Production of Methane Hydrate Inhibitor:

Study on N-Methyl-2-Pyrrolidone as Kinetic Hydrate Inhibitor

By

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CERTIFICATION OF APPROVAL

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Approved by,

(Siti Sarah Binti Salehudin)

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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.

(WAN IMRAN SYAHMI BIN WAN ZAINUDDIN)

ABSTRACT

This paper discuss on effectiveness of N-Methyl-2-Pyrrolidone (NMP) as kinetic hydrate inhibitor compared to Polyvinylpyrrolidone (PVP). Through the experiment, hydrate phase equilibrium of pure methane, NMP and PVP are determined. This will help in understanding the phase equilibrium behavior and effect on the phase equilibrium line using different inhibitor; NMP and PVP.

Due to insufficient experimental data for this study in open literature and methane hydrate plugging with regard to pipeline flow assurance matter, it has made production of hydrate inhibitor study is important in order to deal with hydrate formation in pipeline. The experiment is carried out by using HYDREVAL equipment in high pressure and low temperature to obtain the phase equilibrium of NMP and PVP.

The findings of this study will give better design of industrial operation in such a way that prevention of gas hydrate formation can be achieved by understanding the behavior of gas hydrate and inhibitor.

ACKNOWLEDGEMENT

First and foremost, praise to Most Graceful, Allah SWT as for his blessings and guidance, through high and low, I am able to complete my final year project without any difficulty. I would like to extend my gratitude to both of my parents for praying towards my success and continuously supporting and encouraging me on any decision been made.

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ABBREVIATIONS AND NOMENCLATURES

1. KHI = Kinetic Hydrate Inhibitor
2. LDHI = Low Dosage Hydrate Inhibitor
3. MEG = Mono – Ethylene Glycol
4. NMP = N-Methyl-2-Pyrrolidone
5. PT Diagram = Pressure-Temperature Diagram.
6. PVP = Polyvinylpyrrolidone

CHAPTER 1: INTRODUCTION

1.1. Background of Study.

Methane hydrate formation is one of flow assurance problem in which methane hydrate plug pipeline flow through its ice – like structure. Methane hydrates are made up of interconnected water molecule through hydrogen bond which creates an open structural lattice that has the ability to encage smaller guest molecule which is methane. There are three main concerns of methane hydrate on flow assurance problems; factors of methane hydrate formation, risk of methane hydrate formation in pipeline and prevention methods of methane hydrate formation in pipeline.

Pipeline rupture and blockage are examples of the effect of hydrate presence in pipeline. This effect can leads to high maintenance cost as well as reduction in generating revenue. Nowadays, inhibitors are usually viewed as one of the solution to prevent hydrate formation in pipeline. Injection of hydrate inhibitor inside the pipeline results in hydrate equilibrium curve shift towards lower temperature which creating smaller hydrates stability zone and eventually greater hydrate free zone. Hydrate dissociation will occurs once the operating point of the system operates under hydrate free zone.

Methanol and glycol are commonly used as thermodynamic inhibitor and polyvinylpyrrolidone (PVP) has been proven to be an effective kinetic hydrate inhibitor. N – Methyl – 2 Pyrrolidone (NMP) often been used to extract hydrocarbon in petrochemical plant. However, NMP has never been used as kinetic inhibitor to control hydrate formation in pipeline. Thus, the effectiveness of NMP as kinetic inhibitor need to be studied and understood in order to provide viable solution for methane hydrate control.

1.2. Problem Statement.

Rapid growth of methane hydrate in pipeline may block the flow – path, rupture the pipeline as well as form ice balls that can acts like dangerous projectile motion while being remediated.

Although thermodynamic inhibitor such as methanol and mono – ethylene glycol (MEG) is effective in preventing methane hydrate formation in a pipeline, the concentration of methanol and MEG need to be added is high as well as costly. Alternatively, low dosage hydrate inhibitor (LDHI) such kinetic inhibitor is able to provide smaller volume used to inhibit methane hydrate. Since the concept of LHDI works at low dosage rates, a study on chemical that can works as kinetic hydrate inhibitor (KHI) is required in order to reduce the occurrence of methane hydrate in pipeline.

1.3. Objectives.

1. To investigate effectiveness of NMP as KHI at different range of pressure and temperature.
2. To determine the optimum concentration of NMP as KHI in lab scale.
3. To compare and evaluate the effectiveness of NMP with commercial hydrate inhibitor, PVP in process of hydrate dissociation.

