CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Gas hydrates are crystalline solids resembling ice in which gas molecules are stored or trapped inside cages of hydrogen-bonded water molecules. At moderately high pressure and low temperature conditions, stable gas hydrates can form. The formation of stable gas hydrates may occur and block gas pipelines (Ostergaard et al., 2005), which lead to safety hazards and huge economic loss.

The preventions of hydrate formation and aggregation to maintain flow assurance cost the oil and gas industry over US200 M annually (Sloan, 2003).

Therefore various techniques that could be used to mitigate the hydrate formation: system heating, depressurization, water removal and inhibition. Under many circumstances, the hydrate inhibition by adding inhibitors is the only viable options. A variety of inhibitors are utilized by the petroleum industry to prevent hydrate plug formation; however, these inhibitors are not designed for high water content production.

As oil and gas are produced from less profitable and/or older wells, there is an increased likelihood of higher water cuts, resulting in more costly inhibition strategies. Various authors have studied hydrate formation from low water cut emulsions with few studies approaching 60 vol% or more (Lachance, 2008; Palermo et al., 2004; Sinquin et al., 2004; Turner, 2005).

There are three types of hydrate inhibitors are currently available to the energy industry for controlling gas hydrates: Thermodynamic hydrate inhibitors (THI), Kinetic hydrate inhibitors (KHI) and Anti-Agglomerant hydrate inhibitors (AA).

Thermodynamic inhibitors, which shift the pressure–temperature hydrate equilibrium curve, and kinetic inhibitors, which delay hydrate formation, are injected proportional to the water volume (or cut), meaning that at higher water cuts, more and more inhibitor is necessary. Alternatively, anti-agglomerants, which allow for hydrates to form but prevent hydrate particle agglomeration, are typically not designed to operate at water cuts above 60 vol% (Sloan and Koh, 2008).

Thermodynamic inhibitors which were the conventional chemical method for hydrate control normally shift the equilibrium dissociation/ stability curve, i.e. the hydrate-aqueous liquid-vapour equilibrium (HLVE) curve, to lower the temperature and higher pressure, thus avoid the hydrate formation. Sodium chloride is one of the examples of thermodynamic inhibitors.

However, adding organic salt also leads to corrosion problems. The shortcomings of the traditional thermodynamic inhibitors stimulated the search for low dosage kinetic inhibitors. Kinetic inhibitors (which do not require water and hydrocarbon mixture to be effective) are usually polymers or copolymers and anti-agglomerants (requires water and hydrocarbon mixture) are polymers or zwitterionic (usually ammonium and COOH) surfactants being both attracted to hydrates and hydrocarbons.

Most of kinetic inhibitors were polymer-based inhibitors. Poly(N-vinylpyrrolidone) (PVP), poly(N- vinylcaprolactam) (PVCap), poly(N-methyl-N-vinylacetamide) (VIMA), poly(N-vinylvalerolactam) (PVVam), poly(acryoyl pyrro- lidine) (PAPYD), and poly(acryloylmorpholine) (PAMOR), Luvi- cap (40 wt% PVCap in EG), and a terpolymer combination VC- 713 (a 37 wt% solution of the terpolymer of N-vinylpyrrolidone, N-vinylcaprolactam, and dimethylamino–ethyl–methacrylate in ethanol), are examples of such inhibitors (Arjmandi et al., 2005; Freer and Sloan, 2000; Lederhos et al., 1996; Karaaslan and Parlaktuna, 2002).

As the gas exploration and production (E&P) moves to deeper seas, the temperature and pressure conditions become more favourable to the formation of hydrate and the existing inhibitors cannot give an economic solution. It has also been identified for some cases that the combination of thermodynamic and kinetic inhibitors is still needed to give better results (Kelland, 2006).

Therefore, there is still a need to discover inhibitors that are more effective than the existing inhibitors. A new class of inhibitors were discovered by (Xiao and Adidharma, 2009), referred to as dual function inhibitors, that could act as both thermodynamic and kinetic inhibitors.

These dual function inhibitors were able to not only shift the equilibrium hydrate dissociation curve to lower temperature and higher pressure, but also delay the formation of hydrate by slowing down the nucleation and/or growth rate.

Substances that have strong electrostatic charges and form hydrogen bonds with water are thus expected to perform effectively on hydrate inhibition. Ionic liquids are such materials that are fitting for this purpose.

Ionic liquids are organic salts that are liquid at room or moderate temperature; common ionic liquids consist of bulky and asymmetric organic cations, such as imidazolium or pyridiniumion, with alkyl chain substituents. The common anions used include tetrafluoroborate (BF4−), dicyanamide(N(CN)2−), nitrate, chloride, and bro- mide.

They have strong electrostatic charges and at the same time their anions and/or cations can be chosen or tailored to form hydrogen bonding with water. Besides these tunable properties, ionic liquids also offer several other desirable properties.

For example, ionic liquids are environmentally friendly solvents due to their stability (Adams et al., 1998; Dupont, 2004; Dupont et al., 2002; Earle et al., 1998; Freemantle, 1999; Osteryoung, 1987; Suarez et al., 1996, 2001, 2003; Wilkes and Zaworotko, 1992) and extremely low vapour pressures.

In addition, ionic liquids are very accessible, given their ease of preparation from relatively inexpensive materials (Huddleston et al., 1998; Suarez et al., 1996; Wilkes and Zaworotko, 1992). These extraordinary properties of ionic liquids motivate us to study their potential use for hydrate inhibitors.

1.2 PROBLEM STATEMENT

The formation of gas hydrate may occur and block gas pipelines, which can lead to safety hazards and huge economic loss. Thus, to prevent the hydrate formation, we use inhibitors to inhibit the hydrate formation. .

A variety of inhibitors are utilized by the petroleum industry to prevent hydrate plug formation; however, these inhibitors are not designed for high water content production.

There are three types of inhibitors that are use nowdays: thermodynamic, kinetic and anti-agglomerant. These chemicals work by altering the chemical potential of the aqueous phase such that equilibrium dissociation curve is displaced to lower temperatures and higher pressures.

Thermodynamic inhibitors, which shift the pressure–temperature hydrate equilibrium curve, and kinetic inhibitors, which delay hydrate formation, are injected proportional to the water volume (or cut), meaning that at higher water cuts, more and more inhibitor is necessary.

Alternatively, anti-agglomerants, which allow for hydrates to form but prevent hydrate particle agglomeration, are typically not designed to operate at water cuts above 60 vol% (Sloan and Koh, 2008).

Methanol is much cheaper than ethylene glycol and triethylene glycol per unit volume and the use of glycols is usually justified on the basis of regeneration (Caroll, 2003). Methanol has a lower viscosity and hence requires less pump horsepower for injection (Son, 2000).

Thermodynamic inhibitor, methanol, is volatile and some of it is lost into the gas phase, as opposed to the aqueous phase where it should be inhibiting hydrates.

Corrosion problems may also result from methanol use because (Hammerschmidt, 1934) there may be dissolved oxygen in the methanol leading to corrosion in the pipe, and (Sloan, 2003) the presence of methanol can reduce the efficiency of some corrosion inhibitors (Hagen, 2010).

Overall, the major challenge with using thermodynamic inhibitors is the large attendant costs when they are required in high concentrations.

Due to the drawbacks of thermodynamic inhibitors, there was search for alternative hydrate inhibiting chemicals. About 15 years ago, the application of low dosage hydrate inhibitors in oil and gas fields as alternatives started (Villano, 2009).

These low dosage hydrate inhibitors include kinetic inhibitors and anti-agglomerants, and numerous applications have been documented in the last five years (Hagen, 2010). The two main differences between low dosage inhibitors and thermodynamic inhibitors are in the concentrations required and the mechanism of hydrate inhibition.

Kinetic hydrate inhibitors (KHIs) act by delaying hydrate nucleation and growth, possibly to a time longer than the residence time of the hydrocarbon in the pipeline or to a time longer than the period the hydrocarbon will spend within the section of the pipeline under the hydrate envelope (Hagen , 2010).

The induction time (or delay 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. Currently available KHIs can prevent hydrate formation for days at sub-coolings of up to 13^{o}C (Stora, 2004).

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 than 13^{o}C) (Hagen, 2010).

Anti-agglomerants are another class of low dosage inhibitors. They act by preventing hydrate crystals from agglomerating into hydrate plugs. They do not prevent hydrate crystal formation but rather ensure that the crystals remain as tiny well dispersed particles within the fluid stream so that the low viscosity fluid can be transported through the pipe without difficulty (Mokhatab, 2006).

Their efficiency does not depend on time or on the degree of sub-cooling of the system (i.e. they are effective in systems with extreme sub-cooling) (Kelland, 2006). The main drawback of current anti-agglomerants is that they are only effective in systems with low water cut (Hagen, 2010).

The new discovery of ionic liquids as inhibitor, As reported by (Xiao and Adidharma, 2008), the dual function thermo- kinetic inhibitors, i.e. inhibitors that able to shift the HLVE curve but also slow down the nucleation/ growth rate are now widely being tested to proof the theory.

Ionic liquids are such materials that are fitting for this purpose, due to their strong electrostatic charges and hydrogen bond with water are expected to act as both thermodynamic and kinetic inhibitors.

Therefore, this project will aim to get the lowest hydrate formation temperature from various water cut compositions and different concentration of salt. Then, with the lowest hydrate formation temperature of preferable water cut and concentration of salt, we will test the effectiveness of ionic liquids on hydrate formation temperature and the induction time.

1.3 OBJECTIVES

The aim of this project is to study on effect of different water cut compositions and concentration of salts on gas hydrate stability. Also, this project aim to study the performance of ionic liquids on gas hydrate inhibitor.

This project is carried out with following objectives:

a) to investigate the effect of hydrate formation temperature on concentration of salt from different water cut compositions.

b) to investigate the effect of hydrate formation temperature on water cut compositions from different concentration of salts.

c) to study the kinetic formation of ionic liquids as gas hydrate inhibitor.

1.4 SCOPE OF STUDY

The scope of study for this project starts by understanding on gas hydrate and the prevention method that have been used in industry.

For the first experiment, different water cut compositions (15%, 30% and 45%) are being tested on 0 ppt (water-in-oil) emulsions, 300 ppt (saline-in-oil) emulsions and 500 ppt (brine-in-oil) emulsions. From here, the lowest hydrate formation temperature from various water cut compositions and concentration of salts are being selected to be use as our base for the next experiment, that is, to show the effectiveness of ionic liquids as gas hydrate inhibitor.

Then, with the lowest hydrate formation temperature of preferable water cut and concentration of salt, we will test the effectiveness of ionic liquids on hydrate formation temperature and the induction time.

The second experiment are then being evaluated to study the effect of hydrate formation temperature and the induction time on five different samples, that is, (1) Blank sample , (2) 1% EMIM BF4,(3) 1% BMIM BF4 ,(4) 10% EMIM BF4 and (5) 10% BMIM BF4. The purpose of testing with blank sample is to verify that with addition of ionic liquids in emulsion will performed better than blank sample.

Further evaluation are carried out by doing the experiments using ionic liquids (current method) by measuring the gas hydrate stability and induction time using differential scanning calorimetry (DSC) in order to determine the effectiveness of ionic liquids as gas hydrate inhibitor.

Using the inhibitors identified, these parameters are being measured.

1. For water cut compositions and concentration of salt experiments,

    - hydrate formation temperature in water cut compositions (15%, 30% and 45 %) and concentration of salts (0 ppt, 300 ppt, 500 ptt).

2. For effectiveness of ionic liquids as gas hydrate inhibitor,

    - hydrate formation temperature (base for water cut and concentration of salt are taken from the first experiment)

    - time in minutes/hours before the nucleation of hydrates

Then, the analyses and comparisons will be done based on the information gathered from research studies and experimental done.

CHAPTER 2
LITERATURE REVIEW

2.1 CLATHRATE HYDRATE

Hydrates of natural gas were first discovered by Sir Humphrey Davy in 1810 (Sloan, 2006) but remained in somewhat of a scientific curiosity until Hammerschmidt reported in 1934 that they could form in natural gas pipelines leading to blockages and reduced or zero flow (Pickering, 1998).

The initial work by Hammerschmidt motivated considerable research activity into the formation of hydrates and their prevention in pipelines and led to development of the first hydrate prediction methods and inhibition techniques.

Early 30`s marked the beginning of an intense research effort on natural gas hydrates by the industry, the government, and the academia. Since then, study on hydrates has been intensified especially after discovery of the vast quantities of hydrates in the earth’s crust.

Clathrate Hydrate are crystalline compounds which occur when water forms a cage-like structure around smaller guest molecules. clathrate is a compound formed by the inclusion of molecules of one kind within cavities in the crystal lattice of another (Webster, 1994).

The generic name, clathrate, is taken from the Latin word 'clathratus1, which means, 'enclosed by bars or grating1 (Barrer and Stuart, 1957; Brown, 1962). Clathrates display no chemical bonding between the host and guest molecules, a condition which is a key characteristic of clathrates. Some clathrates can form without water being present where non-water molecules form the molecular structural array.

There are many examples of clathrates (table 1), which are also known as container compounds (Cram, 1992).

While they are more commonly called hydrates, a careful distinction should be made between these non-stoichiometric clathrate hydrates of gas and other stoichiometric hydrate compounds which occur for example, when water combines with various salts.

Gas hydrates of current interest are composed of water and the following eight molecules: Gas, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide.

Table. 1 .: Common clathrates: Various hosts and guests.

Host	**Guest**
Urea	Straight chain hydrocarbons
Thiourea	Branched chain and cyclic hydrocarbons
Dinitrodiphenyl	Derivatives of diphenyl
Phenol	Hydrogen chloride, sulfur dioxide, acetylene
Water (Ice)	Halogens, noble gases, sulfur hexaflouride, low molecular weight hydrocarbons
Zeolites	Wide range of adsorbed substances
Cellulose	Water, hydrocarbons, dyes, iodine

Hydrates normally form in one of three repeating crystal structures shown in Figure 2, Structure I (sI), a body-centered cubic structure forms with small natural gas molecules found *in situ* in deep oceans. Structure II (sII), a diamond lattice within a cubic framework, forms when natural gases or oils contain molecules larger than ethane but smaller than pentane.

sII represents hydrates which commonly occur in hydrocarbon production and processing conditions, as well as in many cases of gas seeps from faults in ocean environments.

