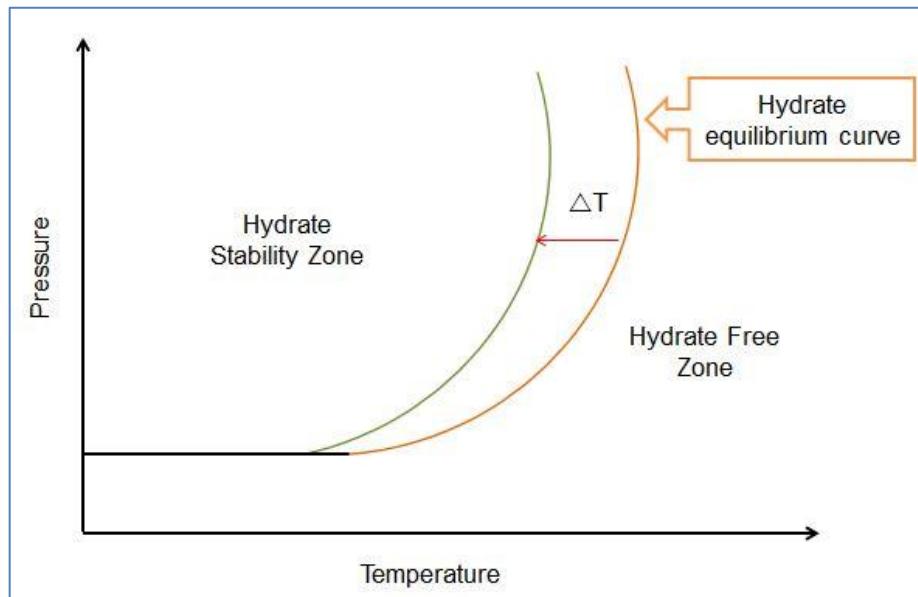


Figure 3 : Hydrate stability zone and hydrate free zone is separated by the equilibrium phase of hydrate.

There are few methods of exploitation have been proposed i.e. thermal simulation, depressurization and usage of hydrate inhibitors. Thermal simulation is the method where hydrates sediments are heated until above the hydrate equilibrium temperature at the prevailing pressure by steam flooding or injection of hot water. On the opposite, the depressurization method decreased the pressure of hydrates sediments below the hydrate equilibrium pressure at the prevailing temperature. This method requires the hydrates formation to be on top of a layer of free gas. In order to decrease the pressure, the free gas is released [5] [6].

These two methods are visualized in below diagram, where for the thermal simulation method, heat is transferred through the cap rock to the hydrate cap. The Earth temperature will increase above the hydrate equilibrium curve after the heat transfer, causing dissociation and guest hydrate will flow to the free gas formation. And as for the depressurization technique, the free gas underlies the hydrates formation need to be released before the hydrates can be dissociated.

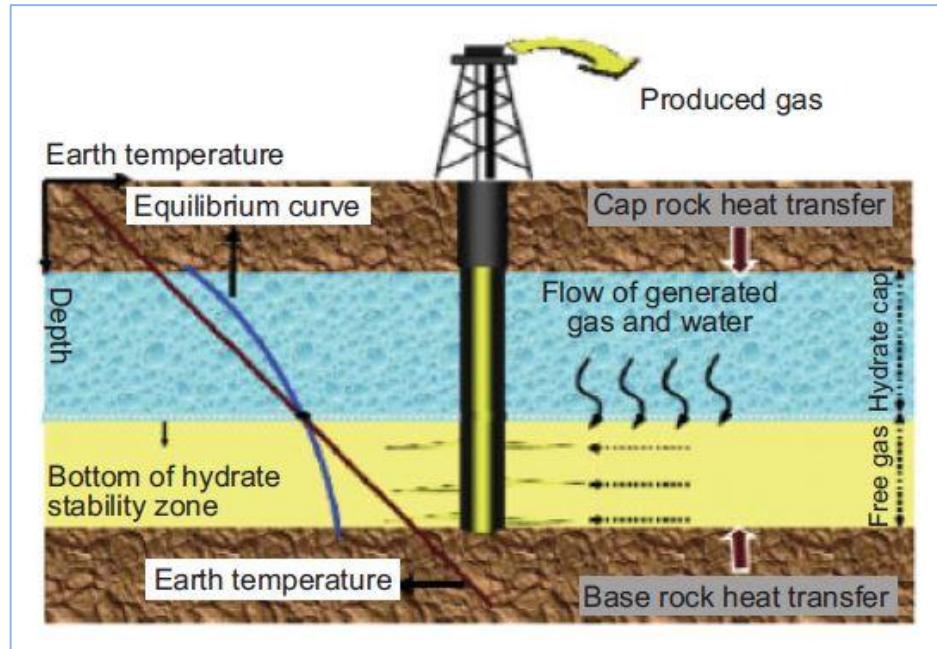


Figure 4 : Visual representation of thermal simulation and depressurization method [7].

On a different note, the third method can also be beneficial in flow assurance problems, besides being an alternative to exploit naturally deposited hydrates. The injection of hydrate inhibitors can shift the equilibrium curve of hydrates to a lower temperature, putting the in situ hydrate condition to be in hydrate free zone, hence dissociation occurs. The objective of this method is to create less hydrate stability zone, by disturbing the hydrate stability condition. At the same time, this inhibitor also can slow down the process of hydrate formation [8] [9]. Hydrate inhibitor is commonly used to delay the hydrates formation in the pipelines or processes facilities. There are two types of inhibitor commonly used, thermodynamic inhibitor and kinetic inhibitor. Usually, thermodynamic inhibitor consists of alcohol based inhibitor while kinetic inhibitor consists of polymer based inhibitor [10].

## 1.2 PROBLEM STATEMENT

For many years, geoscientists and engineers had been searching alternatives energy source for future. Current conventional crude oil which is the main source of energy is estimated will reach its peak of production at 2035, then later will start to decline and is expected could supply for 40 more years [2]. **Soon, earth will be lack of fuel source.** An as alternative to the problem, people start to exploit the unconventional hydrocarbons (e.g. shale gas and coal bed methane). Gas hydrates or methane hydrates to be exact is one of the potential alternatives could replace the conventional fossil fuel resource [5]. However, for many years, even until now, **the hydrates research has been focused on flow assurance**, where the hydrates had been seen as problematic.

According to Japanese Research Consortium for methane hydrate website, the methane gas has been successfully extracted from methane hydrate layer (for the first time ever) by thermal stimulation in 2002 and depressurization method in 2008 [11]. Eventhough the two methods (i.e. thermal stimulation and depressurization) are proven to be applicable in field production, **there are drawbacks analyzed from each method.** In order to produce hot water used in the thermal stimulation method, another form of energy is used. This shows the poor energy efficiency in this method, as energy used to produce source of energy [6]. In addition, the Soviet researchers pointed out that this method is not economically viable [6]. For depressurization method, it is proven to be a more viable recovery method, qualitatively and quantitatively [6] [11]. However, this method is only applicable to the hydrate layer formed on top of free gas. The free gas is needed to lower the pressure below the hydrate equilibrium pressure, by having it released [6]. The injection of hydrate inhibitor has been tested in Messoyakha Field but with a high concentration 96 wt% of methanol. High concentration may add more expenses and negative environmental effects.

In 2005, methane hydrates were found in Gumusut Kakap Field, Sabah, interpreted by 3D seismic and core sample [12]. As come to date, **no applicable technology that can be used to extract the method.**

### **1.3 OBJECTIVES**

1. To investigate the effectiveness of BMIM-Cl (i.e. ionic liquid) as hydrate inhibitor at different range of pressure and temperature.
2. To examine the effects of concentration of hydrate inhibitor on hydrate formation
3. To compare the performance of BMIM-Cl as hydrate inhibitor with the literature data.

### **1.4 SCOPES OF STUDY**

The author has narrow down this research on unconventional hydrocarbons of gas hydrates to the exploitation of methane hydrates in Malaysia. The study will be focused on ocean environment which is suitable for Malaysia. There are three types of methane hydrate extractions, but the study will be focused on the usage of hydrate inhibitor. It is known that hydrate inhibitor consists of two types of inhibitor, ionic liquid and polymer-based inhibitor. This study will focus to ionic liquid as hydrate inhibitor. The ionic liquid will be used in this study is BMIM-Cl.

