



UNIVERSITI  
TEKNOLOGI  
PETRONAS

## **HYDRATES INHIBITION USING IONIC LIQUID**

By

**NOR AMIRAH BINTI RAZALI**

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

Petroleum Engineering

JUNE 2012

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

---

(MS. MAZUIN JASAMAI)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JUNE 2012

## **CERTIFICATION OF ORIGINALITY**

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

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(NOR AMIRAH BINTI RAZALI)

## ABSTRACT

The formation of gas hydrates in gas and oil production and transmission pipelines leads to severe safety problems and huge economic loss, which has been the subject of long-standing problems. Gas hydrates can form in both gas producing and oil-producing wells. Conditions that favors gas hydrates formation is a combination of low temperature (around 32°F to 60°F) with high pressure (>600psia) for crystalline structures to form and also high concentrations of the gas stream and presence of H<sub>2</sub>O. As exploration and production moves to deeper seas, temperature and pressure conditions in the field favors hydrate formation, and thus the existing thermodynamic hydrate inhibitors are still not believed to give an economic solution. It has also been identified for some cases that the combination of thermodynamic and kinetic inhibitors is needed to give better results. This research examines on the application of Ionic Liquids as hydrate inhibitors and the discovery of dual function thermo-kinetic inhibitors, and thus its effectiveness is analyzed. The objectives is to compare the effectiveness of ionic liquid between EMIM-BF<sub>4</sub> and BMIM-BF<sub>4</sub> as hydrate inhibitor and to identify the most effective concentration for ionic liquid as the hydrate inhibitors. Experiment is conducted using differential scanning calorimeter (DSC). From the results, Ionic Liquid is observed to be effective at delaying the hydrated nucleation time and also shifting the hydrate phase equilibrium. From the laboratory experiment shows that EMIM-BF<sub>4</sub> is found to be more effective than BMIM-BF<sub>4</sub> since the induction time for EMIM-BF<sub>4</sub> is longer than BMIM-BF<sub>4</sub>. Ionic Liquid is observed to be effective at a low concentration compared to the conventional ways and therefore are expected to have significant economic and environmental advantages.

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## CHAPTER 1

### INTRODUCTION

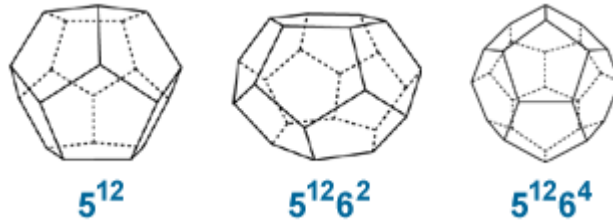
#### 1.1 Background of Study

Gas hydrates are solid crystalline compounds, composed of water and gas (Sloan, 1990). For the formation of gas hydrates to occur, the physical conditions of the flow must be fulfilled. One of the conditions that favors gas hydrates formation is a combination of low temperature (around 32°F to 60°F or 0 °C to 15 °C) with high pressure (>600psia= 4MPa) for crystalline structures to form. Apart from that, it is observed that high concentration of the gas stream, pressure pulsation of the gas stream or the introduction of small crystals of hydrate all hasten the formation of the hydrates (Hammerschmidt, 1934). With the conditions stated, it furnishes almost ideal conditions to accelerate the hydrates formation.

Free water molecules form a metastable crystal lattice, which is stabilized by light gas molecules (C1 – C4 paraffins, carbon dioxide, and hydrogen sulfide) occupying the crystal cavities. Methane hydrates are gas hydrates where the guest molecules are methane. Natural gas compounds can form three types of hydrate structure, cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). It is listed in Table 1 below and depicted in Figure 1. The specific hydrate structure formed is mainly determined by the size of the gas molecules trapped in the cavities. (Khalik M. Sabil, 2009)

**Structures I and II:** Two primary types of hydrate structures are known to exist commonly in nature, termed simply, structure I and structure II. These structures represent different arrangements of water molecules resulting in slightly different shapes, sizes, and assortments of cavities. Which structure forms depends on various aspects of the available guest gas. Methane preferentially forms structure I.



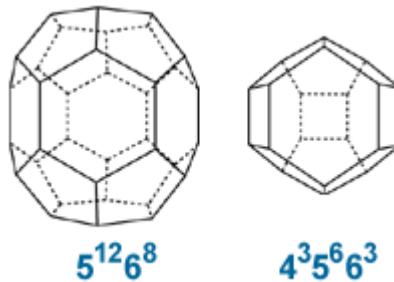


**Figure 1: Types Of Cavities Present In Structure I And II Methane Hydrates.**

Type	sI		sII		sH		
Cavity	Small	Large	Small	Large	Small	medium	Large
Structure	$5^{12}$	$5^{12}6^2$	$5^{12}$	$5^{12}6^4$	$5^{12}$	$4^3 5^6 6^3$	$5^{12}6^8$

**Table 1: Hydrate Crystal Structure**

**Structure H:** Structure H hydrates are rare, but are known to exist in the Gulf of Mexico, where supplies of thermogenically-produced heavy hydrocarbons are common. It is probable that other, more exotic, hydrate structures remain to be discovered.



**Figure 2: Cavities Unique To Structure H Methane Hydrates**

Hydrates have been of interest to the natural gas industry only in the last half century, although gas hydrates have been known for almost two centuries. Gas hydrate was the cause of plugging natural gas pipelines, which lead to the regulation of gas water-content, the development of improved methods of prevention of hydrate plugs, including the injection of hydrate inhibitors into the gas stream (Hammerschmidt,1934). Whenever very small amounts of water are in the gas, the potential exists for hydrate formation. The formation of gas hydrates in gas and oil production and transmission pipelines leads to severe safety problem and huge economic loss, which has been the subject of long-standing problems. The problems in this gas industry trigger the research

of hydrate prevention and mitigation, which may also benefit the recovery of methane from the natural hydrate deposits in the subsea sediments.

Therefore, various methods were developed to mitigate the formation of gas hydrate. The techniques include system heating and depressurization, water removal, and inhibition. In many cases, the hydrate inhibition by adding inhibitors to the system is the only viable option. There are two types of inhibitors that are used nowadays: thermodynamic and kinetic inhibitors. These two inhibitors should be distinguished from hydrate anti-agglomerants, which prevent the hydrate crystals from agglomerating and accumulating into large masses but do not inhibit the hydrate formation. Thermodynamic inhibitors shift the equilibrium hydrate dissociation/stability curve. The shortcomings of the traditional thermodynamic inhibitors stimulated the search for kinetic inhibitors (Lovell and Pakulski, 2003).

Kinetic inhibitors, on the other hand, retard the hydrate formation by slowing down the hydrate nucleation or growth rates (Englezos, 1993; Koh, 2002; Kvenvolden, 1993; Sloan and Koh, 2008). In the deep sea gas exploration, this type of inhibitor delays hydrate formation to a time longer than the residence time of the fluid in the hydrate-prone section of pipeline. Therefore, in this project, kinetic and thermodynamic inhibitor is investigated on its effectiveness to inhibit hydrate formation.

To evaluate the effectiveness of kinetic and thermodynamic inhibitors, the typical apparatuses are rocking cell chambers, autoclave cells (Arjmandi et al., 2003), flow loops (Peytavy et al., 2008). This project employs approach to measure emulsion characteristics by applying differential scanning calorimetry (DSC), in order to obtain a detailed analysis of the inhibitors.

## **1.2 Problem Statement**

Formation of gas hydrates in pipelines is causing serious operational and safety problems. In petroleum exploration and production operations, gas hydrates can cause partial or total blockages in pipelines and processing facilities. The problem is considered hazard in deepwater drilling, which can potentially block the blowout preventer (BOP) stack, kill lines and chokes, and obstruct the movement of the drill strings (Bahman Tohidi, 2005). This has brought new challenge for hydrate prevention in transportation. The crystallization of hydrate particles generally leads by forming solid plugs, to the blockage of pipelines, and thus to the shutdown of production facilities. The removal of hydrate plugs is generally difficult to achieve. A shutdown of several days or weeks may be necessary prior to the restarting of the production, and indeed, it may lead to pipeline abandonment as well.

Hydrate blockages in a subsea flowline system are most likely to be found in direction change areas in well, pipeline and riser parts of the system, and are rarely found in the tubing below the downhole safety valve and the flowlines after platform. Hydrates may appear anywhere and anytime in an offshore system when there is natural gas, water and suitable temperature and pressure. Hydrates may also occur in the drilling fluids that are used in deep offshore drilling operations, leading to severe threats towards the operation safety. All of these will result in catastrophic economic losses and ecological risks. Figure 3 shows a image of areas where hydrate blockages may occur in a simplified offshore deepwater system from the well to the platform export flow line.