The newest hydrate structure H (sH) named for its hexagonal framework, has cavities large enough to contain molecules the size of common components of naphtha and gasoline. Some initial physical properties, phase equilibrium data, and models have been determined for sH and one instance of *in situ* sH in the Gulf of Mexico has been found.

Since information on structure H is in the fledgling stages, and since it may not occur commonly in natural systems, most of this structure in Figure 1 concerns sI and sII. The unit cell of structure I hydrate composts of two 5^{12} cages, six $5^{12}6^{2}$ cages and 46 water molecules.

The unit cell of structure II hydrates composts of sixteen 5^{12} cages, eight $5^{12}6^{4}$ cages and 136 water molecules. Plus, structure H composts of three 5^{12} cages, two $4^{3}5^{3}6^{3}$ cages, one $5^{12}6^{8}$ cages and 34 water molecules.

In all three structures, typically there is only guest molecule within each cage and in order to form hydrates, the size of the guest molecules cannot be too larger or too small compared to the size of the cavities.

Structure I gas hydrate is emphasized in this chapter and is often referred to as Gas hydrate. This gas hydrate can contain very large amounts of Gas. The maximum amount is fixed by the clathrate geometry which translates to 164 volumes of Gas at standard conditions to one volume of Gas hydrate (Davidson et al., 1978).

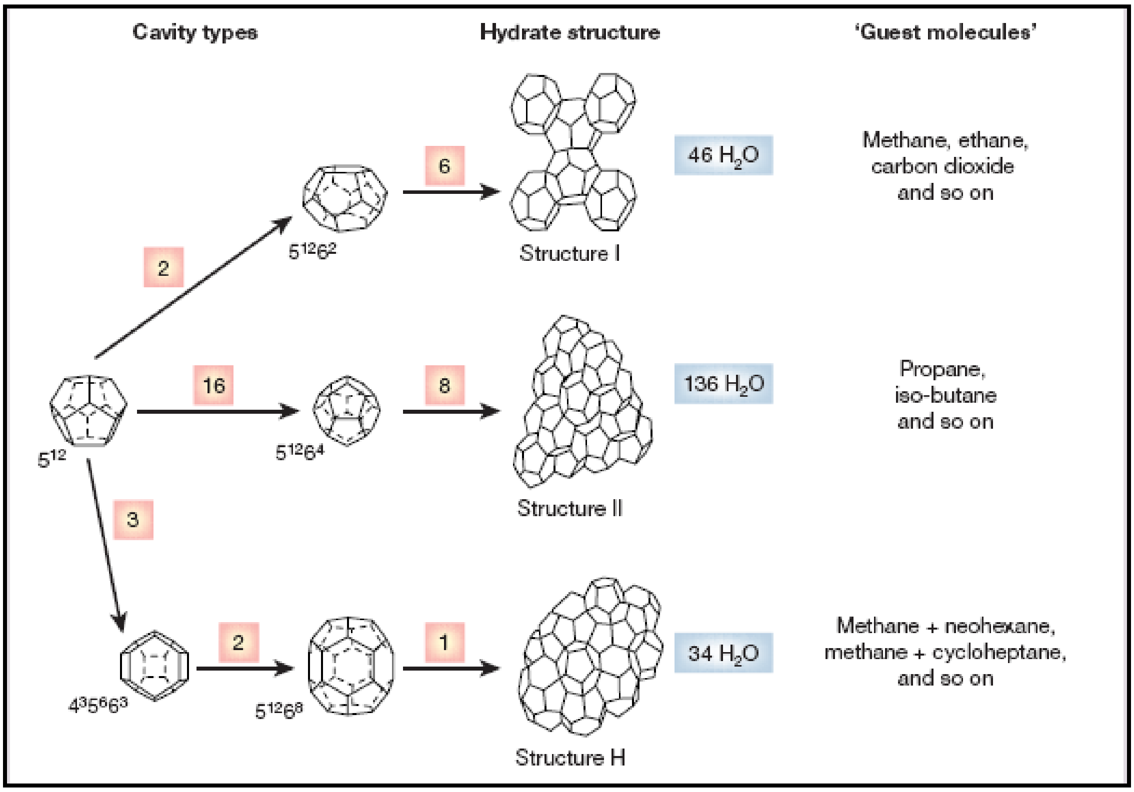


Figure.1 .: The three common hydrate unit crystal structures (Taken from Sloan, 1998)

2.2 HYDRATE FORMATION

For stable hydrate crystals to form in oil and gas production systems, four essential elements must be present: a supply of hydrate forming guest molecules (refer to table 3), access to a supply of water conditions of low temperature and high pressure.

In multiphase oil and gas production pipelines containing hydrocarbon gas and liquid phases together with a free water phase, hydrate form preferentially at the water-hydrocarbon interface having the highest availability of hydrate forming molecules.

Thus, in gas-condensate-water, hydrate tend to form at the abundant gas-water interfaces, whereas in low GOR, gas-oil-water systems they tend to form at the oil-water interfaces.

Although in the case of gas-oil-water systems, the distribution of the oil and water phases (i.e. water-in-oil or oil-in-water dispersions) also plays a key role in determining which interfaces govern the formation of hydrates as does the gas-oil-ratio (GOR) which determines the extent of gas-water interfaces.

As shown in Figure 3, the white region covers pressures and temperatures at which hydrates are set thermodynamically unstable and therefore ‘hydrate free’ as indicated. The region labelled ‘hydrate risk’ is where stable hydrate can exists, although in practice they may not form due to a failure to nucleate and or slow formation kinetics.

In the ‘hydrate zone’ the degree of supercooling is sufficient such that hydrate form spontaneously (Anselme, 1993).

Table 2: Molecules Identified as Potential Hydrate Formers

Natural Gas	**Condensates/Oils**	**Process Industry**	**Academic**
Nitrogen	Benzene*	Ethylene	Inert gases
Carbon Dioxide	Cyclopentane*	Propylene	Oxygen
Hydrogen Sulphide	Cyclohexane*	Other Olefins	Cyclopropane
Gas	Methylcyclopentane*		
Ethane	Adamantane*		
Propane			
Butane*			
Isobutane			
Neopentane*			

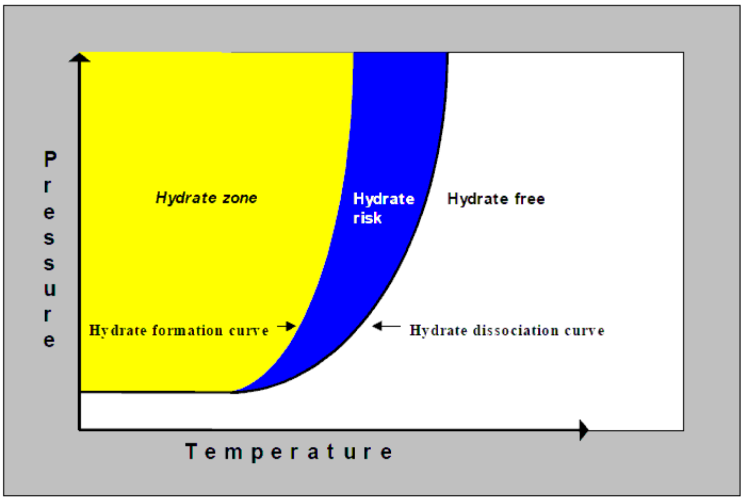


Figure 2: Typical Hydrate Formation Diagram (Taken from Sloan, 2008)

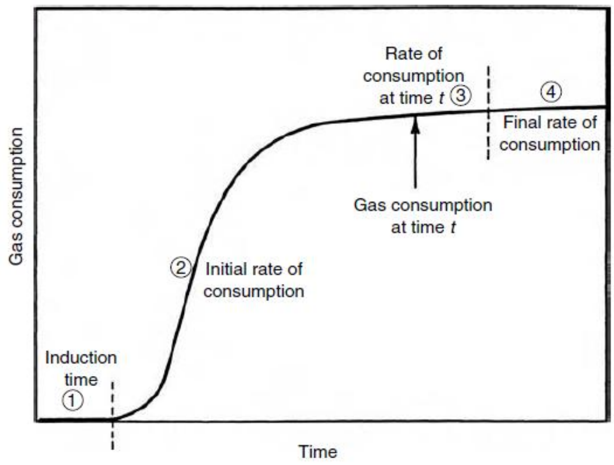
2.3 HYDRATE DISSOCIATION AND INDUCTION TIME

As an example of hydrate nucleation and growth, consider the gas consumption versus time trace in Figure 3, for an agitated system operated at constant pressure and temperature. An autoclave cell, containing, is pressurized with gas and brought to hydrate formation (*P, T)* conditions. The gas is added from a reservoir to maintain *constant pressure* as hydrates form with time. The rate of consumption of gas is the hydrate formation rate that can be controlled by kinetics, or heat or mass transfer.

The induction time is marked as 1 and includes the time taken for crystal nuclei to form which are not visible to macroscopic probes. The induction time is defined in practice as the time elapsed until the appearance of a detectable volume of hydrate phase or, equivalently, until the consumption of a detectable number of moles of hydrate former gas. During the induction period, the temperature and pressure conditions are within the hydrate stable region.

However, hydrate does not form within this period because of meta stability (i.e., the ability of a non equilibrium state to persist for a long period of time). The growth period (in region 2) is where very rapid hydrate growth occurs. During the growth period, gas is being concentrated in the hydrate cages—hydrated gas molecules are more densely packed than those in the vapor. As the water is consumed by hydrate formation, the slope of the gas consumption trace eventually decreases with time (points 3–4).

(3)



(4)

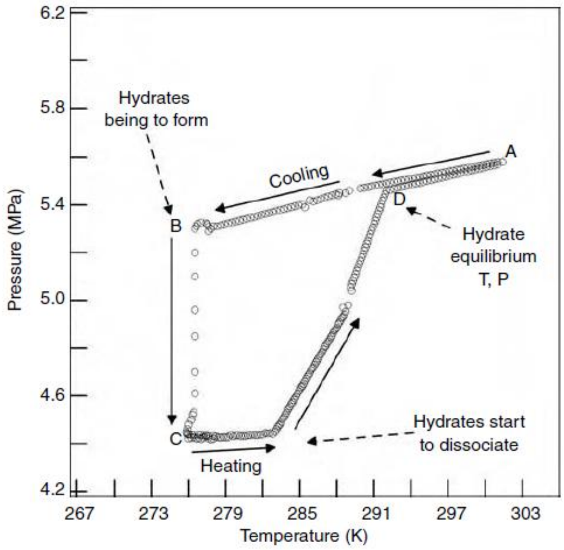


Figure : (3) Gas consumption vs. time for hydrate formation. (Taken from Lederhos et al., 1996). (4) Temperature and pressure trace for formation of simple Gas hydrates (Taken from Ouar et al., 1992).

An alternative hydrate formation and dissociation experiment is shown in the temperature and pressure trace of Figure 4. In this case, the volume is constant and the temperature is changed during the experiment. In the experimental apparatus an agitated autoclave cell, housing a sight glass window contains water, that is pressurized with gas to the upper rightmost temperature and pressure.

As the cell temperature is lowered the pressure decreases, principally due to gas contraction as well as increased gas solubility upon cooling *at constant volume*. Neither gas nor water is added to the system during the experiment. The metastability of the system prevents hydrate forming immediately at Point D (at the hydrate equilibrium temperature and pressure; figure (4)).

Instead the system pressure continues to decrease linearly with temperature for a number of hours, without hydrate formation occurring (A to B is the induction period, cf. 1 in figure (3)). At Point B, hydrates begin to form. The pressure drops rapidly to Point C (about 1.01 MPa or 10 atm in 0.5 h). B to C is the catastrophic growth period (cf. 2 in figure (3)).

Hydrate dissociation begins when the cell is heated from Point C in figure (4), so that the system pressure increases, at first slowly and then sharply along the step dissociation line (between Points C and D). Finally at Point D, the hydrates are completely dissociated, as confirmed visually through the sight glass. The hydrate equilibrium condition (or hydrate dissociation temperature and pressure) is given by Point D. Usually 1–2 days (for reactors on this scale) of experimental effort are required to traverse the loop as shown in figure (4).

In order to avoid obtaining an erroneous dissociation temperature and pressure, the dissociation part of the loop must be performed at a sufficiently slow heating rate (about 0.12 K/h) to allow the system to reach equilibrium (Tohidi et al., 2000; Rovetto et al., 2006). The temperature difference between the temperature at Point D to that at Point B is called the sub-cooling.

As illustrated in figure (4), there is a fundamental difference in hydrate initiation and dissociation due to the associated gas and liquid phases being disorderly on a molecular level, while the hydrate crystals are orderly in nature. Entropy favours disorder over order, so the initial hydrate formation is hindered by a long, metastable period (induction period).

During this period, the disorderly gas and liquid water begin to rearrange into the orderly hydrate crystal structure. Conversely, dissociation begins relatively rapidly after the hydrate is removed from the temperature and pressure stability region.

2.4 INHIBITORS

Hydrate can form at pressure and temperature found in natural gas and oil pipelines causing blockages, especially when temperature fall significantly such as when closing in a well or flowing gas through a choke. Together with other potential solid depositions, such as waxes, asphaltenes and scales, hydrate pose a serious potential problem for the offshore industry. In addition, the remediation of hydrate blockages can also present significantly technical difficulties (Metha, 2001) with major cost complication.

As mention earlier, the formation of hydrates requires four essential elements to be present: a supply of hydrate forming guest molecules, a supply of water and a combination of high pressure and/or low temperatures. Strategies for hydrate mitigation and remediation often modify one or more of these elements to destabilise the hydrate and thus remove the problem.

In a pipeline, hydrate masses usually form at the hydrocarbon-water interface, and accumulate as flow pushes them downstream. The resulting porous hydrate plugs have the unusual ability to transmit some degree of gas pressure, while they act as a flow hindrance. Both gas and liquid can frequently be transmitted through the plug; however, lower viscosity and surface tension favors the flow of gas.

