

GAS PIPELINE HYDRATE MITIGATION USING IONIC LIQUID

by

SIVANESAN SANTHASWDI

12861

Dissertation submitted in partial fulfillment of
The requirements for the
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Petroleum Engineering Programme
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(PETROLEUM ENGINEERING)

Approved by,

Dr. Khalik M.Sabil

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2013

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.

SIVANESAN SANTHASWDI

Abstract

Gas hydrate formation in gas pipeline often results in blockage and shutdown of these pipeline to mitigate the problem. Gas hydrate is a crystalline structure formed from water that host a low weight gas molecule. Natural gas hydrate occurs with presence of water, gas, high pressure and low temperature. As gas production moves to deepwater, the problem becomes serious due increase in pressure drastically and sub cooling temperature. As compare to other inhibition methods chemical inhibitors highly favored due to efficiency and economical factor. There are two type chemical inhibitors available. Thermodynamic inhibitor shifts the hydrate equilibrium curve meanwhile low dosage inhibitor retards or slow down hydrate growth over time. However both inhibitors have major drawback that require serious attention. Ionic liquid (IL) have been selected as novel approach to inhibit gas hydrate formation. IL full fills criteria as dual hydrate inhibitor, thermodynamic inhibitor and kinetic inhibitor. For this experiment two of IL [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br have been tested. The experiment is conducted using High Pressure Micro Differential Scanning Calorimetry (HP μ DSC). Both ILs is tested at effective concentrations to for thermodynamic and kinetic inhibition. Experimented ILs shows promising result by shifting hydrate stability curve to lower temperature region and delays the hydrate formation.

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Abbreviations and Nomenclatures.

KHI	Kinetic Hydrate Inhibitor
THI	Thermodynamic Hydrate inhibitor
LDHI	Low Dosage Hydrate Inhibitor
AA	Anti Agglomerate
IL	ionic liquid
GEP	Gas Export Pipeline
TDP	Touchdown Point
MEG	Monoethylene Glycol
MeOH	Methanol
EMIM	1-Ethyl-3-methylimidazolium chloride
PEO	Polyethylene Glycol
HP μ DSC	High Pressure Micro Differential Scanning Calorimetry

Chapter 1: Introduction

1.1 Background study

Gas hydrates are ice-like crystalline molecular complexes formed from mixtures of water and suitably sized 'guest' gas molecules. Water as host forms a lattice like structure through hydrogen bonding trapping lower molecular weight gases into the structure such as methane, carbon dioxide and ethane. Gas hydrate formation is not a chemical compound either occurs by chemical reaction as the gas molecules does not react with water lattice structure. Combination of high pressure and low temperature enables formation of gas hydrate. 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.

Gas hydrate structure is divided into three common types of structures type I, type II and type H. The type of hydrate formed depends on the size of the gas molecules included in the hydrate [1]. Structure (type I) consists of 46 water molecules commonly made up of small gas molecule's methane and ethane. Meanwhile, structure (type II) consists of 136 water molecules usually made up of larger guest molecule's propane. Structure (type H) seldom forms consist of 34 water molecule's requires a small and large gas molecule to be stable.

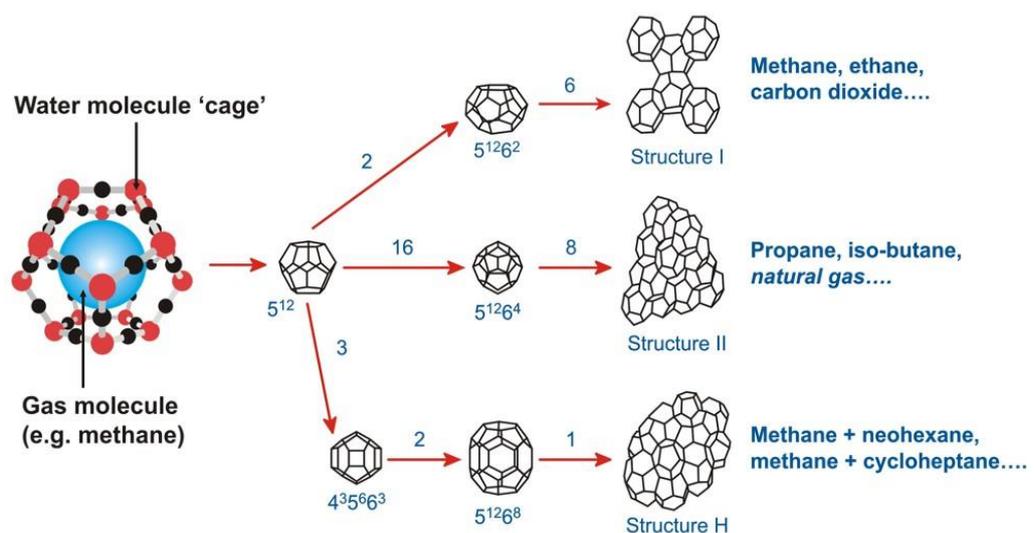


Figure 1: Type of hydrate structure [2]

In gas pipeline, formations of gas hydrate have been discovered to occur frequently causing restriction to gas flow. Especially in gas flow line for drilling and production of gas for deep water, formation gas hydrate often occur due to high pressure and low temperature involved. The hydrate causes blockage and plugging that leads to cause catastrophic failure, resulting in equipment damage, injury, and even loss of life. It is essential to implement a strategy to prevent or manage hydrates for uninterrupted production in a safe and cost-effective manner.

Various research activities were carried out to mitigate this problem immediately. Thus knowledge from the research leads to development of various methods to prevent hydrate formation through gas dehydration, maintaining gas pressure and temperature above ideal condition for hydrate formation and injection of chemical inhibitor [3]. Chemical inhibitors are separated into two types of inhibitors that is thermodynamic inhibitor and low dosage inhibitor [4]. This two groups of inhibitors delivers performance with different mechanism to inhibit hydrate formation. These chemical inhibitors also have certain limitation and drawbacks.

1.2 Problem statement

Gas hydrate formation have tendency to agglomerate and adhere to the wall of the pipeline causing plugging. Plugging in gas production line and transmission leads to severe safety problem and economic losses [5]. As for example, hydrates may agglomerate into a plug that divides the pipe segment into two pressure sections with the section upstream of the plug being under high pressure and the section downstream of the plug being under low pressure[3]. A rupture can occur in the high pressure section or the pressure differential may become large enough to propel the plug as a solid projectile through the pipe segment which can be very dangerous and can lead to major incidents including loss of lives. It also could damage the equipment's and personnel safety hazard working in surrounding environment.

The problem further amplified by winter and cold region of the world where the surrounding temperature drops to near freezing point. During 1929, in

Kazakhstan the pipe was clogged and this problem occurs especially during winter seasons. It was suspected for “ice” formation inside the gas pipeline. To prevent this problem from occurring again the gas flow was dehydrated before delivered along the pipeline. But further investigation shows the “ice” forms at temperature above water freezing point. The sample of clogged material was obtained and heated. The sample observed to release natural gas. Previously suspected “ice’ was a gas hydrate in crystallize structure to be clogging the pipeline [6] .

As more gas field found in deep water zone, gas production have move to deep-water zone. Deep water gas production is exposed to drastically low temperature and high pressure. The deep water hostile environment encourages hydrate formation [7] , especially in deep sea tie back and risers. A gas field operated by TOTAL located in Gulf of Mexico, the Matterhorn field with water depth 2800 ft. The gas produced from Matterhorn field was transported to gathering facility through Gas Export Pipeline (GEP). The GEP inlet pressure and temperature are approximately 1325 psig and 105°F, for a production of 22.5 MMscfd. At the riser touchdown point (TDP) pressure and temperature are approximately 1480 psi and 40°F .During pipeline pigging operation in March 2006, its found hydrate plug formation in the pipeline. Mixture of gas and condensate residual with water initiates hydrate formation causing increase in pigging pressure [8].

1.3 Objective and scope of study

The objective of this project is given below:

1. To determine the performance of ILs as (KHI) by measure the induction time of hydrates formation.
2. To determine the performance of ILs as (THI) by measure onset temperature of hydrates dissociation.

1.4 Relevancy of the project

Hydrate formation in gas pipeline causes a lot of problem for flow assurance in oil and gas industry which requires serious attention. Presence of hydrate leads to production and economic loss as well causing safety and environment hazard. Demand for highly effective and practical inhibitor to mitigate gas hydrate formation. IL is proven to have dual function inhibitor as thermodynamic inhibitor and kinetic inhibitor. IL only required at low dosage to mitigate the hydrate formation and environment friendly as it's an organic salt. Therefore, further studies would carry out regarding IL to prove its capability as inhibitor in mitigating gas hydrate.

Chapter 2: Literature review

2.1 Gas hydrate formation

Introduction of natural gas to water molecule with presence of high pressure and low temperature condition accelerates formation of gas hydrate in the system.[1]. Gas hydrate ideally forms at suitable temperature (5- 25 C) and pressure condition (4MPa to 10Mpa)[9].Gas hydrates exist due to the ability of water molecules to form ice structure, through hydrogen bonding, stabilized by small, non-polar gas molecules. By the inclusion of the gaseous component, the structure, which alone is thermodynamically unstable, becomes stabilized .Gas molecules are physically enclosed in the cavities of the water lattice, and they are released from the cavities only under appropriate circumstances, when the water lattice breaks down. Thus, the gas components filling the cavities are not directly bonded to the water molecules of the framework. It is for geometrical reasons that they cannot leave the hydrogen-bonded water molecule lattice until it collapses.

