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ABBREVIATIONS AND NOMENCLATURES

[BMIM][BF4]   - 1-butyl-3-methylimidazolium tetrafluoroburate

[EMIM][BF4]   - 1-ethyl-3-methylimidazolium tetrafluoroburate

HP   - High Pressure

IL   - Ionic Liquid

KI   - Kinetic Inhibitor

LDHI   - Low Dosage Hydrate Inhibitor

PVP   - Polyvinylpyrrolidone

THI   - Thermodynamic Inhibitor

μDSC   - Micro Differential Scanning Calorimeter

CHAPTER 1: INTRODUCTION

1.1 Project Background

Flow assurance is one of the major challenges in the oil and gas industry. The term 'Flow Assurance' was originated from the phrase **'Garantia de Fluxo'** or guarantee of flow' coined by PETROBRAS in the 1990's. Generally, the term defined the overall process, techniques, strategies, equipments, facilities, and technologies involved to allow optimum and unobstructed flow or production of hydrocarbon from the reservoir to the point of sale. Diverse flow assurance problems discussed in recent years, involving handling of organic and inorganic deposits such as gas hydrates, wax, asphaltene, and scale in hydrocarbon productions, at which engineers trying to get these problems solved by various means of science and technologies.

Hydrates or also known as gas clathrates forms under high pressure, low temperature conditions in the presence of water molecules acting as the 'host' that encase a smaller 'guest' molecules such as methane (CH_4), ethane (C_2H_6), carbon dioxide (CO_2), nitrogen(N_2) and hydrogen sulphide (H_2S) (Sloan,1991). In a simple language, gas hydrates is described as a form of blockage in the pipeline that will introduce interruption to the flow of hydrocarbon.

Common nuisance with hydrates is blockage of transmissions line (Fig. 1 and 2), plugging of blow out preventer and pipelines (Sloan, 1991). Hydrates blockage in the gas pipeline has been found by Hammerschmidt as early as 1930s (Koh and Sloan, 2007) marked the starting point at which extensive research has been conducted to understand hydrates formation in pipelines as well as its mitigation solutions.
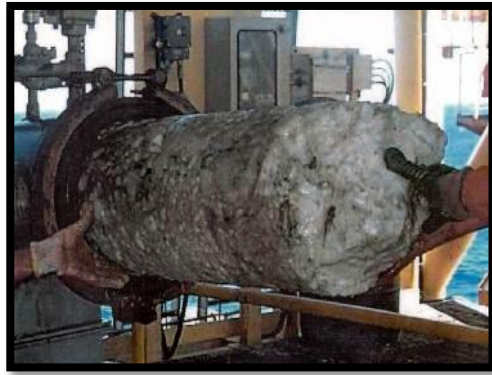
Figure 1: Hydrate formation in transmission line

Figure 2: Formation of hydrate in pipeline

Conventionally, hydrates have been dealt by Thermodynamic Hydrate Inhibitors (THI) at which it is attempt to disrupt the thermodynamic stability of the hydrates in terms of its composition, temperature or pressure. The four main prevention and control activities are through gas dehydration, pressure maintaining by keeping operating temperature above hydrate formation pressure or below than the hydrate equilibrium pressure, heating the gas to a temperature above hydrates equilibrium temperature and by introduction of chemical injection into the gas flow (Igbaonosi and Opara, 2011).

The two significant limitations with commonly used THI using chemical injection of glycol or mono ethylene glycol (MEG) is they are used at high concentration (10-60 wt%) (Kelland, Svartaas and Dybvik, 1995) and consequently leads to high cost expenditure (Igbanosi and Opara, 2011).

The shortcomings of THI have stimulated the industry to search for another type of inhibitors known as Low Dosage Hydrate Inhibitors (LDHI). Different from THI, LHDI works by changing the rheological properties of the hydrate formation (Paez, Blok, Vaziri and Islam, 2001) and are required in small concentrations. As of now, two types of LDHI that have been widely reported are Kinetic Inhibitors (KI) and Anti-Angglomerants (AAs). KI delays the induction time of hydrates while AAs prevent blockage by preventing hydrate to agglomerate.

Commonly studied KI so far reported involved water–based polymers such as poly(vinylpyrrolidone) (PVP) and poly(vinylcaprolactam) (PVCap). Despite their success as inhibitors, there is still ongoing research to enhance KI effectiveness using non-polymeric organic molecules (Villano and Kelland, 2010).

It has been reported very recently that ionic liquids (ILs) is one such organic salts that has become a new option as KI due to its high electrostatic charges to form hydrogen bonds with water molecule thus prevent hydrate formation (Xiao and Adidharma, 2008). Its ability to act as dual functions as thermodynamic and kinetic inhibitors is also one of the interesting revelations that draw the attentions of the industry for further research and analysis.

1.2 Problem Statements

1.2.1 Hydrate formation causes flow interruptions, economic losses and safety hazards.

In 1934, Hammerschmidt reported that the formation of gas hydrates was responsible for blocking pipelines. However, because formation of hydrates is favourable whenever all 4 elements which are high pressure, low temperature and availability of hydrate gas and water exists in a system hydrate can form in any segment of an oil and gas field. Among the possible locations that favour hydrate formations are transmission lines, gathering system, well tubing and casing (Sloan, 1991).

Deep water drillings are one such environment at which hydrates has a very high formation potential. As drilling water depths increases, the potential for its formation during drilling operation also increases. High hydrostatic pressure of the seafloor and low ambient temperature increases the likelihood of hydrate formation in choke lines, drilling risers, blow out preventers (BOP's) and subsea wellhead (Barker and Gomez, 1989).

In the case of formation of hydrates in the pipelines, as hydrates is accumulated over time the two pressure sections will formed due to the plugging forms in the pipeline. It will create a high pressure section between the plug and the well and low pressure section between the plug and recovery division. Pressure rise in the upstream section of the pipeline can cause pipe blow up due to the pressure ramp. Plugging of pipeline can also behaves like a projectile that can cause pipeline damage as the pressure difference between the sections dramatically increases (Chatti, Delahaye, Fournaison, and Petitet, 2004). Thus, not only that hydrates causes production losses as it plugs the pipelines during hydrocarbon flow, it will also causes threats towards production equipments and introduce serious safety hazards towards the operation environment.

Therefore, to avoid serious damage to the pipelines, several techniques have been applied in order to inhibit or dissociates its formation. Conventionally these methods

are carried out by gas and water removal, installation of heating system, temperature and pressure control and chemical injections (Sloan, 1991). These techniques or preventative measures incur large commencement cost expenditure as well as causes production time loses due too well work over operations.

1.2.2. Inhibition techniques using Thermodynamic Inhibitors (THI) is not preferable.

A conventional technique to prevent hydrates formation is by deployment of Thermodynamic Inhibitors using chemicals. The most commonly used chemicals so far are methanol and mono ethylene glycol. It acts by modifying the hydrate phase formation by reducing the temperature for hydrate to forms or increasing the hydrate formation pressure. (Igbaonusi and Opara, 2011).

Despite its usefulness in dealing with hydrates formation, this method however constitutes its own drawbacks. Its main disadvantage lies in the amount needed, as the normal effective concentration for the chemical will be around 10-60% (Kelland, Svaartas, Dybvik, 1995). Thus, because it is needed at high concentration the cost of applying this technique is also high depending on the requirement of the concentration needed at particular field. For example, the costs can range from US$ 50 per BBL in the Gulf of Mexico up to US$ 150 per bbl offshore West Africa (Cochran, 2003).

Besides that, other limitations of THI method includes (1) large storage volumes and pumping requirements required leads to significant capital costs, (2) methanol is volatile thus reduce its amount available for inhibition, (3) corrosion problems as oxygen may dissolved in methanol that causes corrosion in the pipe (4) THI inhibitors may reduce the effectiveness of corrosion inhibitors applied, (5) over use of methanol can result in contaminating the oil and causing it to be devalued, and (6) chemical used is less environmental friendly may draw the concerns with environmental and regulatory issues(Cochran, 2003).

In conclusion, the major challenge with application of thermodynamic inhibitors is due to its large operational costs and required at high concentration.

1.3 Objectives and Scope of Study

1. To test the effective concentration of two (2) imidazolium (1-butyl-3 methylimidazolium tetrafluoroborate [BMIM][BF$_4$] and 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF$_4$]) based ionic liquid (ILs) as KHI using Micro Differential Scanning Calorimeter (µDSC).

2. To measure the effect of ionic liquid (ILs) on inhibitions of hydrates and its ability to delay induction time for hydrate to form.

3. To compare the induction time of ionic liquid (ILs) with other commercially used water-based polymer- polyvinylpyrrolidone (PVP) inhibitor.

1.4 Relevancy of the Project

This project is relevant to the need of the oil and gas industry in the effort to address flow assurance problem related to hydrates. The drawback of hydrates causes problems which could lead to production and economic losses as well as causing many health, safety and environment (HSE) issues. Therefore, continuous research will be needed to find best practical and economically attractive solution to mitigate gas hydrates especially to look for a better inhibitors compared to the existing ones. As reported by many researchers, ionic liquid is an example of an inhibitor that could functions as an effective inhibitor as it is required at low concentration, an organic salts, non volatile, and has been classified as a 'green inhibitors'. Therefore, this project attempt to find a new mitigation solution utilizing ionic liquids as the inhibitors through laboratory testing and analysis to prove that it has the potential to perform as an inhibitor to mitigate hydrate formation better than the widely used method.

1.5 Feasibility of the Project

The project is divided into 3 phase of execution phases (Figure 3) which are; (1) Preliminary research and literature review, (2) Experimental works and analysis and (3) Documentation.
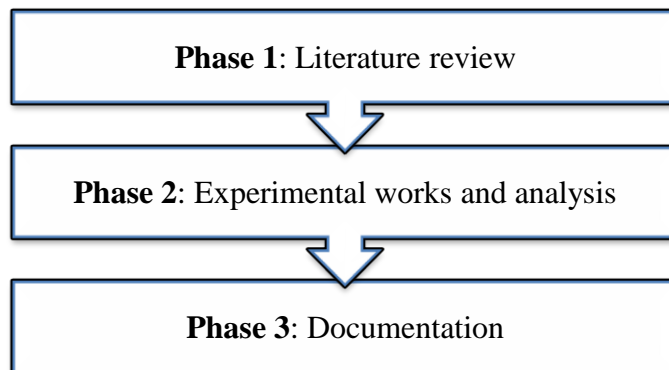
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│        Phase 1: Literature review            │
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│   Phase 2: Experimental works and analysis   │
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│        Phase 3: Documentation                │
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Figure 3: Project phases

Three months had been allocated for research studies in order to have a better insight and background on gas hydrates current research related to the industry. In addition to that, experimental design, materials and apparatus requisitions and lab training were carried out prior to Phase 2 of the project execution. At the end of the Phase 1, complete interim report on the project is submitted to meet the course outlined.

Experimental work is executed as soon as week 2 of the semester. This is whereby all the data and result are gathered and analyzed to summarize the findings of the projects. The project progress is reported to the Supervisor at the end of week 7 to improve the early discussion made based on the interpreted data. At the end of the process, recommendation and improvement idea are summarized to improve the findings for further research and improvisation of the study.