1.4. Scope of Study.

This project requires a comprehensive understanding on formation of methane hydrate in terms of factors lead to methane hydrate formation, associated risk of methane hydrate formation is pipeline as well as efficient and economical prevention methods. The area of focus for this project is prevention of methane hydrate in pipeline. Three types of hydrate exist; thermal control, depressurization and chemical hydrate inhibitor. However, chemical hydrate inhibitor will be the main focused of this study. There are two type of hydrate inhibitor which is thermodynamic inhibitor and LHDI. NMP and PVP are used to serve as LHDI and thus effectiveness of NMP as KHI are being studied and experimented.

Lab work will be carried out to prove the effectiveness of the NMP as KHI. Weight percent usage of NMP in this study must less than 1 wt% in order to satisfy the concept of LDHI. HYDREVAL equipment is used to measure hydrate phase behavior while observing hydrate formation. This equipment is designed to determine hydrate thermodynamic stability experimentally into oil and gas phase.

CHAPTER 2: LITERATURE REVIEW

Successfully transporting hydrocarbon stream from field to processing plant is very crucial in oil and gas industry. Ensuring flow assurance of a pipeline which is used to transport multiphase fluid is very challenging task when dealing with formation of hydrate in the pipeline. Unlike ice, hydrates are able to solidify above 0 °C at a given pressure [1].

2.1. Hydrates.

Clatharites, from the Latin word for 'cages' which another name for gas hydrates are crystalline compound formed by water and light hydrocarbon. The hydrates are ice – like crystals compose of 'cages' of water which referred as host molecules surround the 'guest molecule' which is hydrocarbon. Examples of guest hydrocarbon are methane, ethane, butane and propane. Although the guest molecule is contained in cages of host molecule, there is no bonding exist between each other. Thus, the guest molecules are free to rotate inside the cages built up from the host molecule [10].

In order for hydrate to form, it requires three conditions:

1. High pressure and low temperature.
2. Guest molecule or also known as hydrate former.
3. Host molecule – water.

Hydrates cannot form if they does not meet one of the condition as per mentioned. Thus, by eliminating any of the three conditions, formation of hydrate in pipeline can be prevented. With regards to flow assurance case, guest molecule – natural gas in pipeline is the desired product. Therefore, eliminating the other two conditions is the best option in flow assurance case.

According to Carrol (2003), there is other phenomenon that enhance the hydrate formation; turbulence, nucleation site and free-water. Turbulence phenomenon occurs in two ways which is high velocity and agitation. Hydrate formation is favored in regions where the fluid velocity is high [10]. By observing the hydrate formation curve, region on left of the curve shows the hydrate formation region while region on the right is hydrate free region [1].

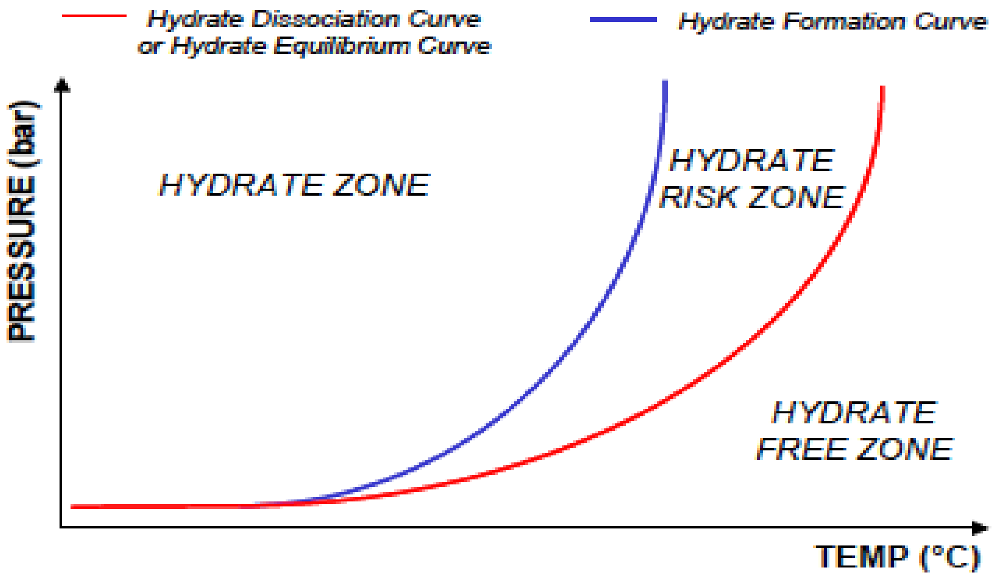

Figure 1: Hydrate formation curve [1].

Hydrates are being categorized by water molecules arrangement in crystal structure. There are three basic hydrate structures to form from natural gases, structure I (sI), structure II (sII) and structure H (sH) [11]. Normally, sI and sII is the most commonly encountered in petroleum business. In general, sI is formed by small molecule such methane or ethane while sII is formed by guest molecule that is bigger than sI guest molecule such as propane and iso-butane. As for sH, larger molecule such iso-pentane form the hydrate structure.