### **1.5 RELEVANCY AND FEASIBILITY OF PROJECT**

The study on gas hydrates has been an important research in oil and gas industry since methane hydrates is one of the acknowledged unconventional reservoirs. The performance of the ionic liquid is examined and compared with the literature data. It is projected that the outcome of this project be able to add new research on the studies of hydrates. And with this discovery, the hydrate inhibitor may be explored with other variables in order to produce the best inhibitor. According to the Gannt Chart plan, this project is able to be completed within the time provided. The equipment to carry out this project is also available in UTP. Samples and conditions of experiment are carefully selected to make sure all expected results are achieved. This project is feasible as it is completed within the time given, and the availability of the equipment.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 METHANE HYDRATES**

Hydrates are the condition where water acts as a host structure and is composed of cages which will trap the other molecules present [2]. The guest molecules that usually trapped in the host crystal lattice are the lighter hydrocarbons. The most common hydrocarbon-hydrate is the methane hydrates. Methane hydrate is the methane molecules of  $\text{CH}_4$  trapped in crystalline solids of water,  $\text{H}_2\text{O}$  formed at the high pressure and low temperature [13]. There are few conditions (other than high pressure and low temperature) suitable for methane hydrate formation. According to Geology.com, the four conditions are ;

- 1) Sediments or sedimentary rocks below Arctic permafrost
- 2) Deposited sediments along continental margins
- 3) Deep-water sediments (e.g. ocean or lake)
- 4) Under the ice of Antarctic

The methane molecule in the solid hydrate is deposited from biogenic gas and thermogenic gas [2]. From its name, the source of hydrates can be determined. Biogenic gas produced from the organic matter buried in the seafloor sediment interacted with the ocean microbial life while thermogenic gas produced deep in the Earth through the catagenesis process which means cracking of larger molecules of kerogen [2].

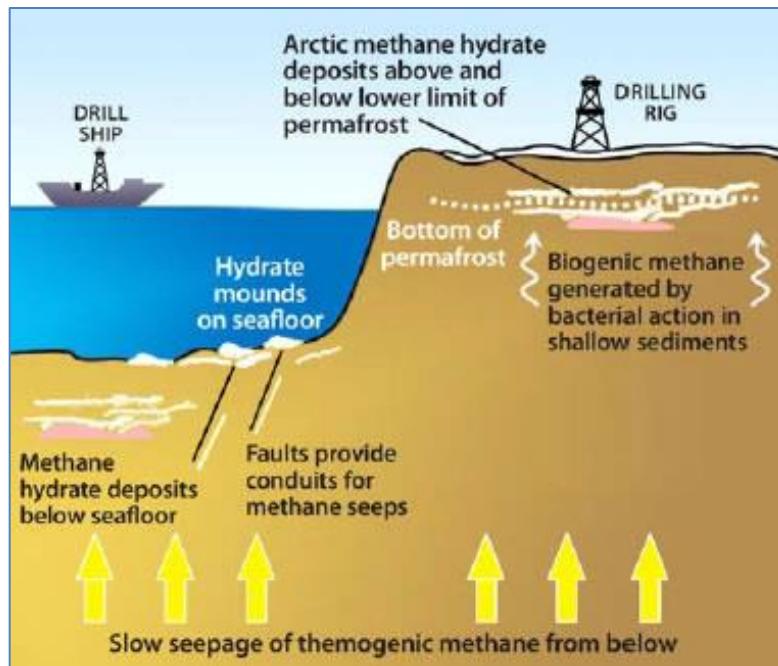


Figure 5 : Methane hydrates deposition at continental margin and under permafrost [14].

Based the phase diagram below developed by Kvenvolden & Lorenson (2001), [15] the temperature and pressure range for methane hydrates formation for both environment can be known. For permafrost area, the temperature range from  $-20^{\circ}\text{ C}$  to  $15^{\circ}\text{ C}$ , with the temperature of  $-20^{\circ}\text{ C}$  to  $0^{\circ}\text{ C}$  is mixture of gas hydrates and ice, while for ocean environment the temperature range quite small, from  $0^{\circ}\text{ C}$  to  $15^{\circ}\text{ C}$  but in deeper formation of 300 m to 1600 m below seafloor compared to in permafrost area, the hydrates formed at 190 m to 1600 m.

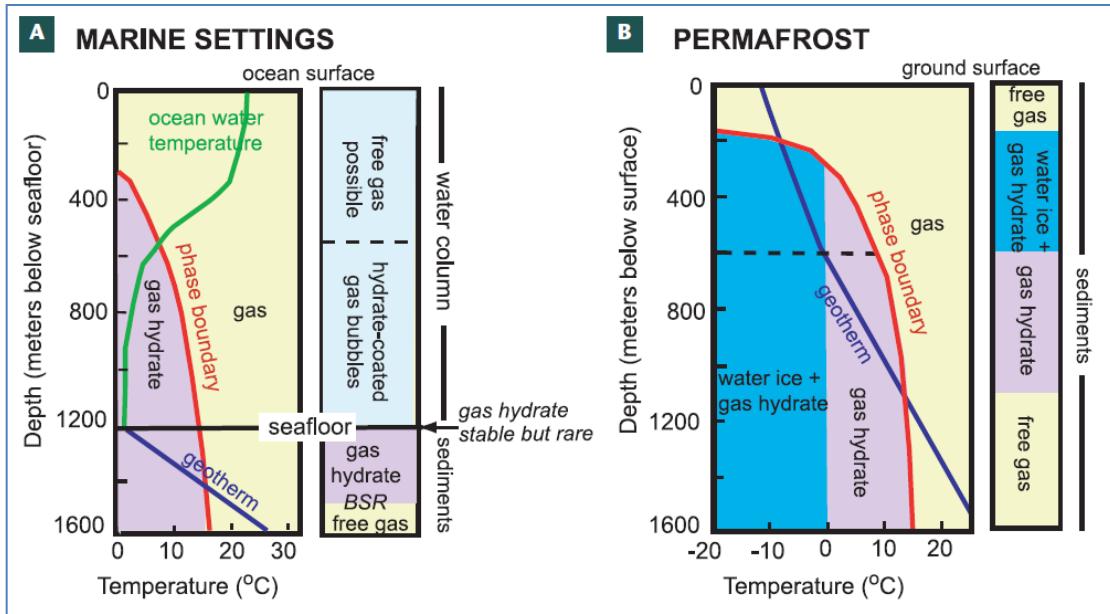


Figure 6 : Phase diagram of methane hydrates in (a) marine settings and (b) permafrost [15].

## 2.2 METHANE HYDRATE EXTRACTION

The common methods of exploitation of methane hydrate are thermal simulation, depressurization and hydrate inhibitor injection [5]. Most of recent studies suggest that depressurization has the highest efficiency in methane hydrate production but with low rate of reaction [5]. Hence, many current ongoing researches focus on combination of thermal simulation and depressurization. For example, Xiao-sen et al (2013) conducted an experiment on gas production from methane hydrate using steam assisted gravity drainage (SAGD) which combine thermal methods (e.g. well heating) with pressurized simulator. In this study, the SAGD method is used to increase the temperature and at the same time the pressure of the vessel where the hydrates formed is decreased. The pressure is decreased by the releasing the gas inside the vessel. As the temperature increase and the pressure is decreased out of hydrate equilibrium phase, the hydrates will dissociate. However, this experiment's result shows that combination of the two methods seems insignificant.

Eventhough depressurization has the highest efficiency, in many cases, the usage of hydrate inhibitor is the only viable option [10]. The equipment used to test the hydrate dissociation by using various variables is high pressure differential scanning calorimetry ( $\mu$ DSC). In one experiment by Gupta et al (2010),  $\mu$ DSC is used to determine the heat of hydrate dissociation.

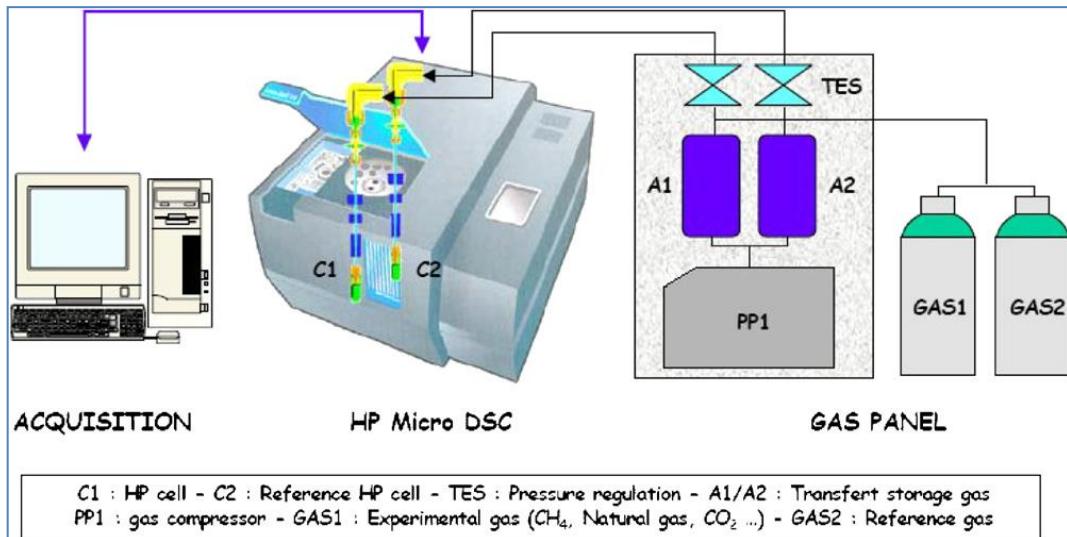


Figure 7 : Equipment setup for microDSC to determine heat of hydrate dissociation [16].