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 Clathrate Hydrates

Flow assurance problem associated with hydrates formation were first arose and reported by Hammerschmidt in 1934 that hydrates would cause obstruction and interruption to the oil and gas transmission pipelines (Sloan, Subramanian, Matthews, Lederhos, and Khokhar,1998). Problems with this snow-like solid is that it may block flow lines, valves, and wellheads thus directly reducing production efficiencies (Kelland, 2005).Therefore, vast research have been carried out in attempts to study the significance of hydrates towards the oil and gas industry to prevent substantial economic loses as well as for safety reasons.

Gas hydrates or commonly regard as gas clathrates is a form of crystalline solid solution which forms as a result of small 'guest' molecules being entrapped by the water 'host' molecules (Sloan, 1991). The three identified structures of gas hydrates are structure I, II and H (Fig. 4). The structures are composed of different combinations of cavity types and sizes, and may be stabilized by different hydrocarbon molecules. To form the hydrates, the guest molecule shall not be too large or too small in size compared to the water cavities. In order for the hydrate structure to be stable, it has to be partially filled with the guest molecules (Azmi, Mukhtar, and Sabil).

Structure I has a body-centred structure at which normally formed by methane, carbon dioxide as the guest molecules while on the other hand structure II has a shape of diamond lattice within cubic framework and made up of bigger guest molecules which bigger than ethane but smaller than pentane (Sloan, 1991). Structure H is a new type of hydrates structure on the other hand has a hexagonal framework. Structure II Hydrates is commonly encountered hydrates in production pipeline (Villano and Kelland, 2010).

The potential of hydrate formers molecules is presented in Table 1. The list consists of all hydrate formers found in gases, condensate and oils, process industry as well as academic field. However, Stability of the hydrate forms is only exists when there is availability of smaller 'help' molecules such as methane and nitrogen.
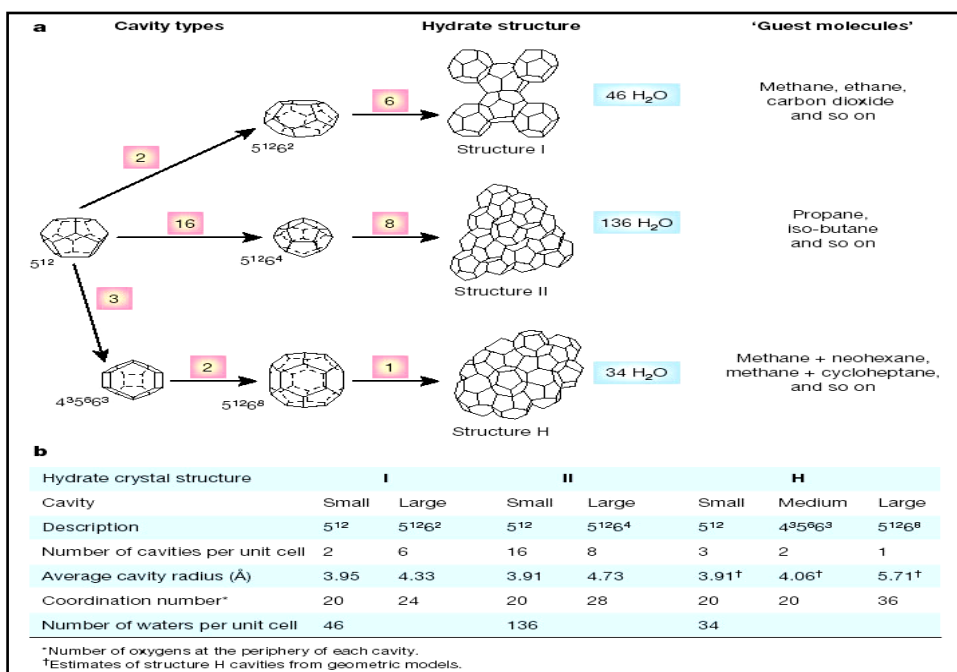
Figure 4: The 3 common hydrate unit crystal structures (Sloan Jr)

Table 1: Examples of molecules identified as potential hydrate formers (Edmonds, Moorwood and Szczepanski, 1998)

Natural Gas	Condensate/oils	Process Industry	Academic
Nitrogen	Benzene	Ethylene	Inert Gases
Carbon Dioxide	Cylcopentene*	Propylene	Oxygen
Hydrogen Sulphide	Cyclohexane*	Other Olefins	Hexafluorosulphide
Methane	Cycloheptane*		Cyclopropane
Propane	Methylcyclohexane*		
Butane*	1-1Dimethylcyclohexane		
Isobutane	2 Methyl butane*		
Neopentane*	2,2 Dimethyl butane*		

*requires presence of smaller 'help' molecule to stabilize structure.

2.2 Hydrate Formation

The science of hydrates formation is favors with the presence of 4 elements, when there is water, hydrates gas molecules and under high pressure and low temperature environments (Sum, Koh, and Sloan, 2009). Hydrates issue are often encountered in deepwater conditions such as in the Gulf of Mexico, North Sea and permafrost regions like Alaska (Kalbus, Christiansen, and Sloan, 1995).

The following Figure 5 is the relationship between pressure and temperature condition for hydrates to form during hydrocarbon transmission from wellhead to the downstream. Formation of the snow like solid falls in the left (hydrate risk) region. This problem area is the main area of concern during production and transportation of hydrocarbon.
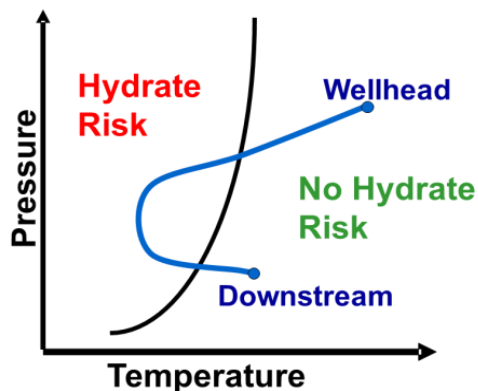

Figure 5: Hydrate formation behaviour in pipelines

Figure 6 is the schematic diagram that shows the relationship between pressure and temperature and the hydrates forming regimes. Based on this figure, two boundaries above and below which two areas of certainty can be observed, which are hydrate free zone and hydrate zone. These two zones are separated by a hydrate risk zone (in yellow). The hydrate zone is whereby hydrate will form spontaneously while at hydrate free zone no hydrate will form due to stability. Sub-cooling (ΔT) is defined as the difference between the thermodynamic of hydrate formation and ambient temperature of the surrounding.
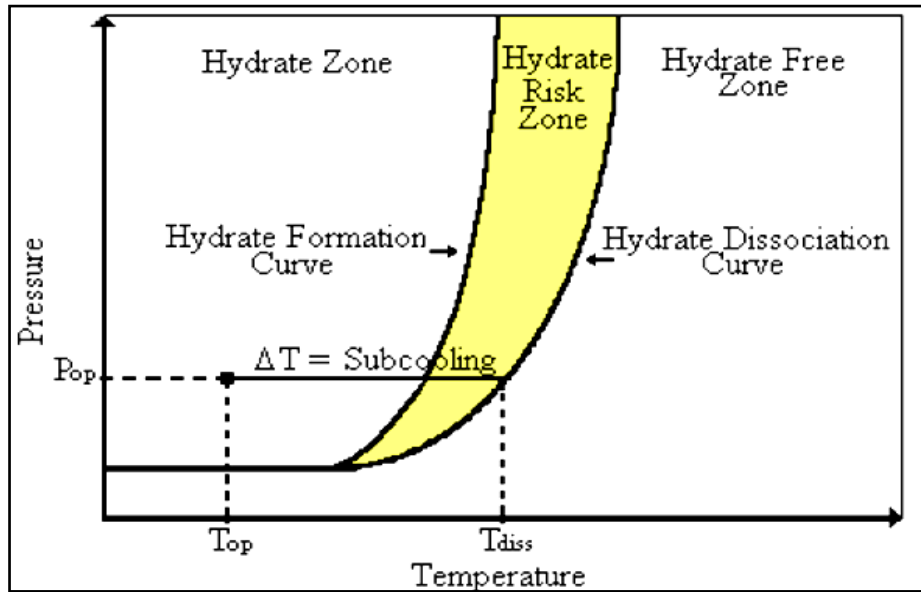
Figure 6: Pressure-temperature graph for a typical natural gas hydrate formation (Paez, Blok, Vaziri and Islam, 2001).

Figure 7 on the other hand is the CO_2 hydrate phase diagram based on Sloan and Koh, 2008. In this diagram, the stable hydrate formation boundaries (shaded region) can be clearly indicated.
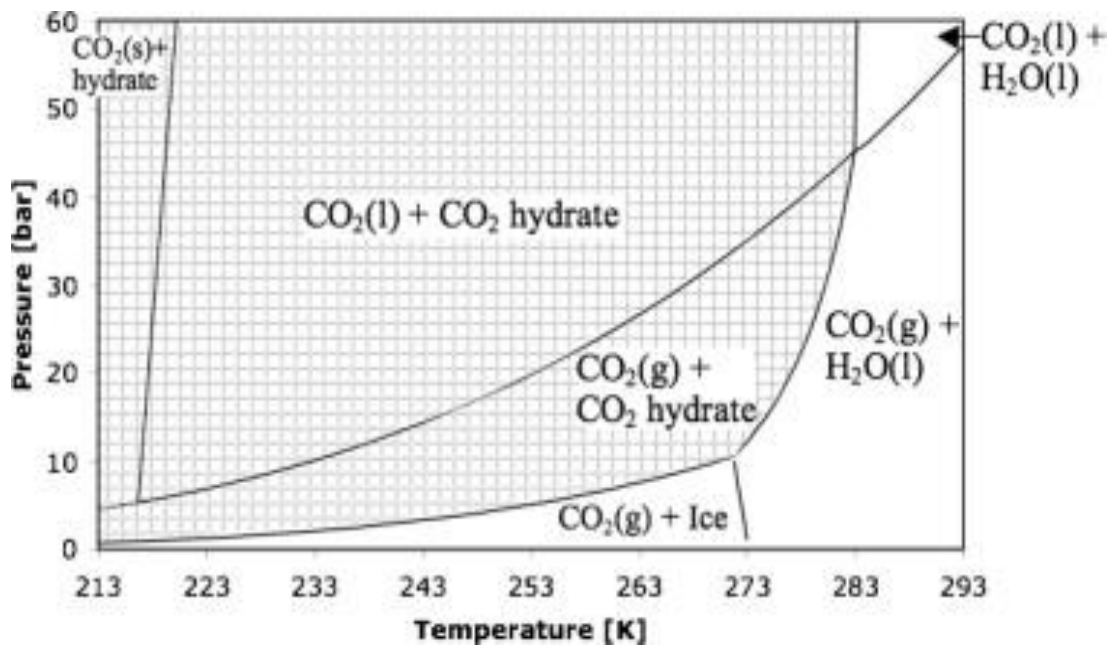

Figure 7: CO₂ Hydrate phase diagram (Sloan and Koh, 2008)

Formation of hydrates involved in 2 processes which are nucleation and stable growth process (Sloan, 2007). Hydrate nucleation refers to the process at which formation and growth of the hydrate nuclei to it critical size. Growth of water and gas molecules takes place at the same time. They act as the precursors to the nucleation process at which it requires a supersaturated environment. Gas molecules will dissolve in water and create the supersaturated condition through the liquid phase at the interface of water and gas molecules. After some time, nuclei of hydrates will form and continues its growth with sufficient gas presence. Nucleation of hydrates is however a probabilistic phenomenon and so is its induction time (Xiao and Adidharma, 2009)

2.3 Thermodynamic Inhibitor

The conventional method used to prevent hydrate formation is by keeping the hydrocarbon system out of the hydrate formation zones. This is carried out by adjusting the thermodynamic stability of the hydrates with the help of thermodynamic hydrates inhibitors (THI) such as methanol and mono ethylene glycol (MEG). Addition of these materials will displace the hydrate dissociation curve to lower temperature or higher pressure (Kelland, Svartaas and Dybvik, 1995). The method is similar to the process of adding anti-freeze to water to lower the freezing point (Chochran, 2003). However for the inhibitors to work, it is added at high concentration; normally 10-60 wt% leads to high operations costs and may arise health, safety and environment (HSE) problems due to large amount of chemical usage (Philips, and Grainger, 1998).

