INHIBITING GAS HYDRATION USING SURFACTANT

by

NURFARAH SHAZLINA BINTI ZULKIFLI

Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) Petroleum Engineering

JUNE 2012

University Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Inhibiting Gas Hydration Using Surfactant

by

Nurfarah Shazlina Binti Zulkifli

A project dissertation submitted to the Geoscience & Petroleum Engineering Department Universiti Teknologi PETRONAS in partial fulfillment of the requirement for the BACHELOR OF ENGINEERING (Hons) PETROLEUM ENGINEERING

Approved,

Pn. Mazuin Jasamai Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS TRONOH, PERAK

June 2012

CERTIFICATION OF ORIGINALITY

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

(Nurfarah Shazlina Binti Zulkifli)

ABSTRACT

Gas hydrates are clathrates that will form in the presence of water and small hydrocarbons at elevated pressure usually higher than 600 psia and in condition of lower temperatures $(0^{\circ}C - 15^{\circ}C)$. The structure of the gas hydrates is crystalline and they pose a big problem to the oil and gas industry as they can result in loss of production. Their presences in pipelines have been a serious economic concern especially they can cause serious operation and safety problem. Anti-Agglomerants (AAs) are injected and the purpose is to prevent the agglomeration and deposition of hydrate crystals such that transportable hydrate slurry is formed. Surfactants will be used and it is designed to attack hydrate surfaces and will disrupt the hydrate growth process. The surfactants are also known to stabilize water in oil emulsions. The equipment that I will use to determine the most effective concentration of the surfactant to inhibit the gas hydrates for my project is Differential Scanning Calorimetry (DSC). At concentrations above 1 wt % or between 0.25 - 0.5 wt % of the aqueous phase, these chemicals showed some positive effects. Other than that, compared to conventional method which is Thermodynamic Hydrate Inhibitors (THIs), AAs is used in low concentration. Thus, it can lead to very substantial cost savings and environmental friendly product.

ACKNOWLEDGEMENTS

First of all, the author would like to express the utmost gratitude to her project supervisor, Pn. Mazuin jasamai for her continuous support, knowledge, and guidance provided throughout the progression of this project. The author would also like to thanks all the lab technicians and beloved colleagues, who had helped, advised, guided and shared a lot of knowledge along with the progression of the experiments conducted for the project. Thousands thanks to the author's family for their never ending support given that kept her moving to complete the project. Finally, thanks to the author's own Universiti Teknologi PETRONAS, for the facilities, laboratories and consumable provided for her.

TABLE OF CONTENT

CERTIFICATION OF APPROVAL
CERTIFICATION OF ORIGINALITYii
ABSTRACT iii
ACKNOWLEDGEMENTiv
TABLE OF CONTENTS
LIST OF FIGURESvii
CHAPTER 1 INTRODUCTION
1.1 Background Study1
1.2 Problem Statement
1.3 Objective
1.4 Scope of Study4
CHAPTER 2 LITERATURE REVIEW
2.1 Hydrate formation
2.2 Hydrates Controlling Methods in Industry
2.3 Types of Anti-Agglomerants Inhibitors11
2.4 Experiments
2.5 Industrial AA Applications14

CHAPTER 3 METHODOLOGY	16
3.1 Research Methodology	16
3.2 Experiment Apparatus	17
3.3 Sample Preparation	19
3.4 Mode of Operation	21

4.1 Hydrate Formation in Emulsion	22
4.2 Anti-Agglomerant Inhibitor Effectiveness	24

CHAPTER 5 CONCLUSION & RECOMMENDATION	25
5.1 Conclusion	25
5 2 Decommon lation	26
5.2 Recommendation	

REFERENCES

LIST OF FIGURES

Figure 1 Hydrates formation diagram
Figure 2 Structures of hydrates
Figure 3 Gas hydrates plug in a pipeline7
Figure 4 Pressure-temperature graph for a typical nature gas hydrate10
Figure 5 KHI vs. AA11
Figure 6 Structure of Shell's quaternary AAs (R1 = long chain hydrocarbon tail; R2
= n-butyl, n-pentyl, or isopentyl; M = N or P; X is an optional spacer group)14
Figure 7 Perkin Elmer Pyris 1 Differential Scanning Calorimetry (DSC)17
Figure 8 Schematic drawing of a typical DSC thermogram
Figure 9 Hanna Instruments HI 180 E-1 Magnetic Stirrer - Compact
Figure 10 Hydrate formation and dissociation trends of emulsions through cooling-
heating process during ramped mode test in terms of temperature
Figure 11 Hydrate formation and dissociation trends of emulsions through cooling-
heating process during ramped mode test in terms of time23