**Figure 3: Example of Hydrate in Pipeline**

As an example of hydrate problems in oil production industry, there are more than 10 oil producing stations in both North and South are a operation of Petroleum Development Oman. With desert environment, the ambient temperature in Sultanate of Oman can drop to as low as 5 °C during winter, when hydrates form in several gases lift lines. The condition has caused affected wells to cease production, however being controlled temporarily by use of methanol as hydrate inhibitor. Due to HSE issues concerned with application of methanol, other alternative chemicals are to be examined to replace methanol as hydrate inhibitor with more cost effective and safety (Nengkoda & Taha, 2009)

The existing kinetic inhibitors, however, are still believed to give an economic solution especially at high pressure and large degrees of super cooling. It has also been identified for some cases that the combination of thermodynamic and kinetic inhibitors is still needed to give better results (Kelland, 2006). Therefore, there is still a need to discover inhibitors that are more effective than the existing inhibitors.

### **1.3 Objectives and Scope of Study**

The objectives of this study are:

- To compare the effectiveness of ionic liquid between EMIM-BF<sub>4</sub> and BMIM-BF<sub>4</sub> as hydrate inhibitors.
- To identify the most effective concentration for ionic liquid as the hydrate inhibitors
- To determine the efficiency of selected Ionic Liquids to the induction time of hydrate formation.

The scope of study includes:

- Conducting research on the theory and definition of terms related to the study.
- Conducting experiments to determine hydrates dissociation at different concentration of the inhibitor and to see the effectiveness of selected Ionic Liquids to delay the hydrate formation and shift dissociation curve when two parameters are varied i.e., pressure and temperature.

### **1.4 The Relevancy of the Project**

Hydrates formation is becoming problematic in the deepwater exploration since now there are many projects on deepwater exploration. As there were need of an effective hydrate inhibitor which is also economic to use. Using Ionic Liquid as Kinetic Hydrate Inhibitor (KHI) and Thermodynamic Inhibitor, engineers can overcome this problem. This also helps in deciding on investment on the particular field. The shortcomings of the traditional thermodynamic inhibitors stimulated the search for new type of kinetic inhibitors.

## **1.5 Feasibility of the Project**

This project is a straight forward experimental research. This project can be done within time frame given that everything goes fine. The objective can be achieved if the procedures are closely followed.

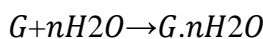
## CHAPTER 2

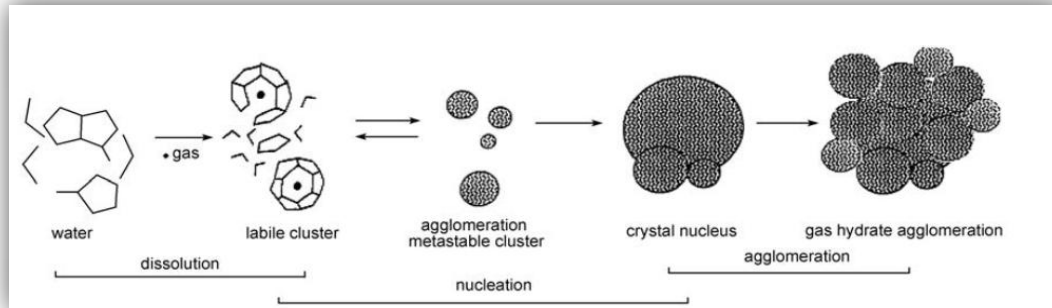
### LITERATURE REVIEW

#### 2.1 Hydrate Formation and Dissociation

Four components are required to form gas hydrates: water, light hydrocarbon gases, low temperature and high pressure. If any one of these components is absent then gas hydrates will not form. Hydrate problems can appear during normal production, but transient operations are often more vulnerable. For instance, during a shut-in, the temperature of the subsea line drops to that of the surrounding environment. Given sufficient time under these high pressures and low temperatures, hydrates will form.

Gas hydrates are ice-like crystalline inclusion compounds that form at high pressure ( $>600\text{psia} = 4\text{Mpa}$ ) and low temperature (around  $0\text{ }^{\circ}\text{C}$  to  $15\text{ }^{\circ}\text{C}$ ) conditions by hydrogen bonds of water molecules, with the assistance of gases such as methane, ethane, propane and butane. On the other hand, hydrocarbons heavier than butane generally do not form hydrates. There are three common crystal structures for gas hydrates named SI, SII, and SH. The network of the structure I is a centered face cubic system which appears with light components such as methane or carbon dioxide. Structure II network is of diamond type with 24 cavities per mesh. SII is the most common because of the normal distribution of hydrocarbons in petroleum. The structure H network of hexagonal type is constituted of 6 cavities. This SH appears for molecules of important size such as cycloalkanes, but at support gas as methane is always necessary in order to stabilize the structure. Basically, gas hydrate formation is expressed by the following equation:



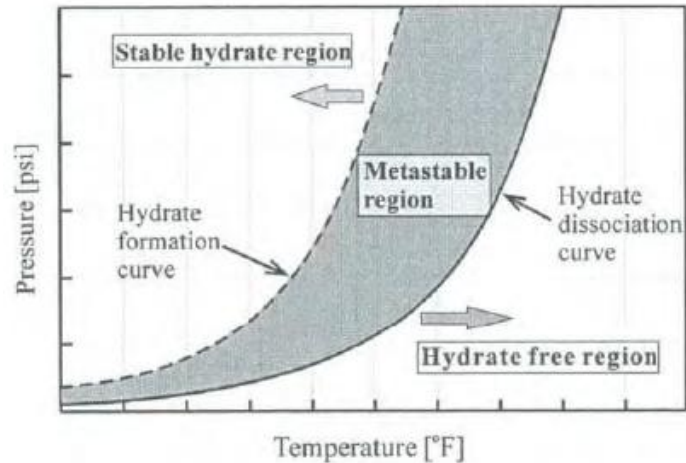


**Figure 4: Gas Hydrate Formation Process**

As shown in Figure 4, gas hydrate formation can be divided into gas dissolution, hydrate nucleation and agglomeration stages. Under condition of gas hydrate formation, water molecules form quasi-cavities by hydrogen bonds. When gases dissolve, gas molecules are entrapped into these quasi-cavities and form labile clusters. These clusters could agglomerate together, which are in quasi-equilibrium with labile clusters until the species reach a critical radius to form stable hydrate nuclei. Finally the hydrates grow catastrophically when hydrate nuclei agglomerate.

Hydrate formation and dissociation curves are used to define pressure/temperature relationships in which hydrates form and dissociate. These curves may be generated by a series of laboratory experiments, or more commonly, are predicted using thermodynamic software such as Multiflash or PVTSIM based on the composition of the hydrocarbon and aqueous phases in the system. The hydrate formation curve defines the temperature and pressure envelope in which the entire subsea hydrocarbons system must operate in at steady state and transient conditions in order to avoid the possibility of hydrate formation.

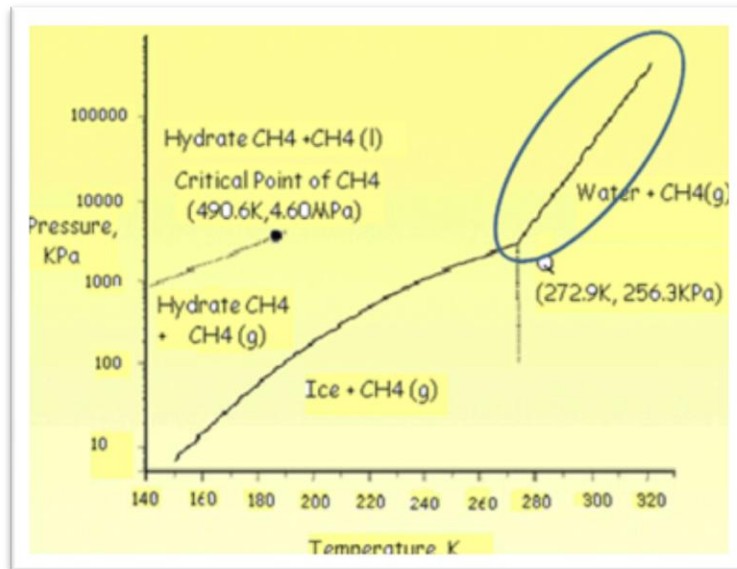




**Figure 5: Hydrate Formation and Dissociation Regions**

Figure 5 shows an example of these curves, which shows the stability of natural gas hydrates as a function of pressure and temperature. To the right of dissociation curve is the region in which hydrates do not form; operating in this region is safe from hydrate blockages. To the left of hydrate formation curve is the region where hydrates are thermodynamically stable and have the potential to form. This does not mean that hydrates will necessarily form or formed hydrates will cause operational difficulties. The stability of hydrates increases with increasing pressure and decreasing temperature.

