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TITLE: THE KINETICS OF GAS HYDRATE FORMATION USING SODIUM DODECYL SULPHATE AS THE PROMOTER

PREPARED BY:
MUHAMMAD SHAFIQ BIN MOHAMED ARIFF (13739)

SUPERVISOR: DR. BHAJAN LAL

Dissertation submitted in partial fulfillment of the requirements for the Bachelor of Engineering (Hons) (Chemical Engineering)

May 2014

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

The Kinetics Of Gas Hydrate Formation Using Sodium Dodecyl Sulphate As The Promoter

by

Muhammad Shafiq bin Mohamed Ariff

13739

A project dissertation submitted to the Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL)

Approved by,

____

(Dr. Bhajan Lal)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

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 the original work contained herein have not been undertaken or done by unspecified source or persons.

MUHAMMAD SHAFIQ BIN MOHAMED ARIFF

ABSTRACT

This final year project will be studying on the kinetic formation of gas hydrates using sodium dodecyl sulphate as the promoter. This report encompasses of background study, problem statement, objectives and scope of study, literature review on gas hydrates and SDS, proposed methodology for carrying out the experiment, project timeline management and lastly conclusion. Our main problem statement is the increasing greenhouse gas emission and the energy intensive carbon dioxide capture calls for a cheaper and more effective alternative. Furthermore, depleting fossil fuels also seeks for alternative energy source. Gas hydrate is seen to have a high potential for carbon dioxide capture and as well as an energy source but unfortunately the current rate of hydrate formation is not in favour of time. Hence, this project studies gas hydrate formation kinetics to increase its formation rate by using promoters. This project is mainly about identifying the optimum concentration of Sodium Dodecyl Sulphate as the promoter for gas hydrate formation. The gas involved in this experimental work is carbon dioxide and methane. This is identified by calculating the induction time of gas hydrate formation and apparent rate of formation of gas hydrate at different SDS concentrations. At the end of the experiment, the data collected will enable us to understand better on how carbon dioxide and methane hydrate can be produced and are believed to be used for in-situ carbon dioxide sequestration through methane hydrate dissociation. Through two semesters of experimental work, which the first half denotes a deeper understanding of the theories of kinetics of gas hydrate whilst the second half will encompass the experimental work to address the problem statements identified.

ACKNOWLEDGEMENT

This final year project would not have been possible without the support of many people. The author wishes to express his gratitude to his supervisor, Dr. Bhajan Lal and Behzad Partoon for their patience, motivation, enthusiasm and continuous support of this hydrate study. Their guidance helped the author in all the time in writing of this thesis. The author would like to express his appreciation and very special thanks to them for their guidance, support and valuable advices throughout this project.

The author also wishes to express his appreciation to all of his fellow friends, for their helps and supports throughout this project. His sincere appreciation also extends to all of his colleagues and others who have provided assistance at various occasions.

In addition, the author would also like to convey million thanks to Universiti Teknologi Petronas for providing the financial means and laboratory facilities in Carbon Dioxide Capture Research Centre.

Last but not least, the author wish to express his love and gratitude to his beloved families for their understanding and endless love, through the duration of his studies.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Gas hydrates is an interesting field to explore mainly because of its potential to become an excellent gas storage facility, future energy source, and the use of the dissociation energy in refrigeration processes. In Malaysia, our rapidly growing oil and gas industry has been contributing to more greenhouse gases. It is believed that this project will soon address the possibility of carbon dioxide sequestration and to transport methane, an energy source in hydrate form.

Since the beginning of the 20th century, the production of natural gas has encountered difficulties with the plugging of piping by the deposition of crystals, first thought to be ice crystals. These crystals are in fact hydrates of natural gas which can appear far above the temperature at which ice is formed. They are inclusion compounds which result from the combination of water with some of the components of natural gas, and primarily methane.

Gas hydrate formation can be promoted using surfactant chemicals such as Sodium Dodecyl Sulphate. Surfactants lower the surface tension between the gas and water interface and allows for quicker gas hydrate formation.

1.2 Problem Statement

Gas hydrate certainly has its own drawbacks. According to Hammerschmidt, water vapor in natural gas is a nuisance to the flow of gas as it gets plugged due to hydrate formations at a relatively higher temperature than normal freezing point of water (Hammerschmidt, 1934). Hence, gas hydrates blocks pipelines and increases pressure that may lead to blowouts and leakages. Natural gas hydrates for an example is a real threat to the environment. Exploitation of these methane hydrates at unfavorable circumstances could damage the marine ecosystem and global warming could raise the hydrate temperature above equilibrium point and induce release of harmful methane (Chatti, Delahaye, Fournaison, & Petitet, 2005).

In whole, the bigger problem that the oil and gas industry facing is the ever increasing greenhouse gas emission. To overcome this, although there are various ways of carbon dioxide capture, they are mostly energy intensive. Through gas hydrate formation, carbon dioxide capture is seem plausible. Unfortunately, another obstacle in this potential method is the rate of gas hydrate formation that takes more than 3 days. (Mohebbi & Behbahani, 2014).