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Gas hydrates are clathrates in which water molecules form hydrogen bonded network enclosing roughly spherical cavities that are filled with gas molecules. Hydrate-former include nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, and butane which are the main components of natural gases. The formation of gas hydrates in natural gas pipe lines depends primarily upon the pressure, temperature and composition of the gas-water vapour mixture. After these primary conditions are fulfilled, the formation of the hydrates is accelerated by high velocities of the gas stream, pressure pulsations or inoculation with a small crystal of the hydrate (Hammerschmidt, 1934).

The conservative method that was used previously to prevent hydrates is Thermodynamic Hydrate Inhibitors (THI) such as methanol and mono ethylene glycol. THIs are used at very high concentrations (10-60 wt. %) which are costly on offshore developments and onshore processing facilities. Low dosage hydrate inhibitors (LDHIs) have been researched and developed over past 15 years as an alternative method to control gas hydrates (Kelland, 2006) and indeed they are more cost-effective and environmental friendly.

LDHI are divided into two categories; kinetic hydrate inhibitors (KHIs) and Anti-Agglomerants (AAs). KHIs are mostly polymeric compounds while all AAs have surface active properties. AAs in general are surfactant based molecules, which allow the hydrate crystals to form but manage the size of the crystals so that they can be dispersed in hydrocarbon fluid. AAs are typically used for severe hydrate conditions and long shut-in period. AAs molecules must have hydrophilic "head" attaching to a surface of hydrate particle and hydrophobic "tail" to repel other hydrate particles; thus preventing hydrate agglomeration. All surfactants having hydrophilic and hydrophobic functionality have some AAs properties. The effectiveness of AA is examined by using Differential Scanning Calorimetry (DSC). The equipment will measure the amout of heat transfer in different concentration of surfactants used as anti-agglomerant inhibitor. The objective of this study is to determine the effectiveness of surfactants as Anti-Agglomerants inhibitors (AAs) by using Differential Scanning Calorimetry (DSC).

1.2 Problem Statement

Formation of gas hydrates are a major nuisance and danger in oil and gas field operations. Dislodged hydrate plugs can become deadly projectiles and have caused several accidents in oilfield in the past. Gas hydrates can form in any place where water and gas coexist at the right temperature and pressure conditions. This includes drilling, production, transportation, storage and natural gas processing plants.

The removal of hydrate plugs is usually difficult to achieve. A shutdown of several days or weeks may be necessary prior to the restarting of the production, and indeed, it may lead to pipeline abandonment as well. The conservative method like THIs is effective, but large concentrations are required which impacts the project profits. THIs is not cost saving as KHIs and AAs since they are added at high concentrations (10-60 wt. %) to shift the hydrate formation conditions to lower temperatures and higher pressures.

On the other hand, AAs only require low dosage (0.3–3 wt %) to prevent the agglomeration and deposition of hydrate crystals. However, further investigations on the effectiveness of AAs have to be established and comparisons between different inhibitors must be done before the industry can depend on the application of AAs to the production system.

Sultanate of Oman is an example where the hydrate problems occur in oil production industry. There are more than 10 oil producing stations in both North and South area operation of Petroleum Development Oman. With desert environment, the country's ambient temperature can drop as low as 5°C during winter, when

hydrates form in several gases lift lines. The condition has caused affected wells to cease production, however being controlled temporarily by use of methanol as hydrate inhibitor.

Another example of hydrate formation problem at offshore Dutch sector, where an unmanned platform tied back to an onshore terminal via a 17-km subsea pipeline. THI injection was planned for hydrate prevention even though the subcooling was relatively low, 1-5°C. However, due to the actual production temperature was unexpectedly lower and the high production of condensed water, MEG system was unable to treat the hydrates.

Gas hydrates are liable to form in subsea flow lines, the technology for deepwater application is often costly. In many cases, AAs aid in lowering the cost compared to the conventional inhibitors. However, there is limited published information at this time. Thus, data verified from field tests and laboratory tests are highly required to verify the effectiveness of an AA.

1.3 **Objectives**

The main objective of this project is to study the application of Anti-Agglomerants hydrate inhibitors (AAs) and the current chemicals used in the industry for handling gas hydrate formation.