Thermodynamic inhibitors shift the equilibrium hydrate dissociation/ stability curve to lower temperature and higher pressure, thus avoid the hydrate formation. Methanol is such an inhibitor that is quite effective and widely used. However, since exploration and production moves to deeper seas, temperature and pressure conditions in the field become in favor of hydrate formation, i.e., the temperature is colder and the pressure is higher, and the addition of such an inhibitor becomes expensive and environmentally prohibitive; thermodynamic inhibitors, such as methanol, need to be used at high concentration up to 60 wt%. Sodium chloride is another example of a thermodynamic inhibitor. However, adding inorganic salt also leads to corrosion problems.

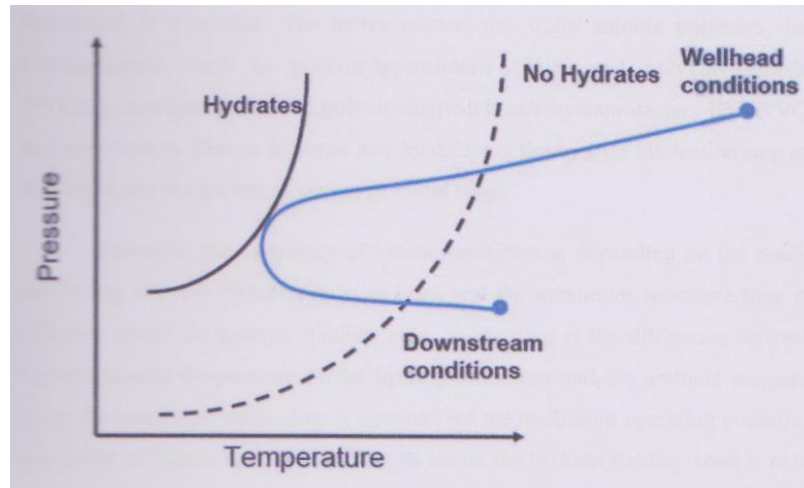


**Figure 6: Phase Equilibrium Diagram of Water-Methane System**

The shortcomings of the traditional thermodynamic inhibitors stimulated the search for kinetic inhibitors. Kinetic inhibitors, on the other hand, do not shift the curve and thus do not prevent the hydrate formation, but delay the hydrate formation by slowing down the hydrate nucleation and/or growth rates. In the deep-sea gas exploration, this type of inhibitor delays hydrate formation to a time longer than the residence time of the fluid in the hydrate-prone section of pipeline. Kinetic inhibitors can be effective at low dosage (<1%) and therefore are expected to have significant economic and environmental advantages.

## 2.2 Hydrate Mitigation Techniques

Hydrate formation is very expensive problem faced by the oil and gas industry, which must be solved in an economically and environmentally appropriate manner. The conventional method employed by the industry to prevent hydrates formation along the flow line is to add THI such as methanol or mono ethylene glycol (MEG), which shifts the hydrate formation conditions to lower temperatures and high pressures (Hammerschmidt, 1934; Solan and Koh, 2008). However, this method has significant economical impacts and technical limitations.



**Figure 7: Application Of Thermodynamic Inhibitor By Shifting Hydrate Formation Conditions**

There are two types of inhibitors that are used nowadays: thermodynamic and kinetic inhibitors. These two inhibitors should be distinguished from hydrate anti-agglomerants, which prevent the hydrate crystals from agglomerating and accumulating into large masses but do not inhibit the hydrate formation.

For thermodynamic inhibitor, it is only effective at high concentrations with respect to the water rate (10 to 60 wt. %), which consequently results in high concerns about Health, Safety and Environment (HSE) risks. For instance, large quantity of methanol leads to high operational expenditure (OPEX), needs large size storage facilities, and cause serious problems in desalting operation and water management. Therefore, studies have been carried out on the replacement of methanol or monoethylene glycol using Low Dosage Hydrate Inhibitors (LDHI). LDHIs can be efficiently used at dosages far lower than that of the THI, where the required concentration for these additives is expected to be in the range of 0.5-4.0 wt.% versus the water rate.

As the gas production and exploration moves to deeper seas, however, the pressure and temperature conditions become more favorable to the formation of hydrate and the existing inhibitors still cannot give an economic solution. It has also been

identified for some cases that the combination of thermodynamic and kinetic inhibitors is still needed to give better results.

In order to shift the equilibrium hydrate dissociation curve to lower temperature and higher pressure or delay the formation of hydrate, the inhibitors are necessarily attracted to water/hydrates, which could prevent the formation of or disrupt the hydrogen-bonded water cage. Prior research related to gas hydrates inhibition focused either on thermodynamic inhibitors, such as methanol, ethylene glycol, and sodium chloride, or on kinetic inhibitors such as poly(*N*-vinylpyrrolidone) (PVP), Luvicap (40 wt% PVCap in EG), and poly(*N*-vinylcaprolactam) (PVCap). These inhibitors either have strong electrostatic charges or form hydrogen bonds with water.

These dual function inhibitors were able to not only shift the equilibrium hydrate dissociation curve to lower temperature and higher pressure, but also delay the formation of hydrate by slowing down the nucleation and/or growth rate. This was possible because the inhibitors were Ionic Liquids that had strong electrostatic charges and at the same time their anions and/or cations formed hydrogen bonding with water. For certain Ionic Liquids, such as tetrafluoroborate Ionic Liquids, possessed excellent kinetic inhibition effects and some thermodynamic inhibition effects.

The new class of inhibitors is dialkylimidazolium-based Ionic Liquids with halide anions. Halides are now chosen because halides are known to have strong tendency to form hydrogen bonding with water. Short alkyls are also chosen for the substituents in the cation heads. Their performance in shifting the hydrate phase equilibrium curve and slowing down the hydrate formation rate is experimentally investigated. To understand the performance of Ionic Liquids in inhibiting the hydrate formation, measuring the electrical conductivity of the Ionic Liquid of interest using a conductivity meter and investigate the strength of hydrogen bonding between water molecules and anions/cations of the Ionic Liquid using infrared spectroscopy is needed.

### 2.3 Effectiveness of Ionic Liquids in Inhibiting Hydrate Formation

It has also been identified for some cases that the combination of thermodynamic and kinetic inhibitors is needed to give better results. This work presents the first account on the application of Ionic Liquids as novel hydrate inhibitors and the discovery of dual function thermo-kinetic inhibitors. These dual function inhibitors are able to not only shift the equilibrium hydrate dissociation curve to lower temperature and higher pressure, but also delay the formation of hydrate by slowing down the nucleation and/or growth rate. Their performances in shifting the hydrate phase equilibrium curve and slowing down the hydrate formation rate are measured in a high-pressure micro Differential Scanning Calorimeter (DSC). These Ionic Liquids are found to act as dual function hydrate inhibitors.