1.3 Objectives

This project aims to study the kinetics of gas hydrate formation using sodium dodecyl sulphate as the promoter. The objectives of this project are:

i) To study the gas hydrate formation mechanism.
ii) To study the influence of SDS as a promoter for gas hydrate formation.
iii) To determine the concentration of SDS that is optimum for gas hydrate formation.
iv) To produce methane hydrate and/or carbon dioxide hydrate using SDS as the promoter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Gas Hydrate

Gas hydrates are crystalline solid compounds each consisting of host water molecules forming a cage-like structure and guest molecules encaged in the structure (Watanabe, Imai, & Mori, 2005). In simple terms, gas hydrates are solid solutions made up of mostly water molecules and gas molecules. The unique property of a hydrate is that the water and gas molecules is not chemically bonded but rather hold by Van de walls forces as way to minimize Gibbs free energy.

Water molecules are made up of hydrogen bonding and creates cavities (host lattice) that can enclose a large variety of molecules (guests). Gas hydrates can conveniently form either below or above the normal freezing point of water. Hydrates occurring naturally in the earth containing mostly methane are regarded as a future energy resource. Although, methane a greenhouse gas will cause a detrimental effect to the environment if it decomposes. Gas hydrates has also been a major problem in the oil and gas industry because the conditions at which they are produced, transported and processed are frequently suitable for gas hydrate formations (Englezos). Natural gas molecules consists of methane, ethane, propane and carbon dioxide (Sloan Jr & Koh, 2007).

2.2 Structures of Gas Hydrates

Gas hydrates have unique structures which is known as cubic structure I (s1), cubic structure II (sII) and hexagonal structure H (sH) as shown in Figure 1. Molecules smaller than 6Å such as methane, ethane, carbon dioxide and hydrogen sulphide makes structure I. Structure II consists of larger molecules (6 Å<d<7Å) such as propone and iso-butane with exception of nitrogen and smaller molecules (d<4.2 Å) that forms as single guests. Structure III (7Å<d<9Å) is of larger molecules such as iso-pentane and neohexane provided in the presence of smaller molecules such as methane, nitrogen and hydrogen sulphide. (Sloan Jr & Koh, 2007) The size of cavities and it's ratio between the large and small cavities distinguishes them from one another.

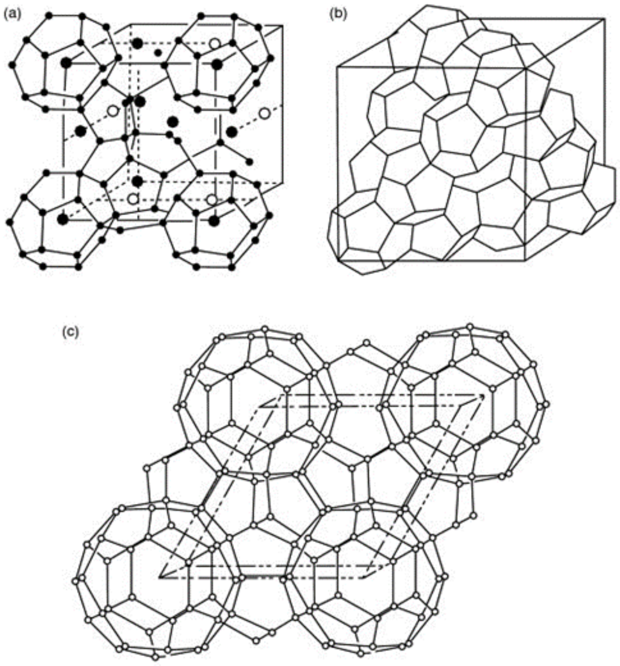


Figure 1: a) Cubic Structure I b) Cubic Structure II c) Hexagonal Structure (Image adapted from Sloan 2007)

Figure 2 also shows the three structures of the gas hydrate in a detailed layout.