Figure 8 shows that the hydrate formation curve has been displaced to a lower temperature with presence of thermodynamic inhibitors (Edmonds, Moorwood and Szczepanski, 1998).

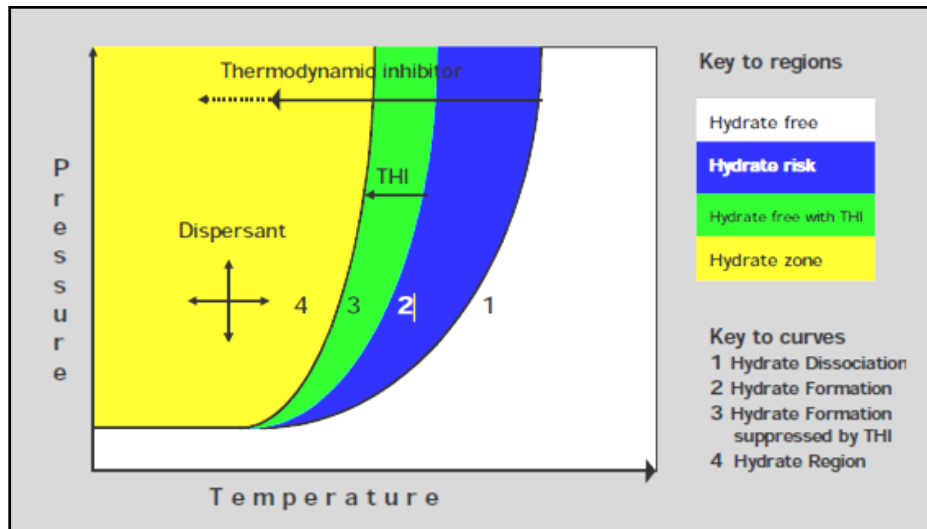**Figure 8: Pressure-Temperature diagram with presence of thermodynamic inhibitors.**

As an example, Figure 9 shows the effects of 5 types of thermodynamic hydrate inhibitors such as salts and alcohol to shift the methane hydrate stability curve to lower down the temperature for hydrates to form (Ellison, Gallagher, Frostman, and Lorimer, 2000).
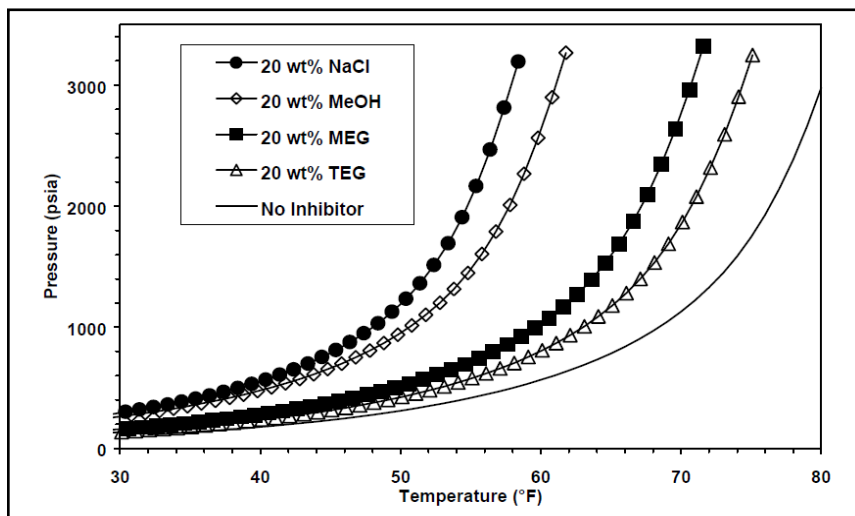

Figure 9: Effects on THI on hydrate stability

Thermodynamic inhibitors are used mainly due to several advantages that it offers. The advantages are; (1) It reduces hydrate formation temperature, (2) the availability of software models to measure its effect on the hydrate dissociation curves, (3) sufficient amount of inhibitors would prevent hydrate formation in most conditions, (4) methanol can inhibit both liquid and vapor phase during transient operations and (5) they are compatible to work in any hydrocarbon system (Cochran, 2003).

On the other hand, limitations of THI method includes (1) large storage volumes and pumping requirements required leads to significant capital costs, (2) methanol is volatile thus reduce its amount available for inhibition, (3) corrosion problems as oxygen may dissolved in methanol that causes corrosion in the pipe (4) THI inhibitors may reduce the effectiveness of corrosion inhibitors applied, (5) Over use of methanol can result in contaminating the oil and causing it to be devalued, and (6) the chemical used is less environmental friendly may draw the concerns with environmental and regulatory concerns(Cochran, 2003).

2.4 Low Dosage Hydrate Inhibitors (LDHI)

Due to the limitations of THI, oil and gas industry are now moving towards the research of new inhibition techniques in which hydrates formation is controlled kinetically. Different from THI, this technique requires only a small amount of concentration or low dosage deployment. The two types of low dosage inhibitors (LDHI) are the kinetic inhibitors (KI) and anti-agglomerates (AAs) also called as dispersant additives.

The principle of KI is that it prolongs the hydrate nucleation and growth or it delays induction time. Efficiency and application of KI depends on two factors which are (1) sub-cooling to which produced effluents are exposed, and (2) residence time of the effluent inside the hydrate stability zone (Jean, Philippe, and Patrick, 2007).

As mentioned before, sub-cooling is the difference between the hydrate dissociation temperature and ambient temperature. At higher sub-cooling, efficiency of KI is reduced, this is because sub-cooling is the driving force of kinetic hydrate formation. So, effectiveness of KHI is highly dependent on the degree of sub-cooling. High value of sub-cooling indicates that less induction time could be achieved (Igboanusi and Opara, 2011).

KI are mainly water soluble polymers with small cyclic amide groups such as pyrrolidone and caprolactam as the active units (Storr, Taylor, Monfort, Roger, 2004). Among the most commonly used KIs includes, Poly (N-vinylpyrrolidone) (PVP) and poly (N- vinylcaprolactam) (PVCap) are among the most frequently tested water-based polymer and found to work effectively as KI (Hagen, 2010; Villano, Fitjen, Schubert, Hoogenboom, and Kelland, 2009; Kelland, 2006).
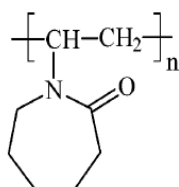
Figure 10:Polyvinylcaprolactam (PVCap)   **Figure 11: Polyvinylpyrrolidone (PVP)**
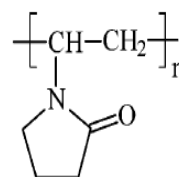
It is also known that some other chemicals can act as synergists to these KIs (Chen, 2010).The main advantage of KIs over thermodynamic inhibitors is that they are effective at very low concentrations (less than1% weight) (Chen, 2010). The major drawback to KIs is that they can only be applied in moderate sub - cooling less than13°C (Hagen, 2010).

On the other hand, Anti-Agglomerant is another category of low dosage inhibitors, or in other words effective at concentration less than 1 weight percent (%). Differ than KI, AA works in a way that it help to keep the hydrate crystal as tiny dispersed particles within the flow stream to ensure easiness of transportation of the crystals (Mokhatab, 2006).

Besides that, its efficiency does not dependent on the degree of sub-cooling as KI does. However, limitation of AA is that they are only effective in low water cut system (Hagen, 2010)

Anti-Agglomerants are usually surfactants in which the head is attracted to the hydrate and the tail is dispersed in the liquid hydrocarbon phase. Therefore the behaviour of AA shows that, a liquid hydrocarbon phase needs to be present for it to be effective (Hagen, 2010). For gas systems, this implies that the gas-to-oil ratio (GOR) should not be too high. Common examples of AA applied in the industry are Polysaccharides and cholesterol-based bile acid.

Nevertheless, the effort of proving that the previously mentioned LDHI would give the best solution is still ongoing. Continuous research to justify and improve preceding limitations of KI is part of the step to look for better inhibitors based on the conclusions developed from prior research as the references.

One of the significant conclusions drawn from those trials is that, material such as methanol and PVP has the ability to inhibit hydrates because it has a strong electrostatic charge and can form hydrogen bonds with the water molecule (Xioa and Adidharma, 2009). So based on this principle, development of new KI using Ionic Liquids (ILs) has been initiate by Xiao and Adidharma in 2008. They concluded that, ILs could function as dual inhibitors. In other words it functions as kinetic inhibitors and thermodynamic inhibitor at the same time.

ILs consists of bulky and symmetric organic cations such as immidazolium or pyrridinium ion with alkyl chain substituent, while the common anions used are tetrafluoroborate (BF_4^-), chloride (Cl^-), and bromide (Br^-). BF_4^- has strong ability to form hydrogen bond with water than any other types of anion.

Properties of ILs fits in such a way that it has strong electrostatic charges and their anions and cations will build hydrogen bonds with the water molecules. In other words, the ions play a very significant function to interfere with the hydrate formation condition.

By nature, ILs is a molten-salt at room temperature that many researchers regard them as a potential green solvent. Other significant features of this solvent are that, they are very stable and has very low vapor pressure makes them nonvolatile (Antony, Mertens, Breitenstein, Wasserscheid, and Carper, 2004).

The two ILs that will be used in this study are shown in the following Figure 12 and 13.