The pressure range for this experiment is from 0.1 MPa to 40 Mpa, supplied by the gas panel. The piston at the gas panel is used to charge the sample with the gas at the pressure stated. The hp  $\mu$ DSC sample cells consist of Hastelloy material to prevent corrosion or contamination, at the same time measure the heat of dissociation. For the measurement, the some DSC sample is filled with hydrate, the remaining is filled with methane gas. At the end of the experiment, the total mass of water is measured and used to calculate heat of dissociation [17].

$\mu$ DSC has the ability to experiment the effectiveness of inhibitor. For the method of inhibitor injection, there are two types of inhibitors, thermodynamic inhibitor and kinetic inhibitor. Thermodynamics inhibitor shift the hydrate dissociation condition, such as phase boundary and hydrate to lower temperatures and higher pressures while kinetic inhibitor delay the hydrate nucleation rate [8].

Besides  $\mu$ DSC, Hydrexal is also one of the equipments used to determine hydrates formation and dissociation condition and examine hydrate inhibitors performance. Hydrexal stands for hydrates studies system. Hydrexal is the medium to study hydrates through four methods, constant volume method (isochoric), constant pressure method (isobaric), constant temperature method (isothermal), and visually [18]. In an experiment conducted by Partoon et al (2012), by using Hydrexal, the isochoric method is used to measure the equilibrium hydrate formation. In this study, the instrument is able to give the evaluation of the hydrate inhibitors thermodynamically where the equilibrium line of methane hydrate is shifted to the lower temperature with the presence of inhibitors [19].

### **2.3 HYDRATE INHIBITOR**

One of the inhibitors commonly used for injection is ionic liquid. Ionic liquid is known as salt in liquid form which has low melting point. It exists as liquid in low temperature [20]. Most of the ionic liquid is hydrophilic. Chloride anion is one of the hydrophilic anions which allow ionic liquid to be miscible with water [21]. Because of that, ionic liquid is chosen and tested as hydrate inhibitor. With this characteristic, ionic liquid can impair the bond between water and gas in the hydrate molecule.

In another study conducted by Richard and Adidharma (2013), [9] the method used to inhibit methane hydrate is injection of inhibitor (i.e. ionic liquid) using microDSC. The ionic liquid is said to have both mechanism of inhibition, thermodynamics and kinetic. The type used in this study is 1-ethyl-3-methylimidazolium chloride (EMIM-Cl) and 1-ethyl-3-methylimidazolium bromide (EMIM-Br). The result stated that the usage of EMIM-Cl demonstrate an increase in inhibition effectiveness as the inhibitor concentration increase.

The dual function characteristic of ionic liquid is advantageous in inhibiting methane hydrate formation. Kinetic inhibition is useful in pipeline transportation because the later the hydrate is formed, more gas can be transported. As for the thermodynamic inhibition, ionic liquid has the ability to shift the hydrate equilibrium phase to a lower temperature, and disturbed the hydrate stability zone. As a result, less hydrate stability zone and more hydrate free zone is created.

As a conclusion, the author will be focusing on hydrate inhibitor injection method since there is a study that shows the effectiveness of the inhibitor (i.e. ionic liquid). There are many types of ionic liquid that can act as hydrate inhibitor and its performance in hydrate inhibition can be examined with different type of equipment. And the results of this project can be compared to the effectiveness of depressurization method.

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 RESEARCH METHODOLOGY**

Below is the flow of the research methodology which ends with experiment to obtain the results, and achieve the objectives planned.

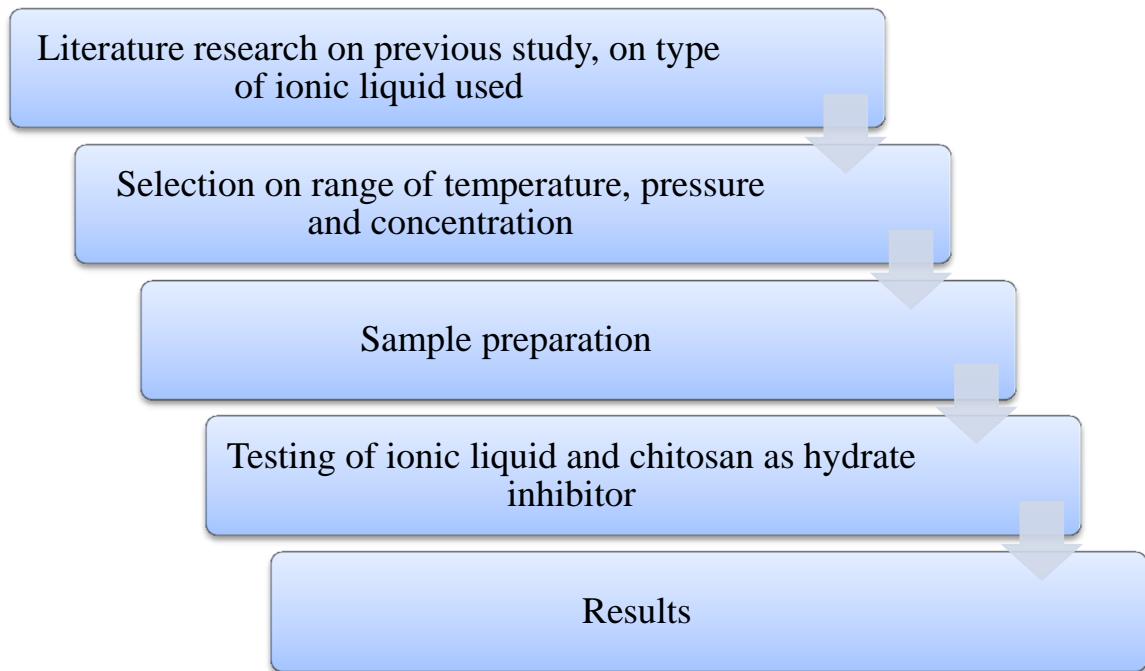


Figure 8 : Flow of research methodology

## 3.2 EXPERIMENTAL METHODOLOGY

### 3.2.1 Experimental Setup

#### *Equipment*

The main equipment used in this experiment is HYDREVAL. Hydrexal has the ability to determine the thermodynamic stability of hydrate formation and dissociation based on four different methods (i.e. isobaric, isochoric, isothermal, and visual method). Hydrexal consists of a fully visual sapphire cell which allows the visual of the sample from top to bottom, and a piston which is equipped with a magnetic stirrer [18].

Table 1 : Features of Hydrexal equipment [18].

FEATURES		ACCURACY
Pressure	3000 psi	0, 1 % full scale
Temperature	-60 ° C to 150 ° C	0.1 ° C
Temperature regulation	± 0.1 ° C	
Cell volume	80 cm <sup>3</sup>	0.01 ml
Stirring mechanism	Magnetic Drive	
Power supply	220 VAC 50 Hz	

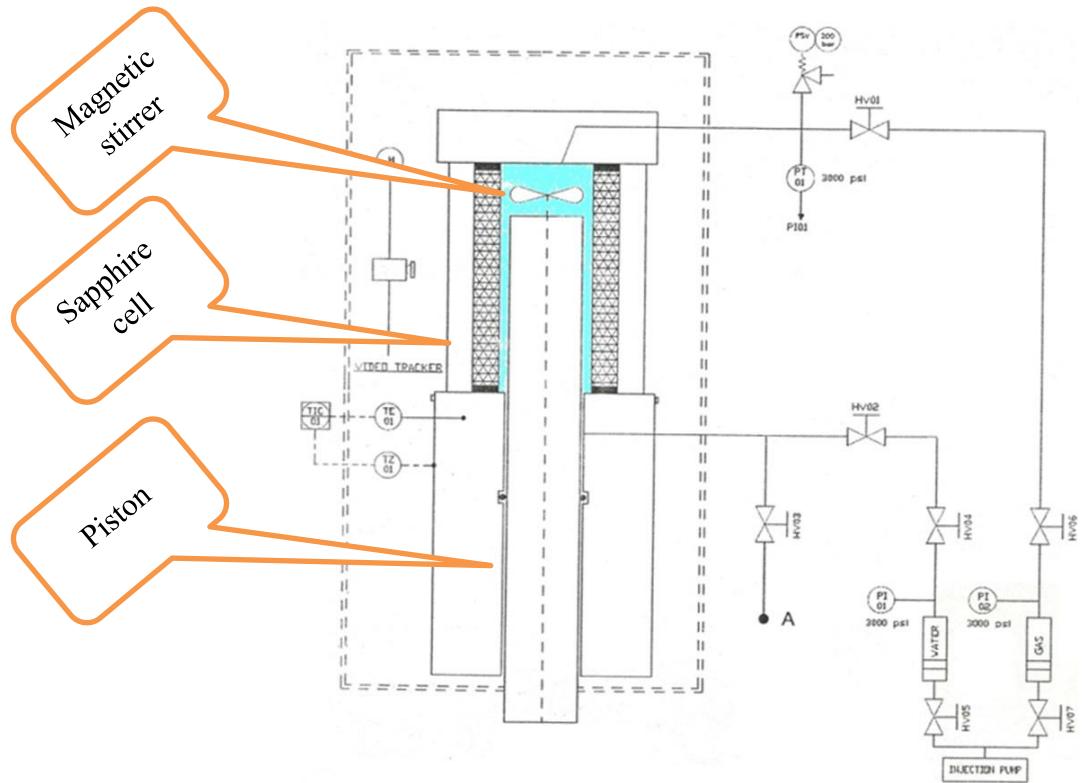


Figure 9 : Schematic diagram of Hydreval [19].