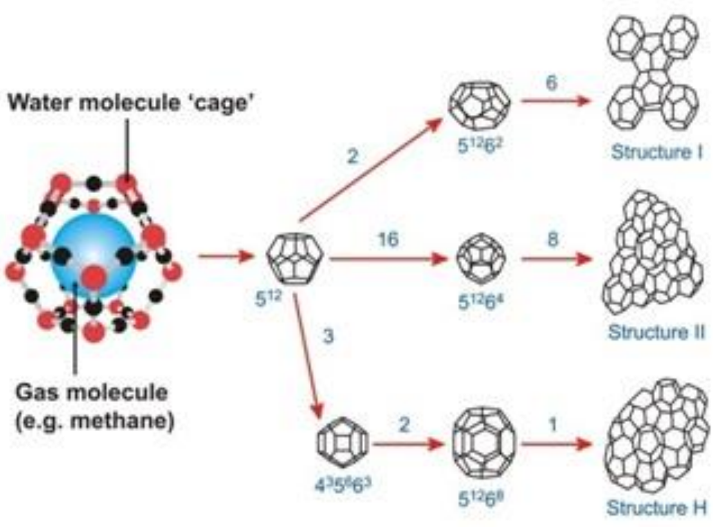


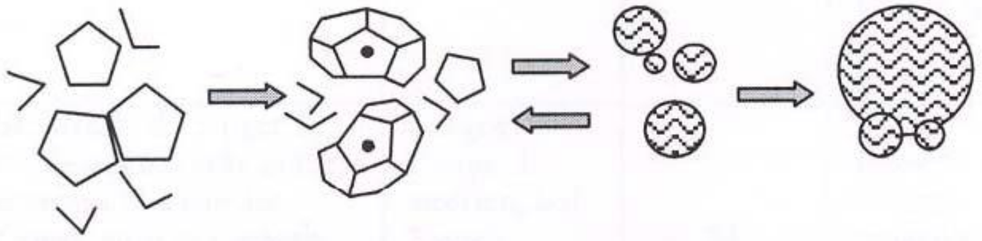
Figure 2: Structure of Gas Hydrate

Image adapted from http://www.pi.ac.ae/cal/events/index.php?com=detail&eID=42

2.3 Gas Hydrate Formation Kinetics

Kinetics of hydrate formation remains as a mystery to many scientist. In the last few decades, vigorous research is being conducted to understand the science behind hydrate formation. Two fundamentals of hydrate formations are the time taken to form a hydrate crystal; induction time and the rate of growth of the crystal. According to (Lederhos, Long, Sum, Christiansen, & Sloan Jr, 1996), gas hydrates form in an autocatalytic reaction mechanism when water molecules cluster around natural gas molecules in structures similar to Figure 2.

The Figure 3 shows the progress of molecular species from water [A] through metastable species [B] and [C], to stable nuclei [D] which can grow to large species. At the beginning of the process (point A), liquid water and gas are present in the system. These two phases interact with each other and form both large and small clusters [B] similar to the hydrate cages of sI and slI. At point [B], the cages are termed "labile"--they are relatively long-lived but unstable. The cages may either dissipate or grow to hydrate unit cells or agglomerations of unit cells [C], thus forming metastable nuclei. Since these metastable unit cells at [C] are of subcritical size, they may either grow or shrink in a stochastic process. The metastable nuclei are in quasi-equilibrium with the liquid-like cages until the nuclei reach a critical radius. After attaining the critical radius [D], the crystals grow rapidly in a period sometimes called catastrophic growth. (Lederhos et al., 1996).



A. Initial condition pressure and temperature in hydrate forming region, but no gas molecules dissolved in water.

B. Labile Clusters Upon dissolution of gas in water, labile clusters form immediately.

C. Agglomeration Labile clusters agglomerate by sharing faces, thus increasing disorder.

D. Primary Nucleation and growth when the size of cluster agglomerates reaches a critical value, growth begins.

Figure 3: Autocatalytic reaction mechanism for hydrate formation)

2.4 Sodium Dodecyl Sulphate

Gas hydrates have high potential as a gas storage since it contains 180+ volumes (stp) of natural gas per volume hydrate. This storage capacity is beneficial for the industry because a) slow release of natural gas from hydrate in the event of leakage, b) flammability is reduced by ice contacts, and c) low pressure storage (Zhong & Rogers, 2000).

Unfortunately, the hydrate formation rate is very slow for our industry standards. In the formation of gas hydrate in a quiescent water-gas system, an induction time is required for the gas to cluster inside the water molecules until concentrations and sizes of the cluster is ideal for hydrate crystallization. After the induction time, crystal growth happens on the water surface. As a result, hydrate formation rate is greatly reduced for gas and water must diffuse through the film of crystals. Although by agitating the water, the crystals can be removed and allow gas to diffuse, it is impractical since stirring consumes significant amount of energy and not sustainable in the longer run. Energy costs increases from stirring as slurry thickens. Stirring mechanisms also invites unnecessary hike in cost in terms of maintenance and equipment capitals. In fact, the slurry formed may limit the hydrate mass in the water to as low as 5% (Zhong & Rogers, 2000).

Sodium dodecyl sulphate also known as SDS will be used as a promoter for gas hydrate formation. SDS is a type of surfactant with the formula $CH_3(CH_2)_{11}OSO_3Na$. It is an anionic surfactant that is amphiphilic (hydrophilic and lipophilic). According to (Karaaslan & Parlaktuna, 2000), SDS have a strong influence on the kinetics of gas dissolution in the water phase as well as on the overall rate of hydrate formation. To determine the effectiveness of SDS, the rate of consumption of gas for hydrate formation will be studied from the temperature-pressure data obtained from the experiment explained in the methodology.

According to (Lin et al., 2004), the presence of SDS could enhance the formation process of methane hydrate. Tests over a SDS concentration range from zero to 2000 ppm performed on gas storage capacity manifested that a maximum storage capacity of 170 standard volume of methane per volume of hydrate (170 V/V) could be achieved at 650 ppm. On the other hand, (Moraveji, Sadeghi, Fazlali, & Davarnejad, 2010) states that increasing SDS concentration increases the gas hydrate formation rate but once CMC is reached the gas hydrate formation is rate is reduced. The CMC for gas hydrate formation is found to be 300 ppm according to figure 4 below.