There are possible methods that can be used to dissociate a hydrate plug (in the pipeline) or hydrate core (in oceanic or permafrost deposits) are: depressurization, thermal stimulation, chemical inhibitor injection, or a combination of these methods.

Here, our interest is more likely to mitigate the hydrate by using chemical inhibitors. The various chemicals available for hydrate prevention fall into three classes: traditional thermodynamic inhibitors, Low Dose Hydrate Inhibitors (LHDI) and the new discovery of dual function (thermo-kinetics) inhibitors. The salient features are summarised below. The detail discussed by Kelland et al., 1996 present good reviews.

Thermodynamic Hydrate Inhibitors (THIs)- These chemicals work by altering the chemical potential of the aqueous phase such that equilibrium dissociation curve is displaced to lower temperatures and higher pressures. They are added at relatively high concentrations (10-60 wt% in the aqueous phase) and examples include methanol and monoethylene glycol (MEG).

THI has been in application for over half a century, and well established thermodynamic models are available for predicting the amount of THI required for hydrate prevention. However, it normally takes a large amount of THI to be effective , as much as 100% based on the volume of the produced water, and a significant portion of it can be lost to the hydrocarbon phase (Bruinsman, 2003).

In addition, high concentrations of THI in the produced water can induce salt precipitation, and crude oils that contain excessive methanol are less desirable to refineries. Therefore, studies have been carried out on the replacement of methanol or monoethylene glycol using Low Dose Hydrate Inhibitors (LDHI). The development of LDHIs has been subjected to a lot of research works for the last eighteen years, and several field testings and deployment for the last twelve years.

LDHIs can be efficiently used at dosages far lower than that of thermodynamics inhibitors, where the concentration for these additives is expected to be in range of 0.5- 4.0 wt.% versus the water rate (Peytavy and Bourg, 2007).

The use of kinetic inhibitors and anti-agglomerants in actual field operations is a new and evolving technology. It requires extensive tests and optimisation to the actual system. While kinetic inhibitors work by slowing down the kinetics of the nucleation, anti-agglomerants do not stop the nucleation, they rather stop the agglomeration (sticking together) of gas hydrate crystals.

These two kinds of inhibitors are also known as Low-Dosage-Hydrate-Inhibitors because they require much smaller concentrations than the conventional thermodynamic inhibitors.

Kinetic inhibitors (which do not require water and hydrocarbon mixture to be effective) are usually polymers or copolymers and anti-agglomerants (requires water and hydrocarbon mixture) are polymers or zwitterionic (usually ammonium and COOH) surfactants being both attracted to hydrates and hydrocarbons.

Kinetic inhibitors were initially discovered in 1991 (Sloan, 1991). Kinetic Hydrate Inhibitors (KHIs)- This class of chemicals does not alter the thermodynamic of hydrate formation but instead modifies the kinetics of hydrate formation. They achieve both by prevention of nucleation and hindering crystal growth.

Kinetic hydrate inhibitors (KHIs) act by delaying hydrate nucleation and growth, possibly to a time longer than the residence time of the hydrocarbon in the pipeline or to a time longer than the period the hydrocarbon will spend within the section of the pipeline under the hydrate envelope (Hagen, 2010).

The induction time (or delay 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. Currently available KHIs can prevent hydrate formation for days at sub-cooling of up to 13°C (Stora, 2004).

KIs are mainly water soluble polymers with small cyclic amide groups such as pyrrolidone and caprolactamas the active units (Stora, 2004). Their effect is time dependent and ultimately hydrates will form and block the pipeline but only if the transit time through the pipelines is sufficiently long, take for instance, following a shutdown.

KHIs are added at lower concentrations (typically less than 1wt% in the aqueous phase). Examples includes Poly(N-vinylpyrrolidone) (PVP), poly(N-vinylcaprolactam) (PVCap), poly(N-methyl-N-vinylacetamide) (VIMA), poly(N-vinylvalerolactam) (PVVam), poly(acryoyl pyrro- lidine) (PAPYD), and poly(acryloylmorpholine) (PAMOR), Luvi- cap (40 wt% PVCap in EG), and a terpolymer combination VC- 713 (a 37 wt% solution of the terpolymer of N-vinylpyrrolidone, N-vinylcaprolactam, and dimethylamino–ethyl–methacrylate in ethanol), are examples of such inhibitors (Arjmandi et al., 2005; Freer and Sloan, 2000; Lederhos et al., 1996; Karaaslan and Parlaktuna, 2002). .

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^{o}C) (Hagen, 2010).

The existing kinetic inhibitors, however, are still not believed to give an economic solution at higher pressure and large degree of supercooling. It has also been identified for some cases that combination of thermodynamic and kinetic inhibitors is still needed to give better results (Arjmandi, 2005). Therefore, there is still a need to discover inhibitors that are more effective than the existing inhibitors.

Anti-agglomerants are another class of low dosage inhibitors. They act by preventing hydrate crystals from agglomerating into hydrate plugs. They do not prevent hydrate crystal formation but rather ensure that the crystals remain as tiny well dispersed particles within the fluid stream so that the low viscosity fluid can be transported through the pipe without difficulty (Mokhatab, 2006).

Anti-agglomerants are usually surfactants in which the head is attracted to the hydrate and the tail is dispersed in the liquid hydrocarbon phase. This implies that a liquid hydrocarbon phase needs to be present for the inhibiting effect of anti-agglomerants to be effective (Hagen, 2010).

For gas systems, this implies that the gas-to-oil ratio (GOR) should not be too high. They are effective at concentrations of less than 1 weight %. Their efficiency does not depend on time or on the degree of sub-cooling of the system (i.e. they are effective in systems with extreme sub-cooling) (Kelland, 2006). The main drawback of current anti-agglomerants is that they are only effective in systems with low water cut (Hagen, 2010).

Dual Function (Thermo-Kinetic) Inhibitors- As documented by (Xiao and Adidharma, 2009), they discovered a new class of inhibitors, that could act as both thermodynamic and kinetic inhibitors. These dual function inhibitors were able to shift the equilibrium hydrate dissociation curve to lower temperature and higher pressure, but also delay the formation of hydrate by slowing down the nucleation and growth rate.

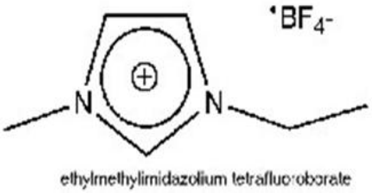
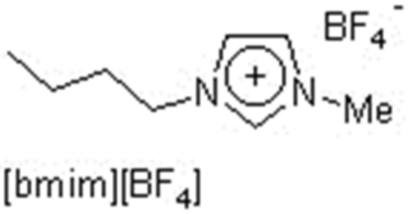
These type of inhibitors were ionic liquids that had a strong electrostatic charges and at the same time their anions and or cations formed hydrogen bonding with water. Ionic liquids are organic salts that are liquid at room or moderate temperature; common ionic liquids consist of bulky and asymmetric organic cations, such as imidazolium or pyridinium ion with alkyl chain substituents.

The common anions used include tetrafluoroborate (BF4−), dicyanamide(N(CN)2−), nitrate, chloride, and bro- mide. They have strong electrostatic charges and at the same time their anions and/or cations can be chosen or tailored to form hydrogen bonding with water.

Besides these tunable properties, ionic liquids also offer several other desirable properties. For example, ionic liquids are environmentally friendly solvents due to their stability (Adams et al., 1998; Dupont, 2004; Dupont et al., 2002; Earle et al., 1998; Freemantle, 1999; Osteryoung, 1987; Suarez et al., 1996, 2001, 2003; Wilkes and Zaworotko, 1992) and extremely low vapour pressures.

Ionic liquids used in this future works are tabulated in Table 3.

Table.3: Ionic liquids used in this studied

Symbol	**Chemical Name**	**Chemical Structure**
EMIM-BF4	1-ethyl-3-methylimidazolium tetrafluoroborate	
BMIM-BF4	1-butyl-3-methylimidazolium tetrafluoroborate	

It is proven that BF_4^- has stronger ability to form hydrogen bond with water than any other types of anion. Thus, in this study, we used both of Ionic Liquids with have tetrafluoroborate. It just that EMIM- BF_4 and BMIM- BF_4 differ to each other only in the alkyl substituent of imidazolium.

It also stated by (Adidharma, 2009), that EMIM- BF_4 performs better than BMIM- BF_4 . This is due to a shorter alkyl in the cation may hinder hydrogen bonding between that BF_4 and water.

2.5 DETECTION OF HYDRATE DISSOCIATION BY USING DSC

The usual way to determine the thermodynamic conditions of the formation of hydrates in drilling muds formulations is to use a PVT cell with visual observation and simultaneous temperature and pressure measurements. This technique requires heavy instrumentation and cannot be used if solid particles are present in the formulation. Moreover, the PVT cell does not give a quantitative evaluation on the kinetic proportion of hydrate formation.

Most recently, an innovative and easy technique based on DSC has been introduced by the French Institute of Petroleum (IFP) to characterize hydrate formation in drilling fluids up to 100 bar (Dalmazzone, 2001). High pressure DSC is an easy and reliable tool for measuring gas hydrate stability conditions in complex fluids such as aqueous electrolyte solutions. It is also appropriate for studies in complex emulsions and suspensions such as drilling fluids.

Compared with the classical PVT techniques, DSC appears as easier and less time-consuming. Furthermore, it requires smaller sample volumes and can be applied to all types of fluids, whatever their density and viscosity. Therefore, this technique could be used as a very efficient tool for deep offshore operations planning.

DSC is defined as a technique in which the difference in energy inputs into a substance and a thermally inert reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program.

A Differential Scanning Calorimetry (DSC) measures the amount of energy (heat) absorbed or released by a sample as it is heated, cooled or held at a constant (isothermal) temperature. The test is conducted by cooling-and-heating water-in-oil emulsified samples prepared.

Apart from that, DSC also have been used to measure emulsion characteristics such as droplet size distributions, emulsion stability, and mass transfer through the dispersion (Dalmazzone et al., 2006).

Due to the distribution of droplets in the emulsion, the interfacial tension of each droplet can adjust the critical nuclei size for hydrate formation in the individual droplets (Sloan, 1990; Makogon, 1981).

This will cause a difference in nucleation time of hydrate in the droplets. Therefore, the isothermal hydrate formation peak can be used as a statistical analysis of the droplet nucleation over time. One emulsified sample essentially can represent hundreds of experiments since each of the dispersed water droplets act as an individual reactor.

In this study, we are focusing on the analysis of formation peaks obtained after varying isotherms durations. This will gives useful information about kinetics of hydrate formation.

It is well known that nucleation studies (determination of induction time and degree of sub-cooling) on bulk solutions are always difficult. In the field of nucleation, studies are preferably performed on emulsions (Clause, 1985). In this study, water-in-oil emulsions or represents a sample to be tested in DSC.

In the DSC thermogram of PerkinElmer (figure.5), the Y-axis is usually expressed in mW or W/gm. The latter is a normalized unit (heat flow/weight of sample). For the Y-axis, analyst need to be aware of heat flow convention i.e. whether endothermic is pointing up or down. Both conventions are acceptable.

Thermal events will appear as deviations from the baseline. The X-axis can be displayed as either temperature or time. The area under the curve is usually calculated as the integration of heat flow over time. The unit for the area under the curve is therefore mJ or J/gm.

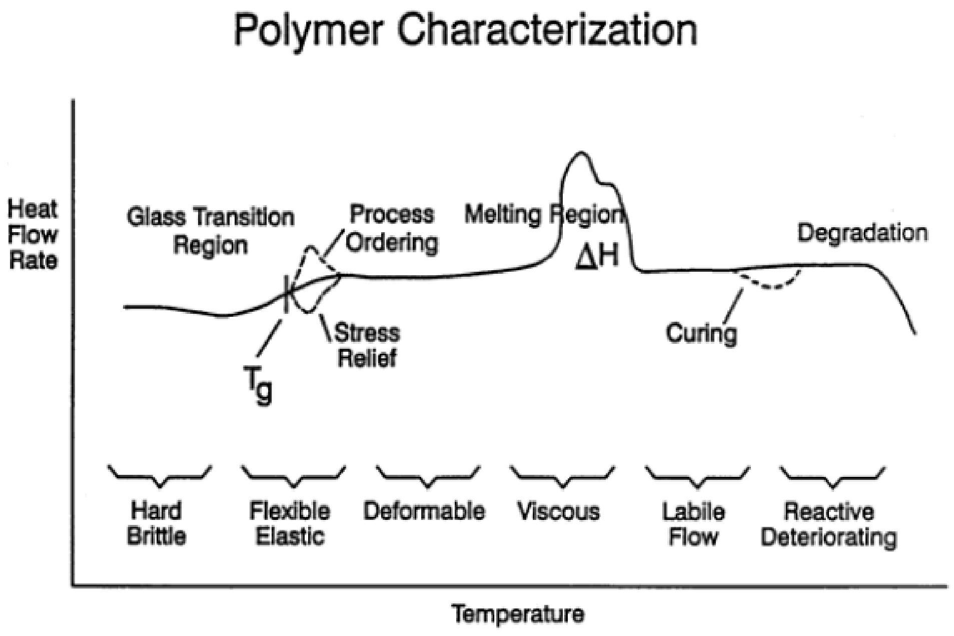


Figure 5: Schematic drawing showing an example of a typical DSC thermogram (Taken from Sloan, 2008)

Figure 6: Perkin Elmer Pyris 1 Differential Scanning Calorimetry (DSC)