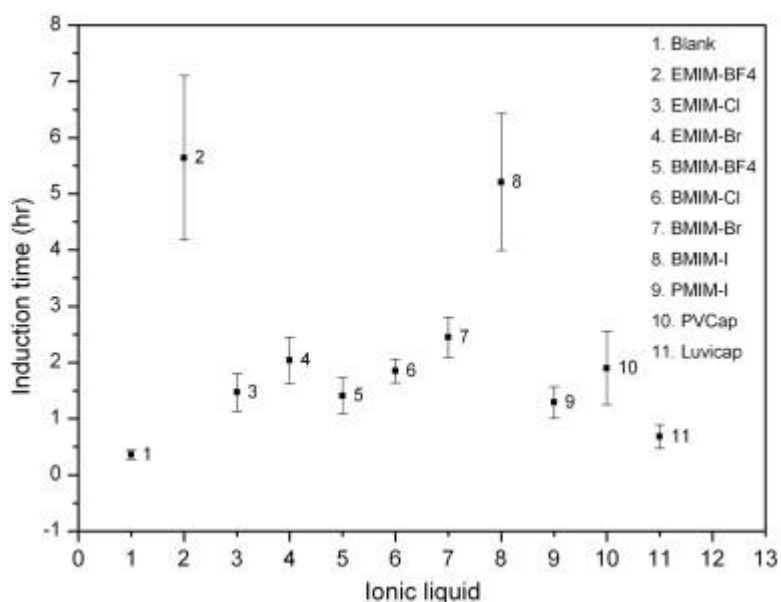
Ionic Liquids have a strong electrostatic charge and form hydrogen bonds with water, thus expected to perform effectively on hydrate inhibition. Ionic Liquids are organic salts that are liquid at room or moderate temperature; common Ionic Liquids consist of bulky and asymmetric organic cations, such as imidazolium or pyridiniumion, with alkyl chain substituents. The common anions used include tetrafluoroborate ( $\text{BF}_4^-$ ), dicyanamide ( $\text{N}(\text{CN})_2^-$ ), nitrate, chloride, and bromide. They have strong electrostatic charges and at the same time their anions and/or cations can be chosen or tailored to form hydrogen bonding with water. Besides these tunable properties, Ionic Liquids also offer several other desirable properties. For example, Ionic Liquids are environmentally friendly solvents due to their stability and extremely low vapor pressures. In addition, Ionic Liquids are very accessible, given their ease of preparation from relatively inexpensive materials.

It is found that the additions of the Ionic Liquids shift the methane hydrate equilibrium phase boundary to the temperature and pressure conditions that are unfavorable for the hydrate formation. The dialkylimidazolium-based Ionic Liquids with the hydroxylated cations exhibit an enhanced effectiveness in inhibiting hydrate formation. For the tetraalkylammonium-based Ionic Liquids, ones with the shorter alkyl substituent's of the cations perform better thermodynamic inhibition effects than ones with the hydroxylated longer alkyl substituents of the cations. Among all of the Ionic

Liquids studied, tetramethyl-ammonium chloride is the most effective one, which is comparable with ethylene glycol.

## 2.4 Induction Time of Hydrate Formation from Samples Containing Ionic Liquids

The induction time is the time elapsing until the moment at which the onset of precipitation can be detected, which is the sum of the time for critical nucleus formation and growth to detectable size. The heterogeneous nucleation rate, thus the induction time, is a probabilistic phenomenon that depends on many factors, such as the cell wall roughness, the presence of impurities and particles in the sample, and the driving force. As a consequence, to compare the performance of different inhibitors, we should measure the induction time using the same apparatus and the same experimental approach.



**Figure 8: The Induction Times of Methane Hydrate Formation from Blank Samples and Samples Containing Different Inhibitors.**

The induction time of hydrate formation from samples with Ionic Liquids are longer than that from blank sample. The kinetic inhibition effect of BMIM-I is almost as good as that of EMIM-BF4. The mean values of induction time of methane hydrate

formation from samples containing 1 wt% BMIM-I and 1 wt% EMIM-BF<sub>4</sub> are about 5.21 and 5.7 h, respectively, which are found to be much better than those of commercial kinetic inhibitors, such as Luvicap and PVCap, and all the other Ionic Liquids. The kinetic inhibition effects of EMIM-Br and BMIM-Br are similar to that of PVCap.

The performance of imidazolium-based Ionic Liquids as a new class of gas hydrate inhibitors has been investigated in a high-pressure micro differential scanning calorimeter. The effects of the anion and cation types of Ionic Liquids on induction time of hydrate formation, on the other hand, are more revealing. Due to their stronger hydrogen bond, tetrafluoroborate Ionic Liquids are found to perform better than other Ionic Liquids and much better than PVP.

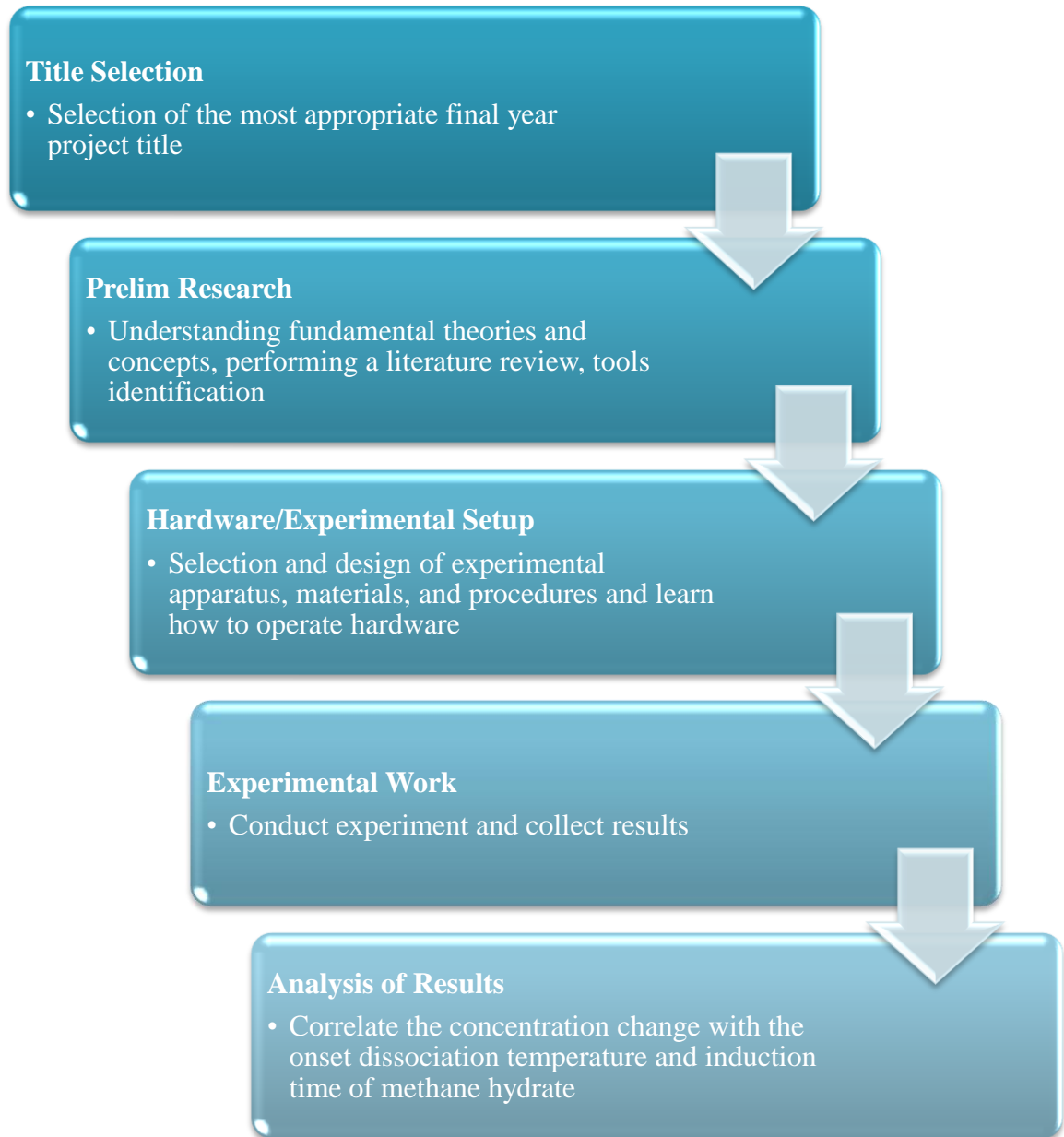
Xiao et. al further investigated the potential of six dialkylimidazolium halide Ionic Liquids as hydrate inhibitors. The Ionic Liquids studied with concentrations of 10wt% shift the equilibrium methane hydrate dissociation curve about 0.2-1.2 K to lower temperature. Among all the Ionic Liquids studied, EMIM-Cl is the most effective thermodynamic inhibitor. The thermodynamic inhibition effectiveness of Ionic Liquids is in the following order: EMIM-Cl<sub>4</sub> > EMIM-Br<sub>4</sub> > PMIM-I<sub>4</sub> > BMIM-Cl<sub>4</sub> > EMIM-BF<sub>4</sub> > BMIM-Br<sub>4</sub> > BMIM-I<sub>4</sub> > BMIM-BF<sub>4</sub>.