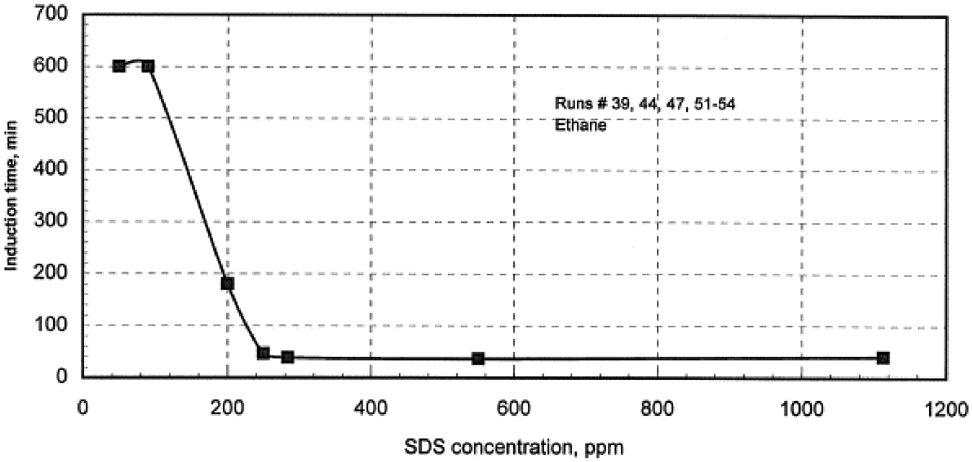


Figure 4 - Graph of Induction TIme vs SDS Concentration

Thus, critical micellar concentration of the surfactant solutions greatly influences the gas hydrate formation and storage capacity. SDS is a better anionic surfactant compared with nonionic surfactant. (Sun, Wang, Ma, Guo, & Fan, 2003).

When (Okutani, Kuwabara, & Mori, 2008) experimented using three different surfactants, sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS) and sodium hexadecyl sulfate (SHS), he found out that SDS having the shortest alkyl chains and the highest in water solubility among the three homologues is very effective for increasing both the rate of hydrate formation and the final water-to-hydrate conversion ratio. SHS having the longest alkyl chains and the lowest solubility is less effective in increasing the rate of the hydrate formation, compared to SDS and STS. With this basis, SDS will be chosen to be studied as a surfactant for gas hydrate formation at different concentrations.

CHAPTER 3
METHODOLOGY

3.1 Materials and Scope of Study

An experiment is conducted to study the kinetics of gas hydrate formations with SDS as the promoter. A special stainless steel batch reactor with a volume of 500 ml and working pressure up to 300MPa is used in this experiment. The temperature and pressure inside the vessel is monitored by a thermocouple and pressure transducer respectively. A magnetic stirrer is placed in the vessel which is then immersed in water bath tank to keep the temperature constant at a desired value. The pressure and temperature data are recorded and stored in a data requisition system. The materials needed for this experiment is as follows:

i) Carbon Dioxide gas 99.99 % purity
ii) Methane gas 99.99 % purity
iii) Sodium Dodecyl Sulphate 98 % purity
iv) Deionized water
v) Batch reactor

The scope of study designed for this project is:

- Pure methane hydrate and pure carbon dioxide hydrate is formed artificially.
- Concentration of SDS is tested as a promoter for carbon dioxide hydrate and methane hydrate formation at a range of 0-2000 ppm for every 100 ppm interval.
- Methane hydrate formation in SDS solutions is investigated at pressure of 55 bar and temperature 273.65K.

- Carbon dioxide hydrate formation in SDS solutions is investigated at temperature of 273.65K and 35 bar

3.2 Experimental Procedures

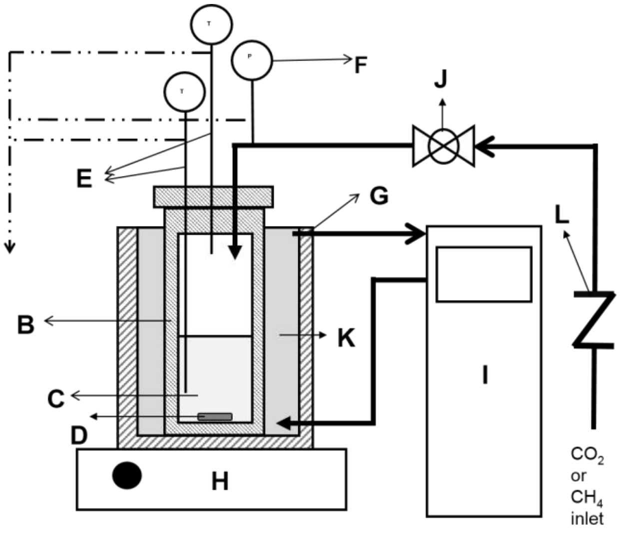


Figure 5 - Kinetic Batch Reactor Setup

The procedure is as follows:

i) Prepare SDS at different concentrations.
ii) Load 100 ml of SDS into vessel and flush with testing gas (CO_2 or CH_4).
iii) Pressurize the vessel according to test gas used.
iv) Switch on stirrer at 500rpm and allow gas to dissolve.
v) After pressure becomes stabilized, reduce temperature to 273 K.
vi) Record changes in temperature and pressure for every second using data requisition system.
vii) End experiment when system remain unchanged for 2-3 hours.