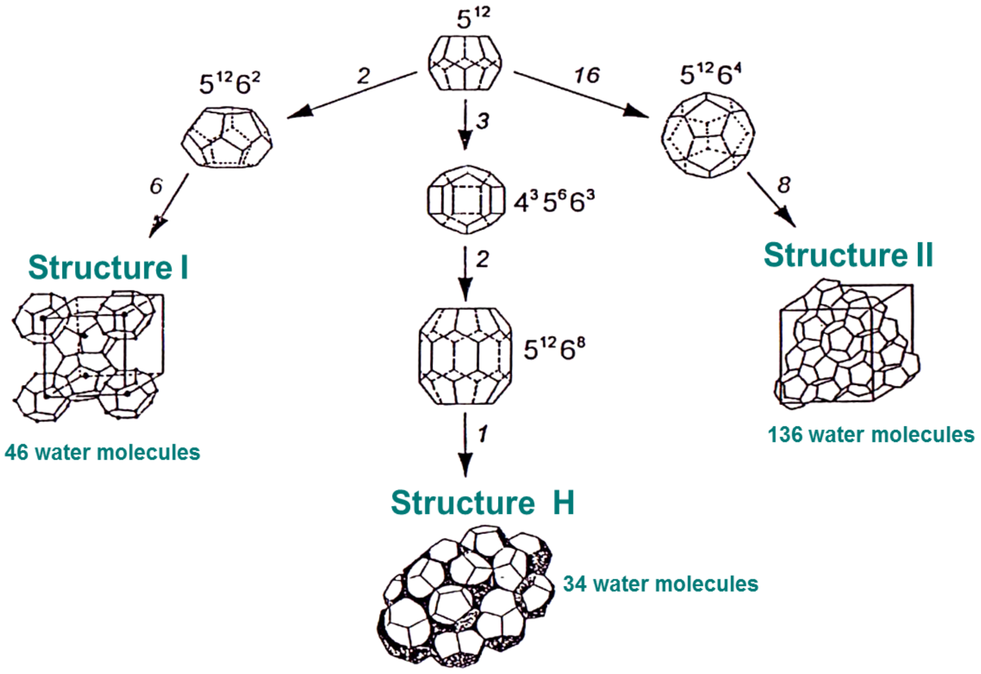

Figure 2: Hydrate structure.

Even though gas hydrate is being considered as problematic in flow assurance case, gas hydrate is actually unconventional source of energy. According to Makogon (2005), potential reserves of gas hydrate are over 1.5 x 10^{16} m^3 and are distributed all over the world either onshore or offshore. Hydrate production however, they face with significant challenges due to the hostile environment in which they exist [12].

2.2. Risk of Hydrate Formation.

Accumulation of solid is one the significant aspect of hydrate formation. This aspect however, it creates problem in flow assurance matter. This is because, same as pure ice, hydrates are able to clog pipeline and hence reduce the flow rate of fluid transport or even worse is damaging equipment. Transient operations such as start – up, shutdown and blowdown are very much likely to trigger the hydrate blockages as this is when temperature of the production system starts to shift into hydrate formation region.

Several risks that commonly associated with hydrate formation are as follows:

- Subsea equipment such as valve and manifold will damage if left un-insulated when hydrate formation occurs.
- Hydrate formation risk increase in long – distance pipeline and remediation process will becomes more complicated because of water holdup location accuracy. Hydrate blockages are common along low spot as water is allowed to accumulate.
- Pipeline rupture may occur if multiple hydrate formation exist and cause trapped pressure.
- Hydrate formation will exist during cold well start – up until the well reach sufficient warm temperature from production. Chemical injection is required to maintain hydrate free zone.
- During depressurization, hydrate may acts as ice ball in projectile motion that can cause rupture at pipeline and subsea equipment.

2.3. Hydrate Countermeasure.

Pigging is one of the common processes used to remove small amount of hydrate from pipeline. Pig tool is used in the pipeline mainly to clean the pipeline in which the tool fits nicely in the pipeline and scrapes solid in it. Examples of solid are hydrate, wax and dirt.

Preventing hydrate formation can be achieved through three methods; heat, depressurization and hydrate inhibitor. Buried pipeline resulting in heat loss to the surrounding as the fluid flows. Thus, it is important to ensure that, there is no point in the pipeline falls in hydrate formation region. Thermal control is one of heat method to prevent hydrate which provides sufficient insulation on the pipeline and subsea equipment that keeps the temperature of the pipeline and equipment from falling under hydrate formation zone. Sufficient cooldown time also necessary in the thermal control system in case of unplanned shutdown operation.