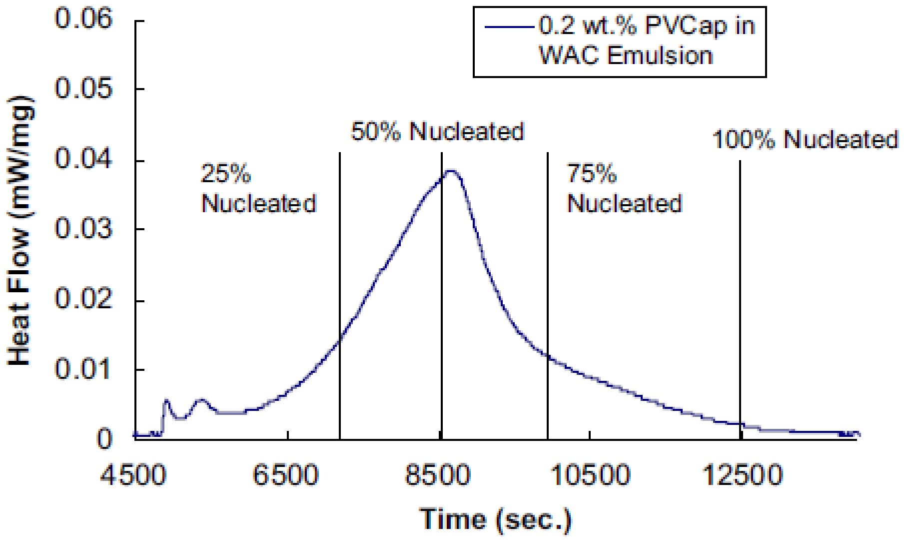


Fig. 7: Example of statistical analysis of the hydrate formation peak in a water-in-West Africa Crude emulsion. (Taken from Sloan, 2008)

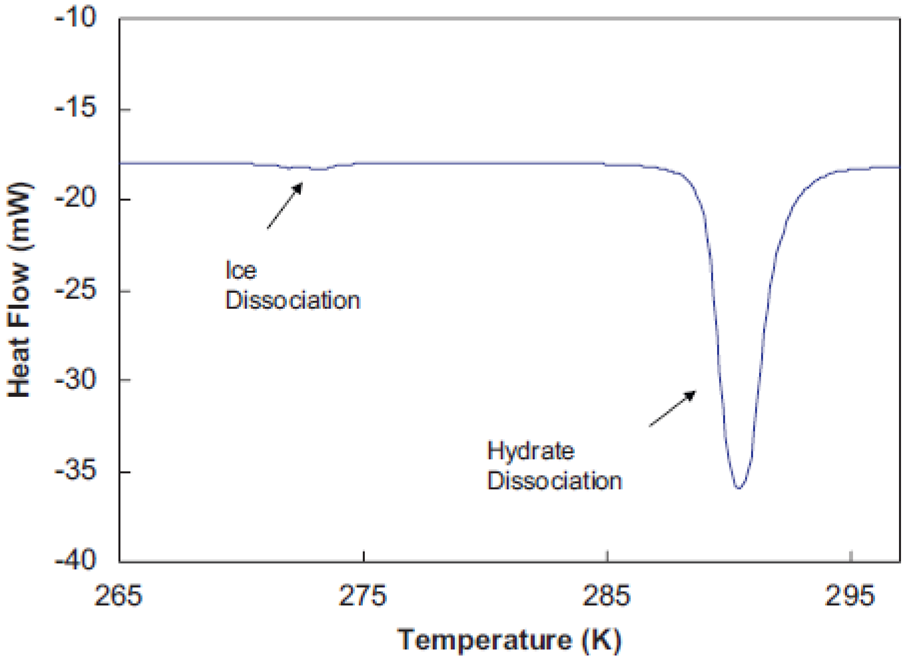


Fig. 8: Hydrate/ ice dissociation peaks showing nearly complete conversion of the emulsified water droplets into hydrate. (Taken from Sloan, 2008)

The above figures show the interpretation of DSC thermogram. Figure 7 shows a typical hydrate formation peak for a water-in-West African crude emulsion with 0.2 wt% polyvinylcaprolactam (PVCap) inhibitor. The Gaussian-like peak can be used as a statistical analysis of the droplets nucleating over time.

It is noted that hydrate nucleation and growth are not decoupled in this peak; however, the droplets in this crude oil are completely converted upon hydrate formation (Lachance et al., 2008).

Fig. 8 shows the dissociation of hydrate after hydrate formation and a subsequent cooling below the homogenous ice formation temperature. The trends show that a miniscule amount of ice was present in the system indicating that there is greater than 97% conversion of water to hydrate formation. Therefore the broad hydrate formation peak does represent the statistical hydrate nucleation time for each droplet over time.

The thermodynamics of hydrate dissociation in this work involves three phases in equilibrium, i.e. gas, liquid and hydrate phases. For a system without any inhibitor, according to Gibbs phase rule, at equilibrium, the number of variables that may be independently fixed (the degree of freedom) is one. When the temperature is set, the equilibrium pressure is fixed and vice-versa.

In this DSC measurement, if the heating rate during the hydrate dissociation process is low enough, the system can be assumed at equilibrium throughout the process, and thus the recorded pressures corresponding to the controlled temperatures represent the equilibrium pressures on the hydrate stability curve.

Since it is known that the onset of the DSC dissociation peak is less affected by the heating rate, the equilibrium pressure and temperature (hydrate stability curve) of such a system is more conveniently determined using the onset of the dissociation peak.

Of course, we can also use the end point or any other point of the dissociation peak to obtain different pairs of equilibrium pressure and temperature, but a slower heating rate will be required to ensure that equilibrium condition can always be approximated during the process.

On the other hand, for a system with one inhibitor, according to the Gibbs phase rule, at equilibrium, the number of variables that may be independently fixed is two. This means, an equilibrium pressure is fixed only when two other variables, such as temperature and inhibitor concentration, are set.

If we knew the concentration of inhibitor in the liquid phase at the onset of the dissociation peak, to obtain the equilibrium pressure and temperature, we would be able to use the same approach as that used for a system without any inhibitor. Unfortunately, this is not the case. The concentration of inhibitor in the liquid phase is known only at the end point of the dissociation peak, which is equal to the concentration of inhibitor loaded into the cell at the beginning of the experiment.

In this study, the approach to determine the ionic liquid inhibitor effectiveness in DSC is to use the first indication of onset of hydrate nucleation. Comparison is then made with the emulsified system without Ionic Liquid inhibitor added, so that effectiveness of ionic liquid inhibitors to the effluent can be observed.

The outcome of the laboratory tests concludes that measuring hydrate formation in water-in-oil emulsions with differential scanning calorimetry (DSC) is effective to determine the efficiency of ionic liquid as inhibitors.

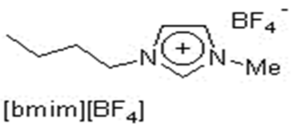
CHAPTER 3

METHODOLOGY

3.1 MATERIALS

The ionic liquids used in this study are fully contributed by PETRONAS Ionic Liquids Centre, UTP, Perak, Malaysia purchased from MERCK- Chemical. We only consider dialkylimidazolium-based ionic liquids, and listed in table 4.

Table.4 : Ionic liquids used in this studies

Symbol	Chemical Name	Chemical Structure
EMIM-BF4	1-ethyl-3-methylimidazolium Tetrafluoroborate	
BMIM-BF4	1-butyl-3-methylimidazolium tetrafluoroborate	

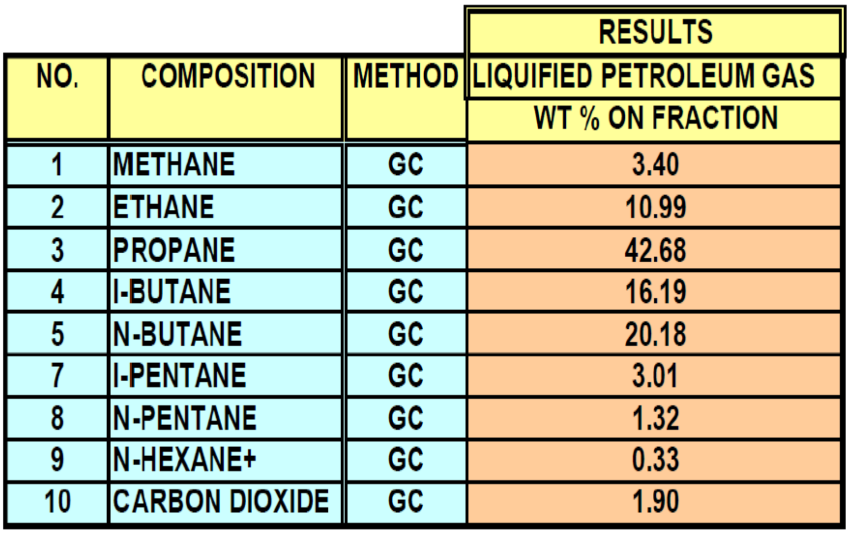
These ionic liquids are water-soluble and relatively not viscous. The anion used in this study is tetrafluoroborate. It have strong electrostatic charges and at the same time their anion can be chosen or tailored to form hydrogen bonding with water. The concentrations of ionic liquids used are 1 and 10 wt%.

Thermodynamic inhibitors are usually used at a concentration of 10wt% or more while kinetic inhibitors are usually used at concentration of less than 1wt%.. To obtain 10 wt% and/or 1wt% polymer solutions, these polymers are then dissolved and/or diluted with water.

Deionized water is used to prepare all of the sample solutions. The sample prepared in water-in-oil emulsions, the crude oil are contributed by PETRONAS Penapisan Melaka, from Miri Crude oil.

The light hydrocarbon analysis is shown in Table .2 .The nitrogen gas are 99.97% purity available in PETRONAS Ionic Liquids Centre, UTP, Perak.

Table.5: Light hydrocarbon analysis Miri Crude Oil.



			RESULTS
NO.	COMPOSITION	METHOD	LIQUIFIED PETROLEUM GAS
			WT % ON FRACTION
1	METHANE	GC	3.40
2	ETHANE	GC	10.99
3	PROPANE	GC	42.68
4	I-BUTANE	GC	16.19
5	N-BUTANE	GC	20.18
7	I-PENTANE	GC	3.01
8	N-PENTANE	GC	1.32
9	N-HEXANE+	GC	0.33
10	CARBON DIOXIDE	GC	1.90

3.2 EXPERIMENTAL APPARATUS

Differential Scanning Calorimetry (DSC) is used to measure the thermal properties of the water-in-oil samples prepared using the magnetic stirrer. DSC is a rapid and versatile technique that can be efficiently used for analytic, kinetic and ionic liquid studies. DSC is a precious tool for hydrate formation studies, especially in complex fluids. The equipment available in the laboratory is product of Perkin Elmer, Pyris 1 DSC.

Technical Specification

Perkin Elmer Pyris 1 DSC

- An Intracooler allowing temperature range of -60°C to +600°C.
- An air shield to prevent moist air from settling into and maintaining the sample holder region dry and frost free.
- Samples as small as 1 mg can be analyzed at rates of up to 300°C per minute.
- Specific heat capacity measurement.
- Power compensating calorimetry

Figure 9: Technical specification of Perkin Elmer Pyris 1 DSC

3.3 SAMPLE PREPARATION

Sample preparation:

The water-in-oil emulsified samples were prepared using a magnetic stirrer. For this experiment, water was added to the oil in a drop-wise manner. There are two experimental works were carried out. First, to determine the water cut that suitable in inhibit the hydrate, between 3 types of different solutions, pure water, saline and brine solutions. Pure water, saline and brine have concentration 0 , 300 and 500 ppt (Pickering, 1998).

The available data on oil density (0.8086 g/mL), brine density (1.19 g/mL) and saline density (1.12 g/mL) are being used and 1mL of sample preparation has been selected as basis. From there, the mass of water and oil are being calculated to prepare the water-in-oil emulsions.

All the samples calculated are tabulated in table 5, table 6 and table 3. Sample calculations are attached in Appendix sections.

Water-in-oil emulsions:

Table 6: Sample calculations of water-in-oil

Watercut (%)	**Voil (ml)**	**Vwater (ml)**	**Moil (g)**	**Mwater (g)**
15	0.85	0.15	0.68731	0.15
30	0.7	0.3	0.56602	0.3
45	0.55	0.45	0.44473	0.45

Brine-in-oil emulsions:

Table 7: Sample calculations of brine-in-oil

Watercut (%)	**Voil (ml)**	**Vbrine(ml)**	**Moil (g)**	**Mbrine (g)**
15	0.85	0.15	0.68731	0.1785
30	0.7	0.3	0.56602	0.357
45	0.55	0.45	0.44473	0.5355

Saline-in-oil emulsions:

Table 8: Sample calculations of saline-in-oil

Watercut (%)	**Voil (ml)**	**Vsaline(ml)**	**Moil (g)**	**Msaline (g)**
15	0.85	0.15	0.68731	0.168
30	0.7	0.3	0.56602	0.336
45	0.55	0.45	0.44473	0.504

Second experiment: Ionic liquids as inhibitor

For the second experiments, upon the computation of oil density, the mass required for different concentrations could be calculated. Before preparing the emulsion, the Ionic Liquid (EMIM-BF4; BMIM-BF4) was added to the water phase at different concentration of 1.0, 5.0 and 10wt% .

All the samples calculated are tabulated in table 5 and table 6. Sample calculations are attached in Appendix sections.

Table 9: Samples preparation for EMIM-BF4

Concentration of EMIM-BF4 in total emulsion	**EMIM-BF4 required (g)**
1 wt%	0.08748
10 wt%	0.9622

Table 10: Samples preparation for BMIM-BF4

Concentration of BMIM-BF4 in total emulsion	**BMIM-BF4 required (g)**
1 wt%	0.08748
10 wt%	0.9622

With the required amount of EMIM/BMIM-BF4 known, all of these inhibitors was added to water and mixed with magnetic stirrer. After that, the solution of this inhibitors dissolved in water was added in a drop-wise manner to prepare the water-in-oil emulsion. A total of nine samples with different water cut would be obtained and four different concentrations of samples would be obtained, which are:

- emulsion with Blank Sample
- emulsion with water cut 15, 30, 45 % water-oil samples
- emulsion with water cut 15,30, 45 % saline-oil samples
- emulsion with water cut 15,30,45 % brine-oil samples
- emulsion with 1,10 wt% EMIM-BF4
- emulsion with 1 ,10 wt% BMIM-BF4

3.4 MODE OF OPERATION

Once the samples are prepared, they will be extracted for the experimental tests using differential scanning calorimetry (DSC). A 5-10 mg of prepared sample (oil + inhibitors), is placed into the sample cell. Then, purified nitrogen gas will be introduced into the sample cell at 303 K (30°C).

The first mode of operation is ramped mode, where the sample will be cooled from 303K (30°C) to 228 K (-45°C) at a rate of 1°C/min. The temperature will then be increased back to 303 K (30°C). This cooling-heating cycle will be repeated three times to observe the effect of hydrate formation in emulsion.