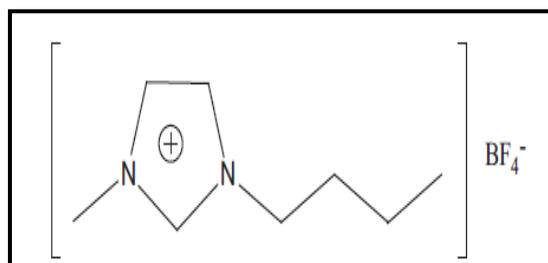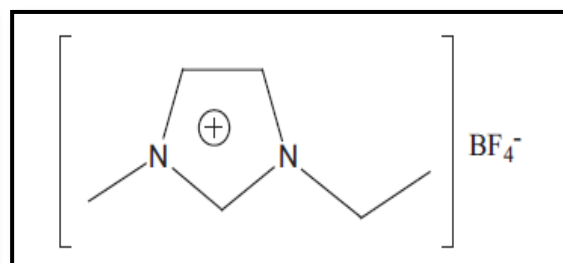Figure 12: [BMIM][BF4]   Figure 13: [EMIM][BF4]

The two ILs are only different to each other only in the alkyl substituent of imidazolium. [EMIM][BF$_4$] performs better than [BMIM][BF$_4$]. The thermodynamic inhibition effectiveness of ionic liquids with a shorter alkyl chain substituent is better than that of ionic liquids with a longer alkyl chain substituent (Xiao and Adidharma,2009).

2.5 Micro Differential Scanning Calorimeter (µ DSC).

Common apparatus used to measure kinetic inhibits effectiveness are rocking cell chambers, autoclaves cells (Arjmandi, 2003; Lederhos, 1996), flow loops (Peytavy, 2008) or differential scanning calorimeter DSC (Koh, 2002; Sivaraman, 2003). These conventional methods are performed by using one sample at a time to measure the induction time of hydrate.

For the purpose of this study a micro differential scanning calorimeter (µ DSC) by SETARAM will be used. The International Confederation for Thermal Analysis and Calorimetry defines µ DSC as a technique in which the heat flux (thermal power) to (or from) a sample is measured versus time or temperature while the temperature of the sample is programmed, in a controlled atmosphere. The difference of heat flux between a crucible containing the sample and a reference crucible (empty or not) is measured.

The measurement of the heat flux versus time will be presented in forms of DSC thermogram as shown in the Figure 14 (SETARAM).
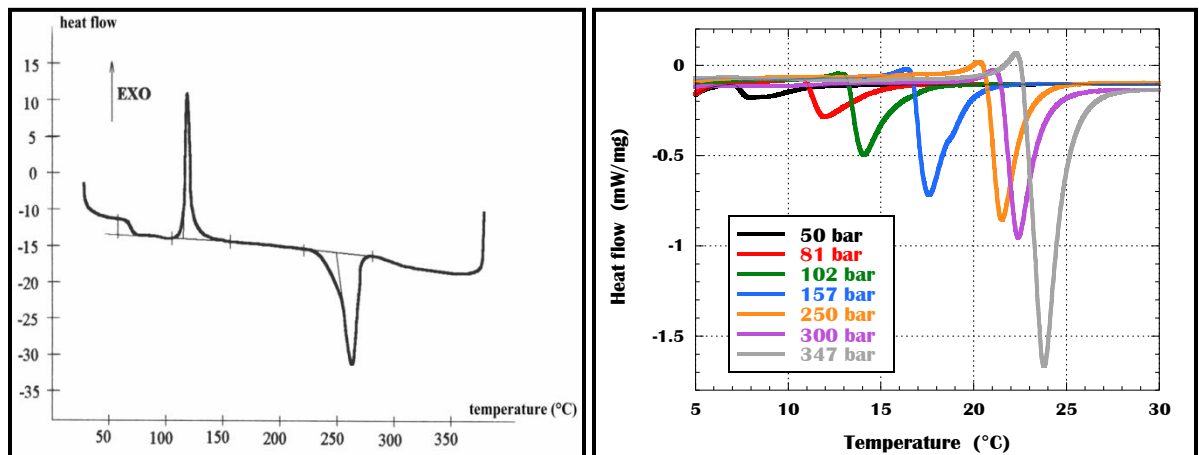
Figure 12: µDSC Thermogram

Based on the thermograms the onset temperature for hydrate to forms and time taken for the induction to take place can be estimated from the peak of the heat flow curve.

CHAPTER 3: METHODOLOGY

3.1 Project Methodology

The project methodology consists of 3 phases of implementations which are preliminary, experimental work and finally discussion and conclusion. Figure 15 summarized all the methodology that is applied throughout the project implementation.

Figure 13: Research Methodology

3.2 Gantt Chart and Key Milestones

Table 2:Gantt chart and key milestones

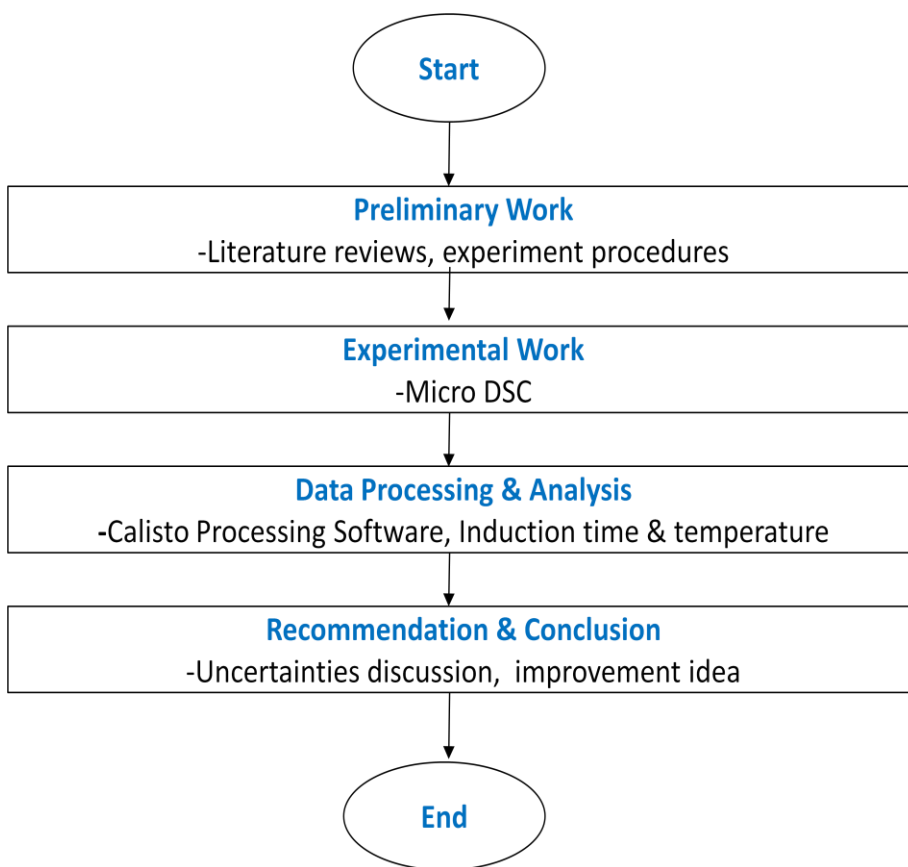| Project Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Reviews		█	█	█	█	█	█																				
Experimental Design							█	█	█																		
Methodology Confirmation										█																	
Materials requisition											█																
Sample Preparation														█	█												
Experimental works																█	█	█	█								
Data Collection and interpretation																				█	█	█					
Comparison against other inhibitors																							█	█			
Recommendation and Improvement																									█	█	█
Key Milestones																											
Preliminary Research Work			█	█	█																						
Submission of Proposal Defense Report						█																					
Proposal Defense									█																		
Project Works Continues										█	█	█															
Submission of Interim Draft Report												█															
Submission of Interim Report													█														
Submission of Progress Report														█													
Pre-SEDEX																				█							
Submission of Draft Report																								█			
Submission of Dissertation																									█		
Submission of Technical Paper																									█		
Oral Presentation																										█	
Submission of Project Dissertation																											█

24

3.3 Materials

A. Ionic Liquids

The two ionic liquids that are tested in this experiment are from two (2) imidazolium based ionic liquid (ILs) which are 1-butyl-methylimidazolium tetrafluoroborate [BMIM][BF4] and 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF4]. Each sample are tested at concentrations of 0.1 and 1.0 wt% against a sample containing no ionic liquid as a control sample

| Figure 14: [BMIM][BF4] | Figure 15: [EMIM][BF4] |

2. Distilled Water (H$_2$O)

Distilled water is used as the aqueous solution to prepare all of the sample solutions and volume of the samples per trial is 60mg.

3. Carbon Dioxide (CO$_2$)

To study the effect of the samples on carbon dioxide hydrates, a tank of carbon dioxide with a purity of approximately 99.99% is used.

3.4 Apparatus

In this experiment, the main apparatus that used is the High Pressure SETARAM micro differential scanning calorimeter (μDSC) by SETARAM Inc. used for measuring the dissociation heat of hydrate. μDSC is build with 2 vessels or a pair of gas-tight high-pressure cells that are made up of Hastelloy C276 with a maximum operating pressure up to 400 bars or 5800 psi.

The 2 vessels are designed to contain 0.5 cm^3 volume of sample and a dimension of 6.4mm internal diameter $\times$15.5mm long. One of them is used as reference and the other contains the sample solution. μDSC can work at a temperature range of -45 to 120 ^0C. The temperature accuracy and precision is ± 0.1 ^0C and ± 0.02 ^0C respectively. Its heating and cooling rate is programmable within 0.001 to $5^0C/min$. As for pressure, it is controlled by a gas charging panel capable of charging to pressures from (5 to 1000) bar, with a pressure deviation of $\pm$ 0.5 bar.
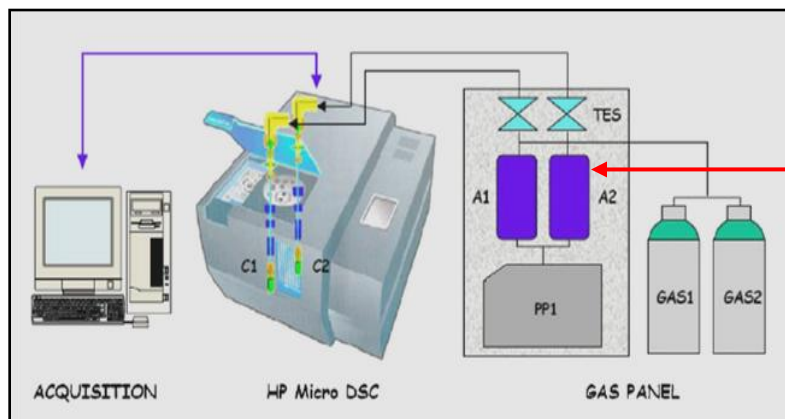

Figure 16: Schematic of μDSC apparatus, high pressure panel and acquisition system.
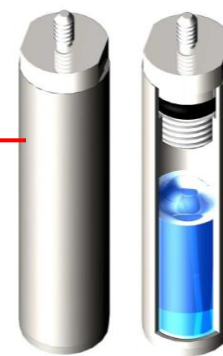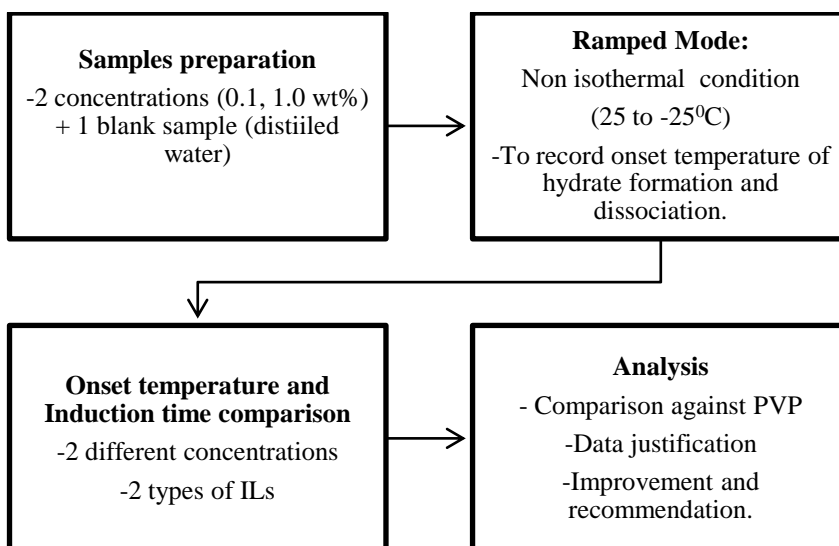
Figure 17: Gas tight HP cell

3.5 Method

Figure 18 : Experimental design

The experimental work started with the preparations of sample solutions for each sample at concentrations of 0.1 and 1.0, wt%. Each sample run is being compared to a reference sample with no IL added to it. The mass of the sample used is kept constant at 60mg. Once the sample is ready the samples it is transferred to the vessel and both the reference and IL sample will be connected to the carbon dioxide gas supply to be charged. Pressure inside the vessel shall then be measured using pressure transducer before it is placed into the calorimetric block of the High Pressure μDSC. To avoid history effects, the previous sample is flushed out using distilled water and pressurizes air.