Hydrate formation can be prevented by reducing the pressure. Reducing the pressure will put the hydrate in unstable phase. This will allow the hydrate to melt but it requires some time for the hydrate to melt. Although this method is possible, it has a major drawback if safety precaution is not been taken into account. Depressurized hydrate can be in projectile shot when a connection is uncoupled for inspection.

As for hydrate inhibitor, chemical is used to prevent formation of hydrate particle by shifting the hydrocarbon equilibrium which resulting in less severe hydrate formation condition. It is important to note that hydrate inhibitor does not prevent hydrate formation but it just inhibit it. Small amount hydrate inhibitor need to exist in the pipeline to prevent hydrate accumulation.

As been stated before, hydrate inhibitor can be classified into two groups, thermodynamics inhibitor and LHDI. Thermodynamic inhibitor tends to shift the hydrate condition to less severe condition by chemical potential alteration of aqueous phase resulting in lower temperature and higher pressure of hydrate dissociation curve. Methanol injection rates on the order of 0.15 to 1.5 m^3/day (1 to 10 barrel per day) are common in petroleum business [10]. Even though the amount seems quite small, but it is costly.

As for LHDI, the chemical dosage that usually used is 1/10 of the volume thermodynamic inhibitor. KHI is one example of LHDI and it works by preventing crystal from forming or in other words nucleation prevention which allowing fluids to be cooled below actual freezing point without crystallization.

2.4. Polyvinylpyrrolidone.

PVP is commonly used synthetic polymers as kinetic inhibitor for gas hydrate formation. [7] PVP consists of five lactam rings which attached to carbon backbone and soluble in water. Other than that, PVP did not hydrolyze to insoluble compound as well as adsorb well on hydrate micro crystals polar surface. This characteristic made the PVP is able to prevent the hydrate formation by eliminating the water which is the host molecule for hydrate formation.

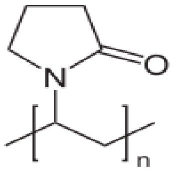

Figure 3: PVP structural formula.

2.5. N-Methyl-2-Pyrrolidone.

NMP is a chemical compound that has five membered lactam rings that is soluble in water. In downstream business, NMP is used to retrieve pure hydrocarbon while processing petrochemical. Other than that, NMP is also hydroscopic which means that it tends to take up water from its surrounding. In processing petrochemical, the treated hydrocarbons are usually produced in contact with water vapors which leads to hydrocarbon produced contain dissolve water. The dissolve water is than will be eliminated by NMP when refining the hydrocarbon. [8]

Moreover, NMP is stable, basic substance which is polar and however there is no possibility of hydrogen bonding. This will probably ensure that the NMP will not form host molecule for hydrate formation. The facts that NMP is able to retrieve hydrocarbon and it has great solvency properties, there is possibility that NMP is able to act as KHI in reducing hydrate formation occurrence in pipeline.

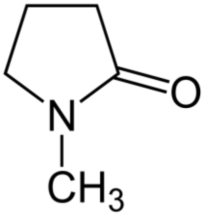

Figure 4: NMP structural formula.

CHAPTER 3: METHODOLOGY

3.1. Research Methodology.

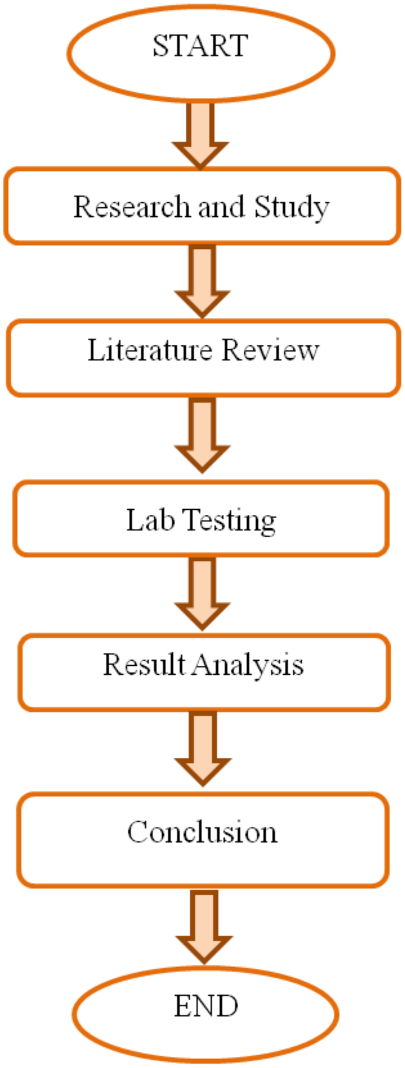

Figure 5: Flow chart of research methodology.