From the data obtained, we can calculate apparent rate constant. It is done by obtaining amount of test gas consumed during hydrate formation. From the mole consumed, the slope of that straight line is calculated to be the hydrate apparent rate constant. The formula is:

$$\frac{dn}{dt} = k(n_t - n^s)$$

where, k is apparent rate constant, n_t is mole of test gas in time t, and n^s is the saturated mole of test gas at the stationary point. Real gas equation

$$PV = ZnRT$$

is used to calculate mole consumed of test gas while compressibility factor is calculated using Peng-Robinson equation of state. (Partoon, Malik, Azemi, & Sabil, 2013). Redlich/Kwong equation can also be used to calculate compressibility factor. Once compressibility factor is calculated, mole of gas (n) consumed at different times can be tabulated. Formation rate is mole consumed per time.

Redlich/Kwong Equation of State is given as:

$$Z = 1 + \beta - q\beta(\frac{(Z - \beta)}{Z(Z + \beta)})$$

Where initial guess of Z =1.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Induction time for CH_4 Hydrate

Induction time is the time elapsed during the nucleation process which is the formation of a stable nuclei. By observing Figure 7, the pressure stabilizes until $t_{1,2,3,4}$ at which sudden pressure drop is detected. The sudden pressure drop is recognized as turbidity point at which hydrates start to form. The pressure keeps decreasing as methane gas is consumed for hydrate formation until the pressure becomes constant. Induction time is the time between time taken for the system to stabilize (tsol) after small pressure drop due to solubility of methane in water and the time taken at the first significant pressure drop ($t_{1,2,3,4}$).

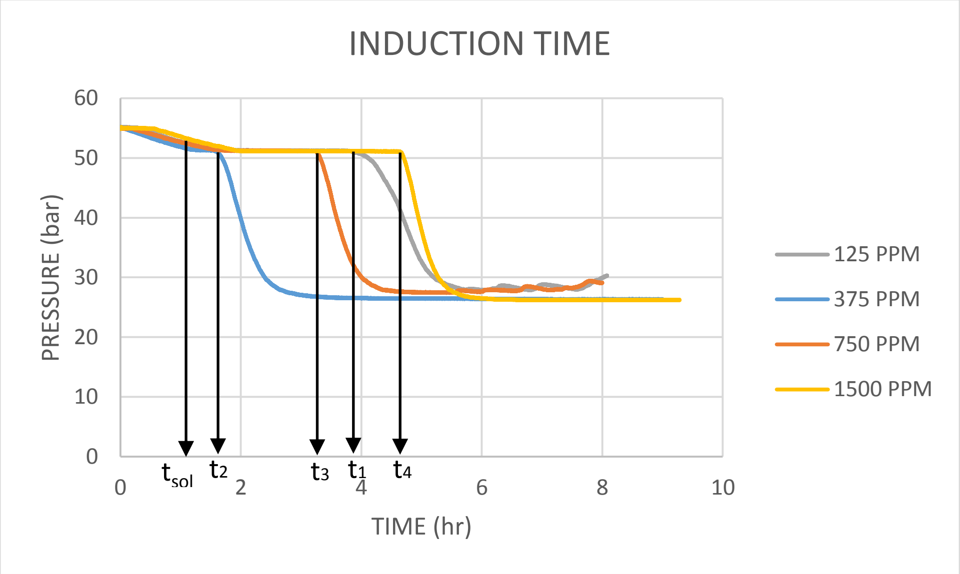


Figure 6 – Induction time for Methane Hydrate Formation

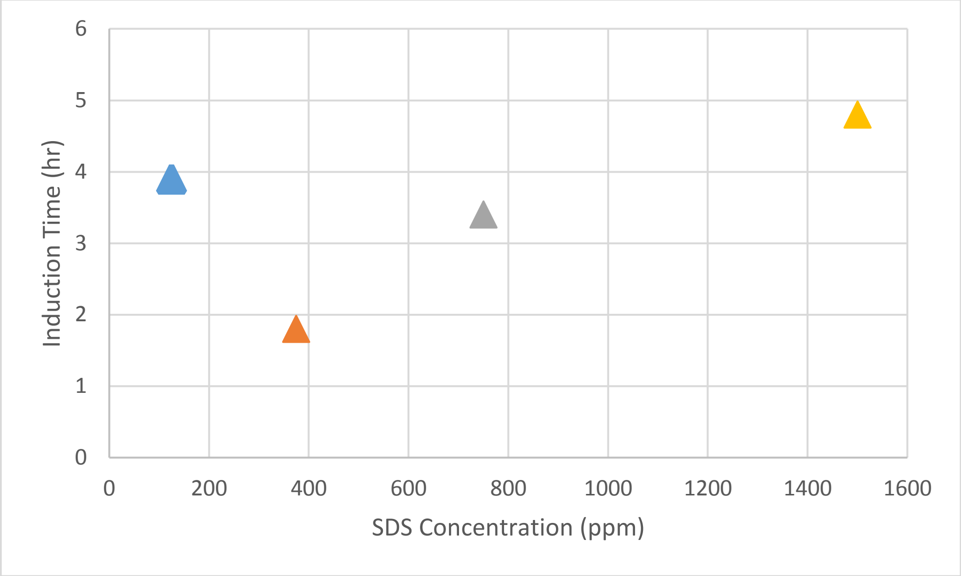


Figure 7: The induction time of methane hydrate in various concentration of sodium dodecyl sulfate solution.