The second objective is to identify the most effective concentration of surfactant to be used as Anti-Agglomerants Inhibitors (AAs) and then carry out laboratory tests in order to verify the effectiveness of Anti-Agglomerants.

The third objective is to determine the efficiency of selected surfactants to the onset dissociation temperature and pressure of hydrate and also to the induction time of methane gas hydrate formation.

1.4 Scope of Study

The scope of study for this project revolves around gas hydrates managing methods in petroleum production system. The main part of this study consists of research on the industry case studies to further understand the gas hydrate handling procedures adopted in the production system. In the second stage, the experiments will be carried out using the surfactant identified as AA. Using surfactant, its effectiveness acting as AA will be measured based on these parameters:

- Concentrations (wt.%) of AA required to prevent gas hydrates effectively
- Time in minutes/hours before agglomeration of hydrates.

The effectiveness of the AA will be measured by using Differential Scanning Calorimetry (DSC) by measuring the amount of heat transfer of the sample and the references. Then, analysis and comparisons will be done base on the data gathered and research studies before.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrates formation

Gas hydrates was first discovered by Sir Humphrey Davy in 1810. But, in 1934, Hammerschmidt reported that the gas hydrates could form in natural gas pipelines leading to blockage and reduced flow. Gas hydrates will form in the presence of water and small hydrocarbons at elevated pressure (> 600 psia) and in condition of lower temperatures ($0^{\circ}C - 15^{\circ}C$). As noted by Mehta et. al., (2000) deepwater production conditions are ideal for the formation of hydrates. The graph below is the pressure-temperature graph for a typical natural gas hydrates.

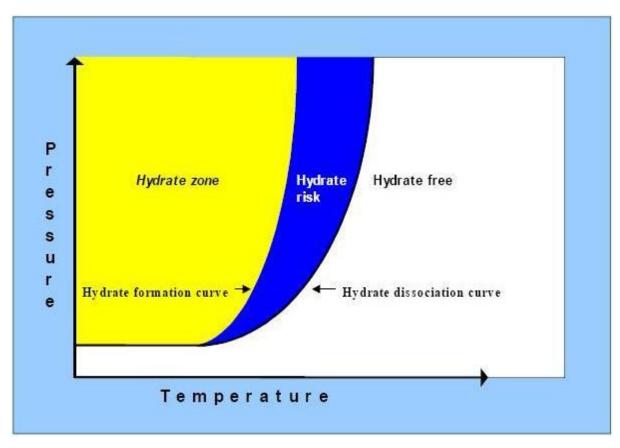


Figure 1 Hydrates formation diagram

The structure of the gas hydrates is crystalline. There are three common crystal structures for gas hydrates named SI, SII, and SH. For structure I, the network is a centered face cubic system which appears with light components such as methane or carbon dioxide. The unit cell of Type I consists of 46 water molecules, forming two types of cages – small and large. While, structure II network is of a diamond type with 24 cavities per mesh and consists of 136 water molecules, forming also two types of cages – small and large. SII is the most common because of the normal distribution of hydrocarbons in petroleum like the oxygen and nitrogen. The structure H network of hexagonal type is constituted of 6 cavities and consists of 34 water molecules, forming three types of cages – two small of different type and one huge. This SH appears for molecules of important size such as cycloalkanes, but support gas such as methane is always necessary in order to stabilize the structure. For my project, I will be focusing on the methane gas hydrate that is classified in structure I. While, the figure below shows the SI, SII and SH structures.

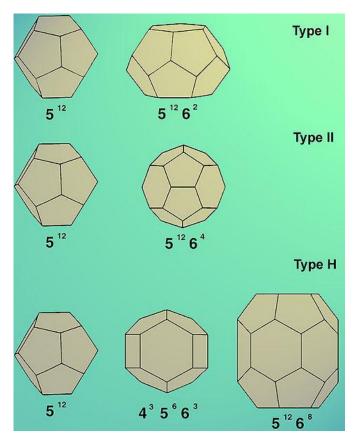


Figure 2 Structures of hydrates

In petroleum E&P operations, gas hydrates can cause blockages in pipelines and processing facilities as shown in Figure 3. In deepwater drilling, hydrates can potentially block the blowout preventer (BOP) stack, kill lines and chokes, and interrupt the movement of the drill strings. This is a new challenge for hydrate prevention in transportation. The crystallization of hydrate particles will form solid plugs then lead to blockage of pipelines and potentially can cause shutdown of production facilities. Thus, it may lead to pipeline abandonment.