3.2. Project Activities.

Table 1: Project activities and its description.

Activities	Descriptions
Research And Study	• Research on methane hydrate formation, hydrate dissociation curve. • Research on chemical properties on N – Methyl – 2 Pyrrolidone (NMP) and its behavior.
Lab Testing	• Perform experiments on N – Methyl – 2 Pyrrolidone (NMP) with hydrate using HYDREVAL equipment • Manipulation of NMP concentration with respect to hydrate dissociation time taken.
Result Analysis	• Analyze the efficiency of N – Methyl – 2 Pyrrolidone (NMP) as kinetic hydrate inhibitor.

3.3. Gantt chart.

Table 2: Gantt chart of Final Year Project II.

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
2	Submission of Progress Report							🟩							
3	Project Work Continues								🟩	🟩	🟩	🟩	🟩		
4	Pre-SEDEX										🟩				
5	Submission of Draft Final Report											🟩			
6	submission of Dissertation (Soft Bound)												🟩		
7	Submission of Technical Paper												🟩		
8	Viva													🟩	
9	Submission of Project Dissertation (Hard Bound)														🟩

3.4. Equipment Required

3.4.1. HYDREVAL Equipment

In this experiment, HYDREVAL equipment can be used determine formation and dissociation of hydrates condition and evaluate inhibitor effectiveness. The equipment is designed to determine experimentally thermodynamic stability of hydrates into melted hydrocarbon. The equipment is based on motor driven PVT cell which can be used in different configuration to run the required test. The equipment chamber is enclosed at one end by the piston of embedded pump and the other by a dedicated cell head made from titanium alloy. The piston is equipped with a magnetic driven stirrer for homogeneous mixing of sample [13].

The following are the equipment specification.

Table 3: HYDREVAL equipment specification

Equipment:	HYDREVAL equipment
Temperature range:	-60°C to 150°C
Temperature accuracy	± 0.1°C
Pressure	3000 Psi
Pressure accuracy	0.1% Full scale
Cell Volume	60 cc
Volume accuracy	0.01 ml
Stirring mechanism	Magnetic drive
Power Requirements:	220 VAC, 50 Hz

Figure 6: HYDREVAL equipment.

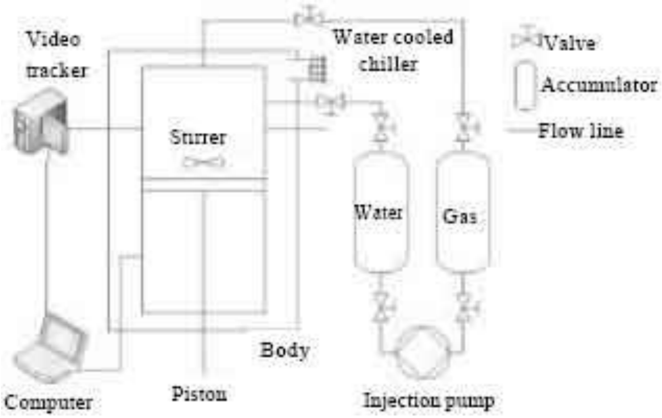

Figure 7: Schematic diagram of HYDREVAL equipment.

Parameters such pressure, temperature and volume can be monitored and observed through available software for interpretation.

3.5. Materials

NMP, PVP and distilled water will be used to prepare the sample. Below are the formula used to prepare 1.0wt% of NMP and PVP.

$$1wt\% = \frac{1.0g\ of\ sample}{mass\ of\ solution} \times 100\% \qquad Equation\ (1.0)$$

Note that the mass of solution is the summation of 1g of sample and mass of distilled water which is equivalent to 100 g. Therefore, the mass of distilled water need to produce 1wt% of NMP and PVP solution is 99g.

3.6. Experimental Procedure.

1) 1wt% solution of NMP was prepared by using equation (1.0).
2) NMP and distilled water were mixed and stirred by using magnetic stirrer. The magnetic stirrer was set at 600 rpm in order to allow NMP dissolve in distilled water.
3) Sapphire cell was washed and ensured to be free from any fluid left inside it.
4) Prepared sample was loaded into the HYDREVAL tank which is connected to sapphire cell.
5) Volume of sapphire cell was set to 55cc.
6) 25cc of prepared sample was loaded above the piston by using pump to fill empty volume above piston and the piston was set to 80cc. 55cc of methane gas was loaded into the empty volume above the piston once the prepared sample has been loaded.