For 125 ppm of SDS, $t_1 = 3.9$ hr

For 375 ppm of SDS, $t_2 = 1.8$ hr

For 750 ppm of SDS, $t_3 = 3.4$ hr

For 1500 ppm of SDS, $t_4 = 4.8$ hr

Figure 7 shows that at SDS concentration of 375 ppm, the induction time is the shortest for hydrate formation while at the highest concentration of SDS at 1500 ppm, the induction time is the longest. Once CMC of SDS is reached, increasing the concentration of SDS does not help to expedite the hydrate formation but prolongs the induction time. The concentration of SDS affects the hydrate formation rate. At higher concentrations, the induction time increases because of the SDS effect on the gas-liquid interface. Because gas hydrate will be formed at gas–liquid interface, the formation of solid layer of gas hydrate on this interface reduces the mass transfer between those two phases and hinders further formation of gas hydrate particles. While, at lower concentration, the presence of SDS prevents hydrate particles from agglomerating at the gas–liquid interface, which leads to prevention solid hydrate layer formation at the interface. This creates the opportunity for more gas–liquid interaction at the interface and possibly increases the number of hydrate nucleus. Therefore, the changes of macroscopic parameters such as induction time can be detected faster. However, if the concentration of SDS is too high, SDS molecules may prevent hydrate nucleus to agglomerate in the liquid phase. This effect will increase the time required for these tiny particles to agglomerate and therefore, prolong the induction time.

4.2 Induction time for CO_2 Hydrate

Similarly, induction time in CO_2 hydrate can be seen from the pressure drop. Although the pressure drop in carbon dioxide hydrate is not significant, at 1500 ppm the pressure drop shows some significance of the other lower concentrations. This shows that for CO_2 hydrate higher concentration of SDS is needed for a shorter and more efficient hydrate formation.

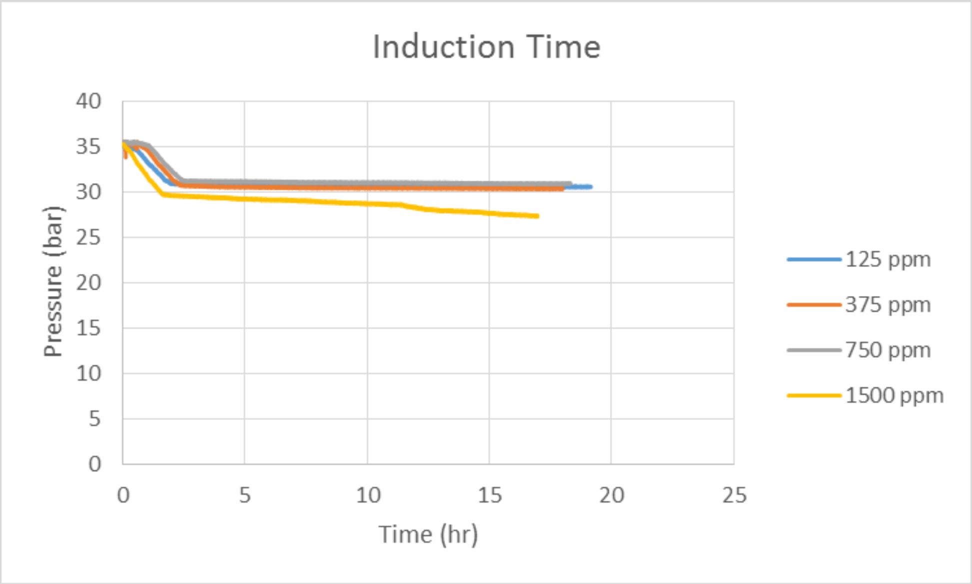


Figure 8- Induction Time for Carbon Dioxide Hydrate

4.3 Apparent Rate Constant for CH_4 Hydrate

Apparent formation rate constant is the constant derived from the equation of slope of number of mole consumed over time. Hydrate formation starts when the methane gas is consumed in the reactor is this is detected by the pressure drop in the system. The gas dissolves in the SDS solution to form hydrate and this is shown in Figure 8 where the sudden increase in peak is the hydrate formation period for different SDS concentrations. Once it reaches a constant value it indicates that the hydrate formation has been completed. As SDS concentration increases, the number of mole of methane gas consumed also increases. This is due to SDS being an effective kinetic promoter for hydrate formation by agglomerating the gas-liquid interface. More gas can be dissolved and trapped inside the water molecules for hydrate formation. However, as explained before after reaching the limit of gas that can be dissolved in the water, no more hydrate can be formed. At higher concentration of SDS solutions, micelles is formed in the reactor. The presence of micelles may be the main reason of reducing the gas consumption by hydrate formation. The presence of micelles in the solution may lead to reduction of amount of free water, and therefore, less water molecules can be converted to the hydrate crystals. The final result would be the reduction of gas consumption during the hydrate formation process.