Three main component of the equipment is the piston, the sapphire cell and the stirrer. The distilled water mixed with ionic liquid will be in through the lower inlet and the gas will be in through the upper inlet. The stirrer is needed to mix the sample and the gas, to form hydrate. Both sample and gas will be mixed in the sapphire cell. The piston is used to set the volume to be filled in each fluid.

## **Materials**

The materials used in this experiment are methane gas ( $\text{CH}_4$ ), distilled water ( $\text{H}_2\text{O}$ ), ionic liquid obtained from Petronas Ionic Liquid Centre (PILC), 1-butyl-3 methylimidazolium chloride (BMIM–Cl) and chitosan as additive. Table below shows the physical details on each component.

Table 2 : Detailed description of the component used in the planned experiment

COMPONENT	STATE OF MATTER	CHEMICAL STRUCTURE	MOLAR MASS
$\text{CH}_4$	Gas	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	16.043 g/mol [22]
$\text{H}_2\text{O}$	Liquid	O-H-O	18.01528 g/mol [23]
BMIM–Cl	Solid	 $\text{C}_8\text{H}_{16}\text{N}_2^+ \text{Cl}^-$	174.67 g/mol [24]

## **Experimental Details**

Table 3 : Material and condition for the experiment

Sample	Concentration
• 1-butyl-3-methylimidazolium chloride (BMIM –Cl)	1 wt%
• Distilled water	
Pressure	30 Bar and 60 Bar

### 3.2.2 Procedures

#### 1) Sample Preparation – BMIM-Cl and Chitosan

The concentration of all samples will be in terms of weight percent, and the concentration of BMIM-Cl used in this experiment is 1 wt%. The sample will be prepared using below equation :

$$\text{wt \%} = \frac{\text{mass of solute powder (g)}}{\text{mass of solution (g)}} \times 100$$

The mass of the solution is 100 g. The mass of solute powder is calculated, based on the concentration. The solute powder is then mixed with distilled water, using the magnetic stirrer, which set to 600 rpm for 1 minute.

Table 4 : Calculation for mass of water and mass of solute powder

1 wt% of BMIM-Cl / 1 wt% of Chitosan
$1 \text{ wt \%} = \frac{\text{mass of solute powder}}{100 \text{ g}} \times 100$
Mass of solute powder = 1g
Mass of distilled water = 100g - 1g = 99g

#### 2) Measurement of Hydrate Equilibrium Point

This experiment utilized the Hydrexal based on isochoric which means constant volume in order to obtain hydrate equilibrium points. After the sample is prepared, the sample will be loaded in the tank connected to the sapphire cell. Before the sample is loaded into the sapphire cell, the cell is washed using distilled water and vacuumed at least for two times to make sure no fluid left in the sapphire cell. The volume of the sapphire cell is then set to 55 cm<sup>3</sup>. Figure below shows the condition before sample is loaded.

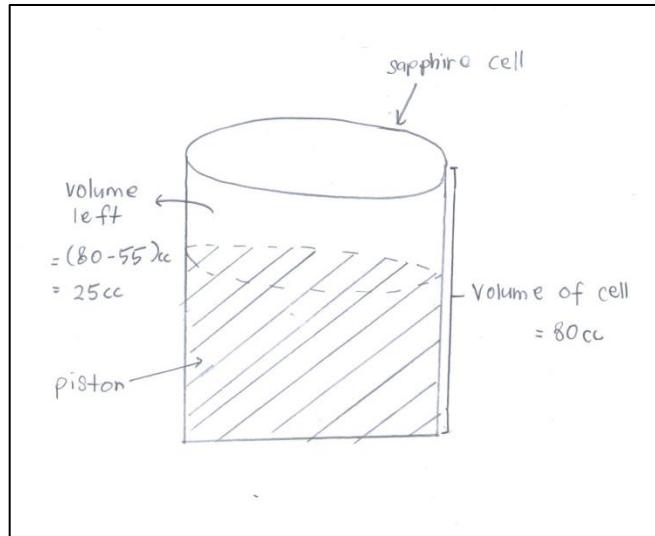


Figure 10 : Position of piston set at  $55 \text{ cm}^3$

$25 \text{ cm}^3$  of sample is loaded using the pump to the empty space above the piston. Then the piston is set to  $80 \text{ cm}^3$  and methane gas is loaded to the sapphire cell. Since there is already  $25 \text{ cm}^3$  of sample, mathematically the volume of methane gas is equal to  $55 \text{ cm}^3$ . The start pressure is 30 Bar which is approximately 420 psig ( $\pm 70$  psig) and is controlled by the pressure gauge at the gas tank. The equipment is left for several hours to make sure pressure is stabilized and no leak around the sapphire cell.

While pressure is stabilized, temperature is set in the equipment software. Table 5 shows the temperature setpoint for 30 Bar.

Table 5 : Temperature setpoint for 30 Bar.

Temp. Setpoint (°C)
7
5
3
1
0
-1
-4
-5
-4
-3
-1
0
0.8
1
1.3
1.5
1.7
2.6
3
3.5
4
4.6
5
6
7

This temperature setpoint is the temperature of hydrate formation and dissociation and it is obtained from the pure methane equilibrium. In this experiment, the temperature data taken from Nakamura (2003) [25]. The temperature is set from high temperature to low temperature, and back to high temperature. Once pressure is stabilized, the stirrer is switched on, and the experiment is started. The stirrer is used to mix the sample and methane gas, to form hydrate. The temperature of the cell is decreased at first and later increased back to the beginning. The temperature measured is recorded.

The experiment will end once the equipment done measuring temperature and pressure, and results are obtained for 30 Bar. The graph is analyzed to obtain equilibrium pressure and temperature. The same sample is used, and experiment is continued for pressure 60 Bar. In order to increase the pressure, the piston is pushed upwards, by means the solution is compressed. Same procedure is applied once pressure is set and stabilized.