Figure 3 Gas hydrates plug in a pipeline

2.2 Hydrates controlling methods in industry

At high pressure and low temperatures gas hydrates can form and block the pipeline. As the method to prevent this from happening, a pipeline is either a) insulated/buried to keep the well stream outside of the hydrate forming region, or b) the well stream is treated with anti-freezes such as methanol or ethylene glycol that can lower the thermodynamic temperature for hydrate formation and it is known as the conservative method called Thermodynamic hydrate inhibitor (THI).

THI will shift the hydrate formation conditions to lower temperatures and high pressures were employed by the industry to prevent hydrates formation along the flow line. However, this method has major economical impacts because it becomes more and more costly and has technical limitations. THIs are only effective at high concentrations with respect to the water rate (10 to 60 wt. %). Therefore, studies have been carried out on the replacement of methanol or mono ethylene glycol using Low Dosage Hydrate Inhibitors (LDHI).

In the early 1970s, a Russian engineer called Kuliev (Kelland, 2006) was experiencing gas hydrate problems in his gas wells. He decided to try adding surfactants to the top part of the wells and it was discovered that the hydrate problem went away. That was the first recorded example of using a low dosage of a chemical to prevent hydrate plugging.

A common thread of thermodynamic hydrate control is that the water/gas system is kept outside the hydrate envelope. Hydrates will never form in a thermodynamically prevented system. While, LDHI allow producers or operators to pump and transport the gas/water at hydrate conditions without forming any hydrate blockage.

8

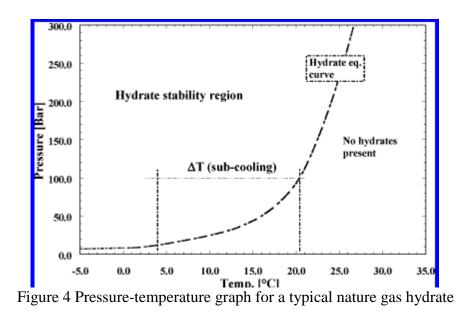
LDHIs are more cost savings and are used at lower dosage than the THI, where the required concentration for these additives is expected to be in the range of 0.3-3.0 wt.% versus the water rate. For commercial applications, LDHI can be subdivided into two basic categories:

- Kinetic Hydrate Inhibitors (KHIs)
- Anti-Agglomerators (AA).

KHIs are generally water-soluble polymers and they act as gas hydrate antinucleators, although most of them delay the growth of gas hydrate crystals. The time to the formation of the hydrate crystals is called the induction time. AAs will allow hydrates to form but they prevent them from agglomerating and subsequently accumulating into large masses. The hydrate particles will remain small, welldispersed and non-adherent.

An AA enables the hydrates to form as transportable non-sticky slurry of hydrate particles dispersed in the liquid hydrocarbon phase. In general, the water cut for AAs should be below approximately 50% otherwise the hydrate slurry gets too viscous to transport (Kelland, 2006). Besides, AA is effective for severe conditions and during extended shut-ins.

The best AAs perform at higher subcoolings experienced in subsea pipelines and for prolonged shutins when pipeline flow is stopped (Firoozabadi et. al, 2008) compared to KHIs. The subcooling (Δ T) is a measure of the driving force for hydrate formation in a system. The difference between the hydrate equilibrium temperature and the operating at a given pressure (Figure 4) is the definition of subcooling.



Anti-freezes from the conventional method which is THI are often used at concentrations of 20 to 40 wt %. On the other hand, the modern method (LDHI) has discovered work at 0.3 to 3.0 wt % of the produced water. Although the chemicals are several times more expensive than the anti-freezes glycols, the concentrations used could still lead to considerable savings. There are also many side benefits of using anti-freezes such as reduced storage and injection facilities.

A wide range of OPEX savings, possible extended field lifetime and multimillion dollar CAPEX savings, are economic drivers for choosing LDHIs instead of the conventional method, Thermodynamic hydrate inhibitor (THI).

The effectiveness of the anti-agglomerant will be measure by using Differential Scanning Calorimetry (DSC). DSC measure the amount of energy (heat) absorbed or released by a sample as it is heated, cooled or held at contstant (isothermal) temperature. Not only can the DSC perform consistent measurements, but it is also the ideal, cost-effective solution for quality control and educational labs due to its rugged, reliable and easy-to-use design.