7) The experiment begins with initial set pressure of 30 bar (435 psig). The pressure can be control by pressure gauge at gas tank and the equipment was left for two hours in order to ensure the pressure is fully stabilize and no leakage occurred around the sapphire cell.
8) Temperature range was set while the pressure was stabilizing. The temperature setpoint for 30 bar are as follows:

Table 4: Temperature setpoint for Pressure = 30 bar.

Temperature setpoint (°C)	
7	1
5	1.3
3	1.5
1	1.7
0	2.6
-1	3
-4	3.5
-5	4
-4	4.6
-3	5
-1	6
0	7
0.8	

9) Stirrer was switched on once the pressure has stabilized. This is to ensure methane gas and prepared sample is mixed to form hydrate. The equipment will measured temperature and pressure at every temperature setpoint. The experiment ends once all temperature set point has been measured.
10) Repeat step 7 till step 9 for pressure at 60 bar (870psig) with the following temperature setpoint.

Table 5: Temperature setpoint for Pressure = 60 bar.

Temperature setpoint (°C)	
14	8.4
10	8.6
7	8.8
4	9
2	9.5
3	10
4	10.4
5	11
6	11.6
7.2	12
7.4	12.3
7.6	12.8
7.8	13
8	13.4
8.2	14

11) Graph obtained from the software was analyzed to get the equilibrium point (pressure and temperature).

CHAPTER 4: RESULTS AND DISCUSSION

Equilibrium Point Measurement For Presence of NMP In Methane Hydrate.

Equilibrium data for presence of NMP in methane hydrate was obtain and measured from HYDREVAL once all temperature setpoint has been measured by the equipment for 30 bar and 60 bar respectively. The measured data is then was plotted in order to determine the equilibrium point for both pressure at 30 bar and 60 bar. In figure 8, pressure-temperature (PT) diagram shows the equilibrium point at which the two intersection points meet. Each equilibrium point for pressure at 30 bar and 60 bar are as follows.

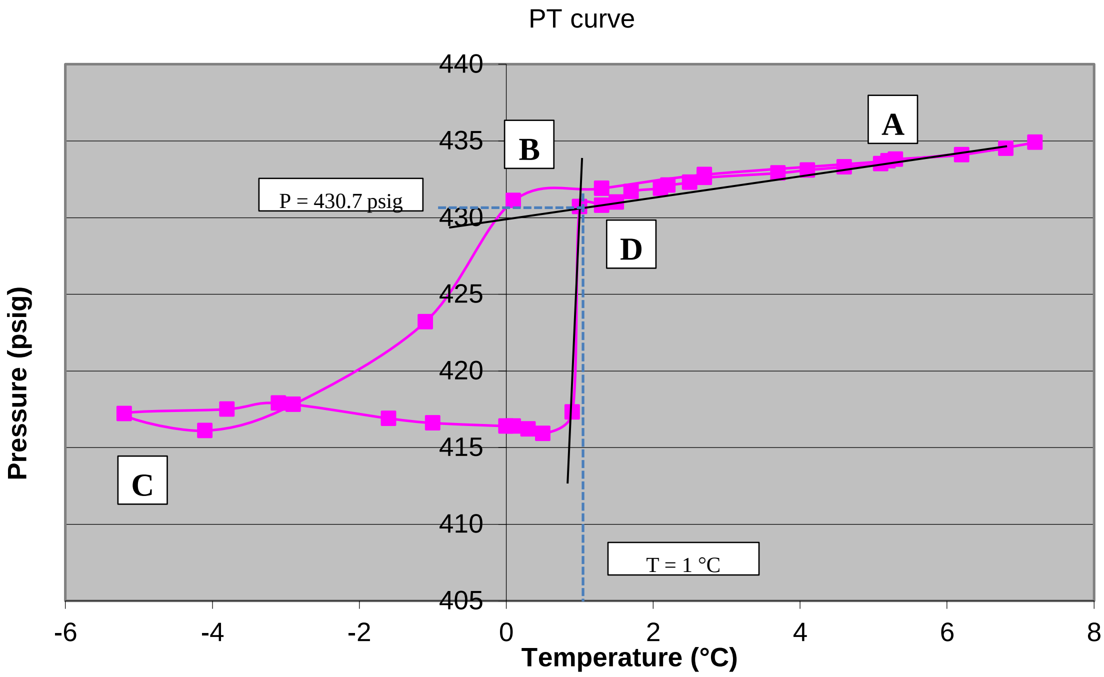

Figure 8: PT diagram of 1wt % NMP with methane at 30 bar.

Table 6: Measured equilibrium point of NMP.