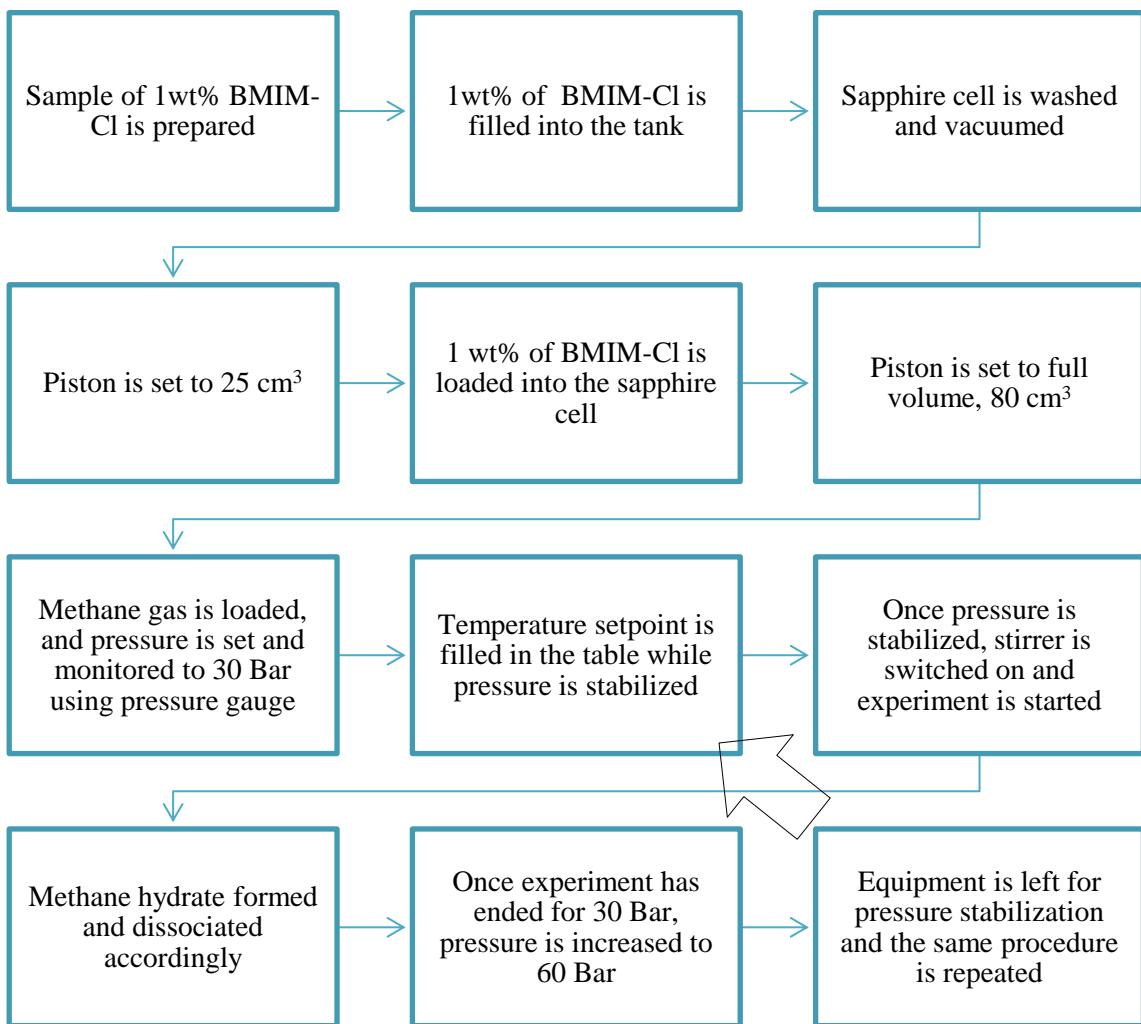


Figure 11 : Flow of the experiment for 1 wt% of BMIM-Cl + methane gas at pressure 30 Bar and 60 Bar

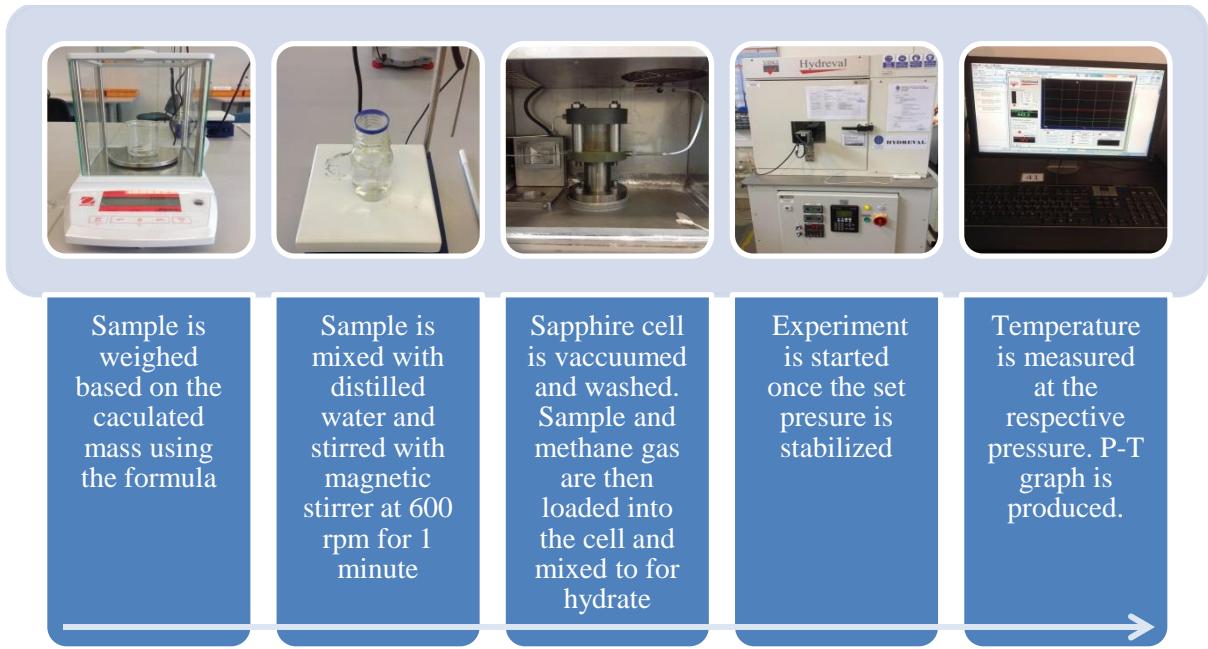


Figure 12 : Summary of the experimental procedure

### 3.3 GANTT CHART AND KEY MILESTONE

#### 3.3.1 Key Milestone

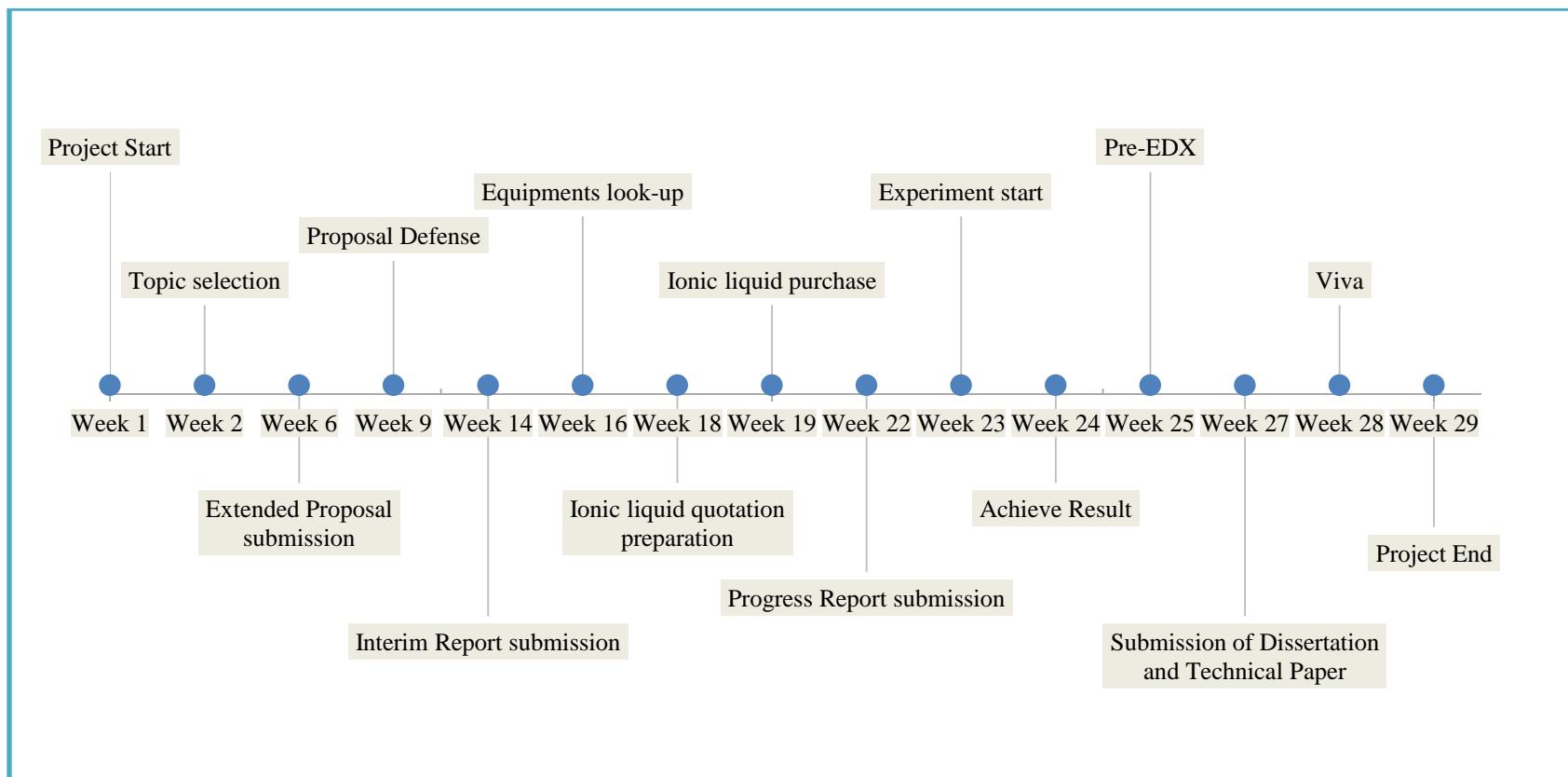


Figure 13 : Weekly key milestone of this project

### 3.3.2 Gantt Chart

Table 6 : Gantt chart of FYP 1 and FYP 2

No	Details	FYP 1							FYP 2						
		1- 2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	23-24	25-26	27-28
1	Selection project title														
2	Preliminary research work														
3	Extended Proposal submission			●											
4	Proposal Defense				●										
5	Research work on materials and equipment														
6	Submission of Interim Report							●							
7	Pre-experimental preparation • Understanding equipment • Purchasing materials														
8	Submission of Progress Report											●			
10	Experimental work														
11	Pre-EDX											●			
12	Submission of Draft Report											●			
13	Submission of Dissertation and Technical Paper												●		
14	Viva														●

## CHAPTER 4

### RESULTS AND DISCUSSION

Before moving on to the analysis of the results, the trend of the graph obtained from the experiment is explained as per below. Sloan (2008) discussed the curve obtained from experiment of hydrate dissociation and formation where the volume is constant and temperature is changed. This is similar to the experimental condition of this study.