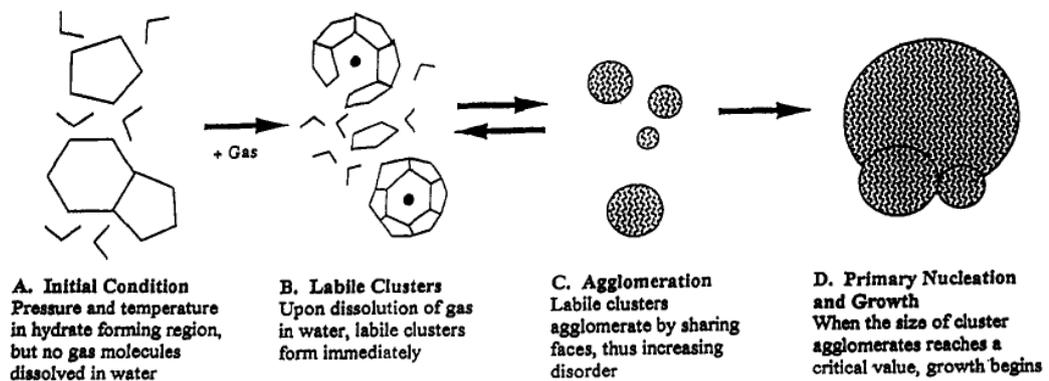


Figure 2 : Autocatalytic reaction mechanism for hydrate formation [10]

Formation of hydrate begins with a simple process called hydrate nucleation. Hydrate nucleation could be defined as minor group of water and gas which grow and scatter out in an attempt to achieve critical size for continued growth [11] . In Figure 2,exhibits growth of hydrate plug from water to metastable species then to

stable nuclei which occurs in sequence[10] . Based on Figure 2, at point A, the presence of water and gas could be observed in the system. Water forms unsteady cluster around a low weight gas molecule. At point B, formation of small group of cluster could be observed. Size of the cluster depends on gas molecule size. Structure I and structure II most favorable to form at this stage. The cluster usually disintegrates or grows further to form gas hydrate. Moving on to point C, the unsteady cluster or known as labile cluster starts agglomerating into metastable nuclei. At point C the metastable either shrink or grow until the nuclei reach the critical radius. Finally at stage D, the nuclei have reached critical size so the crystal grows swiftly over time [11].

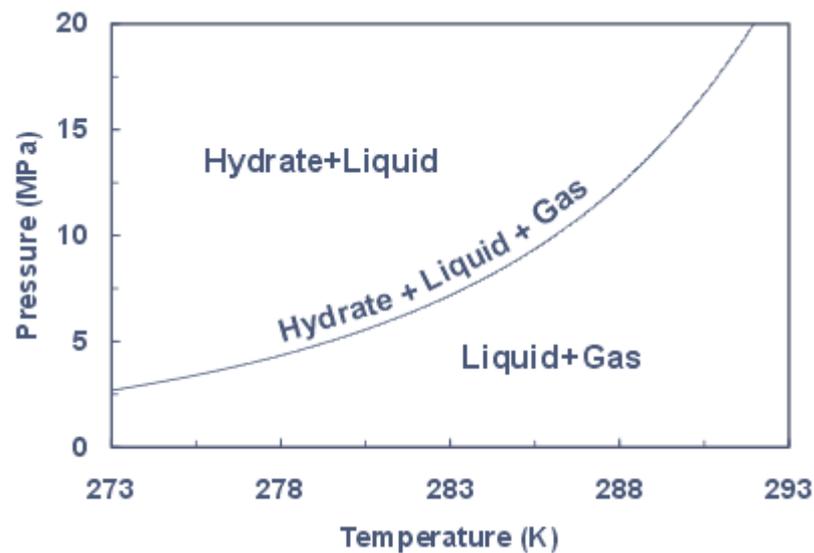


Figure 3 : Pressure versus temperature phase diagram [12]

Figure 3 indicates hydrate formation equilibrium curve. The curve could be plotted based formation of hydrate at a temperature for any given pressure or vice versa. The area on the left side of the curve dictates ideal condition for hydrate formation and area on the right dictates hydrate disassociation zone where hydrate cease to exist. The equilibrium curve is obtained by controlling parameters especially the temperature and pressure. Model parameters derived through laboratory measurements are made by forming hydrates and slowly heating or depressurizing the sample until it totally disassociates [13]. The experiment usually

performed in non-isothermal mode to determine the onset temperature of methane hydrate [14].

2.1 Gas hydrate inhibition technique

Currently commercially utilized hydrate chemical inhibitor could be divided into two groups of inhibitors as below:

1. Thermodynamic Hydrate Inhibitor (THI)
2. Low Dosage Hydrate Inhibitor (KHI)

2.1.1 Thermodynamic hydrate inhibitor (THI)

Thermodynamic Hydrate Inhibitor (THI) functions by shifting the hydrate equilibrium curve to left side of the curve making hydration formation and stability zone smaller compare to hydrate dissociation zone. Injection of THI suppresses the hydrate nucleation temperature further to lower region. This means the curve moved to lower temperature region corresponding higher pressure in general as described in Figure 3[14] . Commonly used THI in industry is methanol and ethylene glycol. THI requires high volume and concentration of injection to mitigate hydrate formation. Usually methanol needs to be injected 30wt % to 51wt% concentration. THI also offers recovery and regeneration of the used THI at end after usage [15].

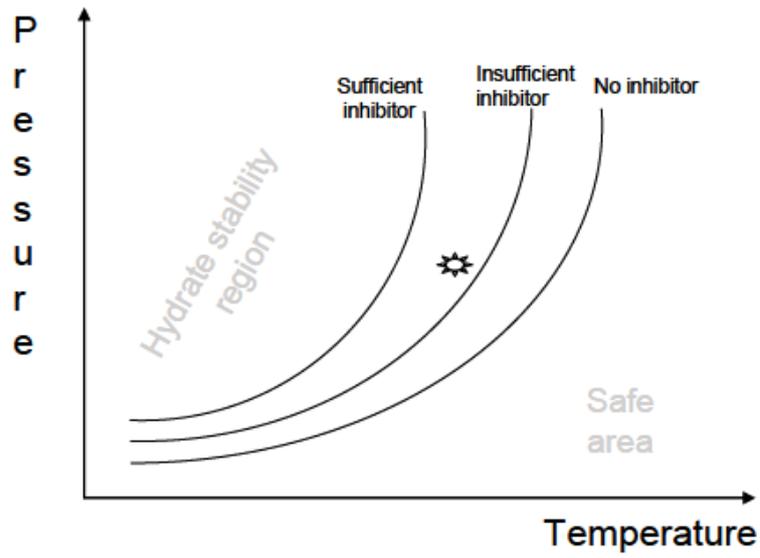


Figure 4: Thermodynamic inhibitor performance graph [16]

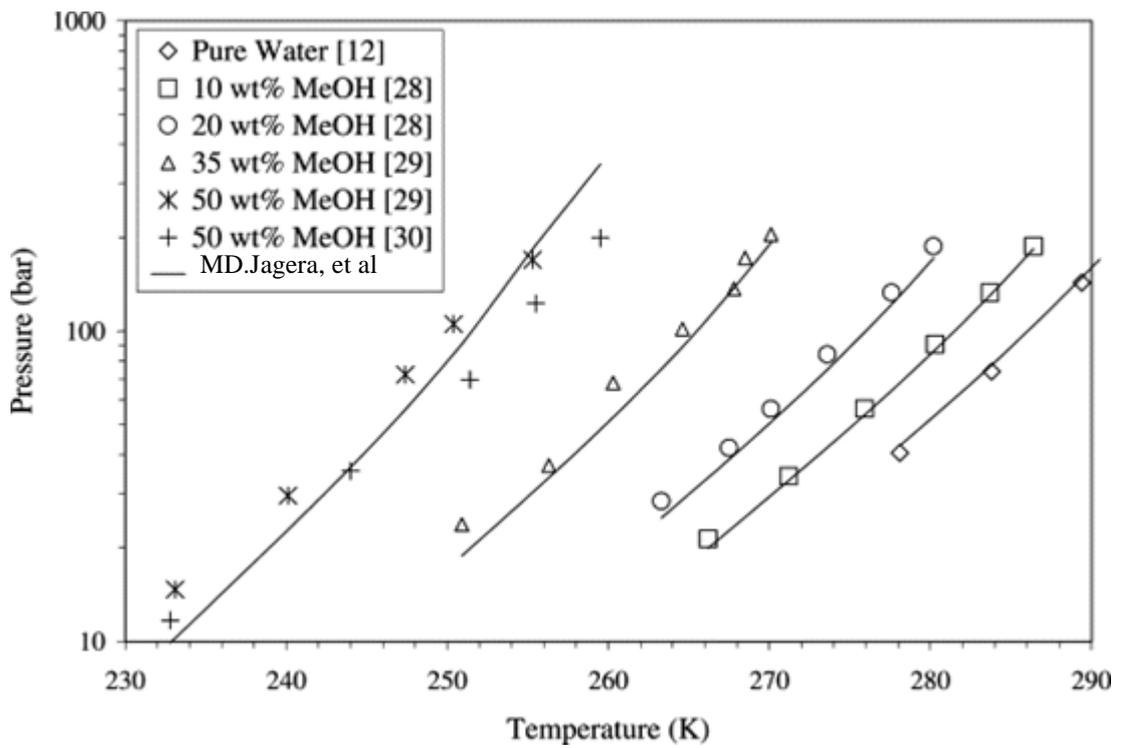


Figure 5 : Predictions for methane hydrate inhibition with methanol [17]