The experiment is conducted at non isothermal conditions or ramped mode. The objective of the non isothermal conditions is to see the onset temperature at which hydrates start to form and dissociates at pressure 30 bars (isobar condition). This experiment consists of both cooling and heating steps. The start temperature will be at 25^0C and cooling will be down to -25^0C below hydrate formation range and heated again to room temperature. Heating rate throughout the experiment is set at constant value of 0.5^0C /min to be able to see the hydrate formation

behaviour with or without inhibitor. The elapsed induction time for hydrates formation in both samples with and without inhibitors is measured and compared to see the effect of ILs in delaying the hydrates formation.
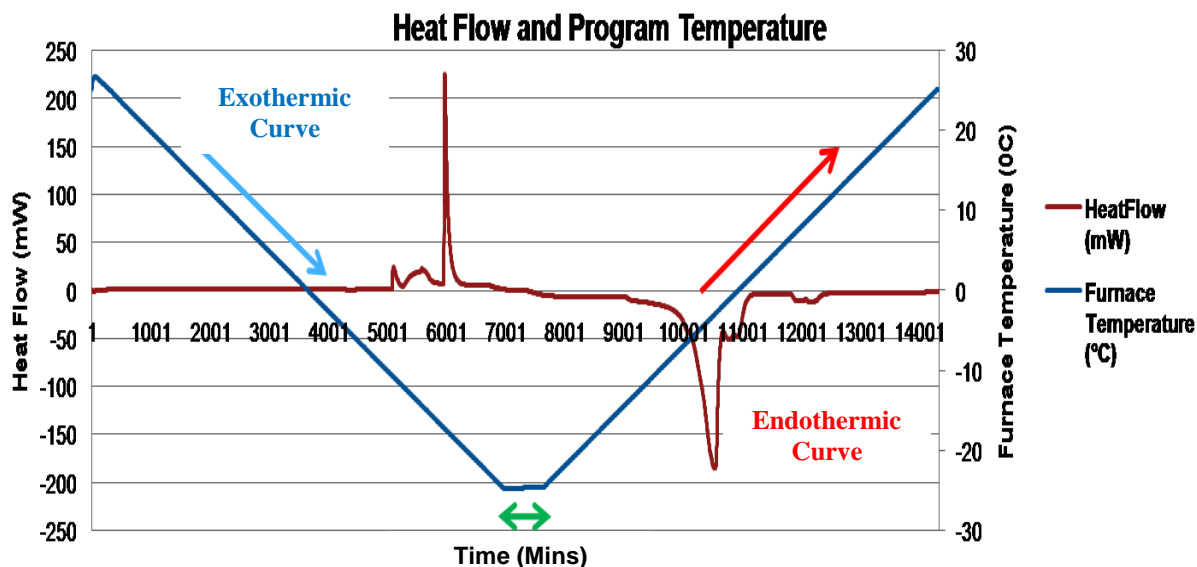

Figure 19: Experiment Program

The effectiveness of the ionic liquids to delay the hydrate formation is measured in terms of the induction time at 2 different concentrations of ionic liquids applied. The second method to determine the best ionic liquid is by comparing the result between the two imidazolium samples at the same concentration sets.

Table 3: Temperature program at pressure 30 bar

			Ramped Mode			
No.	**Start Temp**	**End Temp**	**Heating/Cooling rate ^{0}C/Min**	**Duration (min)**	**Gas Use**	**Remarks**
1	25	25		10		Stabilizing
2	25	-25	0.5	60		**Cooling**
3	-25	-25		10	CO_2	Hold
4	-25	25	0.5	60		**Heating**
5	25	25		10		Stabilizing

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Determination of the induction and dissociation time of gas hydrate is made based on the exothermic and endothermic transformation curves displayed that are shown on the thermogram.

- **Exothermic transformation:** Represents the process of the nucleation and growth of hydrate nuclei to a critical size at which the induction time range is measured between the onset and offset time.
- **Endothermic transformation**: Represents the dissociation of the hydrates and its dissociation time range (measured the same way as its induction time).

Note that prior an ice peak will be seen prior to hydrate formation and also prior to its dissociation
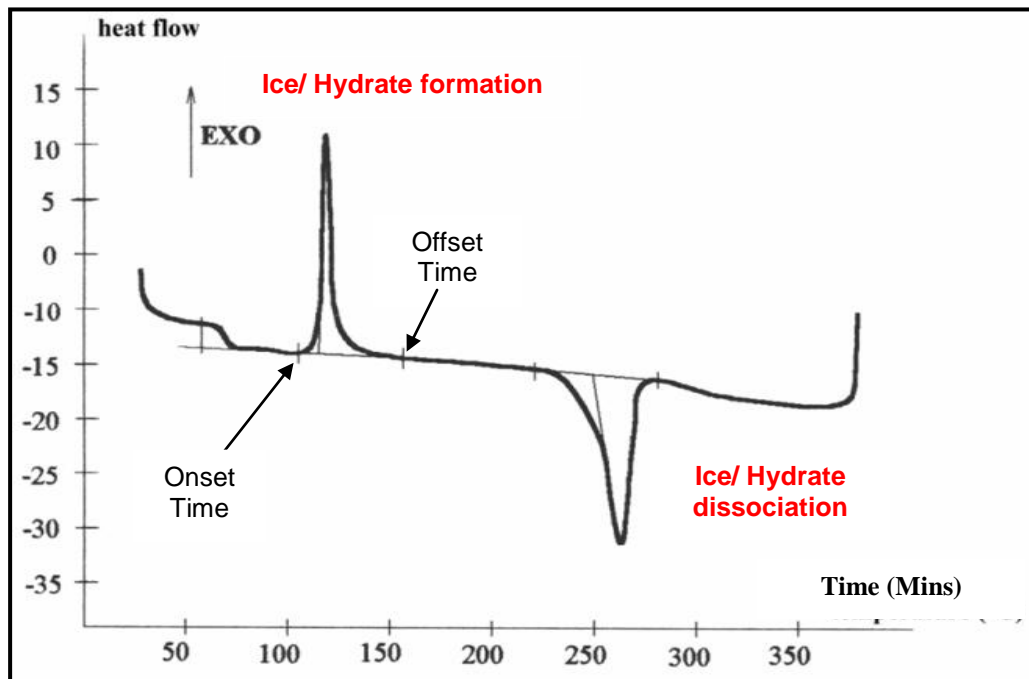

Figure 20: Exothermic and endothermic curve

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Effect of Ionic Liquid on Hydrate Induction and Dissociation Time

The result of all samples for 0.1 and 1.0 wt% concentration against the blank sample were plotted on the same graph and zoomed particularly on the exothermic and endothermic process to be able to see the effect of ILs towards the range of formation and dissociation time of hydrate.

Induction time is measured to represent the behaviour of the kinetic of the CO_2 hydrate crystallization. It is the time elapsed during nucleation process which includes the formation of gas water cluster and their growth to form stable nuclei (Sloan and Koh, 2007). The following sections discussed the interpretation of the result based on the data recorded using micro DSC.

a) Hydrate Formation

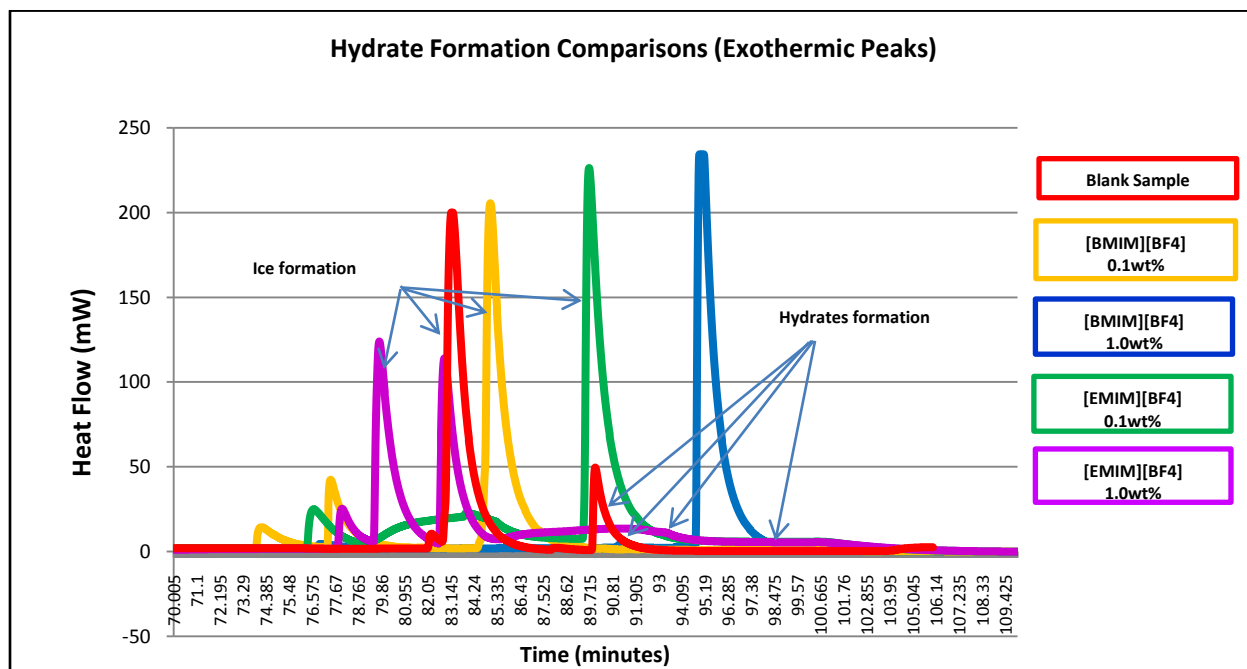**Figure 21: CO$_2$ Hydrate formation curve**

Figure 21 shows the exothermic curves of all samples tested and zoomed at time 70 to 110th minutes in which all formation peak curves occurred. Based on the curves, 2 exothermic peaks are observed for each samples tested.