## CHAPTER 3

### METHODOLOGY

#### 3.0 METHODOLOGY

##### 3.1 Research Methodology

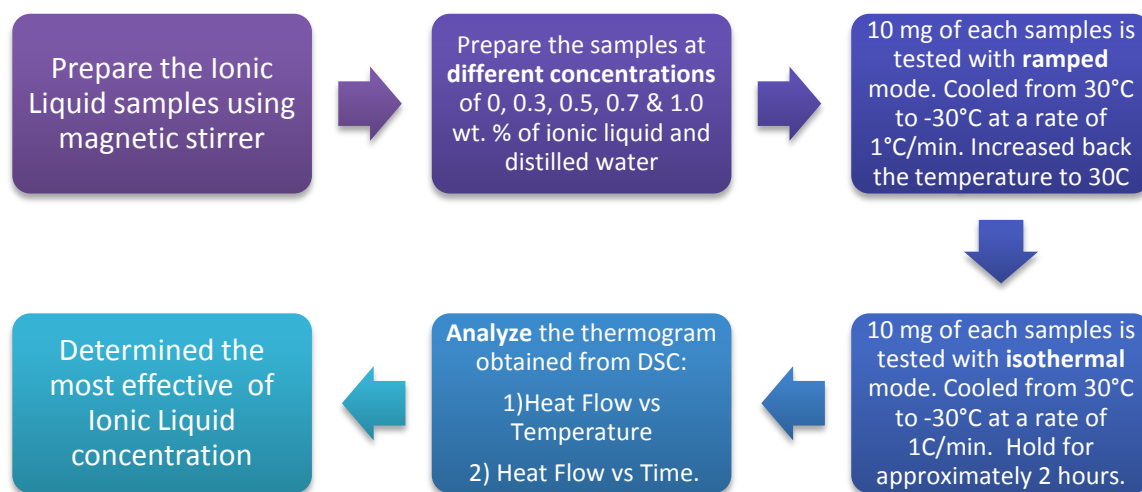


**Figure 9: Flowchart Representation of Project Methodology**



Initial stage in achieving this project objectives involved research and study prior to the submission of preliminary report. The Journal Chemical Engineering Science, Journal Chemical Engineering Data and textbook references have been studied to acknowledge the application for Ionic Liquids and hydrate inhibitors.

### 3.2 Experimental Methodology



**Figure 10: Flowchart Representation of Experimental Methodology**

The solution of ionic liquid samples was prepared using a magnetic stirrer. For this experiment, ionic liquid is added to the water in a drop wise manner. Before preparing the sample, Ionic Liquid will be added to the water phase at different concentration of 0.3, 0.5, 0.7 and 1.0 wt% of the total sample. Ionic liquid is water soluble and can dissolve in water.

In order to determine the amount of mass of ionic liquid to be added to distilled water, first the density of ionic liquid is determined. For example, the volume was

distributed to obtain a 1 wt% in the samples. Therefore, the mass required to prepare different concentration of samples was based on the sample calculation shown.

$$\text{Weight Percent} = \frac{\text{Weight of Solute}}{\text{Weight of Solution}} \times 100\%$$

2 Ionic Liquid which is EMIM-BF<sub>4</sub> and BMIM-BF<sub>4</sub> with different concentrations of samples would be obtained which are:

- Distilled water with 0.3 wt% Ionic Liquid
- Distilled water with 0.5 wt% Ionic Liquid
- Distilled water with 0.7 wt% Ionic Liquid
- Distilled water with 1.0 wt% Ionic Liquid

Once the samples are prepared, they will be tested for the experimental tests using the DSC. About 5 to 10 mg of the sample will be placed into the sample cell. Then, the sample will be purged by purified nitrogen at 30°C. The sample will be cooled from 30°C to -30°C at a rate of 1°C/min. Then, the temperature will be increased back to 30°C. This cooling-heating process will be repeated three times to observe the effect of hydrate in the emulsion. This is also the first mode of operation for this project.

Another procedure is isothermal mode. This is where the sample will be cooled from 30°C to -30°C at a rate of 1°C/min and it will be held for about 6 hours. Upon the hydrate formation, the sample will be heated to dissociate the hydrates. This procedure will be repeated two times in order to observe the effect of hydrate in the emulsion. The experiment result will be indicated in thermogram analysis of the parameters of heat flow, temperature and time for all four samples tested.

The results and analysis obtained through experimental studies of selected Ionic Liquids will be compared to another type of ionic liquid to analyze the effectiveness of the selected Ionic Liquids in inhibiting hydrate formation.

### 3.3 Experimental Apparatus

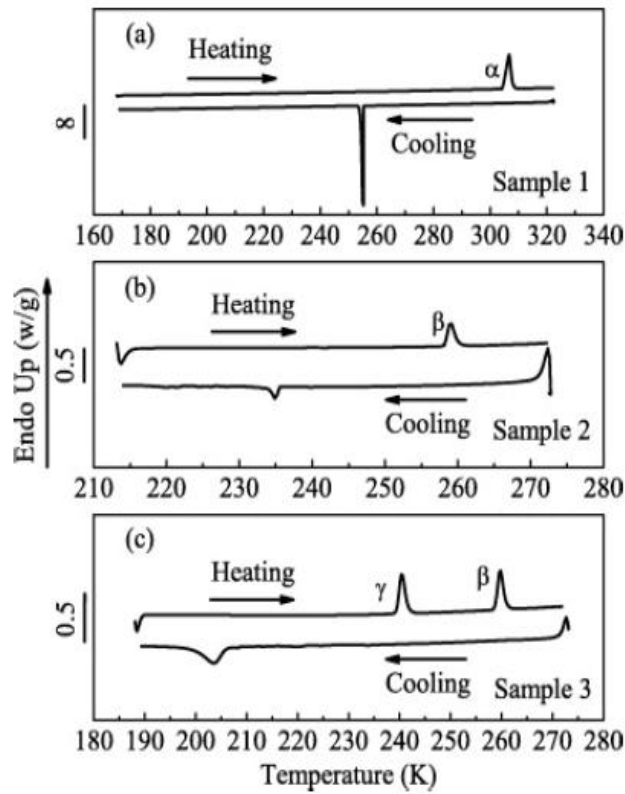
The experimental studies of Ionic Liquids will be conducted using PerkinElmer's Pyris 1 Differential Scanning Calorimetry (DSC). StepScan is a software product for use with PerkinElmer's power compensation Pyris 1 DSC. Differential Scanning Calorimetry (DSC) is used to measure the thermal properties of the water-in-oil samples prepared using the magnetic stirrer. It facilitates the collection of accurate specific heat capacity data by repeatedly measuring the heat flow to a known amount of sample at a constant heating rate. It is also used to obtain the dissociation temperature of nitrogen hydrate and the induction time of nitrogen hydrate formation.

DSC measures the amount of heat flow into the samples (endothermic) and away from the samples (exothermic) when the specimen undergoes thermal transition. The experimental apparatus is shown in Figure 10. The pressure within the sample cell is measured using a high sensitive digital pressure transducer manufactured by MENSOR with an accuracy of 0.010% of full scale. The pressure data are acquired synchronously with the heat data measured by DSC.



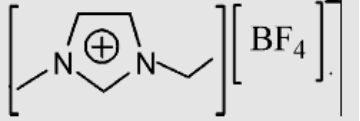
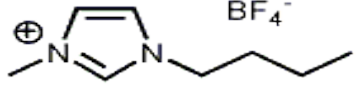
**Figure 10: Perkin Elmer Pyris 1 DSC**

In the DSC thermogram of Perkin Elmer, the Y axis is usually expressed in mW or W/gm. The latter is a normalized unit (heat flow / weight of sample). For the Y-axis, analyst need to be aware of heat flow convention whether endothermic is pointing up or down. Both conventions are acceptable. Thermal events will appear as deviations from the baseline. The X-axis can be displayed as either temperature or time. The area under the curve is usually calculated as the integration of heat flow over time. The unit under the curve is therefore mJ or J/gm.



**Figure 12: Samples of Thermogram Generated By *Perkin Elmer Pyris 1 Dsc***

For this project, two imidazolium-based Ionic Liquids are selected as potential hydrate inhibitors based on literature review:

Symbol	Chemical name	Chemical structure
EMIM-BF <sub>4</sub>	1-ethyl-3-methylimidazolium tetrafluoroborate	
BMIM-BF <sub>4</sub>	1-butyl-3-methylimidazolium tetrafluoroborate	

**Table 2: Imidazolium-Based Ionic Liquid**

### 3.3.1 Conditions that favor gas hydrate formation

There are four factors that can contribute to the hydrates formation:

- i. High pressure (>600psia = 4MPa)
- ii. Low temperature (32°F to 60°F or 0°C to 15°C)
- iii. Water (either in the form of liquid or water vapor)
- iv. Hydrate formers (C1, C2, C3, C4, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>S)

The common hydrate problem in the petroleum industry is methane hydrate. But this project used nitrogen as carried gas instead of methane due to limited availability of the methane gases. There are slight difference between methane hydrate phase behavior and nitrogen hydrate phase behavior as shown in the Figure 13 and Figure 14.