Another mode of operation is isothermal mode, where the sample will be cooled from 303 K (30°C) to 258 K (-15°C) at a rate of 1 °C/min, and held for approximately 3 hours. Upon the hydrate formation, the sample will be heated to measure the induction time of hydrate formation from all the samples.

The experimental results will then be indicated in thermogram analysis of the parameters of heat flow (mW), temperature and time for all samples tested.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EFFECT OF HYDRATE FORMATION TEMPERATURE ON CONCENTRATION OF SALTS FROM DIFFERENT WATER CUTS

The sample prepared are tested in three concentration of salts; 0, 300 and 500 ppt. From these concentrations, we observed the lowest hydrate formation temperature on different concentration of salts from different water cuts. The water cuts being tested are 15 %, 30 % and 45 %.

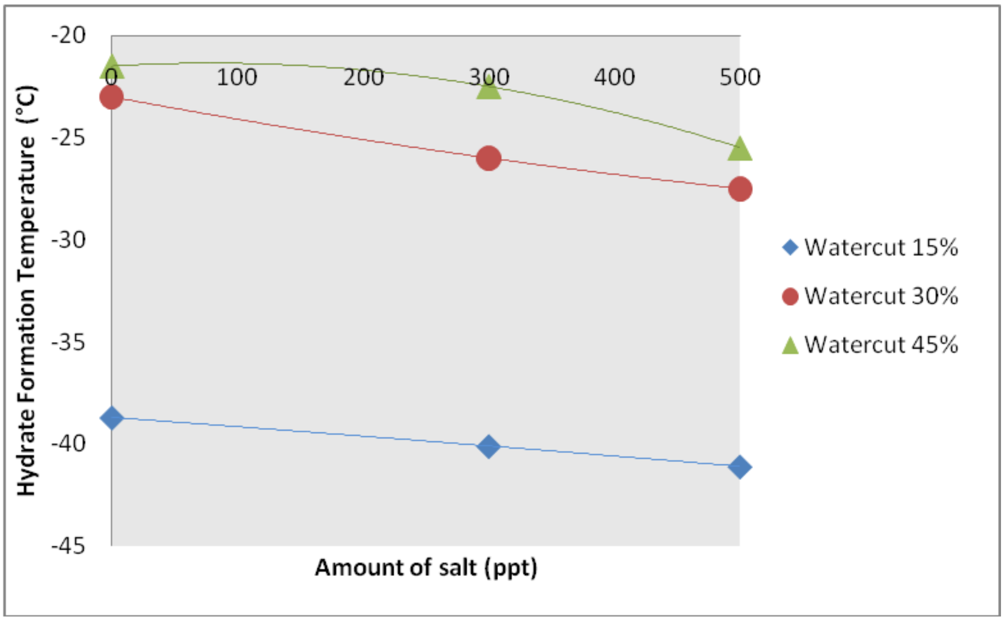


Figure.10: Effect of hydrate formation temperature on concentration of salt from different water cuts

The purpose of this experiment is to find the lowest hydrate formation temperature on different concentration of salt from different water cut compositions. The lowest hydrate formation temperature are then evaluated and use in the second part of this study, that is to use the lowest formation temperature on this water cut and then show the effectiveness of ionic liquids as inhibitor.

The experiments were performed by using ramped mode. A water-in-oil emulsion samples were cooled using temperature ramping to determine the hydrate formation temperature. The sample will be cooled from 303K (30°C) to 228 K (-45°C) at a rate of 1°C/min. The temperature will then be increased back to 303 K (30°C). This cooling-heating cycle will be recorded to observe the effect of hydrate formation in emulsions.

Figure 10 reports a formation temperature/ concentration of salt recorded from DSC thermogram. From these figure, for water cut 15%, the hydrate formation temperature were -38.7,-40.1,-41.1 °C. For water cut 30%, the hydrate formation temperature are much more lower than water cut 15 %, which is, -23,-26, -27.5°C.

The difference in term of shifting the temperature are around 10-15 °C for different concentration of salts. For water cut 45 %, the hydrate formation recorded are -21.5,-22.5,-25.5 °C. The hydrate formation temperature for 30% and 45 % water cuts trend are much more similar compared to 15% and 30 % water cuts. Thus, gas hydrate formation temperature is directly proportional to the water cut.

From Figure 10, it can been concluded that the lower hydrate formation temperature are at lower water cut. Water cut 15% has the lowest hydrate formation temperature compare to others. The decreased in water cuts can inhibit hydrate formation by lowering the hydrate formation temperature.

Therefore, at lower water cut, we will get lower hydrate formation temperature. In term of cost, less inhibitor necessary and it will not cost us more than practice.

As the best efficiency has to be reached at the lower cost, this type of experimental approach is a very useful composition to get the lowest hydrate formation temperature. Thus, we select water cut 15% as our base to proceed to next experiment, that is to show the effectiveness of ionic liquids as inhibitor.

4.2 EFFECT OF HYDRATE DISSOCIATION TEMPERATURE ON WATER CUTS FROM DIFFERENT CONCENTRATION OF SALTS

The sample prepared are tested in three different water cuts; 15%, 30% and 45%. From this water cuts, we observed the lowest hydrate formation temperature on different water cuts from different concentration of salt. The concentration of salt was being tested are 0, 300 and 500 ppt.

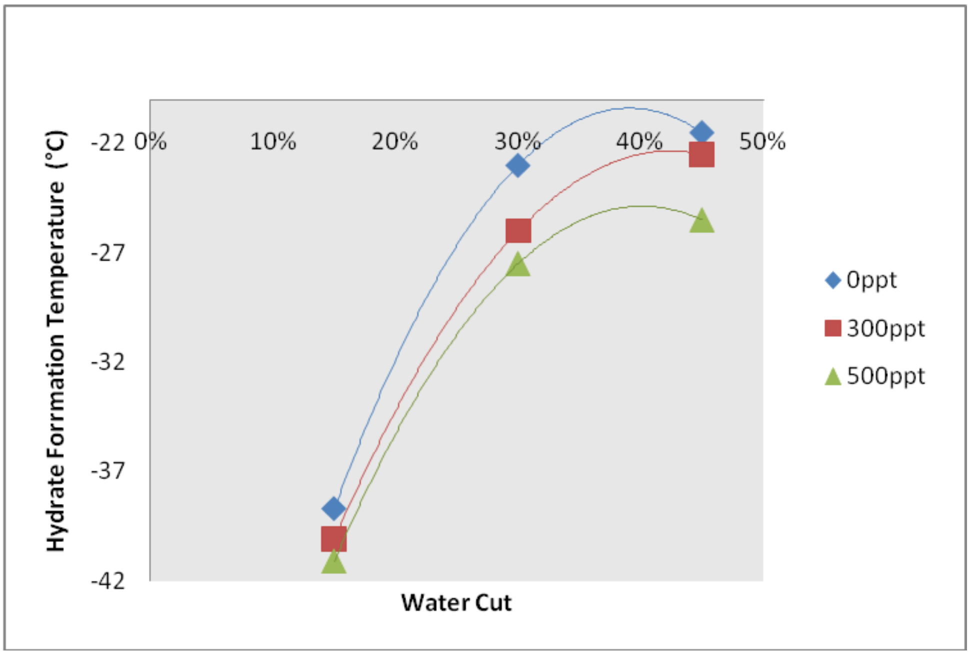


Figure 11: Effect of hydrate formation temperature on water cuts from different concentration of salts

The purpose of this experiment is to find the lowest hydrate formation temperature on different water cuts from different concentration of salt. The lower hydrate formation temperature are then evaluated and use in the second part of this study, that is to show the effectiveness of ionic liquids as inhibitor, which are the second parts of this studies.

The experiments were performed by using ramped mode. A water-in-oil (0 ppt), saline-in-oil (300 ppt) and brine-in-oil (500 ppt) emulsion samples were cooled using temperature ramping to determine the hydrate formation temperature.

The sample then cooled from 303K (30°C) to 228 K (-45°C) at a rate of 1°C/min. The temperature will then be increased back to 303 K (30°C). This cooling-heating cycle will be recorded to observe the effect of hydrate formation in emulsions.

Figure 11 reports a formation temperature water cuts recorded from DSC thermogram. From this figure 13, for pure water, the hydrate formation temperature were –38.7,-23,-21.5 °C . For saline, the hydrate formation temperature is much more lower than pure water, which is, -40.1,-26,-22.5°C.

The difference in term of shifting the temperature are around 1-3 °C for different concentration of salts. For brine , the hydrate formation recorded are -41.1,-27.5,-25.5 °C. The hydrate formation temperature for saline and brine trend are much more similar compared to pure water and saline. Thus, hydrate formation temperature is indirectly proportional to the concentration of salts.

From experiment conducted, we can conclude that at higher concentration of the salt, we will get the lower hydrate formation temperature value. The increased in concentration of salt can inhibit further hydrate formation. There were free water phases remaining in the samples because salt are mostly excluded from the formed hydrate particles and it become concentrated in the remaining water phase.

This showcased that salinity plays a crucial role in preventing hydrate blockages by given the lower hydrate formation temperature. Thus, it have been concluded that, the higher the concentration, the easier the hydrate problem is to manage.

As indicated earlier, this phenomenon lies in the fact that salt becomes concentrated in the remaining liquid water phase as hydrate forms. As a result, the higher concentration of salt may have come out of the hydrate region, while the lower concentration of salt still favors continued hydrate formation. Thus, saline solution have been selected as our base for the next experiment, that is, to show the effectiveness of ionic liquid.

4.3 EFFECT OF HYDRATE FORMATION TEMPERATURE WITH/ WITHOUT IONIC LIQUIDS

The purpose of this experiment is to compare the effect of hydrate formation temperature with ionic liquids and the blank sample.

The experiments were performed by using ramped mode. Five emulsion samples, (1) Blank sample (30% water cut, 500 ppt), (2) 1% EMIM BF4 (30% water cut, 500 ppt), (3) 1% BMIM BF4 (30% water cut, 500 ppt), (4) 10% EMIM BF4 (30% water cut, 500 ppt) and (5) 10% BMIM BF4 (30% water cut, 500 ppt) were cooled using temperature ramping to determine the hydrate formation temperature.

The sample then cooled from 303K (30°C) to 228 K (-45°C) at a rate of 1°C/min. The temperature will then be increased back to 303 K (30°C). This cooling-heating cycle will be recorded to observe the effect of hydrate formation in emulsions.

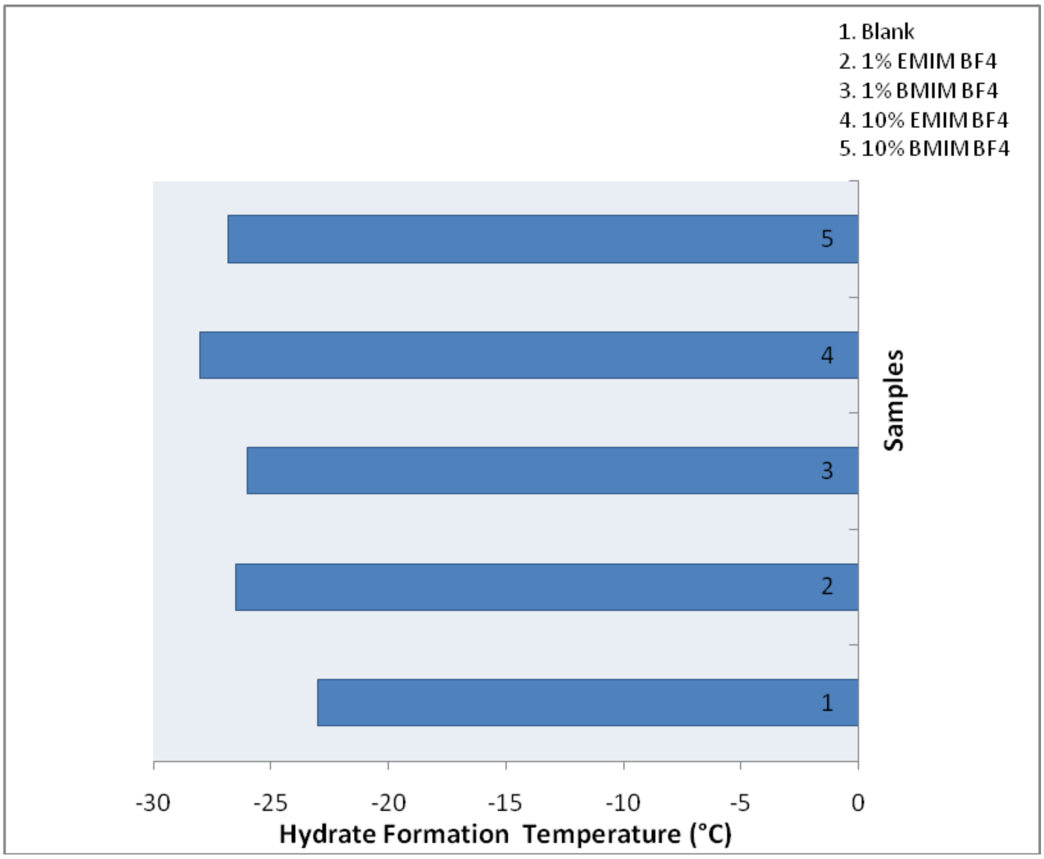


Figure 12: Effect of ionic liquids on hydrate formation temperature

Figure 12 shows that, ionic liquids have the lowest hydrate formation temperature compared to the blank sample because it has strong electrostatic charges and at the same time their cation are can be chosen or tailored to form hydrogen bonding with water.

It shows also that formation temperature in samples containing other ionic liquids is similar. In the pressure range fixed, the ionic liquids studied with concentration 1wt%, could shift the HLVE curve around 3- 3.5(°C) while for 10 wt%, it could shift up to 5(°C). As shown in Figure 12, the inhibition effect is more pronounced when ionic liquids added as inhibitor.

Among all of the ionic liquids that have been studied, 10wt% EMIM-BF4 is the most effective by having the lowest hydrate formation temperature. Thus, ionic liquids performs better and suits for industry purpose. It is proven that, EMIM-BF4 have the shorter alkyl chain substituent compared to others and that is why its better than that of ionic liquids with longer alkyl chain substituent (Adidharma,2009).