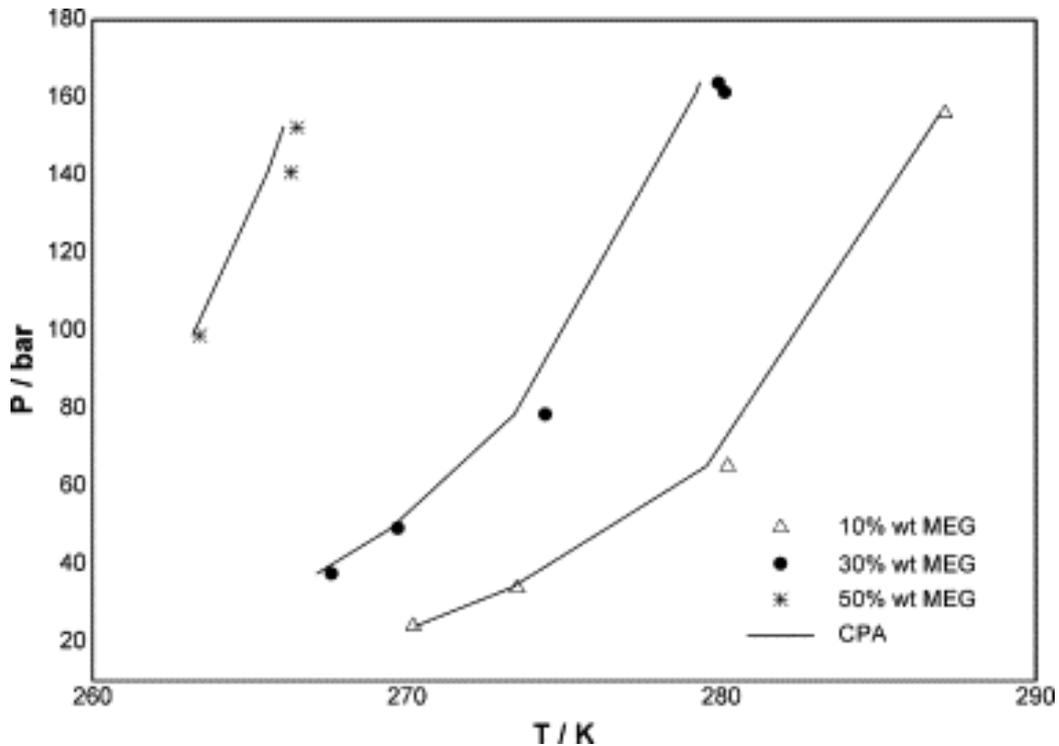


Figure 6 : Prediction of methane hydrate formation in the presence of MEG as inhibitor [18]

Based figure 5 and 6, shows experiment conducted to test efficiency of currently available THI in the market. In diagram 5, the chemical inhibitor that is tested is methanol (MeOH) meanwhile in diagram 6 the tested chemical is monoethylene glycol (MEG). Both graphs is based on the hydrate formation equilibrium curve. Increase in concentration of THI, the further the curve shift to left. This diagram proves THI required high concentration and quantity to depress hydrate formation.

However, methanol is also volatile and has high vapor pressure where most of it is lost to gas phase [19] . Furthermore oxygen also seems come along indirectly due to high amount of methanol injection leading to corrosion. To inhibit the corrosion problem more corrosion inhibitor need to be injection into system [19]. Methanol also causes drop in efficiency and effectiveness of corrosion inhibitor overtime [3]. As gas production and exploration move to deep water operation, usage of THI is not feasible and economical due to high pressure and sub cooling temperature.

2.1.2 Low dosage hydrate inhibitor (LDHI)

Due to a lot of drawback from THI, initiates research and development for better hydrate inhibitor. Low Dosage Hydrate Inhibitor (LDHI) consists of Anti Agglomerate (AA) and Kinetic Hydrate Inhibitor (KHI) [15]. The main difference between LDHI and THI is the mechanism and concentration used [3]. LDHI uses very low dosage to inhibit hydrate mitigation and do not effect hydrate equilibrium curve [20] .

Anti-Agglomerate (AA) prevents hydrate nuclei from agglomerating into hydrate plug [20] . AA is surface active molecules which coats and attach to the hydrate nuclei thereby interfering the growth of hydrate. AA does not prevent formation of hydrate nuclei rather disperse the hydrate into fine particles so low viscosity could flow without any restriction [3] . Furthermore, AA delivers anti-corrosion features and works well together with other corrosion inhibitors [19]. With proper testing and injection, AA capable of achieving best result in hydrate mitigation compares other inhibitors. However, AA has a main drawback that it is only works best in low water cut system. Oil phase need to be present for AA to function and the water cut ranges from 40% to 60% [20].

Kinetic Hydrate Inhibitor (KHI) retards the hydrate formation by slowing down hydrate nucleation or growth rate. KHI delays hydrate nucleation or formation for certain length of time period which is known as induction time [3] . Induction time also could be defined as time taken for hydrate growth to reach size that could be detected [14] . The induction time achievable from KIs depends on the degree of sub-cooling. The higher the sub-cooling, the smaller is the induction time that can be achieved [20]. Currently available KIs can prevent hydrate formation for days at sub-cooling of up to 13 C. KHI also could perform well in high water cut system without problem. One of KHI major drawback is that it only could be used in a system with moderate sub cooling temperature ranging from 5 to 20 F [20] . Research is being carried out to produce better KHI to be used in greater sub cooling temperature.

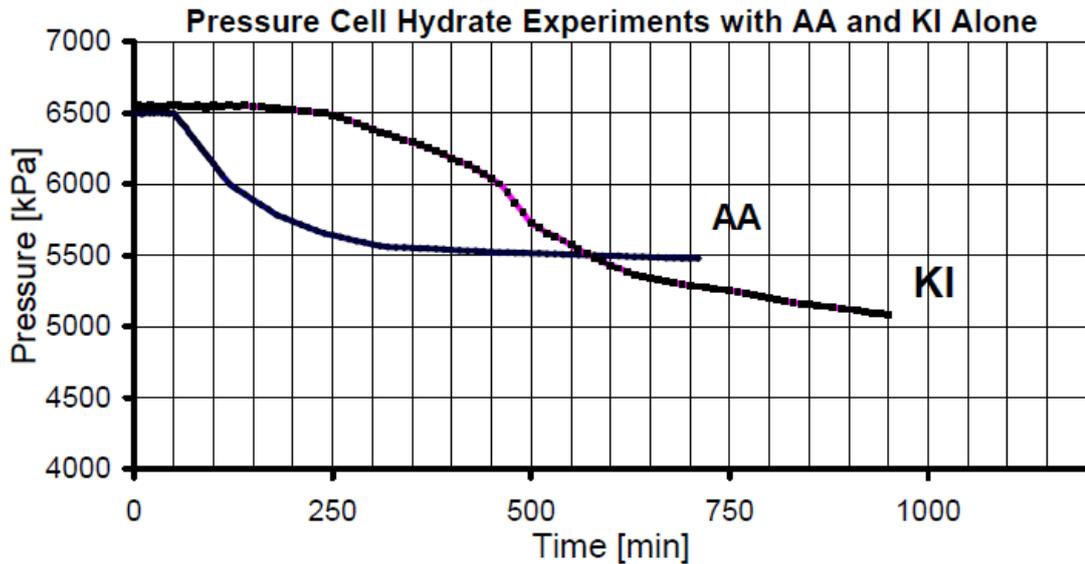


Figure 7 : Pressure cell Hydrate experiments with AA and KHI [19]

In figure 7, shows general scope on KHI and AA performance in inhibiting hydrate formation experiment. Generally the graph displays pressure over time. This phenomena is due to more gas in the pressure cell is dissolved into the solution to form hydrate. For AA sudden drop in pressure indicates rapid hydrate formation and becomes constant. AA do not prevent hydrate formation but discourages hydrates growth and agglomeration so hydrate formed over time have decreased drastically .For KHI the graph drops gradually as time increases . This due to KHI slows growth of hydrate but over time more hydrate is formed is increased.