Chemical	**Concentration (wt %)**	**Measured Pressure (bar)**	**Measured Temperature (K)**
NMP	1	29.696	274.15
		60.000	281.25

Figure 8 shows the result of measured pressure and temperature 1 wt % NMP with methane hydrate at 30 bar. In figure 8, as temperature decreases from point A to point B, energy loss of gas inside the sapphire cell results in reduction in pressure. Transition from point A to point B is determined as cooling process. The diagram shows that there is significant drop in pressure from point B to point C. This is due to methane gas in the sapphire cell has been formed into hydrate. This is point whereby hydrate growth occurs.

Once the temperature starts to increases (heating process occurs) from point C, methane hydrate formed in the sapphire cell start to dissociate. The intersection at point D is determined as the equilibrium point of hydrate dissociation. In figure 8, the measured temperature and pressure for 1 wt% NMP with methane hydrate at 30 bar are 274.15 K and 29.696 bar (430.7psig) respectively.

In figure 9, volume-temperature diagram of 1 wt% NMP with methane hydrate shows that there no change in total volume although the temperature is changing. Therefore, the diagram indicates that the volume is constant throughout occurrence of hydrate formation and dissociation in the sapphire cell.

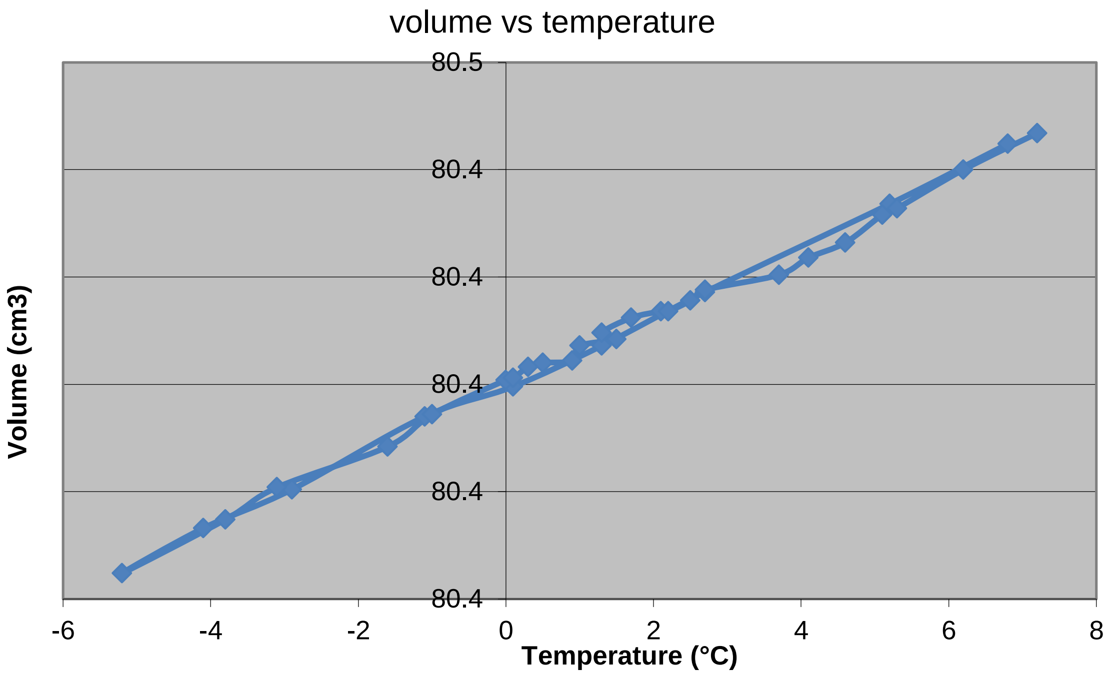

Figure 9: Volume-Temperature diagram of 1wt % NMP with methane gas.