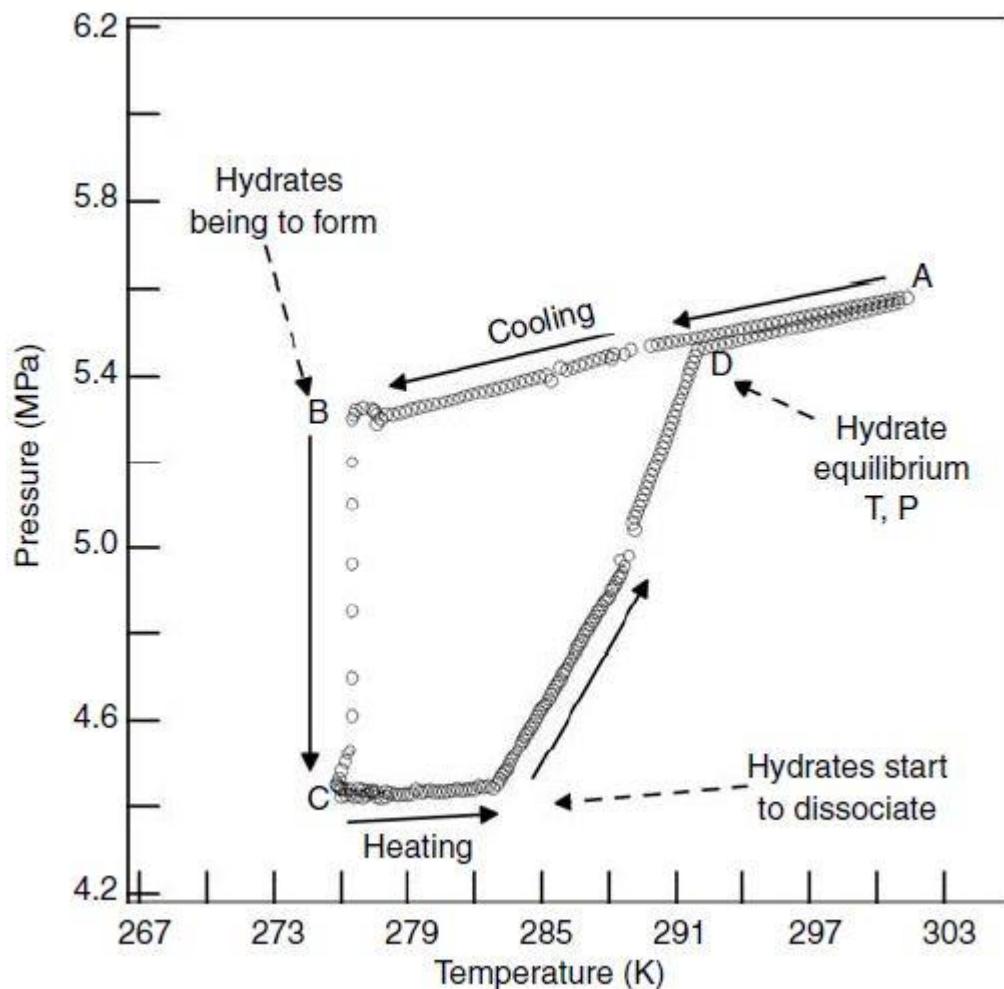


Figure 14 : Pressure vs Temperature curve for hydrate formation and dissociation [25]

As shown in Chapter 3 : Methodology, the temperature of the cell is decreased at first. According to the Figure 14, pressure is decreased when cell cooled down, and this is due to the contraction of the gas. Point A to Point B is the induction time of the hydrate. Point B is when the hydrates start to form and moving to Point C, there is sudden drop in pressure, showing the gas is completely consumed, and caged in the hydrate. As the temperature is increased, the dissociation process occurs and pressure is increased as gas is released. Point D is when the hydrates completely dissociate, and point for hydrate equilibrium pressure and temperature is recorded [25].

#### 4.1 RUN 1 : METHANE GAS + BMIM-CL AT 30 BAR

Table 7 : Experimental condition for Run 1

Sample	Pressure	Pure Methane Equilibrium Temperature
• Methane gas	30 Bar	1.52 ° C
• 1 wt% BMIM-Cl		

For the first run, the pressure is set to 30 Bar. The hydrate equilibrium temperature for pure methane at this pressure is 1.52 ° C. The objective of this run is to obtain a temperature shift, lower than 1.52 ° C for hydrate equilibrium temperature.