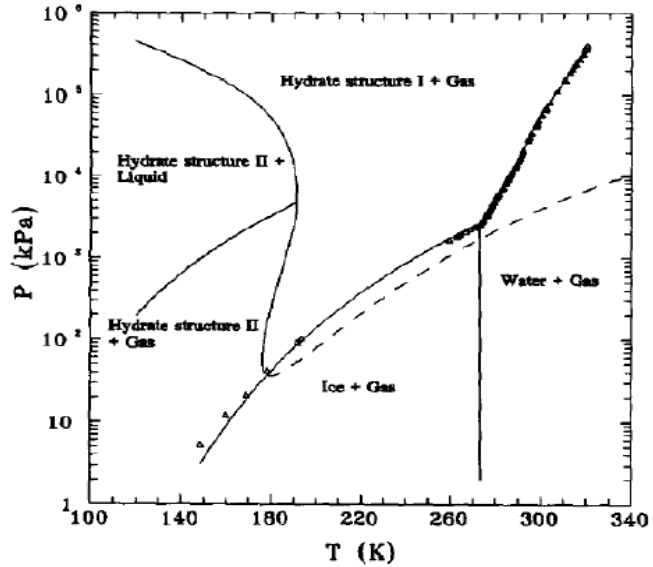


Figure 13: Calculated Phase Diagram for Methane Hydrate. The Dashed Line Represent An Unstable Equilibrium Line Between Hydrate Structures I And Ii And Gas, Where It Cuts The Ice-Gas-Hydrate Equilibrium Line There Is A Change In The Stable Hydrate Structure. (Lundgaard And Mollerup, 1992)

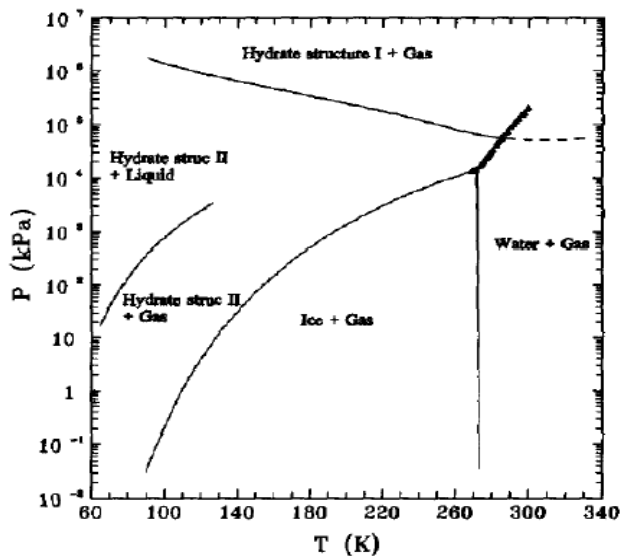


Figure 13: Calculated Phase Diagram For Nitrogen Hydrate. The Solid Line At The Top Of The Diagram Represents The Equilibrium Line Between Hydrate Structures I, Ii And Gas. The Dashed Extension Represents An Unstable Equilibrium Line Between Hydrate Structure I And Structure Ii (Lundgaard And Mollerup, 1992)

### 3.4 Key Milestones and Planning

Activity	1st SEM				2nd SEM			
	O	N	D	J	F	M	A	M
Selection of FYP Topic	Process							
Preliminary Research Studies	Process							
Submission of Extended Proposal Defense	Milestone							
Survey on the availability of experiment apparatus		Process						
Study on how to prepare samples.		Process						
Proposal defense. Present details on methodology of the experiment			Milestone					
Sample Preparation. Distilled water with ionic liquid at different concentration. 100ml of each sample.				Process	Process			
Experiment of effect of temperature on hydrate formation and dissociation with and without ionic liquid						Process		
Completion of the temperature determination at which hydrates formation & dissociation at different concentrations						Milestone		
Completion of determination of the time at which hydrates form at different concentrations						Milestone		
Data analysis						Process	Process	
Report documentation							Process	Milestone



**Figure 11: Gantt chart And Key Milestone through the Final Year Project**

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Hydrate Formation in Samples

Initially, the ramped mode test was used in the DSC to measure the effects of temperature towards the formation of hydrates in the samples. Nine different samples were prepared which are:

- i. Distilled water without Ionic Liquid
- ii. Distilled water with 0.3wt% EMIM-BF<sub>4</sub>
- iii. Distilled water with 0.5wt% EMIM-BF<sub>4</sub>
- iv. Distilled water with 0.7wt% EMIM-BF<sub>4</sub>
- v. Distilled water with 1.0 wt% EMIM-BF<sub>4</sub>
- vi. Distilled water with 0.3 wt% BMIM-BF<sub>4</sub>
- vii. Distilled water with 0.5 wt% BMIM-BF<sub>4</sub>
- viii. Distilled water with 0.7 wt% BMIM-BF<sub>4</sub>
- ix. Distilled water with 1.0 wt% BMIM-BF<sub>4</sub>

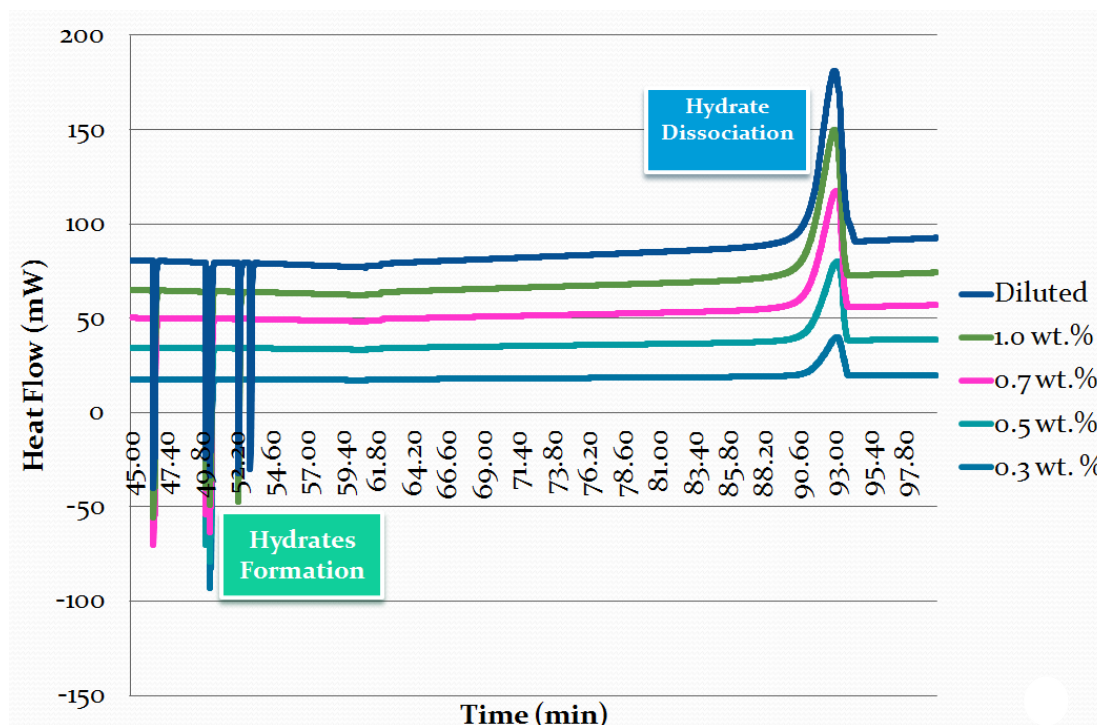
10mg of each sample were first examined by ramped mode. In ramped mode, samples were cooled from 30°C to -30°C at a rate of 1°C/min, and heated back to 30°C at the atmospheric pressure. Nitrogen gas is used as the carried gas during the cooling process. Heat flow vs. temperature data were gathered and plot in the graph.

From this graph, phase transitions can be determined by looking at the dips and peaks of the graph which represent the total heat flow in (endothermic) or out (exothermic) of the samples. Figure 14 shows a thermogram (heat flow vs. time) of the samples of EMIM BF<sub>4</sub>.