2.3 Types of Anti-Agglomerants inhibitors

AAs are a class of low dosage hydrate inhibitor that have been used in the oil industry since mid 90s to prevent plugging of oil, condensate and gas production pipelines with gas hydrates. Anti-Agglomerant inhibitors give operators an additional tool for controlling hydrates in their systems. Compared to kinetic inhibitors (KHIs), Anti-Agglomerant (AAs) inhibit hydrate plugging, rather than hydrate formation. Thus AAs allow hydrates to form but keep the particles small and well dispersed.

Surfactants designed to attack the hydrate surfaces will also disrupt the hydrate growth process. One of the advantages of AA over KHI is fluid viscosity remains low, allowing the hydrates to be transported along with the produced fluids. Emulsification of the produced fluids is not necessary; in fact, AAs have aided in demulsifying several black oil emulsions. In the laboratory, AAs have been shown to be effective up to 4°C below the hydrate formation temperature, at pressures up to 48263 kPa, and for shut-ins up to two weeks in duration. Figure 5 below shows the different between Kinetic hydrate inhibitor (KHI) and Anti-agglomerant (AA).

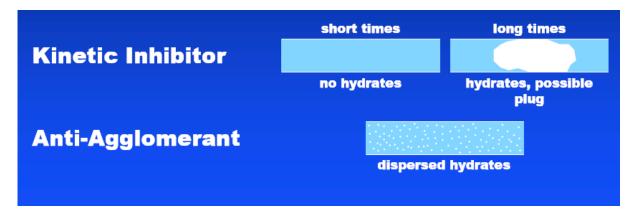


Figure 5 KHI vs. AA

There are a few types of surfactant that can be used as anti-agglomerant. They are divided to three categories:

- 1. Anionic surfactant
 - The head is negatively charged. Examples are carboxylates, sulfates and sulfonates
- 2. Cationic surfactant
 - The head is positively charged. Two common types are long chain amines and quarternary amine salts
- 3. Non-ionic surfactant
 - The head is polar, but not charged. The most common is polyoxyethylenated

AA molecules must have hydrophilic "head" attaching to a surface of hydrate particle and hydrophobic "tail" to repel other hydrate particles; thus, preventing hydrate agglomeration. All surfactants having hydrophilic and hydrophobic functionality have some AA particles.

2.4 Experiments

For this project, laboratory test will be conducted on different samples using Anti-Agglomerant inhibitors to examine the effectiveness on gas hydrate prevention. The apparatus for assessing the effectiveness of an Anti-Agglomerant inhibitors that will be used is differential scanning calorimetry (DSC).

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 constant (isothermal) temperature. The test will be conducted by cooling-and-heating waterin-oil emulsified samples that will be prepared. The anti-agglomerant will be added to the water phase at different concentrations. One of the advantages of using DSC is it allows sample to be tested in small scale and lower amounts of sample per test.

With this technique, heat transfer is measured as a function of time, temperature and pressure and thus detects the phase transition. From here, the approach to determine the anti-agglomerant inhibitor effectiveness in DSC is to use the first indication of onset of hydrate agglomeration. Comparison will be made with the emulsified system without anti-agglomerant added, so that the effectiveness of anti-agglomerant inhibitors to the effluent can be observed.

2.5 Industrial AA applications

An initiative on AAs began in the late 1980s in Norway within the statefunded PROFF research program. There are two projects on gas hydrates were included in the program. The first program was carried out at SINTEF, it studied the consistency of hydrates under flowing conditions. They observed that at a low water conversion, the hydrates were sticky and liable to agglomerate and deposit on the pipe walls. However, at high water conversion, the hydrates were a non-sticky powder that appeared to be transportable in the hydrocarbon phase. Thus, they concluded that if a chemical could be found to prevent the hydrates from agglomerating during the early stages of water conversion, it should be possible to produce transportable slurry of hydrates. (Kelland, 2006)

The second project in the PROFF program was at RF-Rogaland-Research. RF began screening additives in high-pressure cells to observe any inhibiting effects. The best product obtained from the studies was a quaternary corrosion inhibitor from Black smith, which showed some positive AA effect, but unfortunately the work was not taken further.

The mechanism of Shell's quaternary AAs (Figure 5) are designed with a hydrate-philic (hydrate seeking) headgroup and a hydrophobic tail. Being surfactants, the AAs will accumulate at the water-oil interface, where hydrate formation first occurs. The hydrophilic headgroup, which is the quaternary center, will bind to hydrate particles. The butyl/pentyl groups penetrate open cavities on the hydrate surface. The hydrophobic tail will also make the surface more attractive to the hydrocarbon phase.