However, at this point, we do not have a clear explanation on the effect of chemical structure of ionic liquids on hydrate formation temperature. We will further address this in our future work. Thus, it can be concluded that sample contains ionic liquids, have lower hydrate formation temperature, that can inhibit the formation of gas hydrate.

4.4 EFFECT OF INDUCTION TIMES WITH/ WITHOUT IONIC LIQUIDS

The purpose of this experiment is to find the induction time that delaying the nucleation of hydrate in pipelines.

The induction time is an important indicator to characterize the kinetics of gas hydrate crystallization. The induction time is the time elapsing until the moment at which the onset of precipitation can be detected, which is the sum of the time for critical nucleus formation and growth to detectable size (Behar, 1994).

For heterogeneous nucleation, the nucleation rate depends on many factors, such as the cell wall roughness and the presence of impurities and particles in the sample. It is also greatly dependent on the driving force.

The nucleation is thus a probabilistic phenomenon and so is induction time. Since different experimental approaches will obviously give different results, to compare the performance of different inhibitors, ionic liquids, one should measure the induction time using the same experimental approach and the same apparatus.

Five emulsion samples, (1) Blank sample (30% water cut, 500 ppt), (2) 1% EMIM BF4 (30% water cut, 500 ppt), (3) 1% BMIM BF4 (30% water cut, 500 ppt), (4) 10% EMIM BF4 (30% water cut, 500 ppt) and (5) 10% BMIM BF4 (30% water cut, 500 ppt) using isothermal mode.

Isothermal mode are performed where the sample will be cooled from 303 K (30°C) to 258 K (-15°C) at a rate of 1 °C/min, and held for approximately 3 hours. Upon the hydrate formation, the sample will be heated to measure the induction time of hydrate formation from all the samples.

Samples containing 1wt% ionic liquids: kinetic inhibitors are typically used at concentrations of 1wt% or less and samples containing 10wt% are also used in these isothermal runs.

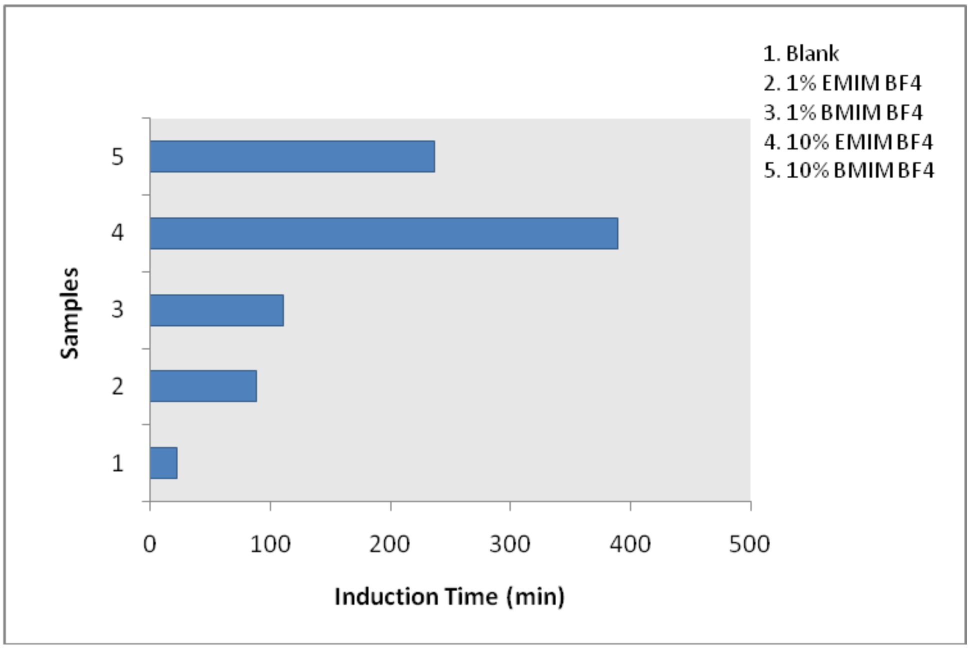


Figure 13: Induction time of hydrate formation from blank samples and samples containing ionic liquids.

As shown in Figure 13, the induction time of hydrate formation from samples with ionic liquids are longer than blank sample. 10wt% EMIM-BF4are found to perform better than other ionic liquids.

At lower concentration of ionic liquids, the shorter the induction time, means, the shorter its retard hydrate formation in pipelines. At higher concentration of ionic liquids, the longer the induction time takes place, means, the longer its retard hydrate formation in pipelines. We will further doing experiment to study on the effect of concentration of ionic liquids on induction later on.

It takes the longer time to delay the hydrate formation. As stated by Adidharma, the structure arrangement of EMIM- BF4, a shorther alkyl in the cation may not hinder the hydrogen bonding between BF4 and water. Thus, it can be concluded that, ionic liquids delay the hydrate formation longer compared to the blank samples.

CHAPTER 5

CONCLUSIONS

The result from this study shows that hydrate formation temperature is directly proportional to the concentration of salt and indirectly proportional to water cut. From this two parameters, we proceed to the next experiment that is to show the effectiveness of ionic liquids as inhibitors.

These ionic liquids are found to lower the hydrate formation temperature and slow down the nucleation or the growth rate. The effect of ionic liquids on HLVE curve are inclusive because we do not vary the pressure. An extension to this particular, that is on HLVE curve will further work later on.

To prove, the effectiveness of ionic liquids as inhibitor, first, the effect of water cut on hydrate formation temperature have been studied. Samples were prepared in blank, oil-in water emulsions in three different compositions, 15%, 30% and 45% water cuts. The reason why is to get the lowest hydrate formation temperature so it can be used as our based on the next experiment.

From the experiment conducted, at lower water cut, we will get lower hydrate formation temperature. In term of cost, less inhibitor necessary and it will not cost us more than practice.

Thus, water cut 15% as our base to proceed to next experiment, that is to show the effectiveness of ionic liquids as inhibitor. As the best efficiency has to be reached at the lowest cost, this type of experimental approach is a very useful compositions to get the lowest hydrate formation temperature.

Then, the effect of concentration of salt on hydrate formation temperature have been studied to find the lowest hydrate dissociation temperature. Samples were tested in three different concentrations, 0, 300 and 500 ppt. From there, it can be concluded that at higher concentration of salt, the lower the hydrate formation temperature.

The increased in concentration of salt can inhibit further hydrate formation. The reason why is, there were free water phases remaining in the samples because salt are mostly excluded from the formed hydrate particles and it become concentrated.

From this two experiments mentioned, water cuts and concentration of salt, it is been selected, 15% water cut and 500ppt as our based to proceed to the next experiment, that is, to prove the effectiveness of ionic liquids as inhibitor.

Among all of the ionic liquids that have been studied, 10wt% EMIM-BF4 is the most effective by having the lowest hydrate formation temperature. Therefore, ionic liquids performs better as gas hydrate inhibitor.

Also, the induction time of hydrate formation from samples with ionic liquids are longer than blank sample. 10wt% EMIM-BF4are found to perform better than other ionic liquids.

In summary, ionic liquids performs better than the conventional inhibitors by having the lowest hydrate formation temperature and delaying the hydrate formation.

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APPENDICES

Appendix (a)

Sample Calculations of

For the second experiments, Upon the computation of oil density, the mass required for different concentrations could be calculated. Before preparing the emulsion, the Ionic Liquid (EMIM-BF4; BMIM-BF4) was added to the water phase at different concentration of 1.0, 5.0 and 10wt% .

	Cut (%)	**Mass (g)**
Oil	70	5.6602
Water	30	3.000
EMIM BF4		X

Sample Calculation of EMIM-BF4

The volume was distributed to obtain a 30 wt% water cut in the samples in 10mL oil-water emulsion. Therefore, the mass required to prepare different concentrations of samples was based on the sample calculation shown.

$$\boxed{\text{Weight Percent} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \text{ X } 100\%}$$

Example calculation for 1wt% EMIM-BF4 in total emulsion:

$$1.0\text{wt\% EMIM-BF4} = \frac{x}{5.6602 + 3 + x} \times 100\%$$

$$0.01 = \frac{x}{8.6602 + x}$$

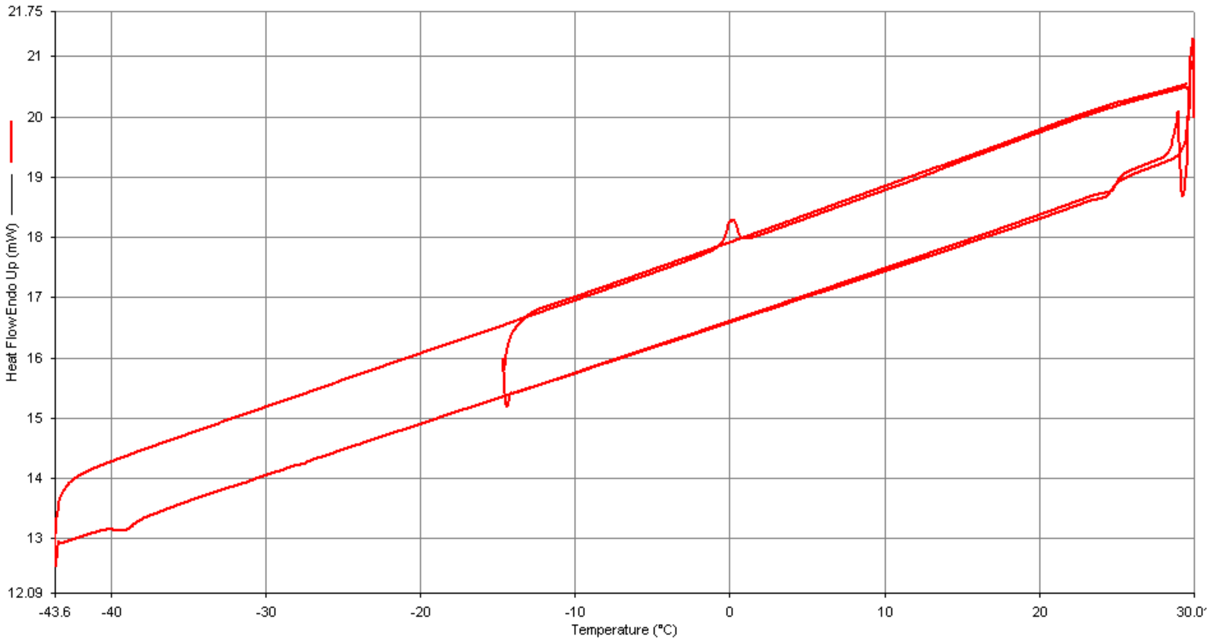
$$x = 0.086602 + 0.01x$$

x = 0.08748 g

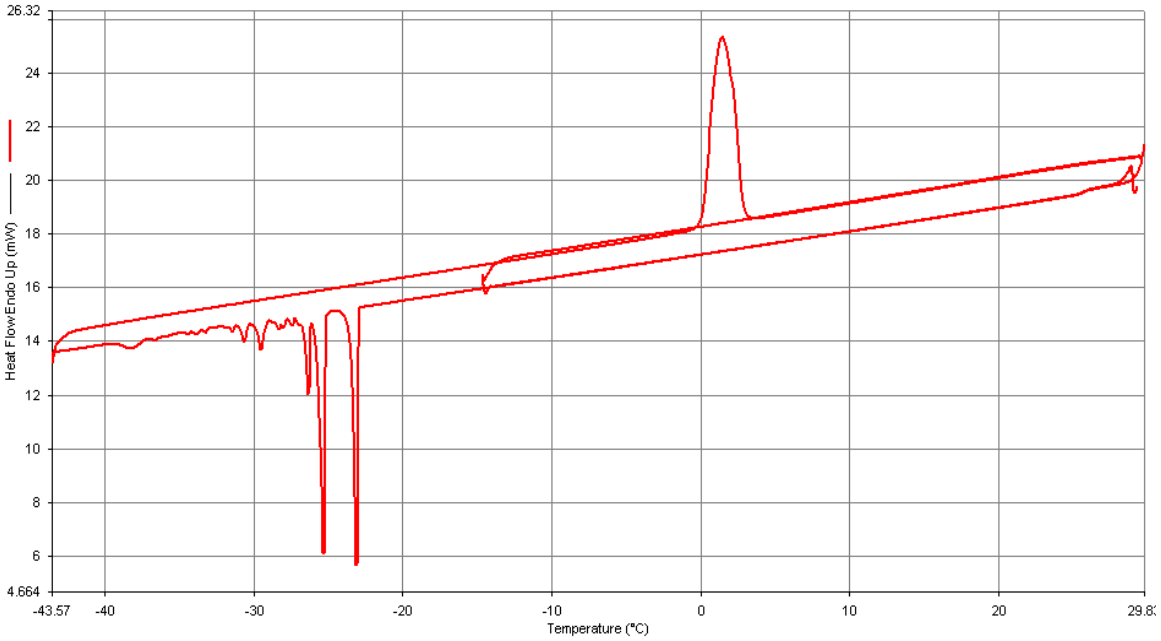
APPENDIX (B)