Based on the Figure 14, generally hydrate started to dissociate at 90 minutes during the heating process. The hydrate formation dips shown are the indication of heat released (exothermic) by the samples in order to transform into another physical state,

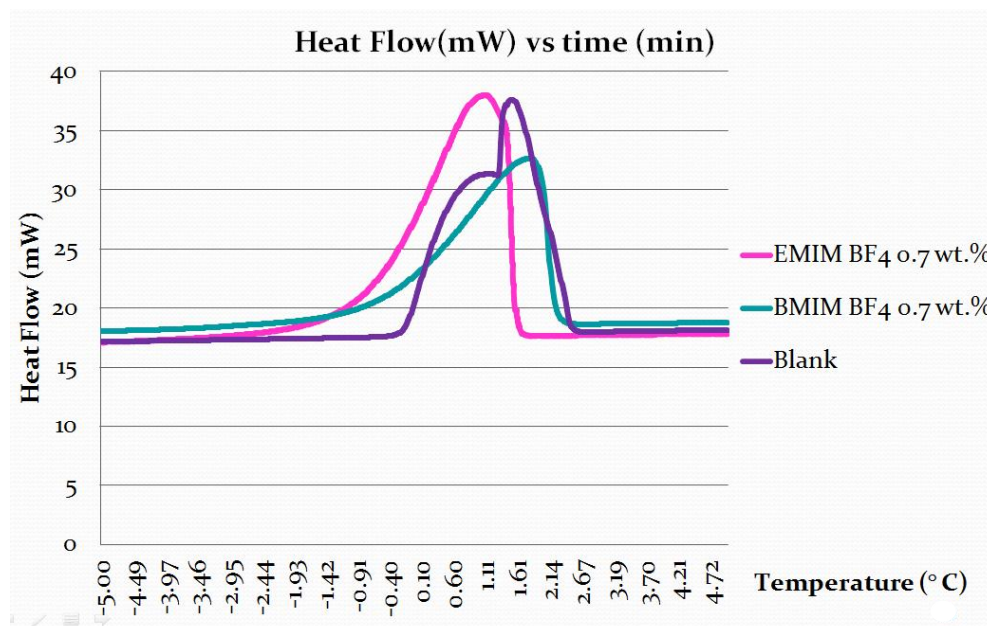


which is from water with ionic liquid to hydrate crystalline state. As the temperature gets lower, the hydrate formed earlier remains as the solid phase.



**Figure 14: Hydrate Formation and Dissociation Trends of Distilled water with Ionic Liquid through Cooling-Heating Process for EMIM BF<sub>4</sub> during Ramped Mode Test**

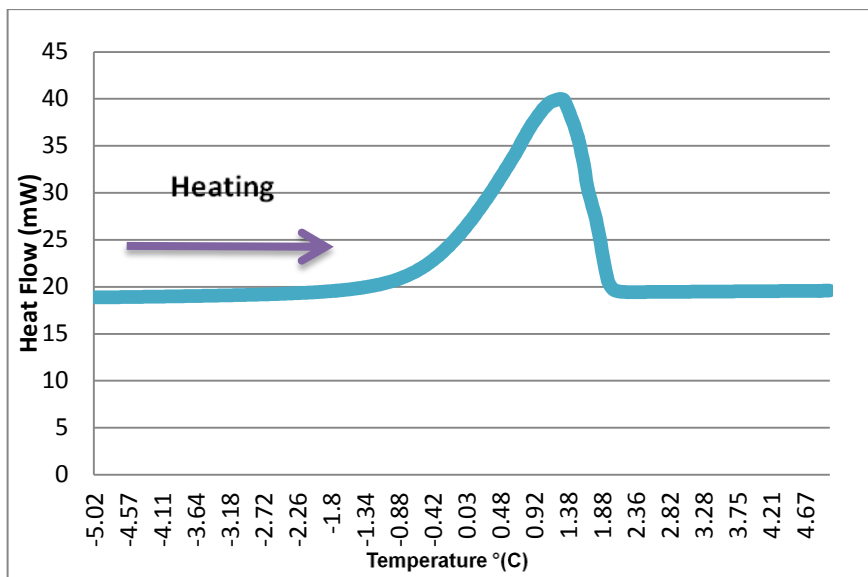
From figure 14, it is observed as the temperature gets lower, hydrates starts to form in the sample, indicated by the peak. On the other hand, after the formation of hydrate and the temperature gradually increased. The hydrate form earlier is observed to have formed at time 53 minutes and. The hydrate dissociation trend is shown in the peak and starts to dissociate at 90.6 minutes. The ramped mode test is carried out with two Ionic Liquid EMIM BF-4 0.3 wt%, 0.5 wt%, 0.7 wt% and 1.0 wt% concentrations. From the results, it is observed that 0.7 wt% concentration is the most effective whereby the hydrate dissociates the fastest which is 90.30 minutes. It can be observed while temperature increases slowly. For Thus, this shows the tendencies of hydrate formation in the samples as the temperature changes.



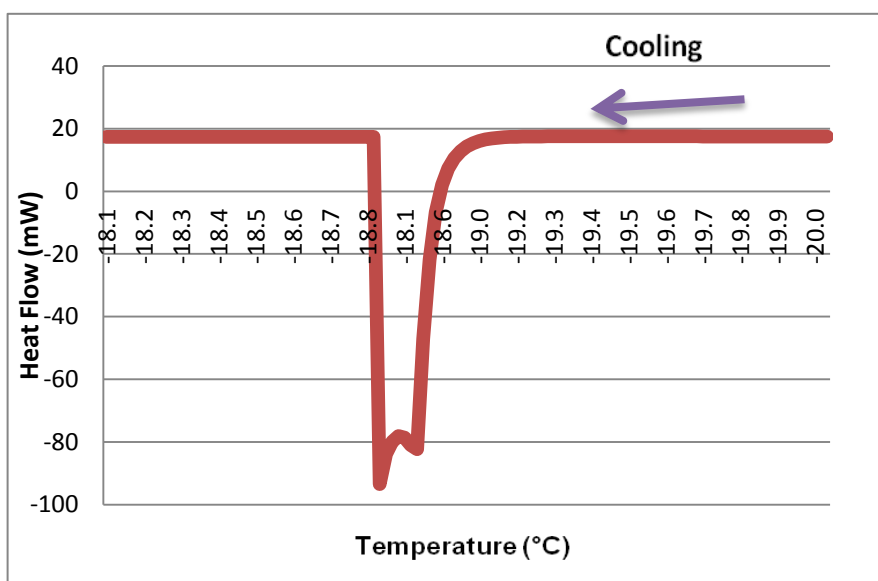
**Figure 15: Hydrate Dissociation Temperature for Three Samples**

As the samples undergo heating process, there are peaks of hydrate dissociation which can be seen at the temperature mere 0°C as seen at Figure 15. This is indication of hydrates formed earlier during the cooling process being dissociated. Heat is absorbed (endothermic) by the samples in order to transform from solid to liquid phase. The results of different concentrations of Ionic Liquid yield from ramped mode test are quite similar, whereby the hydrate formed as samples undergo cooling process and hydrate dissociation trends can be observed while temperature increases slowly.

Thus, this shows the tendencies of hydrate formation in the emulsions as the temperature changes. However, to examine the effectiveness of kinetic inhibitor in delaying the hydrate nucleation, the samples must be tested with isothermal mode in DSC.



(A)



(B)

**Figure 16: Hydrate dissociation (A) and Hydrate formation (B) in distilled water with Ionic Liquid during ramped mode test in DSC**

From figure 16, it is observed as the temperature gets lower, hydrates starts to form in the sample, indicated by the peak. On the other hand, after the formation of hydrate and the temperature gradually increased. The hydrate form earlier is observed to have formed at temperature  $-18.5^{\circ}\text{C}$ . The hydrate dissociation trend is shown in the peak in figure 15(A). The ramped mode test is carried out with two Ionic Liquid EMIM BF-4 and BMIM BF-4 with 0.3 wt%, 0.5 wt%, 0.7 wt% and 1.0 wt% concentrations. The result yields are quite similar, whereby the hydrate formed as samples undergo cooling process and hydrate dissociation trends can be observed while temperature increases slowly. Thus, this shows the tendencies of hydrate formation in the samples as the temperature changes.