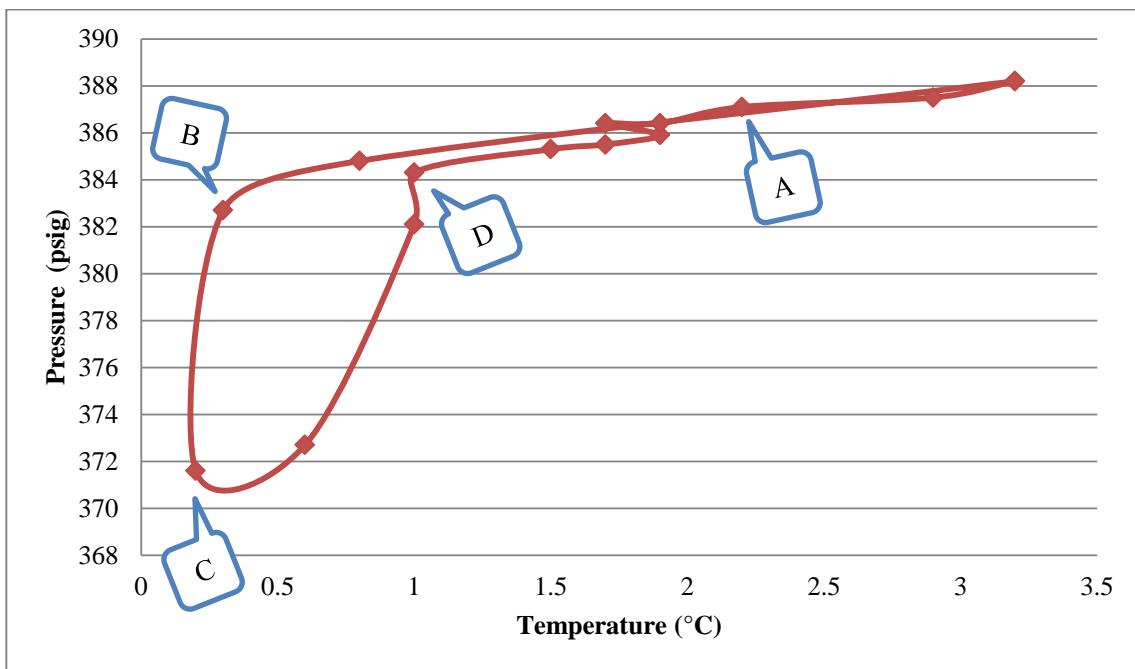


Figure 15 : Pressure vs Temperature Curve for set pressure = 30 Bar

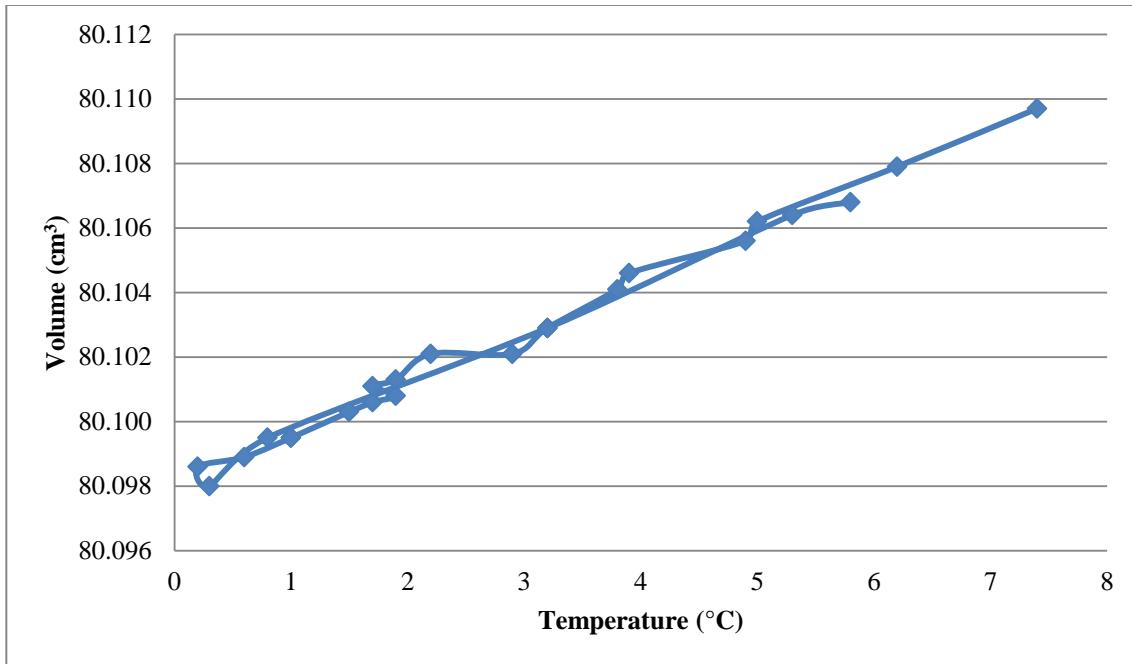


Figure 16 : Volume vs Temperature Curve for set pressure = 30 Bar

As per discussion above, A is the point where the time of hydrate is induction is started. From A to B is the time of induction, B is the point hydrate start to form. The pressure seems to agree with the statement as the pressure is slowly decrease, by mean is the contraction of gas. Based on Figure 15, hydrate is completely formed at point C and this can be justified by the sudden drop of pressure. The methane hydrate is seen dissociated at Point D. Point D is taken as the hydrate equilibrium pressure and temperature. For Figure 16, curve Volume vs Temperature is showing that the isochoric mode is applied, where the volume are approximately constant throughout the experiment,  $80 \text{ cm}^3$ .

Table 8 : Temperature ( $^{\circ}\text{C}$ ) and pressure (psig) for each point

A		B		C		D	
T ( $^{\circ}\text{C}$ )	P (psig)						
2.2	387.1	0.3	382.7	0.2	371.6	1	384.3

#### 4.2 RUN 2 : METHANE GAS + BMIM-CL AT 60 BAR

Table 9 : Experimental condition for Run 2

Sample	Pressure	Pure Methane Equilibrium Temperature
• Methane gas	60 Bar	
• 1 wt% BMIM-Cl		8.41 ° C

For the second run, the pressure is set to 60 Bar. The hydrate equilibrium temperature for pure methane at this pressure is 8.41 ° C. The objective of this run is to obtain a temperature shift, lower than 8.41 ° C for hydrate equilibrium temperature.

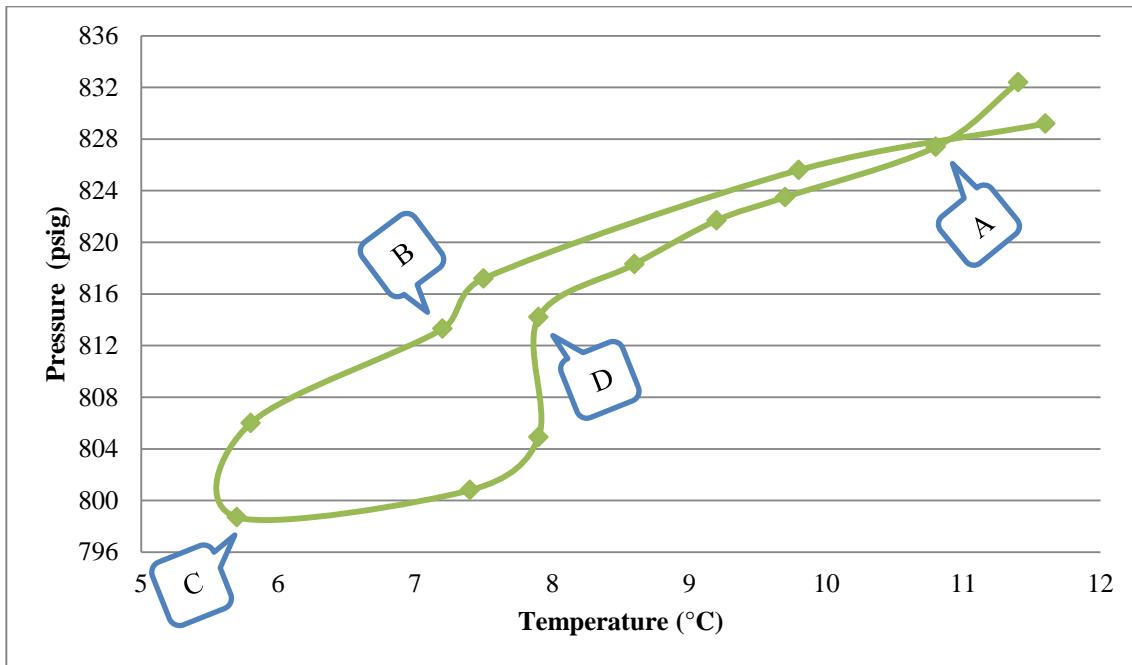


Figure 17 : Pressure vs Temperature Curve for set pressure = 60 Bar

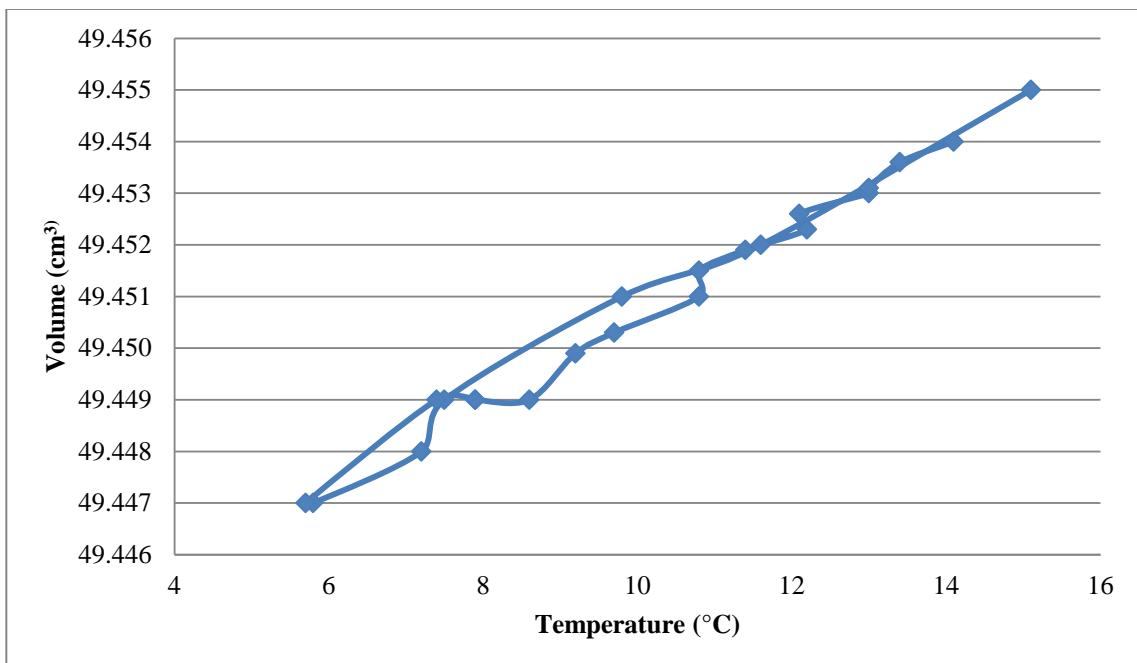


Figure 18 : Volume vs Temperature Curve for set pressure = 60 Bar

Referring to Figure 17, condition before point A is the stabilization of pressure. Point A is the point where the time of hydrate induction is started. The contraction of gas can be seen in the graph, as the pressure decreased, when temperature is cooled down. From A to B is the time of induction, B is the point hydrate start to form. Based on Figure 17 again, hydrate is completely formed at point C and this can be justified by the sudden drop of pressure. The methane hydrate is seen dissociated at Point D. Point D is taken as the hydrate equilibrium pressure and temperature. For Figure 18, curve Volume vs Temperature is showing that the isochoric mode is applied, where the volume are approximately constant throughout the experiment,  $49.5 \text{ cm}^3$ . This value is differ from the previous run, because the solution inside the cell is compressed to increase the pressure inside the cell from 30 Bar to 60 Bar.