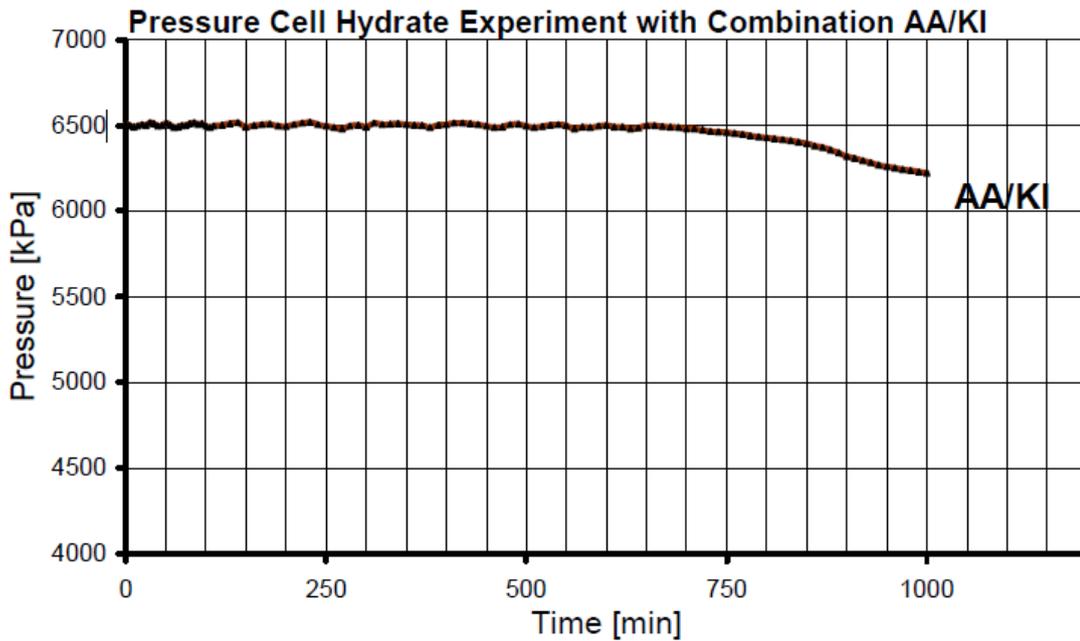


Figure 8 : Pressure cell hydrate experiment with combination AA / KHI [19]

Even though KHI and AA have major drawback, combination of both agent could optimize gas hydrate inhibition. Based on research by Dean Lovell and Marek Pakulski , proves that combination of AA and KHI provides longer induction time. This could be observed in figure 8 where pressure drop could be observed at 700 minute. The combination was used in Crimson Lake Gas Well in Canada with depth of 2800 m [19].

2.1.3 Ionic liquid as gas hydrate inhibitor

Ionic liquid (IL) are organic salt in liquid phase at room temperature [4]. Based on research by Chong Wei Xioa and Hertanto Adidharma[14], IL have properties to be used as gas hydrate inhibitor. Result from IL experiment shows it could shift the hydrate equilibrium curve and also delay hydrate formation time by slowing down hydrate nucleation rate. This indicates IL could use as dual function inhibitor as thermodynamic inhibitor and kinetic inhibitor.

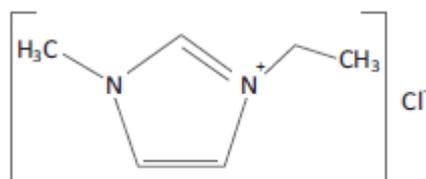


Figure 9 : 1-Ethyl-3-methylimidazolium chloride [4]

Currently used IL is made up of a chain of alkyl cation group and anion. As shown in figure 9, it's a chemical structure of 1-Ethyl-3-methylimidazolium chloride (EMIM-CL). IL have strong electrostatic charges and capable of forming hydrogen bond with water [14] . Nevertheless, IL also have extremely low vapor pressure as not volatile as methanol and relatively inexpensive to be utilized. Only low dosage of IL is required to deliver better performance than present KHI's. Furthermore, the IL be modified with suitable cation and anion to form hydrogen bond with water to interfere hydrate formation [9]. IL also offers option as environment friendly inhibitor as green replacement in the industry.

Based on research by HertantoAdidharma and ChongweiXioa in 2009 have proven that IL possess dual inhibiting properties, thermodynamic inhibiting and kinetic inhibiting [14]. Referring to figure 10, Polyethylene Glycol (PEO) and different types of EMIM chain IL. It could be observed the EMIM liquid manage to shift the hydrate equilibrium curve further than PEO.

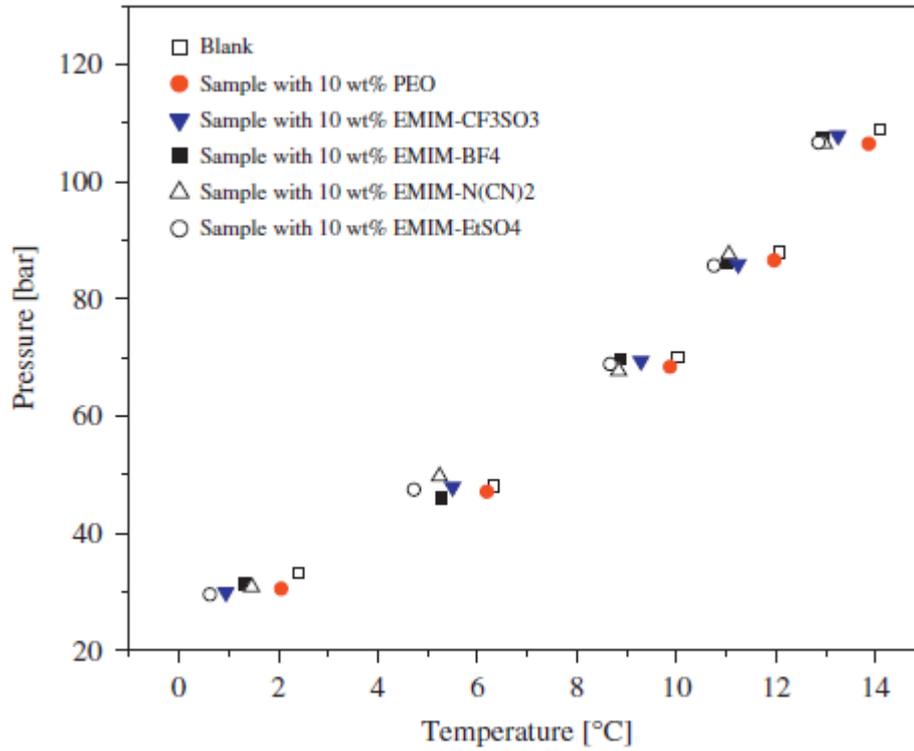


Figure 10 : The effectiveness of EMIM ionic liquids and polyethylene oxide (PEO) in shifting the equilibrium curve [14]

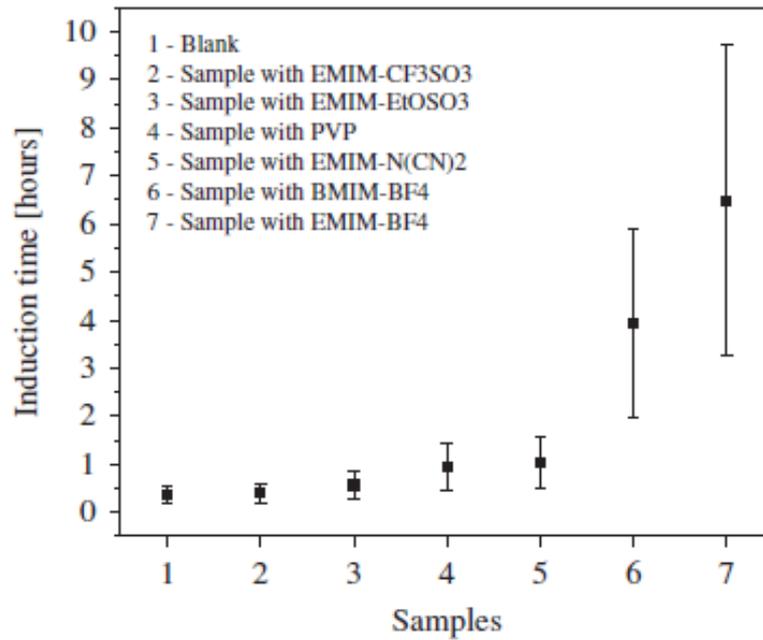


Figure 11 : Induction times of methane hydrate formation from blank samples and samples containing 10wt% inhibitor [14]

Furthermore, figure 11 dictates induction time for hydrate formation to test kinetic inhibiting capability of the inhibitors at same concentration 10wt%. The test is done with polyvinylpyrrolidone (PVP) and different type of EMIM chain IL. It could clearly be differentiated the performance by EMIM-BF4 have longest induction time compare to PVP. Moreover a lot of researches have been carried out to test the potential of IL in inhibiting hydrate formation. Table 1 shows details and summary of the research findings.

Table 1 : Related Researches

Researches	Paper	Result
C.Xiao, H,..Adidharma	Dual function inhibitors for methane hydrate. (2009)	It is found that these ILs have dual function inhibition, due to their strong electrostatic charges and hydrogen bond with water, could shift the equilibrium hydrate dissociation/stability curve to a lower temperature and, at the same time, retard the hydrate formation by slowing down the hydrate nucleation rate, thus are able to act as both thermodynamic and kinetic inhibitors.
C.Xiao 1, N.Wibisono,H.Adidharma	Dialkylimidazolium halide ILs as dual function inhibitors for methane hydrate. (2010)	The halide ILs are found to shift the equilibrium hydrate dissociation/stability curve to a lower temperature and, at the same time, retard the hydrate formation by slowing down the hydrate nucleation rate. To understand the performance of these ILs in inhibiting the hydrate formation, the electrical

		conductivity and infrared spectra of ILs are also obtained and analyzed.
A.R.Richard, H.Adidharma	The performance of ILs and their mixtures in inhibiting methane hydrate formation. (2013)	It is observed that single component solutions of EMIM-Cl demonstrate a progressive increase in inhibition effect with increasing concentration, The mixture of EMIM-Cl and EMIM-Br also shows a synergistic effect at higher pressures. Unlike MEG or NaCl, inhibitors containing EMIM-Cl or EMIM-Br demonstrate an increase in inhibition effectiveness as pressure increases.
BehzadPartoon, Nordiyana M.S. Wong, Khalik M. Sabil*, KhashayarNasrifar, MohdRiduan Ahmad	A study on thermodynamics effect of [EMIM]-Cl and [OH-C2MIM]-Cl on methane hydrate equilibrium line. (2013)	The equilibrium conditions of methane hydrate in the presence of [EMIM]-Cl and [OH-C2MIM]-Cl are measured in this work. The thermodynamic inhibition effects on methane hydrate equilibrium in the presence of these ILs are less significant at low pressures. However, when the pressure is higher than 7 MPa, their thermodynamic inhibition effects are more significant.
L.K Chun , A. Jaafar	IL As low Dosage Inhibitor For Flow	1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF4)

	Assurance In Pipeline. (2013)	was explored in carbon dioxide (CO ₂) gas mixture for its potential application as gas hydrate inhibitors for CO ₂ hydrate (Type I)
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IL future as new groundbreaking hydrate inhibitor has great possibility and potential. It is still in research and development stage to be tested with multiple situation and scenario before being implemented into industry.