Through this experiment, it can be said that the optimum concentration of SDS for methane hydrate formation is at 375 ppm. With low dosage of the promoter, the methane consumption for hydrate formation is better. The apparent rate constant, k, as the gradient of the slope in Figure 8, the apparent rate constant is the highest at 1500 ppm of SDS solution. This shows that the rate of formation can be increased with the addition of low dosage promoter.
This finding is important for the development of gas hydrate-based processes such as those for methane hydrate transportations.

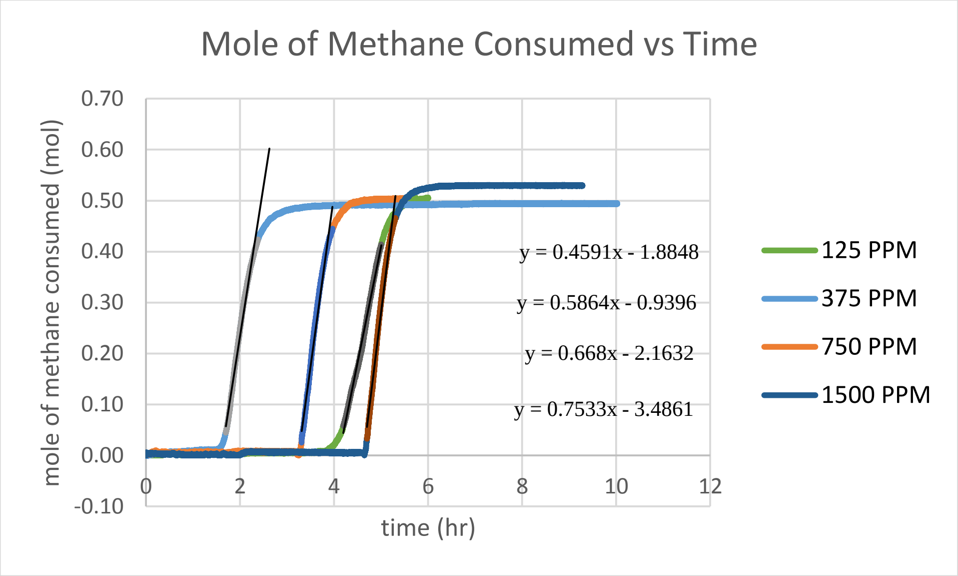


Figure 9- Mole of Methane Consumed vs Time

4.4 Apparent Rate Constant for CO_2 Hydrate

Apparent formation rate constant is the constant derived from the equation of slope of number of mole consumed over time. Hydrate formation starts when the carbon dioxide gas is consumed in the reactor is this is detected by the pressure drop in the system. The gas dissolves in the SDS solution to form hydrate and this is shown in Figure 10 where the sudden increase in peak is the hydrate formation period for 1500 SDS concentration. Once it plums downwards it indicates that the hydrate formation has been completed. As SDS concentration increases, the number of mole of methane gas consumed also increases. This is due to SDS being an effective kinetic promoter for hydrate formation by agglomerating the gas-liquid interface. More gas can be dissolved and trapped inside the water molecules for hydrate formation. However, in CO_2 hydrate case, the possible explanation on why the hydrate formation constant is low is because there might be possible contamination in the supply gas system. CO_2 has diameter of 5.12 Å which fits into hydrate structure I. If impurities were to occur in the CO_2 supply, there are chances for more than 1 hydrate structure to be formed in the same system. Hence, the data shows that pure CO_2 hydrate could not be formed. With a crystal structure change, a different thermodynamic state (three phase temperature and pressure) is required for stability.