#### **4.2 Dissociation Time of Hydrate Formation from samples.**

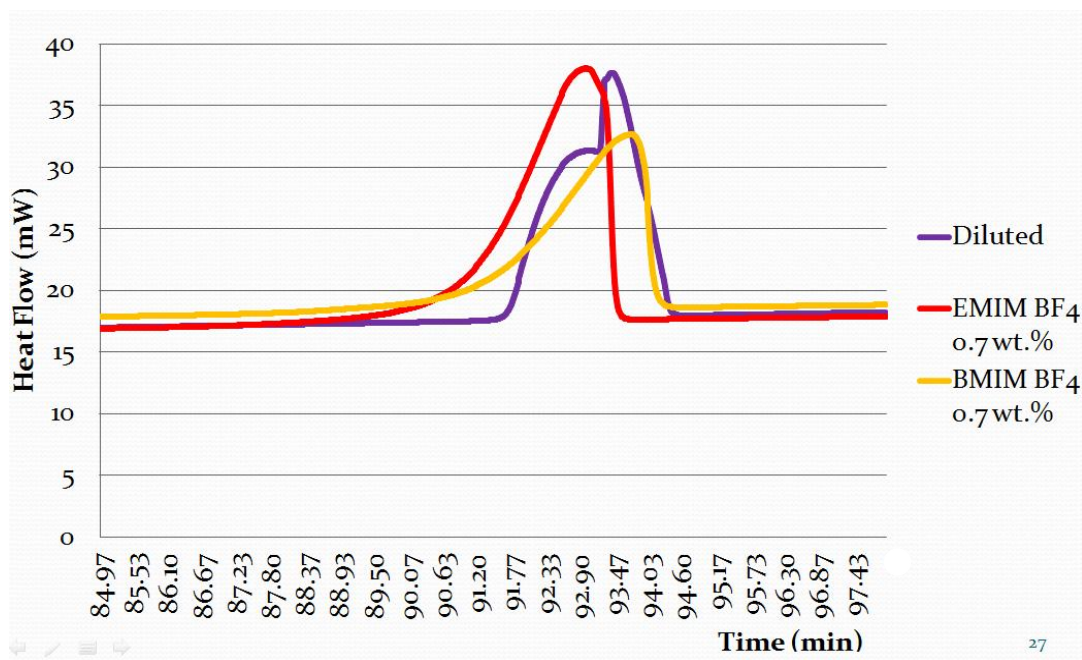
The induction time is an important indicator to characterize the kinetics of gas hydrate crystallization. The induction time is the time elapsing until the moment at which the onset of precipitation can be detected, which is the sum of the time for critical nucleus formation and growth to detectable size (Behar et al., 1994; Verdoes et al., 1992). For heterogeneous nucleation, the nucleation rate depends on many factors, such as the cell wall roughness and the presence of impurities and particles in the sample. It is also greatly dependent on the driving force. The nucleation is thus a probabilistic phenomenon and so is induction time. Since different experimental approaches will obviously give different results, to compare the performance of different inhibitors, one should measure the induction time using the same experimental approach and the same apparatus.

The performance of the best ionic liquid is then investigated at lower concentrations. Examples of thermograms for induction time measurements of hydrate formation from blank sample and samples containing ionic liquids are shown in Figure 17. It demonstrates that the growth of methane hydrate crystal is very quick after it reaches a detectable size.

In this study, the induction time is obtained as the period between the starting point of the isothermal step ( $-12^{\circ}\text{C}$ ) and the onset point of the exothermic peak. As

expected, the induction time of hydrate formation from samples with ionic liquids are longer than that from blank sample.

Based on the effectiveness of both ionic liquid, EMIM-BF<sub>4</sub> is found to be more effective than BMIM-BF<sub>4</sub> since the induction time for EMIM-BF<sub>4</sub> is longer than BMIM-BF<sub>4</sub>. BF<sub>4</sub><sup>-</sup> ionic liquids are found to perform better than other ionic liquids. A possible reason is that BF<sub>4</sub><sup>-</sup> has stronger ability to form hydrogen bond with water than the other types of anion. Although EMIM-BF<sub>4</sub> and BMIM-BF<sub>4</sub> differ to each other only in the alkyl substituent of imidazolium, EMIM-BF<sub>4</sub> performs better than BMIM-BF<sub>4</sub>. A longer alkyl in the cation may hinder hydrogen bonding between BF<sub>4</sub><sup>-</sup> and water.



**Figure 17: Dissociation time for 0.7% wt concentrations for three samples**

Figure 17 shows hydrate dissociation peaks of the solution in the three samples tested, with and without addition of Ionic Liquid as hydrate inhibitor. The comparison is made between each sample by looking at hydrate dissociation time. Referring to heat flow curves as shown, solution with 0.7% wt EMIM BF<sub>4</sub> ionic liquid tends to dissociate hydrate earlier which is at 89 minutes followed by solution with 0.7wt% BMIM BF<sub>4</sub>

ionic liquid at 90.07 minutes. Blank sample dissociate at 91.4 minutes. This shows that EMIM BF<sub>4</sub> is more effective than BMIM BF<sub>4</sub> since the dissociation time is the earliest.

## CHAPTER 5

### CONCLUSION

#### 5.1. CONCLUSION

The application of ionic liquids as dual function thermo kinetic inhibitors that is able to not only shift the hydrate aqueous liquid vapor equilibrium (HLVE) curve but also slow down the nucleation and/or growth rate. Ionic liquids act as dual function thermo-kinetic inhibitors which makes it performs more effectively. Based on research, studies and experiments carried out throughout this period, it is proven that the employment of Ionic Liquid as dual function inhibitors in water with probable hydrate formation is able to increase the flow assurance of the system. The performance of two ionic liquids as a new class of gas hydrate inhibitors has been investigated in a differential scanning calorimeter (DSC) and shows accurately on the effectiveness of Ionic Liquid in delaying the hydrate nucleation and dissociation time. Since Ionic Liquid is very effective in low concentration (<2.0wt%), it is proven that Ionic Liquid is much more effective as hydrate inhibitor compare to conventional inhibitors like methanol and monoethylene glycol (MEG).

The objectives are achieved throughout this project. Hydrates to form in the samples are determined to be at temperature of  $-23^{\circ}\text{C}$ , and dissociate at temperature around  $0^{\circ}\text{C}$ . Hydrates in the sample of distilled water without Ionic Liquid tend to dissociate the latest which is at 91.4 minutes. In the other hand, hydrates in the samples of distilled water with Ionic Liquid of 0.3wt%, 0.5 wt%, 0.7 wt% and 1.0 wt% dissociate earlier. From the results, 0.7% wt EMIM BF<sub>4</sub> ionic liquid tends to dissociate hydrate earlier which is at 89 minutes followed by solution with 0.7wt% BMIM BF<sub>4</sub> ionic liquid at 90.07 minutes & Blank sample dissociate the latest which is at 91.4 minutes. Based on the effectiveness of both ionic liquid, EMIM-BF<sub>4</sub> is found to be more effective than BMIM-BF<sub>4</sub> since the dissociation time for EMIM-BF<sub>4</sub> is shorter than BMIM-BF<sub>4</sub>. 0.7wt% of Ionic Liquid concentration is determined to be the most effective Ionic Liquid as dual function hydrate inhibitor. The study of effect of concentration of induction time

indicates that an ionic liquid concentration of larger than 1wt% does not offer a lot of advantage in retarding the hydrate formation.

The present invention is useful for production, processing and transportation in oil and gas industry, especially for deep sea exploration and production where the operating temperature and pressure favor hydrate formation.

## **5.2. FUTURE WORK RECOMMENDATION**

The existing kinetic inhibitors are still not believed to give an economic solution especially at high pressure and large degrees of supercooling. It has also been identified for some cases that the combination of thermodynamic and kinetic inhibitors is still needed to give better results. Therefore, there is still a need to discover inhibitors that are more effective than the existing inhibitors. On the basis of prior research related to inhibiting the formation of gas hydrates, it can be concluded that materials having strong electrostatic charges or forming hydrogen bonds with water can generally inhibit the formation of gas hydrates. Sodium chloride is an example of material that has strong electrostatic charges. Methanol, polyethylene oxide (PEO), and PVP are examples of materials that form hydrogen bonds with water. Substances that have strong electrostatic charges and form hydrogen bonds with water are thus expected to perform effectively on hydrate inhibition.

Modifications can be carried out through the combination of other ionic liquid that are having strong electronic charges and short alkyls. A longer alkyl may hinder the occurrence of hydrogen bonding between ionic liquid and water. However, this requires further verifications from the laboratory experiments and field applications.



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