Chapter 3 Methodology

3.1 Research methodology

This project methodology consist of 3 phases of implementation which are preliminary, experiment work and finally discussion and conclusion which shown by figure 12 .

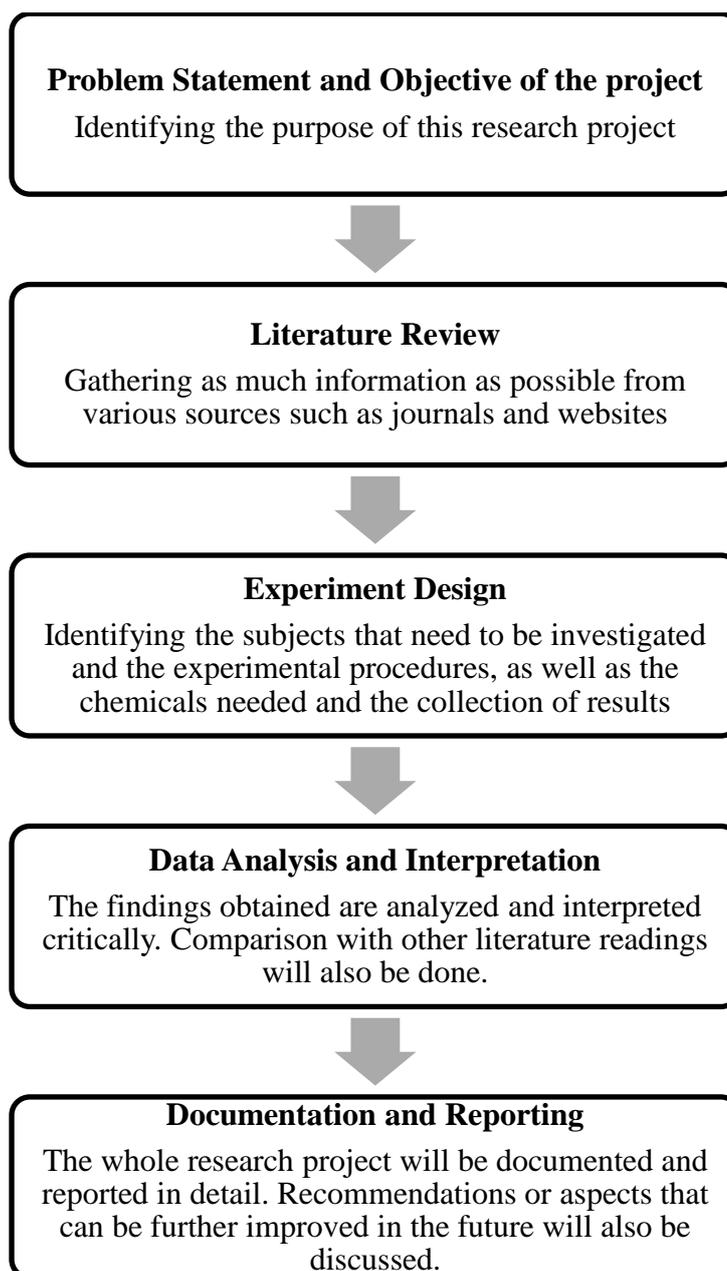


Figure 12 : Research methodology

3.2 Experiment

3.2.1 Experiment apparatus and setup

The High Pressure Micro Differential Scanning Calorimetry (HP μ DSC) is being utilized for this experiment. HP μ DSC measures heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involves endothermic or exothermic processes, or changes in heat capacity. The HP μ DSC can operate at pressures up to 400 bar and at temperatures from -45 to 120 °C. Its sensitivity, as provided by manufacturer is high with are solution of 0.4mW. Advanced Peltier cooling and heating principles are used to control the system temperature. Two gas-tight high-pressure vessels are used for each experiment: one is for reference and the other contains a sample solution. The vessels are made of Hastelloy C276 and each has a volume of 0.33mL. Nitrogen was used as the carried gas as carried to create control environment in the HP μ DSC machine. Pressure controller supplied by SETARAM capable of handling gas pressure up to 200 bar with an accuracy of ± 1 bar. It measures gauge pressure so atmospheric pressure need to be added to the pressure reading taken.

Following the calorimeter is standardized by measuring two standard material melting points. The calibration process carried out according the manual provided by HP μ DSC manufacturer. The results are obtained by measuring melting points at different heating rates. The results further are used in a standard least square method to obtain the coefficients of temperature correction function from which the temperature correction for any scanning temperature and rate can be determined. The software by the HP μ DSC manufacturer is utilized fully to do above procedures. An analytical balance is used to weigh of sample solution and added into the sample vessel. The reference and sample vessels are then connected to a methane gas cylinder. The overall experiment apparatus setup could be viewed in figure 13.

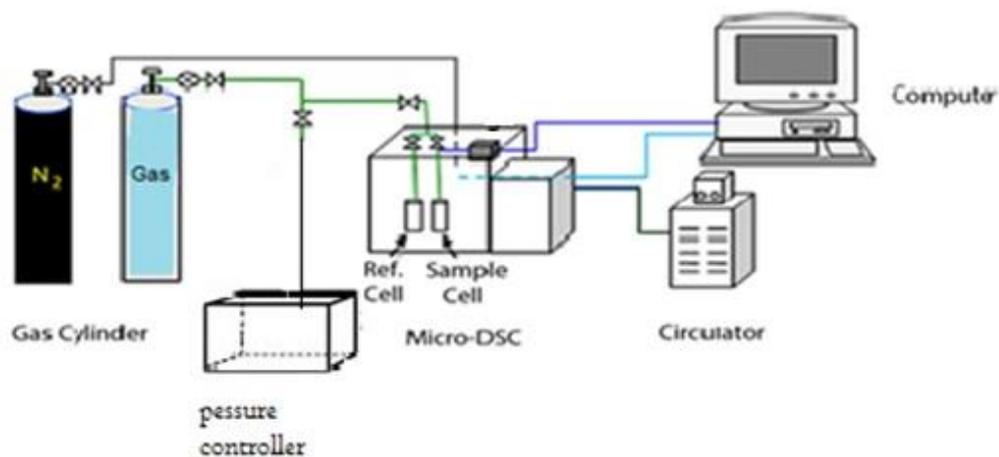


Figure 13 : Experiment apparatus arrangement [5]

3.2.2 Material

The IL that are planned to be used displayed as in Table 2.

Table 2 : Ionic liquid Structure

Component	Symbol	Structure
1-(2-Hydroxyethyl) 3-methylimidazolium chloride	[OH-C ₂ MIM]-Cl	
1-(2-Hydroxyethyl) 3-methylimidazolium bromide	[OH-C ₂ MIM]-Br	

All the chemicals were obtained from IL Centre in UTP. The chemicals are synthesized at the center and purity is of the IL ranges from 90-95%.

3.2.3 Experiment method

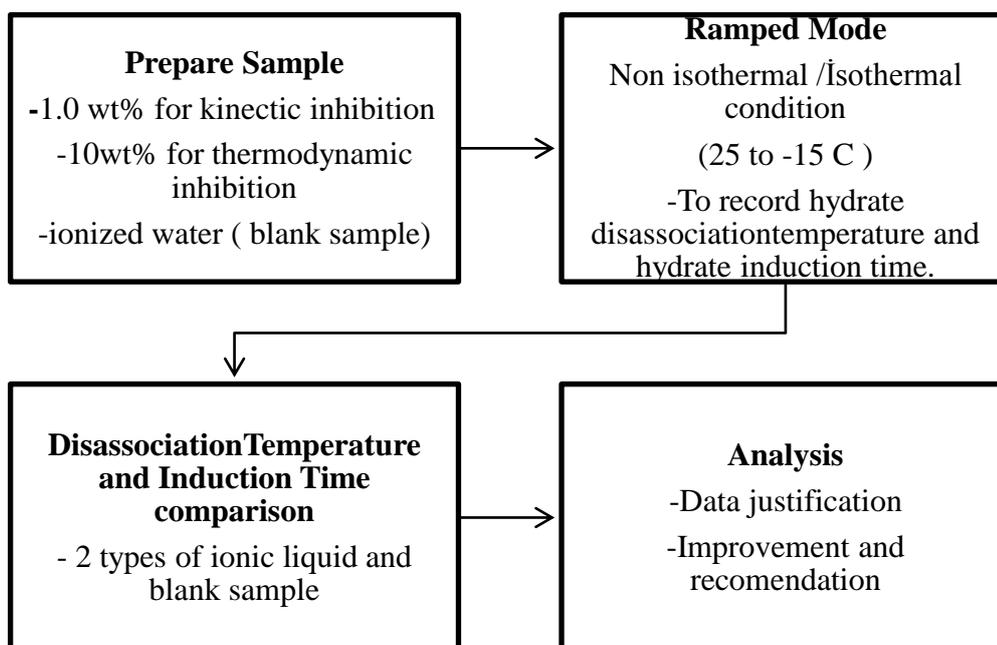


Figure 14: Experiment design

Three types of sample is prepared for the experiment comprising of two IL and ionized water as blank sample. The mentioned two ILs is [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br. Before beginning the experiment the sample vessel is cleaned from any contaminants. The sample solution is injected into the sample vessel and weighed on an analytical balance. Then the sample vessel is placed in the HP μ DSC along with the reference vessel. Methane gas is supplied from gas cylinder into pressure controller to obtain desired pressure before being injected into vessels. Small amount of methane gas is injected into the sample vessel and released out to remove any remaining air inside the vessel. This procedure is to make sure the sample vessel fully filled with methane gas and enables formation of stable hydrate crystal. Methane gas was injected into the vessels after the sample vessel have been fixed in HP μ DSC. The pressures inside the vessels are stabilized using pressure controller.