Theoretically the first peak shows the ice formation while the second peak indicates CO_2 hydrates formation. During the cooling process, ice crystallization occurs prior to hydrate formation. The area under the peak represents the amount of energy released during cooling process. Formation of ice happens before hydrates starts to nucleate explains the 2 peaks observed, at which ice crystallizes more readily than hydrates and most of the water can convert directly to ice. On the other hand, only thin film of hydrate forms at the interface. Hence, the fraction of ice formed is larger than the CO_2 hydrates formed. Thus this explains the differences in the observed size of the 2 peaks.

Table 4: Hydrate Induction Time

Sample	Hydrate Induction Time Range (Mins)	Mean Induction Time (Mins)
Blank Sample	87.53-91.79	89.66
[BMIM][BF4](0.1wt%)	83.34-92.29	87.79
[BMIM][BF4](1.0wt%)	91.35-98.22	94.79
[EMIM][BF4](0.1wt%)	91.08-99.36	95.22
[EMIM][BF4](1.0wt%)	84.59-106.26	95.75

Table 4 is the data recorded for the induction time range and the mean value for CO_2 hydrates starts to form based on the exothermic curves plotted. The results showed a positive improvement in time when ionic liquid being is added in the blank samples. In comparison to the blank sample, at concentration of 0.1wt% [BMIM][BF4] does not show any improvement in delaying the hydrate formation while [EMIM][BF4] shows that the induction time is delayed for about 5.57 minutes. The delay time for [BMIM][BF4] and [EMIM][BF4] at 1.0wt% gives 5.13 and 6.1 minutes respectively.

The improvement in CO_2 hydrate delay time is presented in the following Figure 22. The highest improvement is by [EMIM][BF4] at 1.0wt% with 6.79% induction delay time improvement. On the other hand, only [BMIM][BF4] at 0.1wt% showed to have no improvement to retard the hydrate nucleation process.

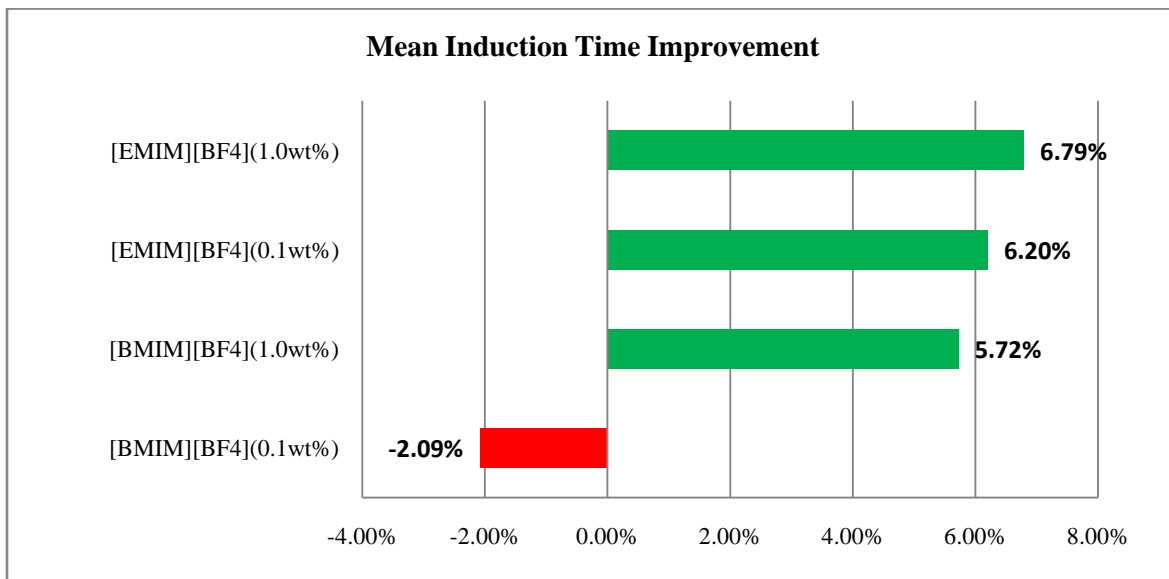**Mean Induction Time Improvement**

Sample	Value
[EMIM][BF4](1.0wt%)	6.79%
[EMIM][BF4](0.1wt%)	6.20%
[BMIM][BF4](1.0wt%)	5.72%
[BMIM][BF4](0.1wt%)	-2.09%

Figure 22: CO₂ hydrate induction time improvement
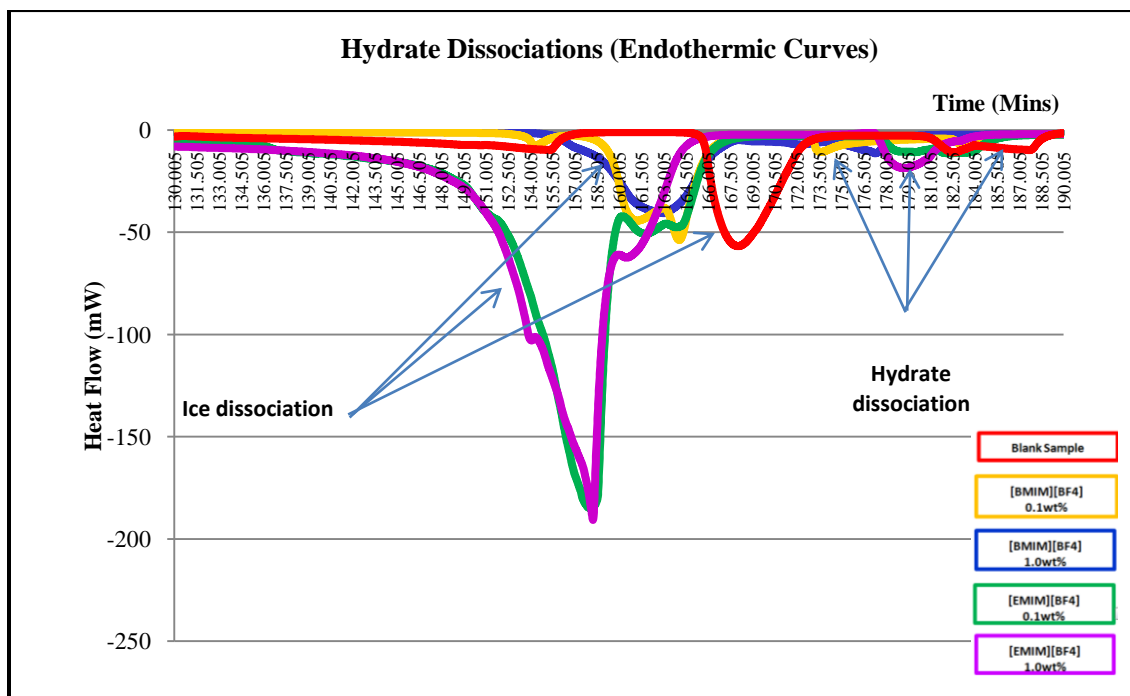
b) Hydrate Dissociation

Figure 23: CO₂ hydrate formation curve

Figure 23 shows the endothermic curves of all samples tested and zoomed at 130 to 190th minutes. The curve represents the behavior of the curves during heating process form -25^0C to 25^0C. The first peaks observed are found to be the ice dissociation while the second indicates the hydrate dissociation.

The interpretation of the ice and hydrate formation can be confirmed during heating process as the hydrate nucleation time cannot be used directly to distinguished between ice and hydrate below $0\ ^0$Celcius (Davies, Hester, Lachance, Koh and Sloan,2008). Thus, based on the endothermic curve, the area under the curve showed that the magnitude of the ice and hydrate dissociation are of approximately the same with the exothermic curves.

Table 5: Hydrate dissociation time

Sample	Hydrate Dissociation Time Range (Mins)	Mean Dissociation Time (Mins)
Blank Sample	184.85-193.98	189.42
[BMIM][BF4](0.1wt%)	178.63-187.52	183.07
[BMIM][BF4](1.0wt%)	179.5-182.7.32	181.20
[EMIM][BF4](0.1wt%)	172.94-190.44	181.69
[EMIM][BF4](1.0wt%)	176.37-181.97	179.17

Table 5 is the data recorded for the dissociation time range and its mean dissociation value. The highest mean induction time is with blank sample, while all other samples with ionic liquid show a shorter time period for dissociation to occur. [EMIM][BF4] at 1.0 wt% gives the shortest dissociation time at 179.17 minutes.

The following Figure 25 shows the effects of ionic liquid towards the dissociation time of the CO_2 hydrates in terms of its mean induction time improvement of hydrate dissociation compared to blank sample.
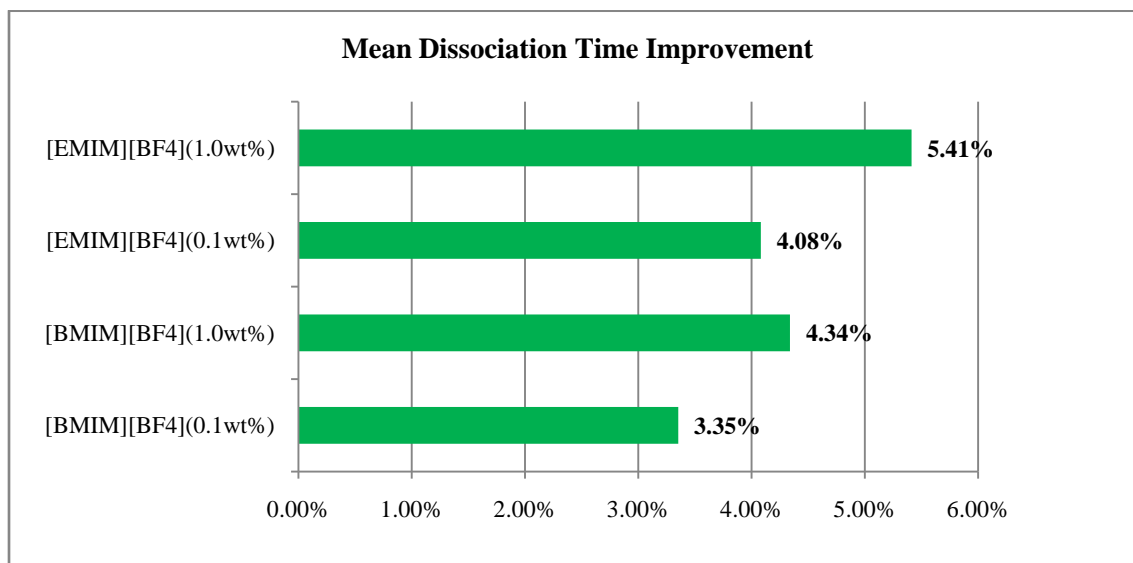

Figure 24: CO_2 hydrate dissociation time improvement

4.2 Comparison between the 2 Ionic Liquid used at Different Concentration

In this section, the comparison between [BMIM][BF4] and [EMIM][BF4] are tested at concentration of 0.1wt% and 1.0 wt% is justified.