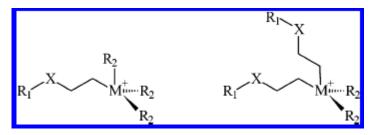


Figure 6 Structure of Shell's quaternary AAs (R1 = long chain hydrocarbon tail; R2 = n-butyl, n-pentyl, or isopentyl; M = N or P; X is an optional spacer group)

In addition, after a comprehensive laboratory evaluation, an AA was selected for field testing in a deepwater, Gulf of Mexico oil well. The product protected the system throughout the 1.5 month trial, including two brief shut-ins.

CHAPTER 3

METHODOLOGY

3.1 Research methodology

This project starts with title selection. 'Inhibiting Gas Hydration Using Surfactant' was the title chosen for the project. Then, the project continues with the prelim research. All the fundamental theories and concepts must be fully understood first before starting to find the literature review and also before identifying the tools that are needed.

The project continued with the detailed research. Here is where further research on gas hydrates inhibitor was made along with the data acquisition, procedures and also learned how to conduct the experiment for the project.

After all information collected, the experiment was conducted and all the results were recorded. The proper elements must be determined include conditions that favour gas hydrate formation, types of inhibitor and samples to be tested.

One condition that favours gas hydrate formation is presence of water or ice. Therefore, the experiment sample to be tested must be ensured to contain water composition. Other conditions that have been determined that could lead to formation of gas hydrates are high pressure and low temperature.

The next element that must be taken into account is the type of surfactant to be used as the anti-agglomerant gas hydrates inhibitor. The most common one is Sodium Stearate. Next is to consider the sample that will be tested for the experiment. The sample will be prepared with water and added with the antiagglomerant inhibitor.

After finish with the experiment, all the results were analysed and the most effective concentration of the surfactant was determined. Lastly, all research findings, literature reviews, experimental works and outcomes were compiled into a final report.

3.2 Experiment methodology

1. Apparatus

Differential Scanning Calorimetry (DSC) will be used to measure the thermal properties of the water-in-oil samples that will be prepared using the magnetic stirrer. This equipment is very versatile and efficient and the one that available in the laboratory is product of *Perkin Elmer*, *Pyris 1 DSC*.



Figure 7 Perkin Elmer Pyris 1 Differential Scanning Calorimetry (DSC)

DSC equipment will measure the amount of heat flow into the sample (endothermic) and away from the sample (exothermic) when the specimen undergoes thermal transition. The substance material is subjected to a controlled temperature program while the difference in energy inputs into a substance and a thermally inert reference material is measured as a function of temperature.

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

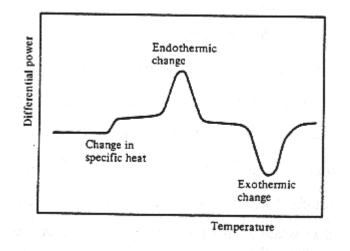


Figure 8 Schematic drawing of a typical DSC thermogram

2. Chemical

The surfactant that will be used as the anti-agglomerant inhibitor for this project is Sodium Stearate.

Chemical formula	Chemical name	Chemical structure
CH3(CH2)16COONa	Sodium Salt of Stearic Acid	"O Na"

3.3 Sample Preparation

Firstly, the water-in-oil emulsified will be prepared by using a magnetic stirrer. The anti-agglomerant will be added to the water phase at different concentration of 0.3, 0.5, 0.7 and 1.0 wt% of the total emulsion.



Figure 9 Hanna Instruments HI 180 E-1 Magnetic Stirrer - Compact

For every sample that will be prepared, each of them will be 100ml of total volume of the distilled water and the anti-agglomerant inhibitor which is the surfactant. Since 1ml is approximately equal to 1g, in order to determine the amount (mass) of the surfactant to be added to water phase, first the volume of the distilled water will be measured. For example for concentration of 0.3 wt% total emulsion:

	Mass (g)
Distilled water	99.7
Surfactant	Х

Simple calculation:

Total mass of surfactant = Total mass of emulsion – total mass of distilled water OR

The mass of surfactant required to prepare the 0.3 wt% concentration of sample was based on the sample calculation shown.