DSC thermograms

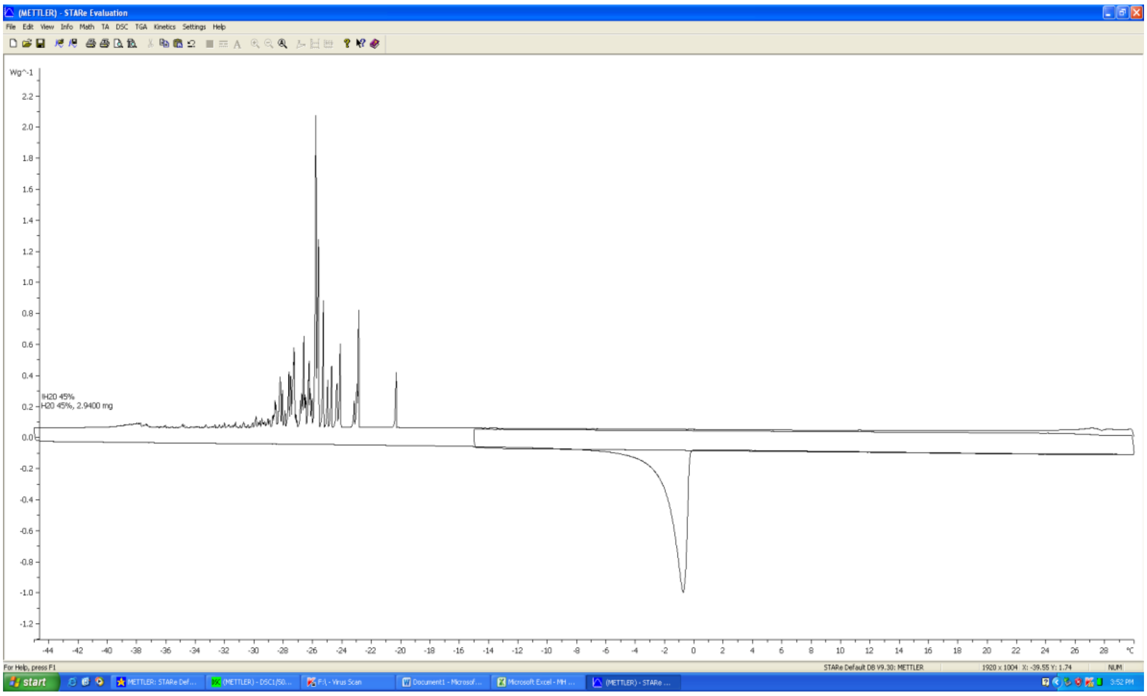
1. Water 15%



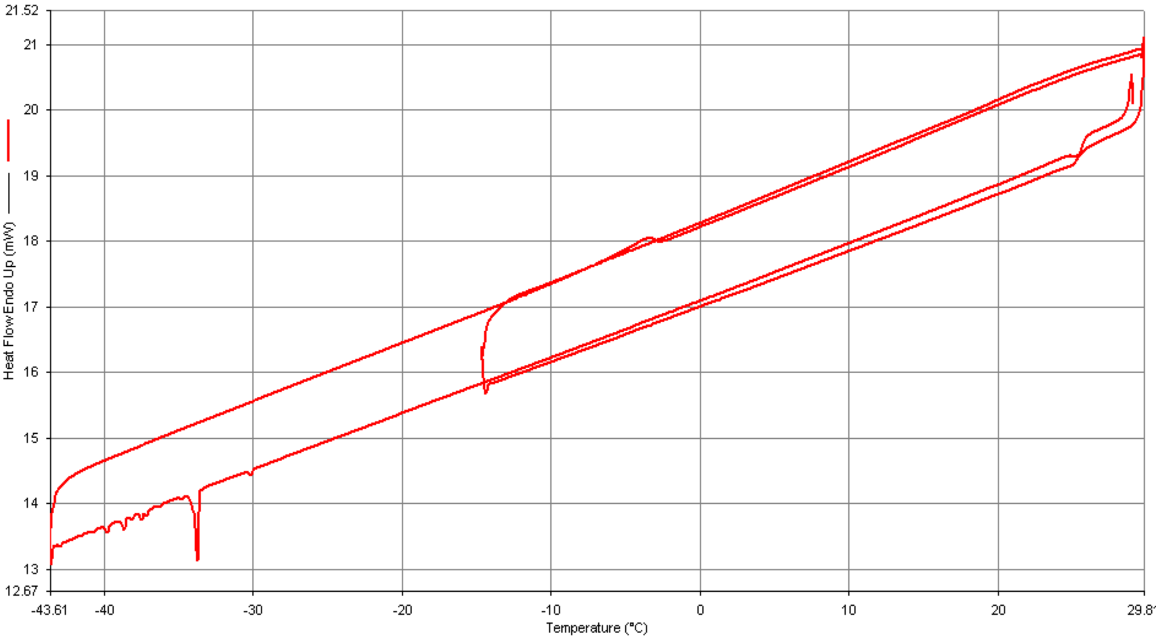
2. Water 30 %



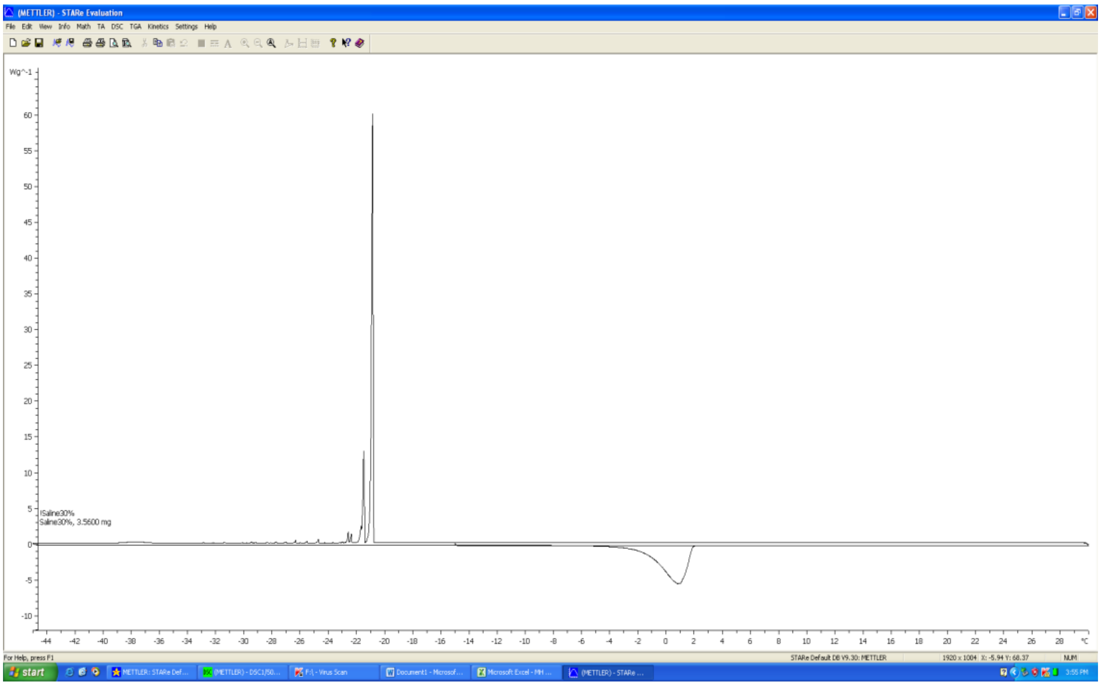
3. Water 45%



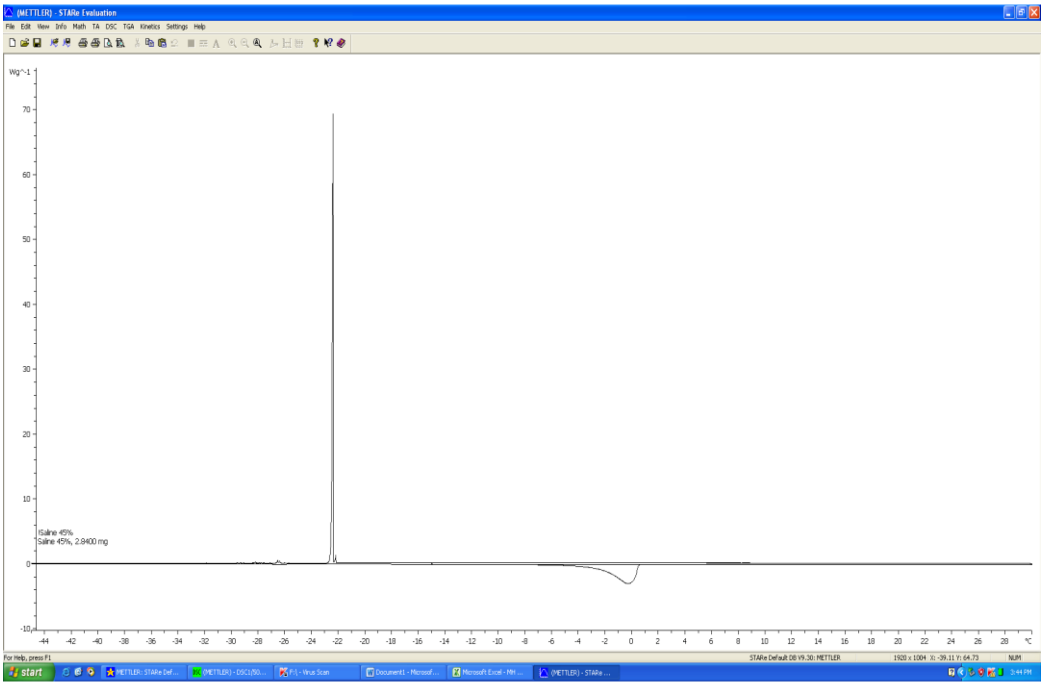
4. Saline 15 %



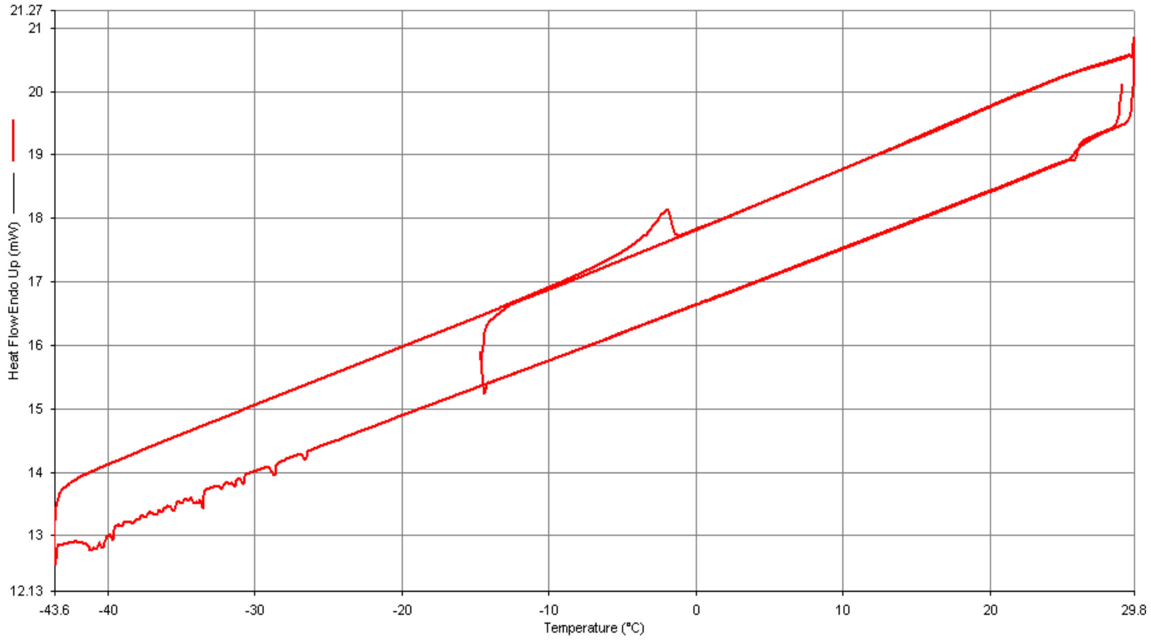
5. Saline 30 %



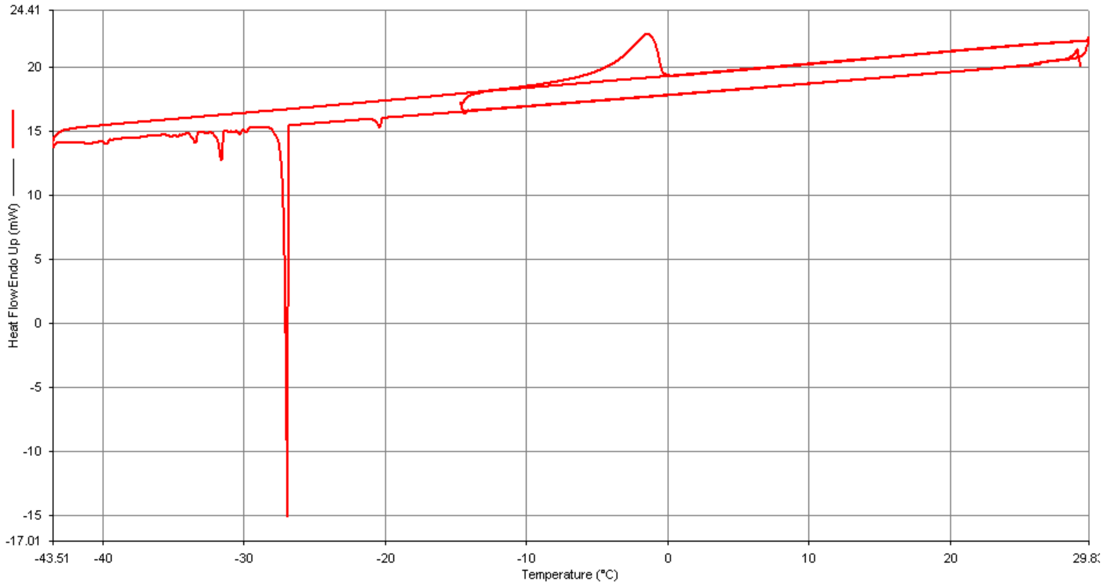
6. Saline 45%



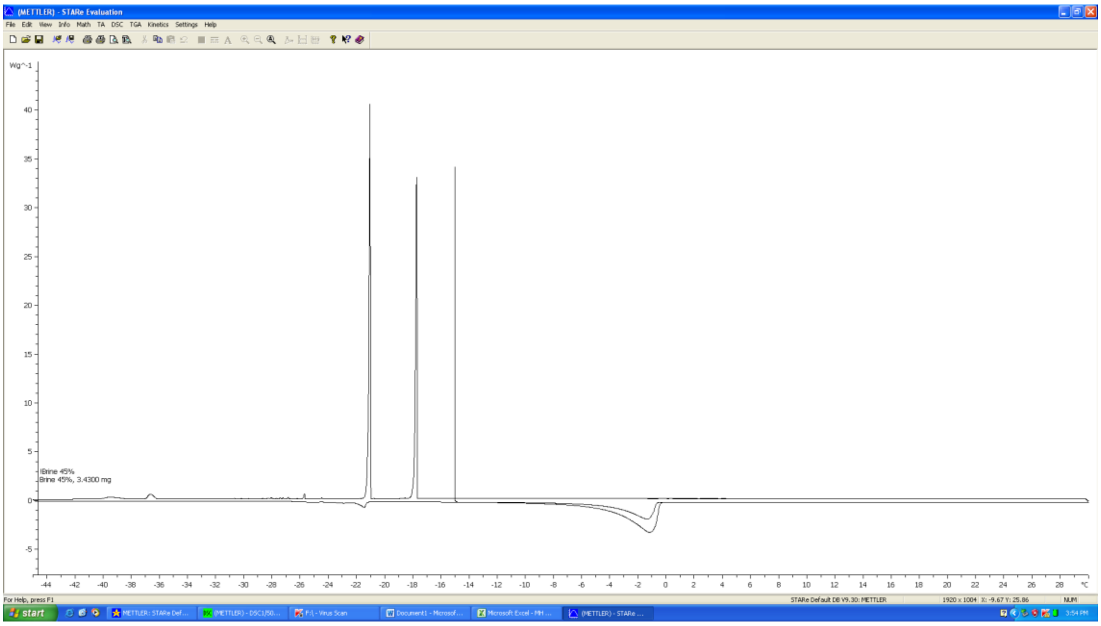
7. Brine 15 %



8. Brine 30%

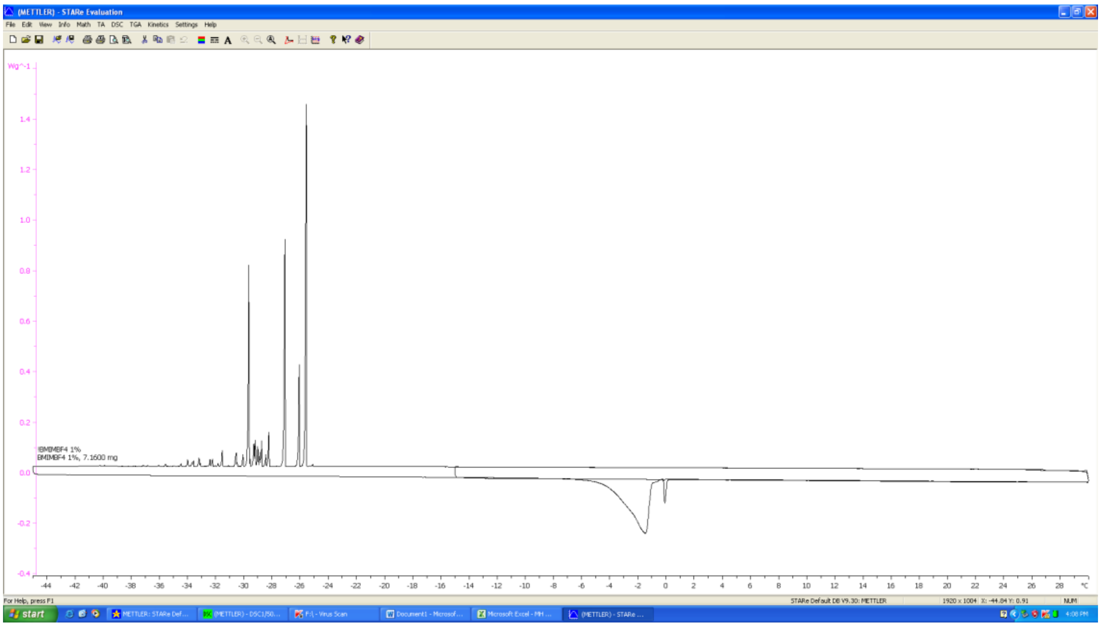


9. Brine 45%

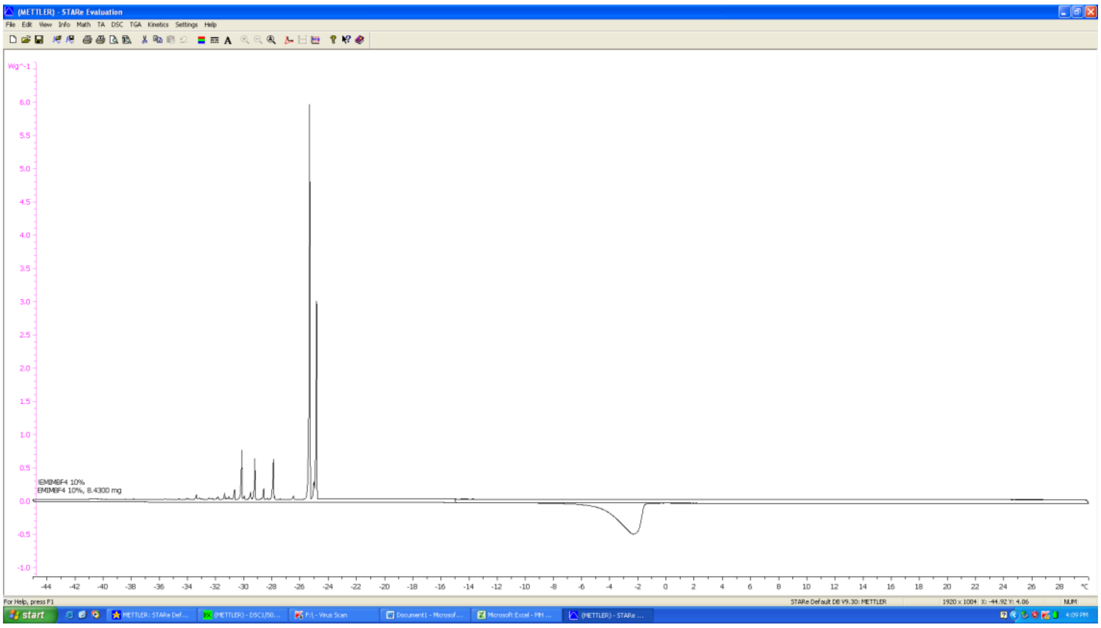


10. EMIM-BF4 1%

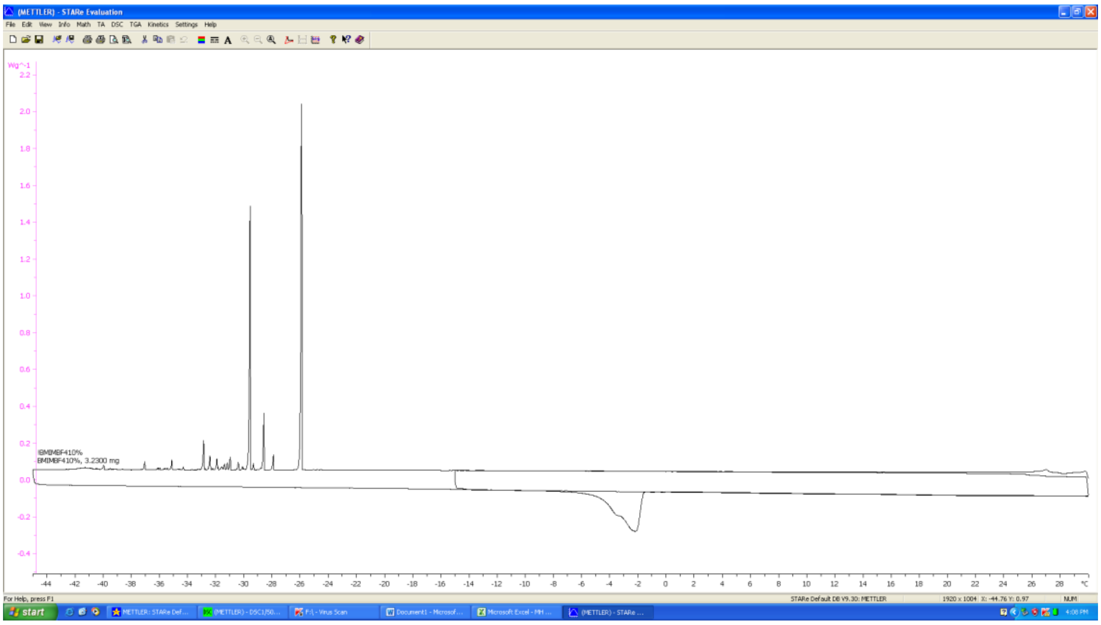
11. BMIM BF4 1%



12. EMIM BF4 10%



13. BMIM BF4 10%



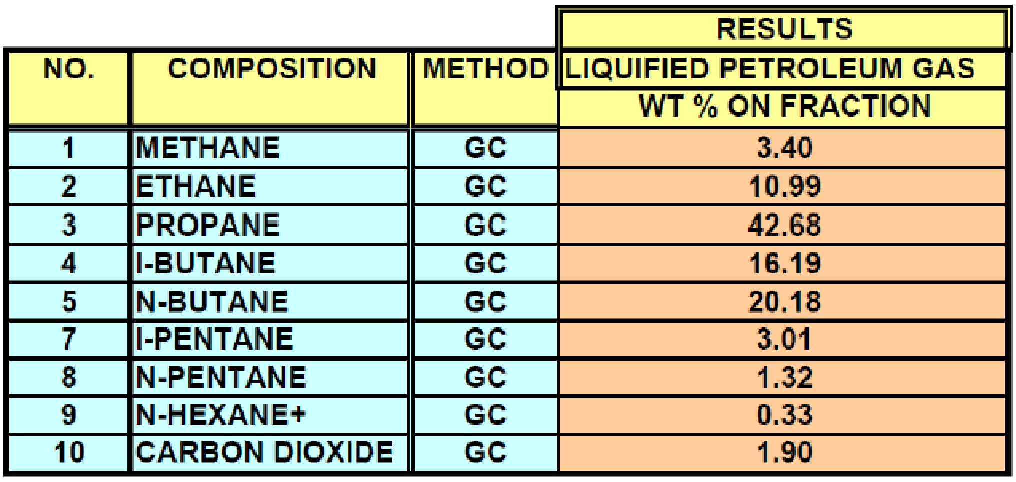
APPENDIX (C)

CRUDE OIL ASSAY REPORT

Crude Oil Assay Report

Sample: Miri Crude Oil
Tested date: 16th October 2009

LIGHT HYDROCARBON ANALYSIS



			RESULTS
NO.	COMPOSITION	METHOD	LIQUIFIED PETROLEUM GAS
			WT % ON FRACTION
1	METHANE	GC	3.40
2	ETHANE	GC	10.99
3	PROPANE	GC	42.68
4	I-BUTANE	GC	16.19
5	N-BUTANE	GC	20.18
7	I-PENTANE	GC	3.01
8	N-PENTANE	GC	1.32
9	N-HEXANE+	GC	0.33
10	CARBON DIOXIDE	GC	1.90

DETAILED HYDROCARBON ANALYSIS

NO.	COMPOSITION	METHOD	RESULTS NAPHTHA (C5 - 140) WT % ON FRACTION	RESULTS NAPHTHA (C140 - 185) WT % ON FRACTION
1	PARAFFINS	DHA	40.54	36.20
2	OLEFINS	DHA	0.00	0.00
3	NAPHTHENE	DHA	48.79	25.48
4	AROMATIC	DHA	10.14	29.59
5	HEAVIES	DHA	0.00	0.00
6	UNKNOWNS	DHA	0.53	8.73
7	TOTAL C3	DHA	0.12	0.00