The experiment is divided into two different modes as below:

1. Non isothermal mode (To obtain disassociation temperature of hydrate).
2. Isothermal mode (To obtain induction time of the hydrate).

Non isothermal mode

This main objective of the experiment is to test thermodynamic inhibition ability of the inhibitor. For this mode the IL is prepared at 10%wt concentration and 51 mg of the sample is injected into the sample vessel. The samples would be tested at 4 different pressures ranging from 51 to 111 bar. The mode is separated into two thermal cycle that is cooling step and heating step. The sample is cooled from 20°C to -15°C at 1°C/min. Then the sample is heated from -15°C to 25°C was done by 0.01°C/ min.

Isothermal mode

This main objective of the experiment is to test kinetic inhibition ability of the inhibitor. For this mode the IL is prepared at 1%wt concentration and 15 mg of the sample is injected into the sample vessel. The each sample would be tested 4 times to obtain average induction time at pressure 111bar and isothermal temperature at -15 °C. This indicates the induction time would be taken at high degree of super cooling. There are 3 steps included in the thermal cycle. The temperature is decreased from room temperature 25°C to a super cooling temperature to -15°C at 4 °C/min rates Celsius over time for the cooling step. After that, is isothermal where the super cooling temperature -15°C is retained to measure the induction time. Then, in heating step the temperature is raised from super cooling temperature -15°C to room temperature 25°C at 4 °C/min rate.

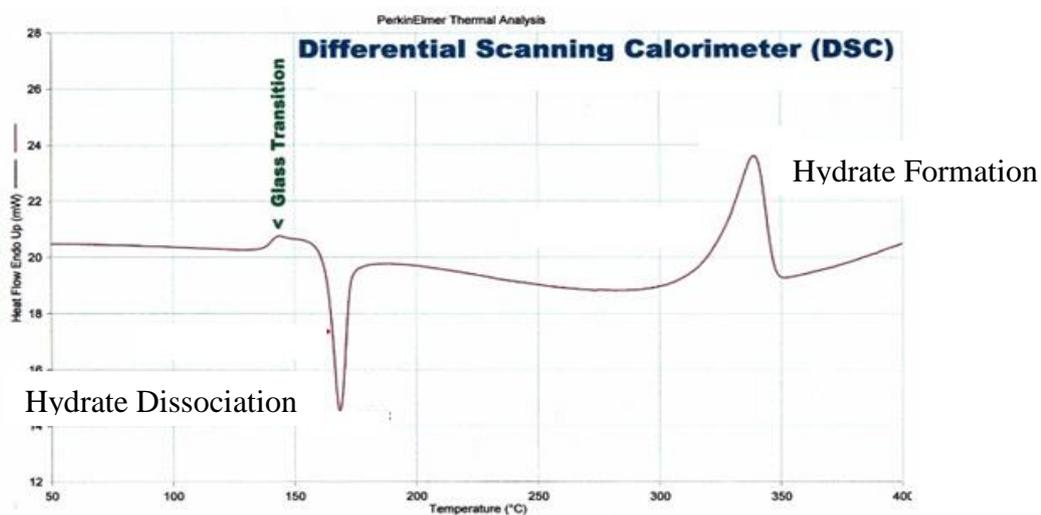


Figure 15 : Exothermic and endothermic curve

The induction time and dissociation temperature of gas hydrate could be identified by exothermic and endothermic curve displayed on thermogram in figure 15. In exothermic peak, the hydrate nucleation and growth occurs to reach critical size. The induction time range is measured between onset and offset time. For exothermic peak, hydrate dissociation occurs. The dissociation is measured between onset and offset temperature.

3.3 Gantt chart & key milestone

Legend	
Completed Task	
Pending Task	

Table 3 : Project activity

	Final Year Project 1													Final Year Project 2														
Project Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Literature Review																												
Experimental Design																												
Methodology Conformation																												
Material Requisition																												
Sample Preparation																												
Experimental Work																												
Data Collection and Interpretation																												
Comparison against other inhibitors																												
Recommendation and Improvement																												

Table 4 : Key milestone

	Final Year Project 1													Final Year Project 2													
Key Milestone	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Preliminary Research Work			■	■	■																						
Submission of Proposal Defence Report						■																					
Proposal Defence									■																		
Project Works Continues										■	■	■															
Submission Of Interim Draft Report											■																
Submission Of Interim Report												■															
Submission Of Progress Report																					■						
Submission of Draft Report																								■			
Submission of Technical paper																								■			
Pre-Sedex																										■	
Oral Presentation																											■
Submission Project Dissertation																											■

Chapter 4 : Result and discussion

4.1.1 Methane hydrate dissociation temperature

To obtain methane hydrate dissociation temperature, the experiment is conducted at non-isothermal mode in HP μ DSC at pressure range from 51 bar to 111 bar. The experiment was divided into two steps that is cooling step and followed by heating step. The sample is cooled from 20°C to -15°C at 1°C/min. Then the sample is heated from -15°C to 25°C was done by 0.01°C/ min. The heating step conducted at slower rate to obtain more accurate hydrate disassociation temperature [5].

As mentioned in previous section, three samples would be tested. That is ionized water as blank sample, 10% wt [OH-C₂MIM]-Cl and 10% wt [OH-C₂MIM]-Br.

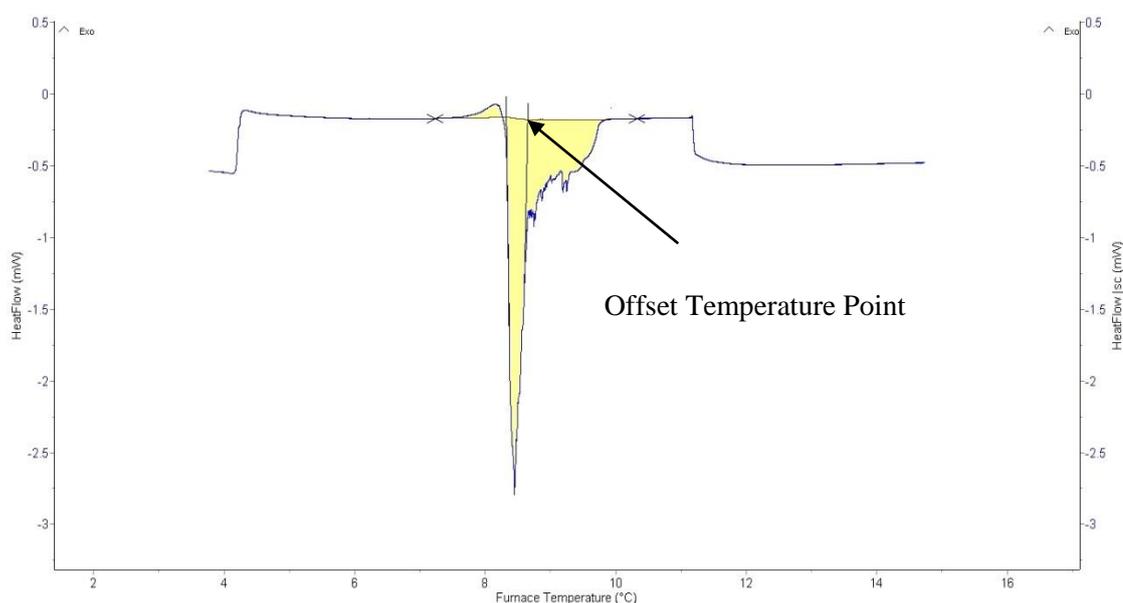


Figure 16 : Determination of methane hydrate disassociation temperature

The offset temperature from the exothermic peak is recorded as methane hydrate dissociation temperature as shown in figure 16 above. Offset temperature is used as dissociation temperature to guarantee the methane hydrate have been fully disintegrated. As can be seen figure 17 displays exothermic peak for in the thermogram for each sample at pressure 71.01 bar.