Based on the discussion before, it can be summarized that the induction time for the samples with ionic liquids has a longer induction time as compared to the blank sample. This is applicable to [BMIM][BF4] at 1.0 wt%, and [EMIM][BF4] at 0.1wt% and 1.0 wt%. Thus, shows that, ionic liquid has a good potential to act as a kinetic inhibitor or delay the growth of the gas hydrates.

Theoretically, ionic liquids are able to perform as a kinetic inhibitor due to its strong electrostatic charges. Both the anion (BF_4^-) and imidazolium cation tailored the formation of hydrogen bonding with water. Thus, these ions functions to interfere with the hydrate formation condition.

In terms of concentration, it can be seen that at lower concentration of ionic liquids the result shows the shorter induction time. Therefore indicates effectiveness of ionic liquids is also dependent on the concentration of the ionic liquids applied. However, because only two concentrations of ionic liquid were tested, it limits the conclusion of the result that the effectiveness of ionic liquid will increase linearly at concentration above 1.0 wt%.

In the case of [EMIM][BF4], the difference in mean induction time between the two concentration is increased approximately 0.6% at 1.0wt%. Further investigation will be carried out to find the optimum concentration in between the two values.

Besides that, comparing the two samples tested, the longest mean induction time recorded is with [EMIM][BF4] at 1.0wt% at 95.75 minutes. This is due to [EMIM][BF4] have a shorter alkyl chain substituent and that is why it is better than that of ionic liquids with longer alkyl chain substituent (Adidharma, 2009) at which in this case is [BMIM][BF4].

4.3 Comparison of Ionic Liquid against Commercial Inhibitor (PVP) at 0.1 wt%

A comparison between [BMIM][BF4] and [EMIM][BF4] ionic liquid to a commercially used inhibitor poly(N-vinyl pyrrolidone) (PVP) is compared at 0.1 wt%. PVP is a type of water-soluble polymer proven as kinetic inhibitor and commonly used in the industry. The PVP data used are based on the experiment conducted by two other Final Year Project students following the same experimental approached.
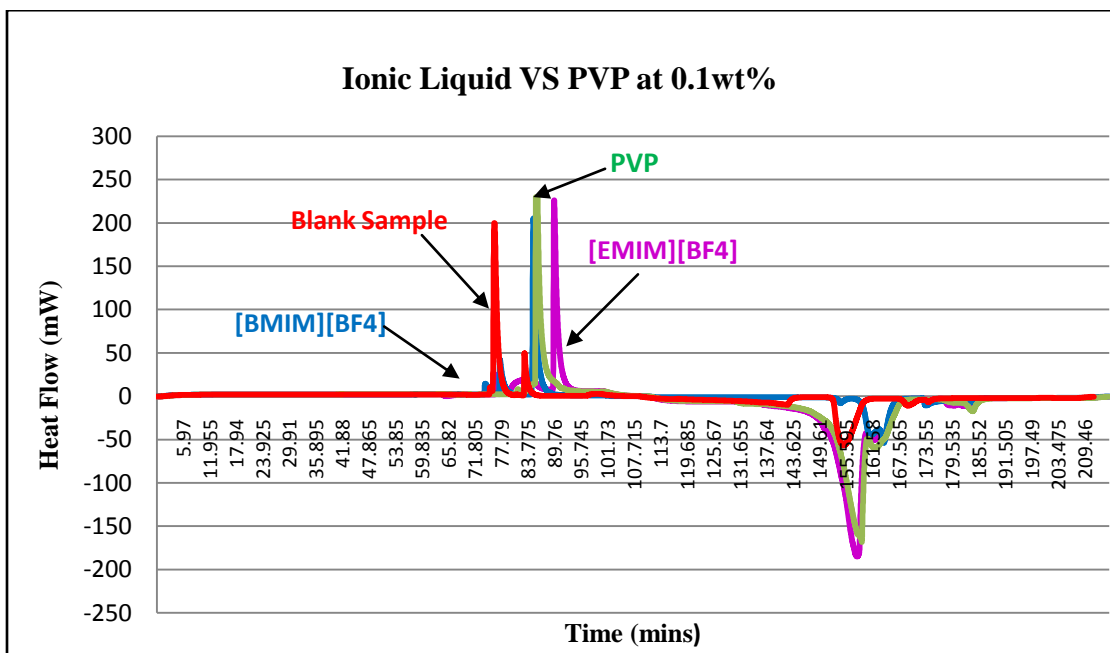

Figure 25: Hydrate Formation and Dissociation of Ionic Liquid VS PVP at 0.1wt%

Based on the exothermic curves, mean time for hydrate nucleation for PVP occurred at 95.10 minutes. This value fells in between the 2 exothermic curves of blank sample and [EMIM][BF4] while [BMIM][BF4] occurs before blank sample. Therefore, at 0.1wt%, [EMIM][BF4] works better than PVP. It gives an indicators than it has the potential to act as a better kinetic inhibitor than the existing KI at as low as 0.1wt%.

4.4 Uncertainties

There are several uncertainties found throughout analysing the experimental results. They are as discussed below:

- *Formation and dissociation peaks* – The peak of the exothermic ice formation peak of 1.0wt% [BMIM][BF4] produced shown a flatten line on top of the peak and there is no maximum in the peak. This erroneous result may be due to the errors during sample preparation. For example, the weight of the sample may exceed the limits of the sample chamber or for the scanning rate of 0.50^0C/min to be effective. In this experiment, all sample should not exceed 60mg weight, otherwise errors could be seen in the produced result.

- *Sample preparation time-* In this experiment, all samples are prepared 3 days prior to its run time. Although all samples were left in the lab for storage at the ambient temperature, the sample solution might have been affected. So, fresh sample prepared right before the run time might be more favourable.

- *History effects-* History effect of other samples run previously might have affect the result as it may not be completely flushed out before loading the new samples and remain adhered to the surface of the vessel. Flushing out using distilled water with alternately applying pressurize air to dry the vessel can reduce the effects.

CHAPTER 5: CONCLUSION

5.1 Conclusion

Based on the literature reviews, experimental activities and data analysis performed throughout this project, the research study has shown fruitful results at which all objectives outlined are achieved.

Effectiveness of the 2 imidazolium based ionic liquid (ILs) which are [BMIM][BF4] and [EMIM][BF4] by using Micro Differential Scanning Calorimeter (μDSC) were compared with the sample with no inhibitors added to it. The result shows that samples with ionic liquid shows a positive improvement to delay the hydrate formation time to a longer time except for [BMIM][BF4] at 0.1wt%. [EMIM]BF4] is found to be a more efficient inhibitor than [BMIM][BF4] at the same concentration. At 1.0wt% it is shown that the mean induction time improvement achieved for [EMIM][BF4] is 6.79% while [BMIM][BF4] only at 5.73%. This difference is due to the molecular structure of the ionic liquid that enhances its ability to inhibit hydrate formation. [EMIM][BF4] has a shorter alkyl substituent that facilitates during hydrogen bonding with the water molecules. A strong electrostatic charge of the ionic liquid is the main properties of ionic liquid to inhibit hydrate formation. In terms of hydrate dissociation time, [EMIM][BF4] at 1.0 wt% gives the shortest dissociation time at 179.17 minutes, with 5.41% improvement compared to blank sample.

Besides that, a comparison against a water-soluble polymer, poly (N-vinyl pyrrolidone) (PVP) at 0.1wt% shows that PVP the induction time is less than [EMIM][BF4] but better than [BMIM][BF4]. Thus [EMIM][BF4] proves that its effect is pronounced and has a potential to act as an efficient kinetic inhibitor even though it is deployed at as low as 0.1wt%.

Therefore, a conclusion that can be drawn out of this is that hydrates formations can be inhibit using ionic liquid as the inhibitors due to the positive improvement shown in the results. Improvement of the result can be achieved by implementation of the suggested recommendation idea discussed.

5.2 Future Recommendations

  To improve the findings of this project several recommendations are made following the discussion and analysis carried out at the end of the project. The followings are the recommended future works to enhance the current research study.

 I. **Experiment mode**

    -To test the formation of hydrate at isothermal (constant temperature) mode to see the effects of hydrate formation at different operating pressure.

 II. **Concentrations**

    -To test the effect of Ionic Liquid at other concentration below 1.0 wt% (0.3, 0.5, and 0.7 wt %) to find the optimum effective concentration.

    -To test its effect at above 1wt% (5 and 10 wt %) on its ability to act as dual inhibitor (thermodynamic and kinetic Inhibitor)

 III. **Cost comparison against other commercial inhibitor**

    -To present the cost analysis of ionic liquid against other kinetic inhibitor and justification of its advantages.

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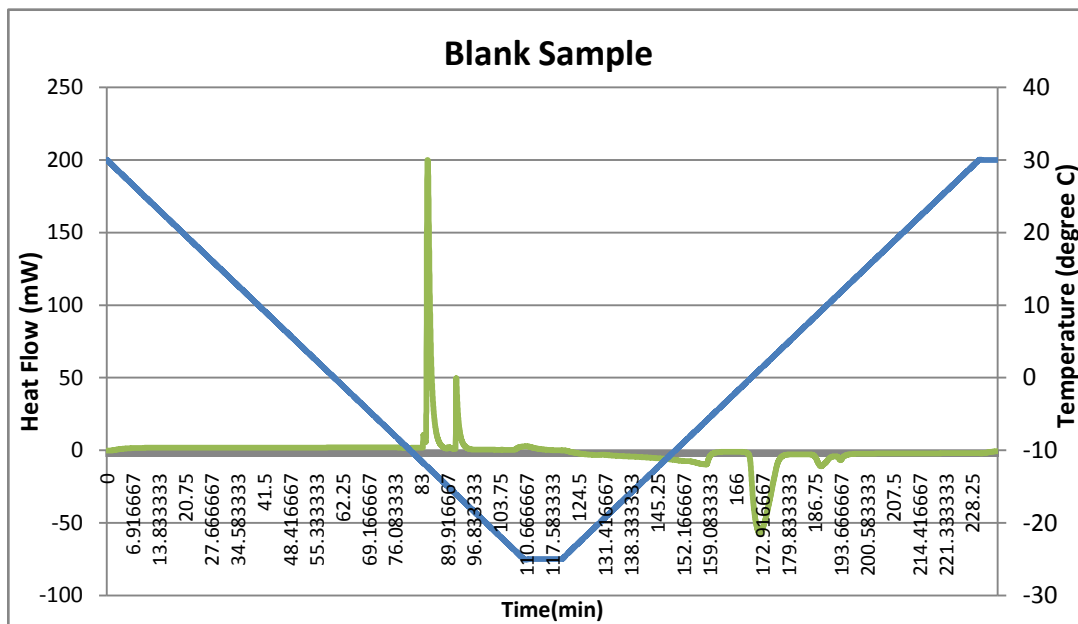.