8	TOTAL C4	DHA	1.78	0.00
9	TOTAL C5	DHA	6.49	0.05
10	TOTAL C6	DHA	18.94	0.54
11	TOTAL C7	DHA	30.60	4.50
12	TOTAL C8	DHA	24.66	15.25
13	TOTAL C9	DHA	13.77	26.83
14	TOTAL C10	DHA	3.09	31.50
15	TOTAL C11	DHA	0.02	10.48
16	TOTAL C11+	DHA	0.00	2.12
17	TOTAL HEAVIES	DHA	0.00	0.00
18	TOTAL UNKNOWNS	DHA	0.00	8.73
19	C4 PARAFFINS	DHA	0.12	0.00
19	C4 PARAFFINS	DHA	1.78	0.00
20	C5 PARAFFINS	DHA	5.57	0.03
21	C6 PARAFFINS	DHA	7.95	0.09
22	C7 PARAFFINS	DHA	7.12	0.45
23	C8 PARAFFINS	DHA	9.24	2.90
24	C9 PARAFFINS	DHA	6.14	7.24
25	C10 PARAFFINS	DHA	2.62	17.40
26	C11 PARAFFINS	DHA	0.00	7.02
27	C12 PARAFFINS	DHA	0.00	1.06
28	C13 PARAFFINS	DHA	0.00	0.00
29	C14 PARAFFINS	DHA	0.00	0.00
30	C5 OLEFINS	DHA	0.00	0.00
31	C6 OLEFINS	DHA	0.00	0.00
32	C7 OLEFINS	DHA	0.00	0.00
33	C8 OLEFINS	DHA	0.00	0.00
34	C9 OLEFINS	DHA	0.00	0.00
35	C10 OLEFINS	DHA	0.00	0.00
36	C11 OLEFINS	DHA	0.00	0.00
37	C12 OLEFINS	DHA	0.00	0.00
38	C13 OLEFINS	DHA	0.00	0.00
39	C5 NAPHTHENE	DHA	0.92	0.02
40	C6 NAPHTHENE	DHA	10.46	0.42
41	C7 NAPHTHENE	DHA	20.44	3.23
42	C8 NAPHTHENE	DHA	10.73	6.82
43	C9 NAPHTHENE	DHA	5.87	9.54
44	C10 NAPHTHENE	DHA	0.36	4.34
45	C11 NAPHTHENE	DHA	0.02	0.89
46	C12 NAPHTHENE	DHA	0.00	0.23
47	POLYNAPHTHENE	DHA	0.00	0.00
48	C6 AROMATIC	DHA	0.54	0.02
49	C7 AROMATIC	DHA	3.04	0.82
50	C8 AROMATIC	DHA	4.68	5.53
51	C9 AROMATIC	DHA	1.77	10.05
52	C10 AROMATIC	DHA	0.11	9.77
53	C11 AROMATIC	DHA	0.00	2.56
54	C12 AROMATIC	DHA	0.00	0.84