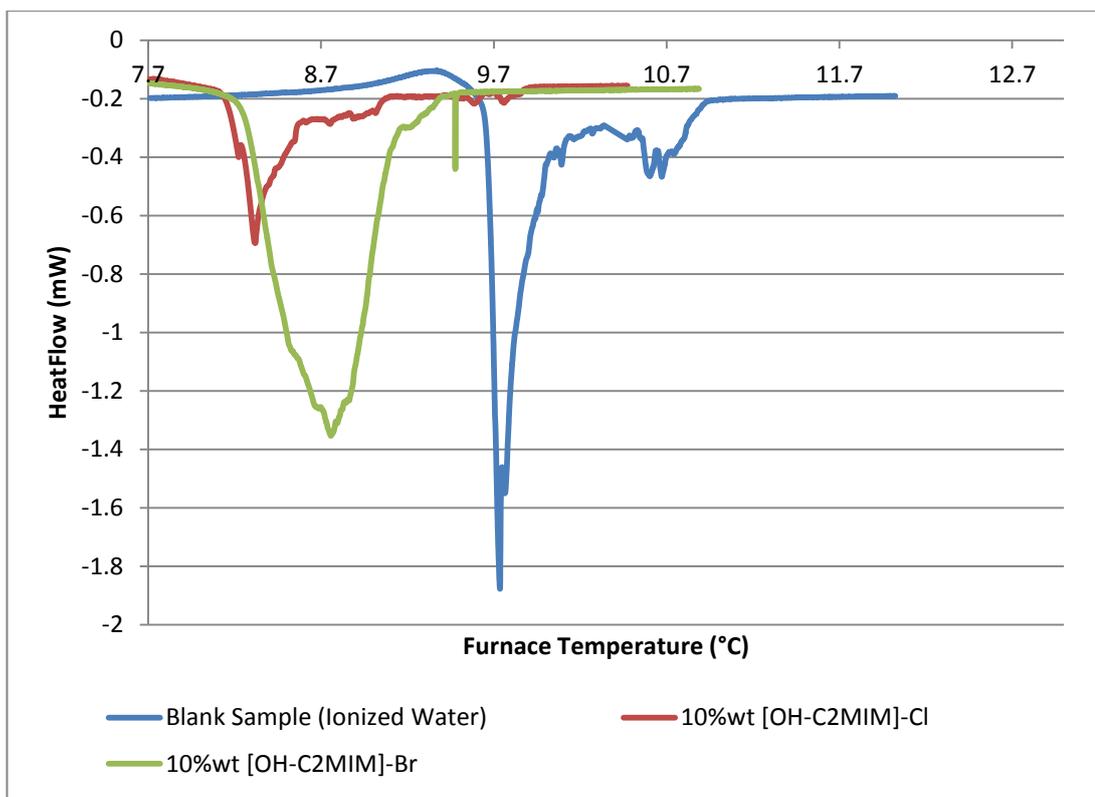


Figure 17 : Thermogram for methane hydrate disassociation at 71.01 bar

Blank sample is tested in this experiment to obtain temperature for each pressure point where the hydrate still remains at equilibrium before being disintegrated. The recorded temperature is then used to generate the hydrate stability graph before proceeding with the IL. The disassociation temperature to be obtained from the IL should not exceed plotted hydrate stability curve.

Presence of ILs, [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br with concentration 10% wt does affect the hydrate equilibrium. For example in figure 17, the methane hydrate disassociation temperature for ILs is lesser compare to the blank sample. The hydrate disassociation temperature for the ILs for each pressure point was recorded. Hydrate stability curve is plotted using data collected as in figure 18. The effectiveness of ILs [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br in shifting the curve could be clearly seen in figure 18. The curve is shifted further to lower temperature region.

Especially IL, [OH-C₂MIM]-Cl is more effective in shifting the graph further compare to [OH-C₂MIM]-Br. This phenomenon is contributed by type of anion present in the IL. Anion -Cl possess stronger electrostatic charges compare to anion

–Br. Furthermore the hydroxyl group cation also believed to improve the inhibition effect of the IL [4]. The methane hydrate disassociation temperature becomes higher as pressure increases. The hydrate structure becomes more stable and compacted as pressure increases. In contrary the shift in curve for the IL becomes more significant as pressure increases.

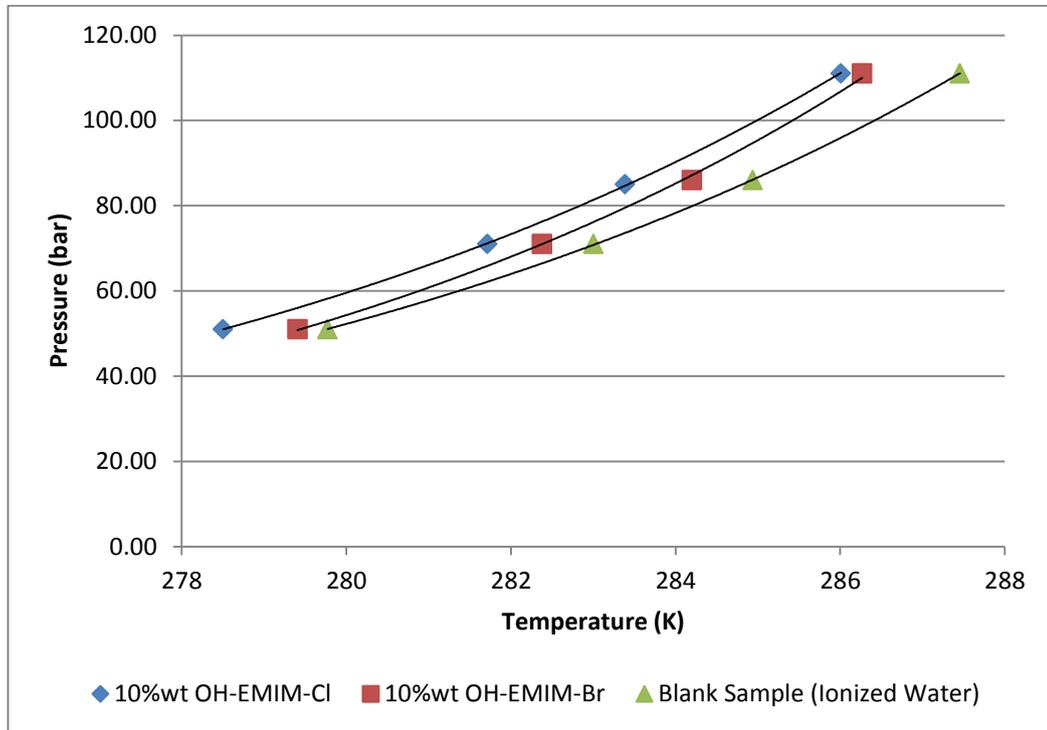


Figure 18 : Methane hydrate stability curve

Average shift temperature (\bar{T}) is calculated using formula below for better understanding of performance of the thermodynamic inhibition by the IL.

$$\bar{T} = \frac{\sum \Delta T}{n} = \frac{\sum_{i=1}^n (T_{0,p_i} - T_{1,p_i})}{n}$$

T_{0,p_i} in the formula represents methane hydrate disassociation temperature for blank sample measured at pressure p_i , meanwhile T_{1,p_i} represents methane hydrate disassociation temperature for IL measured at pressure p_i and n is total number pressure points involved.

Table 5: Average shift in temperature for ionic liquids

Ionic liquid	OH-EMIM-Cl	OH-EMIM-Br
Average Temperature Shifts (K)	1.38925K	0.72925K

Presence of IL managed to shift the disassociation temperature from 0.7 to 1.3 k to lower temperature region as referring table 5.

4.1.2 Methane hydrate induction time

To obtain methane hydrate induction time, the experiment is conducted at isothermal mode in HP μ DSC at pressure 111 bar. There are 3 steps included in the thermal cycle. The temperature is decreased from room temperature 25°C to a super cooling temperature to -15°C at 4 ° C/min rates Celsius over time for the cooling step. After that, in isothermal where the super cooling temperature -15°C is retained to measure the induction time. Then, in heating step the temperature is raised from super cooling temperature -15°C to room temperature 25°C at 4 °C/min rate. During isothermal step there is slight chance for formation of ice when endothermic peak is recorded in the themogram. In order to prevent recording time of ice induction, it is make sure two exothermic peaks is formed during heating step. Presence of two exothermic peaks indicates disassociation of ice and methane hydrate. Ice disassociation occurs at lower temperature compare to hydrate disassociation.

For kinetic inhibition, three samples would be tested. That is ionized water as blank sample, 1% wt[OH-C₂MIM]-Cl and 1%wt [OH-C₂MIM]-Br. Methane hydrate induction time experiment is influenced by certain factors such as cell wall roughness, presence of impurities and particle in the sample [14]. To overcome this factors each sample is tested 4 times with same experiment procedure and the same apparatus.

Methane hydrate induction time is recorded when onset precipitation of hydrate occurs and growth into detectable size [14]. The onset time is recorded from

the endothermic peak as it indicates of initial size of hydrate that is detectable by HP μ DSC as seen figure 19.

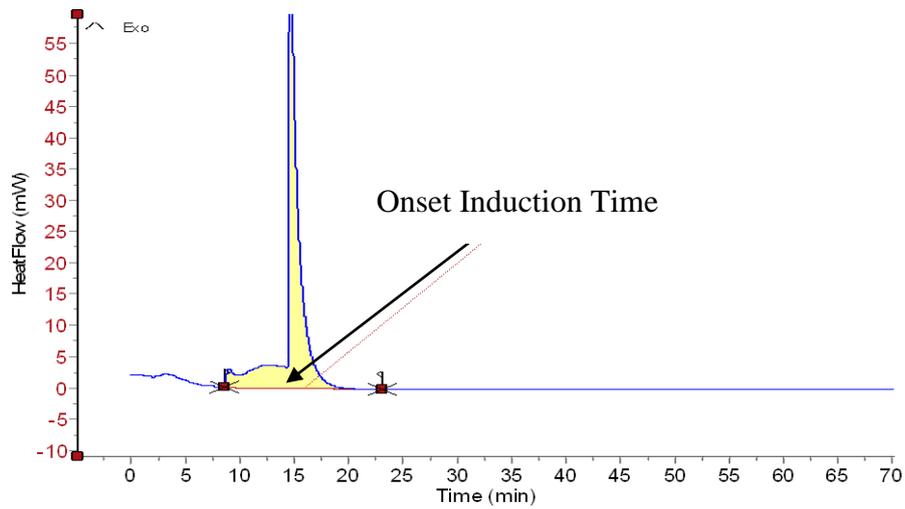


Figure 19 : Determination methane hydrate induction time

Induction time recorded for runs with IL show large difference form the blank sample induction time. Figure 20 displays endothermic peak for each sample.