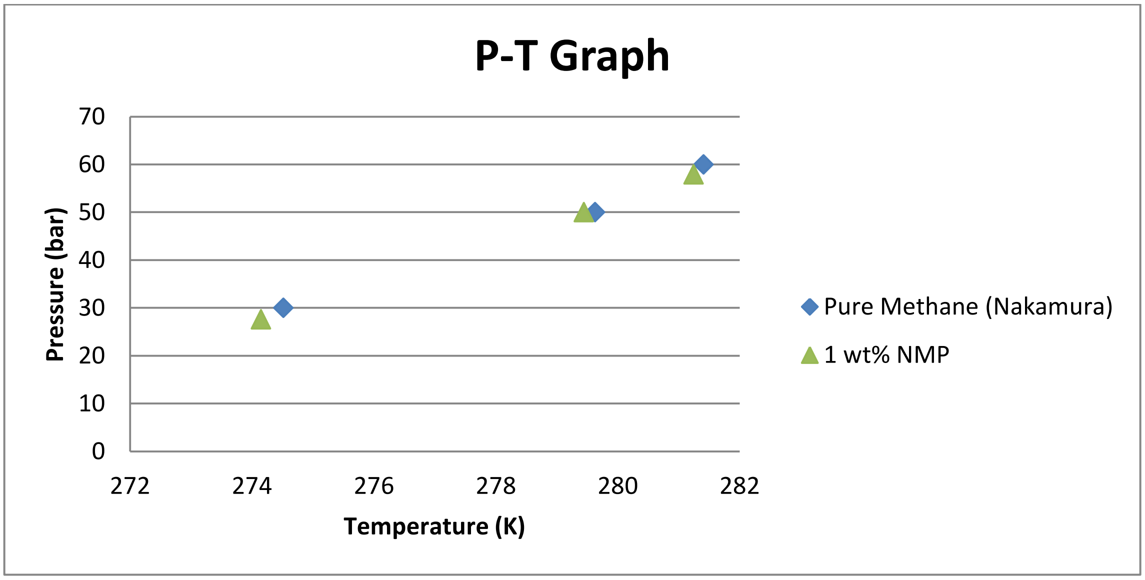

Figure 10: 1wt % NMP with methane hydrate phase boundary.

Figure 10 shows the phase diagram of 1wt % NMP plotted with pure methane phase diagram. From the phase diagram, the two plot were made to observed the effect of 1wt% NMP phase boundary shift with the pure methane phase boundary. From the observation, 1wt % NMP temperature boundary shifted slightly to the left as the pressure is increasing. Note that, area under the phase boundary is note as hydrate free zone while area above the phase boundary is hydrate stability zone. Since 1wt % NMP temperature boundary shifted slightly to the left of pure methane phase boundary, this has widened the area of hydrate free zone and eventually reducing the area of hydrate stability zone. Therefore, it is proven that NMP at 1wt % able to serve as KHI.

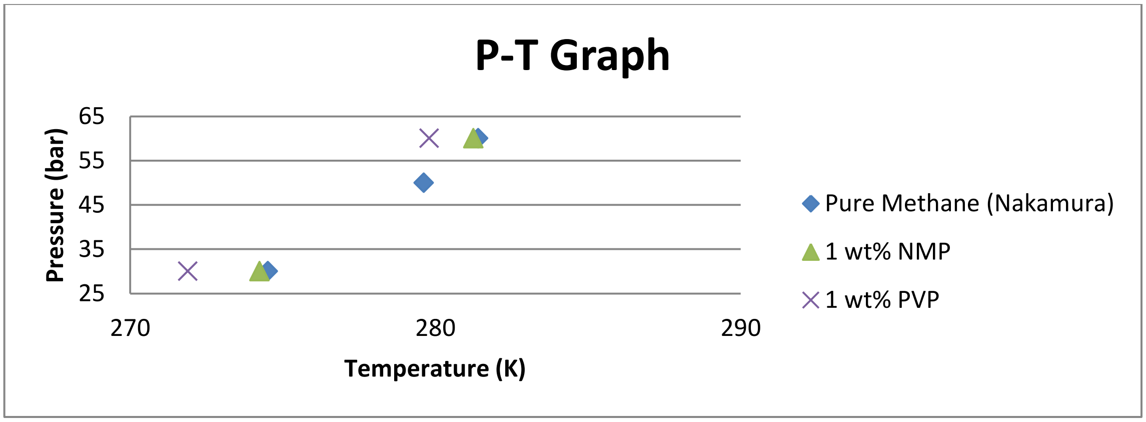

Figure 11: Phase boundary comparison between NMP, PVP and pure methane.

Comparison of 1wt % NMP, 1wt % PVP and pure methane phase boundary are being showed in figure 11. In figure 11, it is clearly seen that although 1wt % NMP are able to shift the phase boundary to the left of pure methane phase boundary, it is not as efficient as 1wt % PVP which yield greater shift phase boundary.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

As for conclusion, flow assurance play big roles in delivering profitability of a company and ensuring fluid transport from field to consumer runs smoothly is a major task to be carried out. Thus studies on KHI become more crucial as it able to prevent hydrate blockage in the pipeline and subsea equipment. This will eventually reduce the amount time used to maintain and repair the damage done due to hydrate formation as well reducing cost of repairing or replacing new pipe and equipment for fluid transport.

Although methane hydrate is viewed as one of the common flow assurance problem, methane hydrate also being viewed as new source of fuel. This is due to each volume of gas hydrate is equivalent to 189 volume of gas at standard condition. It is highly recommended that in the near future studies on production of methane hydrate at medium deep sea sediments and permafrost region are made for better understanding and technology development.

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