Weight percent = Weight of
$$\frac{solute}{solution} \times 100\%$$

$$0.3 wt\% = \frac{X}{99.7 + X} \times 100\%$$

$$0.003 = \frac{X}{99.7 + X}$$

$$X = 0.2991 + 0.003X$$

$$X = 0.3g$$

Concentration of surfactant in total emulsion	Surfactant required (g)
0.3 wt% surfactant	0.3
0.5 wt% surfactant	0.5
0.7 wt% surfactant	0.7
1.0 wt% surfactant	1.0

After the required amount of surfactant is known, the surfactant was added to the water and mixed with the magnetic stirrer. It took for about 2 hours to stir one sample. A total of 4 different concentrations of samples would be obtained, which are:

- Emulsion with 0.3 wt% surfactant
- Emulsion with 0.5 wt% surfactant
- Emulsion with 0.7 wt% surfactant
- Emulsion with 1.0 wt% surfactant

3.4 Mode of Operation

Once the samples are prepared, they will be extracted for the experimental tests using the DSC. About 5 to 10 mg of the sample will be placed into the sample cell. Then, the sample will be inserted by purified nitrogen at 25° C.

The sample will be cooled from 25° C to -30° C at a rate of 1° C/min. Then, the temperature will be increased back to 25° C. This cooling-heating process will be repeated three times to observe the effect of hydrate in the emulsion. This is also the first mode of operation for this project.

Another procedure is isothermal mode. This is where the sample will be cooled from 25° C to -30° C at a rate of 1° C/min and it will be held for about 6 hours. Upon the hydrate formation, the sample will be heated to dissociate the hydrates. This procedure will be repeated two times in order to observe the effect of hydrate in the emulsion.

For this project, ramped mode was used to conduct the experiment. The experiment result will be indicated in thermogram analysis of the parameters of heat flow (mW), temperature and time for all four samples tested.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Hydrate Formation in Emulsion

The ramped mode was used in the DSC to measure the effect of temperature of the formation of hydrate in the samples. Samples were cooled from 25° C to -30° C at a rate of 1° C/min, and heated back to 25° C. Figure 10 and Figure 11 below show the thermogram of the 4 samples.

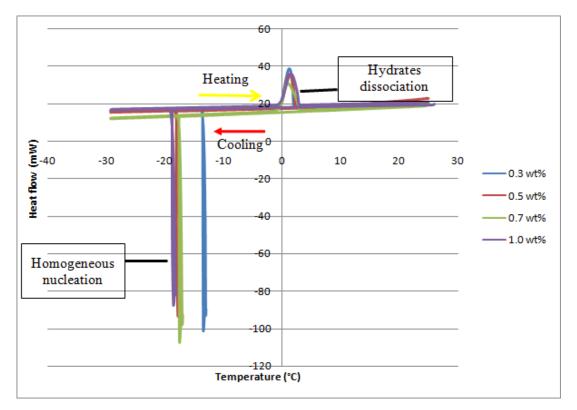


Figure 10 Hydrate formation and dissociation trends of emulsions through coolingheating process during ramped mode test in terms of temperature

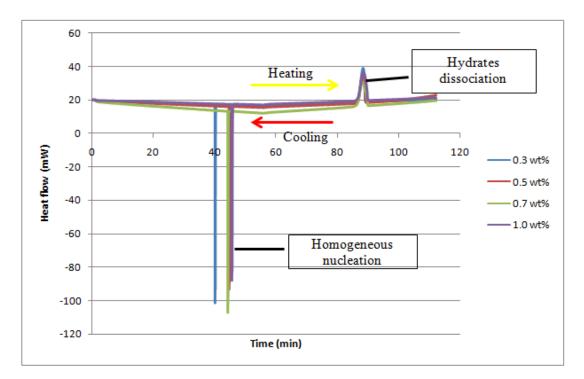


Figure 11 Hydrate formation and dissociation trends of emulsions through coolingheating process during ramped mode test in terms of time

Based on the trends above and in the comparison of the four different samples plotted, the hydrate of the concentration of 0.3 wt% emulsion sample starts to nucleate at the temperature -13°C during cooling process and took 40 minutes to dissociate. The homogeneous nucleation peaks shown are the indication of heat required by the samples in order to transform from liquid to solid phase which is to hydrate crystalline state. When the samples undergo heating process, hydrates of concentration of 0.3 wt% dissociated at the temperature of 0°C. This indicates another phase changes occurred which is from solid to liquid phase.