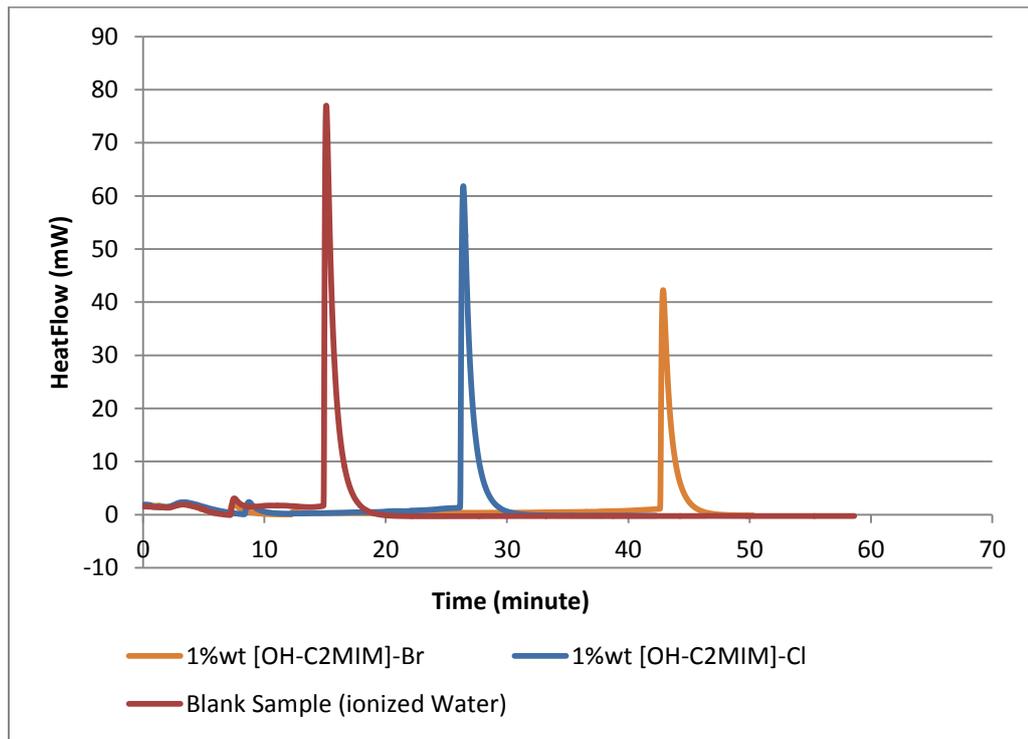


Figure 20 : Methane hydrate induction time thermograph at 111.01 bar and - 15°C for blank sample

Presence of IL, [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br manages to delay and retard formation of the hydrate. . Mean induction time for blank sample is 15.514 minutes meanwhile [OH-C₂MIM]-Br have longer mean induction time 51.328 minutes compare to [OH-C₂MIM]-Cl which delays the hydrate growth up to 23.852 minutes. Type of anion in the IL largely influence outcome of the result. Anion –Br performs better than –Cl due the capable of forming stronger hydrogen bond.

Table 6: Mean induction time for different samples

Sample	Pressure (Bar)	Temperature (°C)	Mean Induction Time (min)
Blank Sample	111.01	-15	15.514
1% [OH-C ₂ MIM]-Cl	111.01	-15	23.852
1% [OH-C ₂ MIM]-Br	111.01	-15	51.328

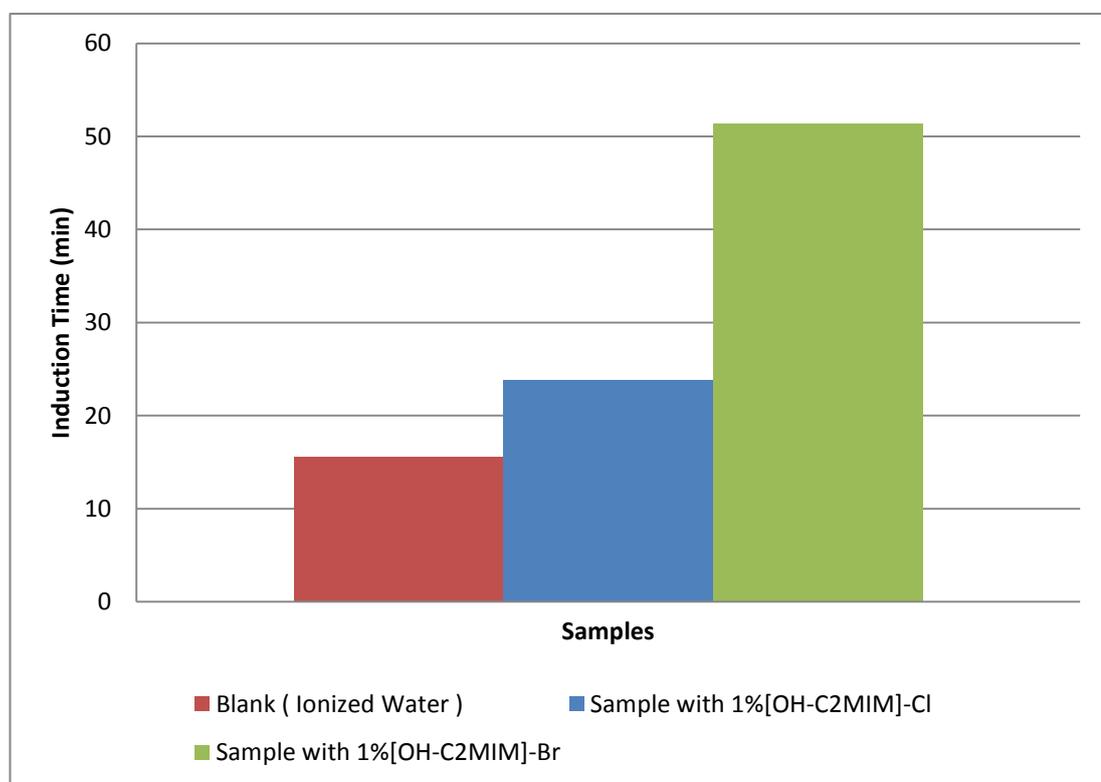


Figure 21 : Methane hydrate induction time at 111.01 bar and -15°C

Chapter 5 Conclusion and future works

5.1 Conclusion

Application of IL as dual function inhibitor has met the objective of this paper. In overall both ILs [OH-C₂MIM]-Cl and [OH-C₂MIM]-Br managed to shift the hydrate stability curve into lower temperature region and retard the growth of hydrate. The performance of both IL was tested in High Pressure Micro Differential Scanning Calorimetry (HP μ DSC). For methane hydrate disassociation temperature part, the IL with 10% concentration was tested at pressure range 51 bar to 111 bar. The hydrate stability curve is shifted to lower temperature region as much 0.7K – 1.3 K. The effect of different anion in the IL could be clearly seen. Anion –Cl delivers better hydrate disassociation temperature compare to anion –Br. This phenomenon is believed due to stronger electrostatic charges possessed by anion –Cl.

Meanwhile for methane hydrate induction, the IL [OH-C₂MIM]-Br is the most effective kinetic inhibitor. The IL is tested with 1% concentration at temperature -15°C and pressure 111 bar. [OH-C₂MIM]-Br delays the hydrate growth for longer period of time compare to [OH-C₂MIM]-Cl. Similar to thermodynamic inhibition, the kinetic inhibition of the IL also influenced by different type of anion. Due to their ability to form strong hydrogen bond with molecule, anion –Br is more effective compare anion –Cl.

Based on literature review, IL has proven to be better in various aspects compare to commercially available inhibitors. For example IL also have extremely low vapor pressure as not volatile as methanol and relatively inexpensive to be utilized. Only low dosage of IL is required to deliver the result. Furthermore the molecule structure of IL could be tailored according to the situation. Further understanding in effect of IL on gas hydrate induction time and disassociation temperature could enable development of better IL.

In overall, IL seems to be promising prospect as new ground breaking hydrate inhibitor. Utilizing IL in oil and gas industry could provide better flow assurance in in the future. As more gas fields being develop the expenses of

maintaining the pipeline increases tremendously. IL as a new class inhibitor could be the solution for hydrate problem being faced for decades.

5.2 Future works

Currently IL is only being tested in environment filled with pure methane gas. In reality the gas that is being piped from gas fields have a different gas composition. To emulate the real flow assurance condition, the IL need to be tested in environment filled with different mixture of gas. Data delivered could determine effectiveness of IL inhibiting gas hydrate in reality.

Furthermore, IL should be tested along with different type's commercial inhibitors. Mixture of IL and commercial inhibitor such as methanol and PVP could deliver a better result. The synergy could shift hydrate stability curve further to lower temperature region and delays the hydrate growth for longer period of time compare to stand alone IL.

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