Table 10 : Temperature ( $^{\circ}\text{C}$ ) and pressure (psig) for each point

A		B		C		D	
T ( $^{\circ}\text{C}$ )	P (psig)						
10.8	827.4	5.8	806	5.7	798.7	7.9	814.2

## 4.2 HYDRATE EQUILIBRIUM CURVE COMPARISON

The equilibrium pressure and temperature for methane hydrate + 1 wt% of BMIM-Cl is obtained and plotted at P-T Graph as shown in Figure 19. The curve is also compared to a few other curves to prove the effectiveness of 1 wt% of BMIM-Cl. The details for each data number is labelled as below :

Data (1) : Pure methane gas [25]

Data (2) : Methane gas + 1 wt% of EMIM-Cl [19]

Data (3) : Methane gas + 10 wt% of MeOH [25]

Data (4) : Methane gas + 1 wt% of BMIM-Cl

Table 11 : Pressure and temperature for literature data

Pressure (Bar)	Temperature ( °C )		
	Pure Methane	1 wt% EMIM-Cl	10 wt% MeOH
30	1.52		-3.41
50	6.63	6.37	1.57
60	8.41	7.76	3.37

Table 12 : Pressure and temperature for 1 wt% BMIM-Cl

1 wt% BMIM-Cl	
Pressure (Bar)	Temperature ( °C )
27	1
35	2.84
50	6.29
57	7.9

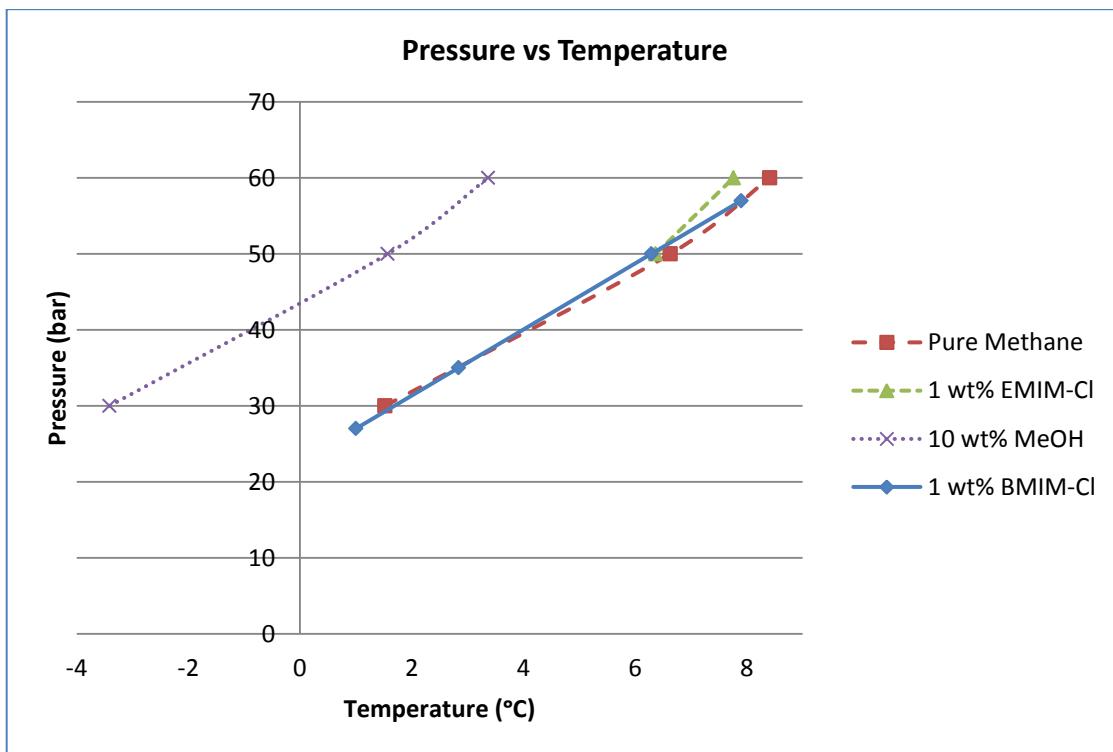


Figure 19 : Hydrate equilibrium curve for methane hydrate and inhibitors

From Figure 19, it can be observed that the result of BMIM-Cl in shifting the pure methane curve to a lower temperature is insignificant. This may be due to limited data and time constraint. This also applies to 1 wt% of EMIM-Cl. The thermodynamic inhibition effects of both ionic liquid cannot be proven from this plot. However, Partoon et al (2012) mentioned in the literature that the thermodynamic inhibition effects are less significant in lower pressure [19]. The results of ionic liquid may be significant if the curves are compared at higher pressure. As for the curves 10 wt% of MeOH, the curve shows quite significant temperature shift proving to be more effective than 1 wt% of BMIM-Cl. However, in order to have a significant result, a high concentration of MeOH (i.e. 10 wt%) is needed in order to obtain a significant result.

### 4.3 TEMPERATURE SHIFT

Since the P-T plot in Figure 19 is not significant and cannot prove or conclude the performance of 1 wt% of BMIM-Cl, the results for BMIM-Cl thermodynamic inhibition is translated into the calculation of temperature shift.

Table 13 : Equilibrium temperature for pure methane hydrate

Pressure	Methane Hydrate Equilibrium Temperature (°C)		
	Pure Methane	BMIM-Cl	ΔT
30	1.5	1.69	-0.19
40	4.07	3.99	0.08
50	6.63	6.29	0.34

Table 13 shows the data for pure methane and sample of 1 wt% of BMIM-Cl equilibrium temperature and pressure. The temperature shifts in Table 13 are calculated using below formula.

$$\Delta T_i = T_{0,P_i} - T_{1,P_i}$$

where  $T_{0,P_i}$  is the methane hydrate dissociation temperature for blank sample measured at pressure  $P_i$ , while  $T_{1,P_i}$  is the dissociation temperature for sample with inhibitor measured at the same pressure  $P_i$  [10].

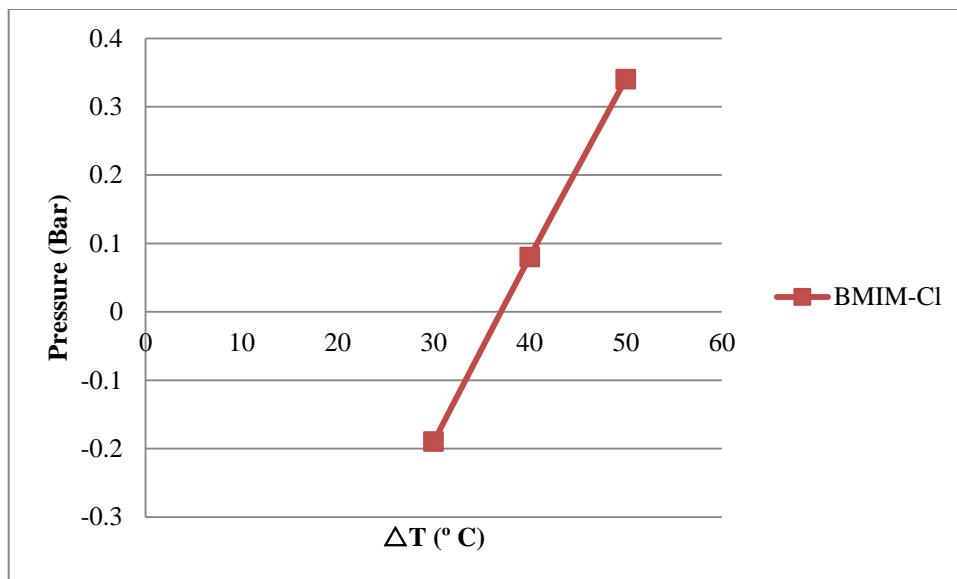


Figure 20 : Pressure vs Temperature shift for BMIM-Cl

Figure 20 is the plot for the pressure vs temperature shift for 1 wt% of BMIM-Cl. At pressure 30 Bar, the thermodynamic inhibition of BMIM-Cl is void because the temperature shift has a negative value, by means the pure methane equilibrium temperature is lower than the equilibrium temperature of sample with BMIM-CL. However, as the pressure increases, the temperature shift also increases. This concludes that the thermodynamic inhibition effect of BMIM-CL is more significant at higher pressure.

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

As a conclusion, BMIM-Cl can be seen as a potential hydrate inhibitor that can be explored more. Eventhough the inhibition effect of BMIM-Cl is not significant due to several constraints throughout the experiment, the equilibrium curve is seen shifted to a lower temperature, especially at higher pressure. At 30 Bar, the result is void but at 60 Bar, the temperature is shifted from 8.41 ° C to 7.9 ° C. In terms of temperature shift calculation, the highest temperature is observed at 50 Bar, with 0.34 ° C of temperature shift. This concludes that the effect of thermodynamic inhibition effect is more significant at higher pressure.

Eventhough the effectiveness is not as significant as MeOH, the research may be continued by adding more manipulative parameters to the study. For example, from literature it is proven that higher concentration gives more significant result, and same goes to higher pressure. Hence, adding more concentration of BMIM-Cl and testing BMIM-Cl at higher pressure may be giving better results. The performance of BMIM-Cl might be enhanced by mixing it with an additive such as chitosan. It is proven that chitosan is able to delay the formation of hydrate, having longer induction time than sample without chitosan [26].

However, ionic liquid is said to have little toxicity. For the future work, it is recommended to find green inhibitor. For example, natural deep eutectic solvent (NADES) can be tested as inhibitor. No previous study has experimented on this material, but this material has similar physical properties as ionic liquid, but in cheaper price [27]. NADES has the ability to maintain the liquid form at room temperature and even lower temperature and remain stable when water is added [28]. Since NADES can be extracted from plant, it will not contain any toxic which is good as green technology.

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