The ramped mode was also carried out on the other samples with 0.5 wt%, 0.7wt% and 1.0 wt% surfactant concentrations. The results yields are different from the 0.3 wt% surfactant concentration sample. But, this shows the tendency of one concentration that can be the most effective to inhibit gas hydrates by preventing agglomeration of gas hydrates crystals.

4.2 Anti-Agglomerant Inhibitor Effectiveness

Starting from concentration of 0.5 wt% emulsion sample, the hydrate nucleated at the temperature different from concentration of 0.3 wt% emulsion sample which is at temperature -17°C and so do the other samples, 0.7 wt% and 1.0 wt% concentrations of emulsions. On the other hand, the three samples took longer time to dissociate and based on the plotted graph, the time taken by the three samples are almost the same which is 45 minutes.

The changes in the concentration of surfactant do not have much difference compared to the 0.3 wt% emulsion sample. This implies that low concentration of anti-agglomerant inhibitor is required on inhibiting gas hydrates effectively. Furthermore, based on the time thermogram, the shorter time the gas hydrates take to nucleate, the better it is (Parlaktuna, 2000). Because, the faster the hydrates formation, the faster they can be dissociated. Thus, the most effective concentration of surfactant to be used as anti-agglomerant inhibitor will be 0.3 wt% of emulsion.

CHAPTER 5

CONCLUSION & RECCOMENDATION

5.1 Conclusion

Based on the researches, studies and experiments conducted throughout this project, it is crystal clear that the development and exploitation of surfactant as antiagglomerant inhibitor with probable hydrate formation at the condition of high pressure and low temperature especially in the pipelines has a great capability to improve the entire flow systems.

The results of the experiments obtained from the Differential Scanning Calorimetry (DSC) have verified the effectiveness of surfactant as anti-agglomerant inhibitor by increasing the nucleation time of the hydrates. Besides that, surfactant is most effective at low concentration of less than 0.5 wt%.

5.2 Recommendation

Anti-aggolerant inhibitor can prevent hydrate blockages in the pipeline and flowline for only few hours, rather than days or weeks. They also can eliminate the methanol toxicity issue that is obtained from the traditional method i.e.; Thermodynamic Hydrate Inhibitor (THI).

Modifications can be carried through changing the concentration of surfactant lower that 0.5 wt%. The emulsion sample may have 0.4 wt%, 0.2 wt% or 0.1 wt% surfactant concentration. However, this requires further verifications from the laboratory tests and field applications.

REFERENCES

Alain Graciaa, Christophe Dicharry, Marie L. Zanota, "*Hydrate Plug Prevention by Quaternary Ammonium Salts*" paper Energy & Fuels, 2005.

Divya Ramaswamy, Mukul M. Sharma, "The Effect of Surfactants on the Kinetics of Hydrate Formation",

http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-141226-MS&societyCode=SPE [accessed 29/10/2011].

J.L. Przybylinski, L.M. Frostman, "Successful Applications of Anti-agglomerant Hydrate Inhibitors" paper SPE 65007, 2001.

L.A. Dybvik, M.A. Kelland, T.M. Svartaas, "Control of Hydrate Formation by Surfactants and Polymers", paper SPE 28506, 1994.

L.M. Frostman, "Anti-Agglomerant Hydrate Inhibitors for Prevention of Hydrate Plugs in Deepwater Systems",

http://www.onepetro.org/mslib/servlet/onepetropreview?id=00063122&soc=SPE [accessed 29/10/2011].

Lynn M. Frostman, "Anti-Agglomerant Low Dosage Hydrate Inhibitors (LDHI's)", http://www.coqa-inc.org/add20010531LDHI.pdf [accessed 29/10/2011].

Mahmut Parlaktuna, Ugur Karaaslan, "*Surfactant as Hydrate Promoters?*", paper Energy & Fuels, 2000.

Malcolm A. Kelland, Thor M. Svartaas, Jorunn Øvsthus, Takashi Namb, "A New Class of Kinetic Hydrate Inhibitor",

http://www.iris.no/internet/student.nsf/199f312efd2a0cacc125680e00635b85/b58dc b01591e3feac125768f004f4a66/\$FILE/Fagernes%20paper.pdf [accessed 29/10/2011].

Marek Pakulski, (2007) "Accelerating Effect of Surfactants on Gas Hydrates Formation", paper SPE 106166.

Wikipedia, "Clathrate Hydrate", <u>http://en.wikipedia.org/wiki/Clathrate_hydrate</u> [accessed 29/10/2011].