APPENDIX A

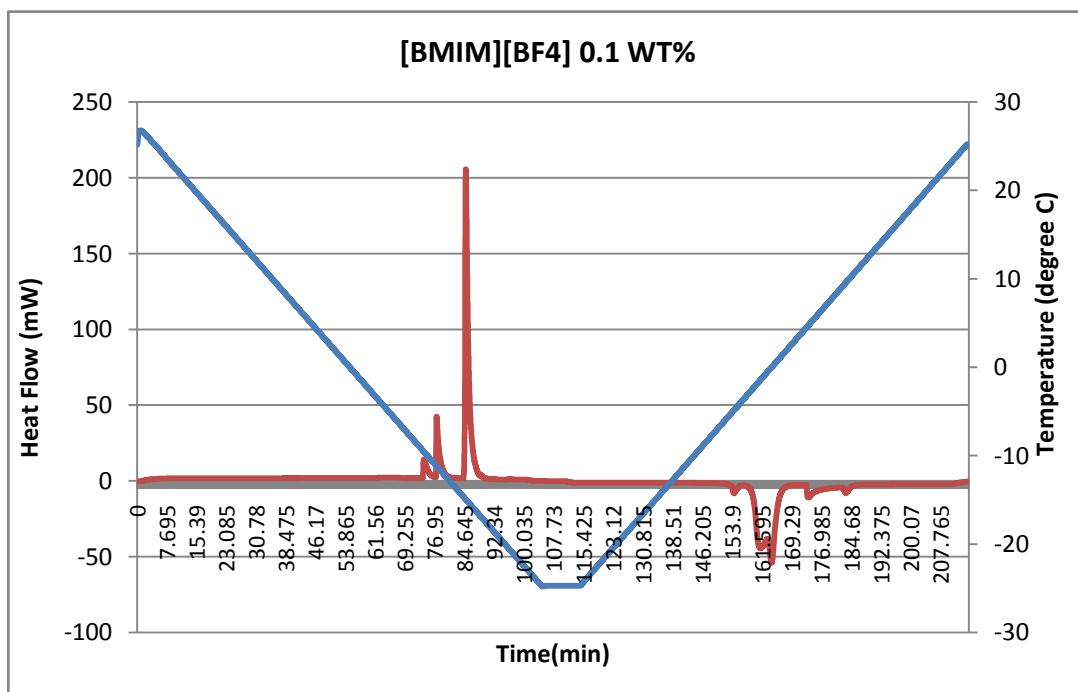**Fig A-1: Blank Sample**

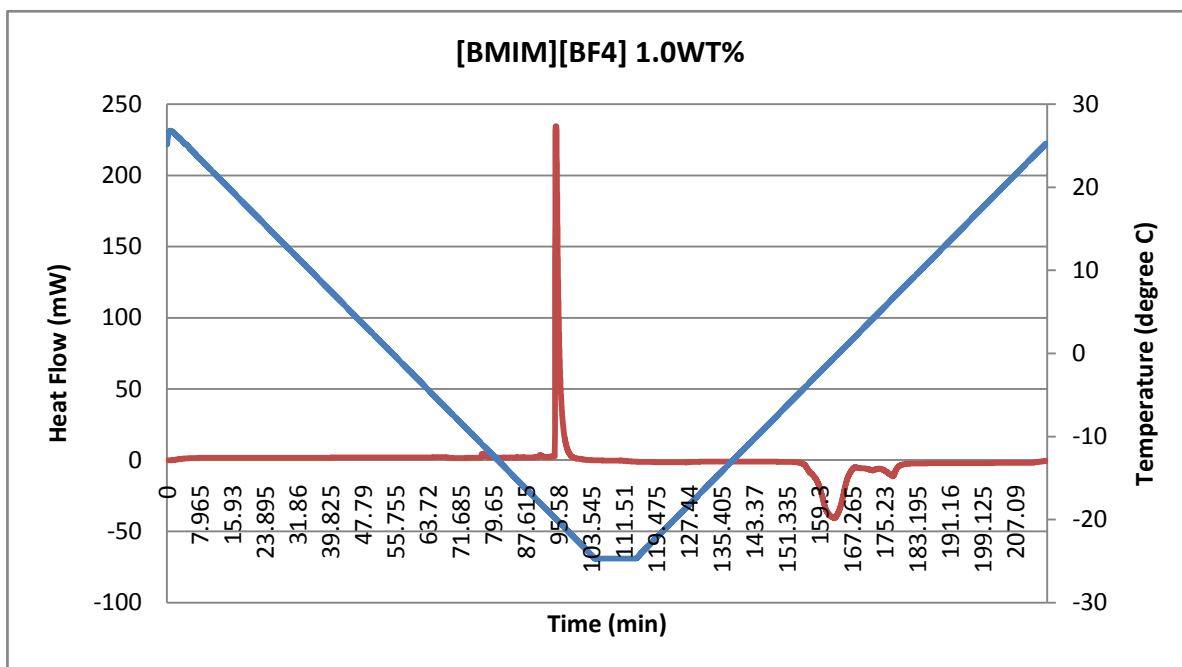**Fig A-2: [BMIM][BF4] at 0.1wt%**

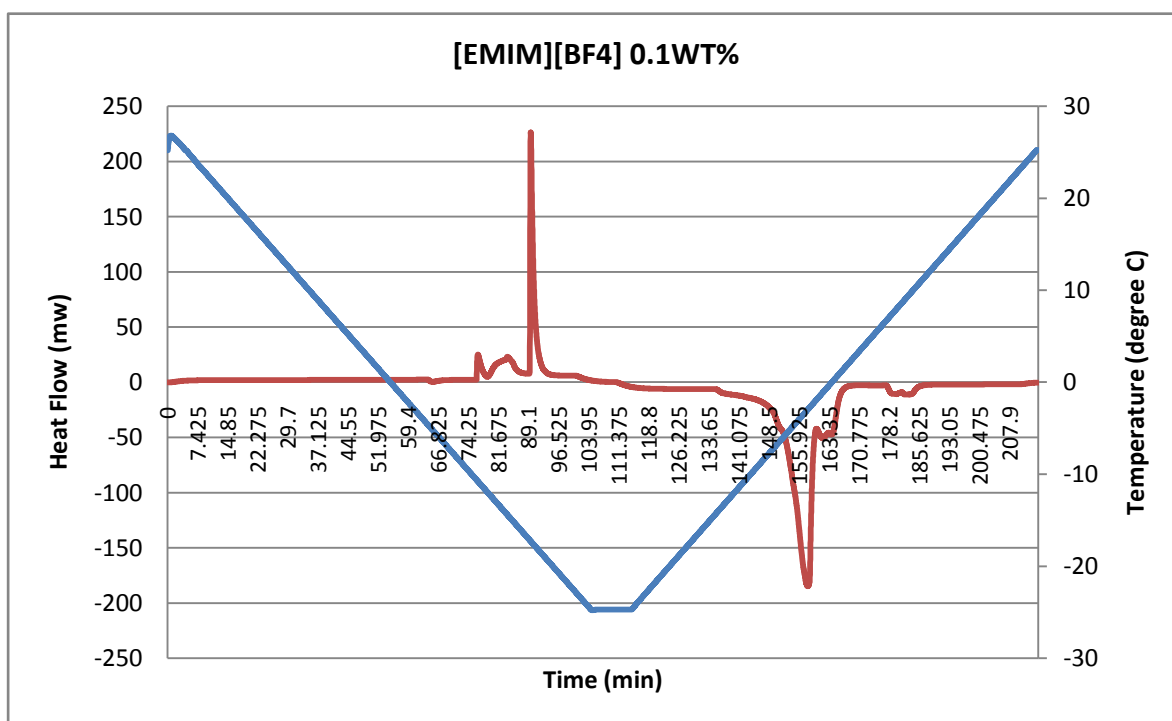**Fig A-3: [BMIM][BF4] at 1.0 wt%**
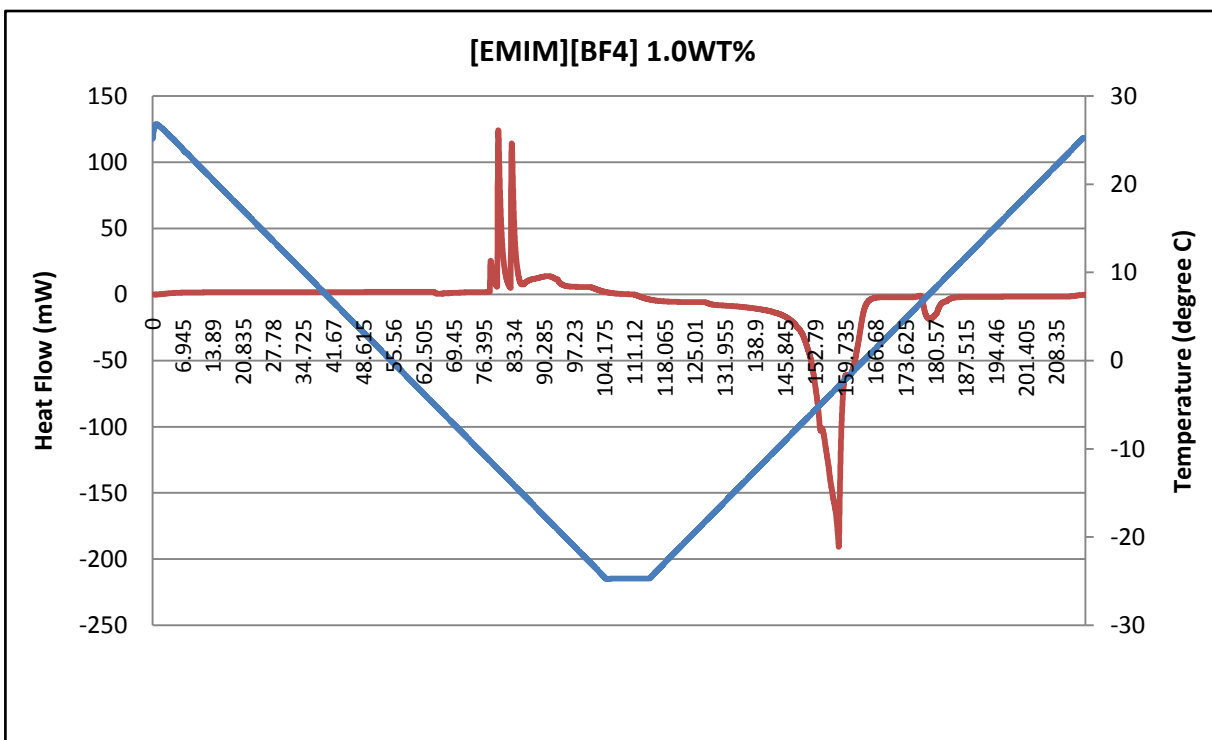

Fig A-4: [EMIM][BF4] at 0.1wt%

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Fig A-5: [EMIM][BF4] at 1.0 wt%

APPENDIX B

B-1 Sample Calculations

Weight Percent (wt%)

Formula:

$$\text{Weight Percent (wt\%)} = \frac{weight\ of\ solute}{\text{weight of solution}} \times 100\%$$

	Ionic Liquid Concentration (wt%)	Mass of IL (g)	Mass of Water (g)	Total mass solution(g)
1	0.1	0.01	9.99	10
2	1	0.1	9.9	10