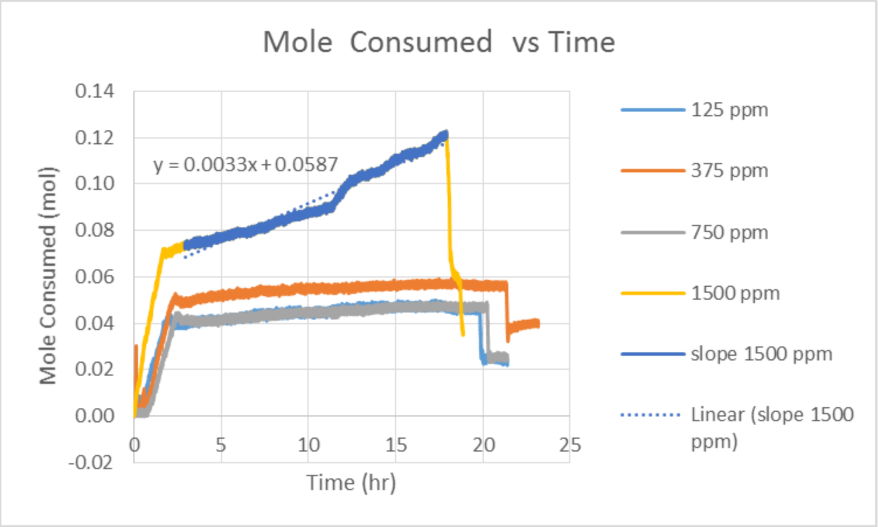
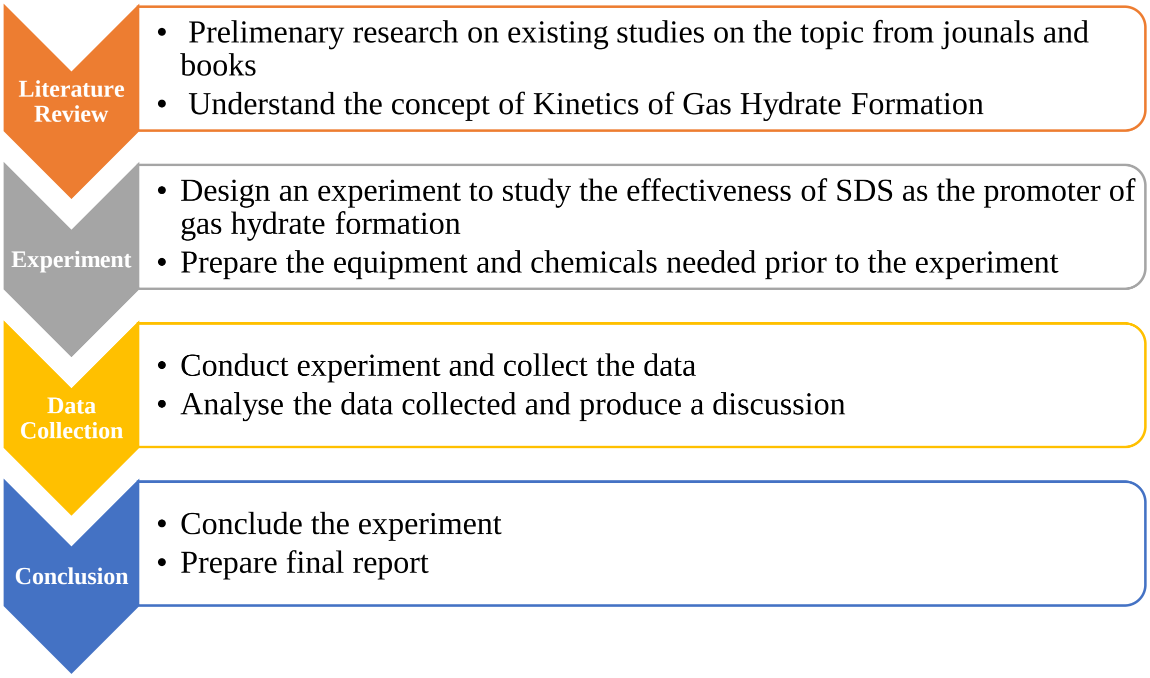


Figure 10 – Mole Consumed vs Time for Carbon Dioxide Hydrate

Through this experiment, it can be said that the optimum concentration of SDS for CO_2 hydrate formation is at 1500 ppm. With high dosage of the promoter, the CO_2 consumption for hydrate formation is better. The apparent rate constant, k, as the gradient of the slope in Figure 10, the apparent rate constant is the highest at 1500 ppm of SDS solution. This shows that the rate of formation can be increased with the addition of low dosage promoter.

This finding is important for the development of gas hydrate-based processes such as those for CO_2 hydrate formation for carbon capture.

4.5 Project Activities



Literature Review

- Prelimenary research on existing studies on the topic from jounals and books
- Understand the concept of Kinetics of Gas Hydrate Formation

Experiment

- Design an experiment to study the effectiveness of SDS as the promoter of gas hydrate formation
- Prepare the equipment and chemicals needed prior to the experiment

Data Collection

- Conduct experiment and collect the data
- Analyse the data collected and produce a discussion

Conclusion

- Conclude the experiment
- Prepare final report

4.6 Gantt Chart and Key Milestone

Description/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Experiment Work	▨	▨	▨	▨	▨	▨	▨								
Submission of Progress Report							■								
Experiment Work								▨	▨	▨	▨	▨			
Pre-Sedex										■					
Submission of Draft Final Report											■				
Submission of Dissertation (soft bound)												■			
Submission of Technical Paper													■		
Viva														■	
Submission of Dissertation (hard bound)															■

▨	Work in progress
■	Deadline

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

Gas hydrate has a high potential to be the next energy source as well as solution for our storage of greenhouse gases. It is definitely a lucrative field to be explored that demands research from all aspects of engineering. With this final year project, it is hope that substantial amount quality data could provide us the necessary information to use SDS as the promoter for gas hydrate formation for carbon dioxide sequestration, methane hydrate as an alternative energy source. Once this research is done, and a better knowledge is gained, more thorough analysis can be performed on the dissociation of in situ methane hydrates while sequestering carbon dioxide as hydrates. (Goel, 2006)

It is highly recommended that carbon dioxide hydrate formation is also studied thoroughly at higher concentration range and eliminate any contaminations in the system to determine the optimum concentration of SDS for its formation. Although CO_2 hydrate was part of the research in this paper, but due to failure in equipment the results have been compromised in this paper.

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