FLOW ASSURANCE:

MICRO AND MACRO-SCALE EVALUATION OF LOW DOSAGE HYDRATE INHIBITORS

2002 – 2005 PROGRAMME

PROGRESS REPORT
March 2003 – November 2003
FLOW ASSURANCE: MICRO AND MACRO-SCALE
EVALUATION OF LOW DOSAGE HYDRATE INHIBITORS

2002 – 2005 PROGRAMME

PROGRESS REPORT

March 2003 - November 2003

November 2003
Heriot-Watt Institute of Petroleum Engineering

This document is confidential. The copyright is rested in Heriot-Watt University, Riccarton, Edinburgh. Third parties must obtain the written authority of the Institute of Petroleum Engineering, Heriot-Watt University, before reproducing the whole or part of the contents, or disclosing the same to others.
# TABLE OF CONTENTS

PERSONNEL AND SPONSORS................................................................................... i

EXECUTIVE SUMMARY......................................................................................... ii

EXTENDED SUMMARY............................................................................................ iii

INTRODUCTION ...................................................................................................... 1.1

VISUAL OBSERVATION BY MICROMODEL EXPERIMENTS ............................... 2.1

KINETIC RIG EXPERIMENTS................................................................................... 3.1

EXPERIMENTS IN HIGH PRESSURE VISUAL RIG............................................. 4.1

HYDRATE NUCLEATION TESTS USING ULTRASONIC WAVES .................. 5.1

DEVELOPMENT, APPLICATION AND TESTING OF ANTI-AGGLOMERATE INHIBITORS................................................................................................................. 6.1

APPENDIX........................................................................................................... A.1
November 2003

PERSONNEL AND SPONSORS

The study was conducted in the Institute of Petroleum Engineering, Heriot-Watt University, under the direction of Professors B. Tohidi, A. Danesh, and A. C. Todd. Experimental and analytical works were carried out by Mr M. Arjmandi, Ms Z. Zain, Mr. R. Burgass, Dr. J. Yang, Dr S. R. Ren, Ms E. Carnegie, Mr. P. Jadhawar, Mr. G. Mali, Mr J. Pantling and Mr C. Flockhart were responsible for manufacture and maintenance of equipment.

The research project is supported by BASF, British Petroleum Plc., Clariant Oil Services, Gaz de France, TOTAL and the UK Department of Trade and Industry, which is gratefully acknowledged.
EXECUTIVE SUMMARY

The ongoing research programme is focused on the investigation of the mechanisms of Low Dosage Hydrate Inhibitors (LDHI) and the evaluation of their performance under different conditions. The main objectives of the research are:

- Development and application of new techniques for studying the mechanisms of hydrate inhibition by LDHIs.
- Evaluation of the performance of current LDHIs at various conditions.
- Guidelines on effective design and deployment of LDHIs
- Guidelines on screening of potential LDHIs using laboratory-based tests

The work in the last six months of the project can be summarised as:

- Investigating natural gas and methane hydrates morphologies in the presence of two PVCAP based kinetic inhibitors (with and without synergist) in different conditions, by visual observations in the high-pressure micromodel set up. The observations suggested that the new LDHI (HI03-22) has affected the morphology of gas hydrates. The morphology is mainly patches of very thin crystal flakes.
- Experiments conducted in the kinetic rigs to test a new formulation kinetic inhibitor (comprising PVCAP, ethylene glycol water and a synergist chemical) at different bulk conditions including shut-in and flow cases. It was found that for achieving the induction times longer than one day, the degree of subcooling should be less than 11°C for natural gas system and less than 9 °C for methane system. At static conditions, longer induction times experienced in the presence of new inhibitor in the natural gas and methane systems.
- The impact of hydrate structure on the performance of PVCAP was investigated. Two binary systems comprising of C1/C2 and C1/C3 were prepared to give similar hydrate stability zones but different hydrate structures. From tests results it appeared that at similar degrees of subcooling and pressures, PVCAP performs much better in structure II hydrate forming systems.
- A windowed kinetic rig was used to observe hydrate formation in different systems (natural gas, methane/propane mixture and pure methane in the presence and absence of PVCAP) and different conditions (mixing and static). The behaviour of PVCAP in the structures II and I hydrates in mixing (flowing) and static condition was also studied. The result showed that in a static situation
PVCAP significantly increases the amount of hydrates formed. In the test with no PVCAP, hydrates formed on the cell walls (in the vapour phase) and at the gas/water interface, however there were few hydrates formed in the bulk of the water phase. In the test with PVCAP hydrate formation appeared to occur in an unusual sequence, which is detailed in the report.

- A series of tests using ultrasonic set-up have been carried out to see how PVCAP inhibit hydrate formation using three different hydrate formers, i.e., THF, carbon dioxide and natural gas. The test results suggest that PVCAP prolongs the induction time of hydrate formation through not only delaying the catastrophic growth but also slowing down hydrate nucleation.

- A literature survey on the development, testing and field application of anti agglomerants was accomplished and some preliminary experiments have been carried out in our laboratory to develop the methodology for testing anti agglomerates using the Kinetics Rigs and the Glass Micromodels. These preliminary experiments have demonstrated that micromodel can provide valuable information to support the results obtained from conventional techniques for evaluating AA LDHIs.
The ongoing research project started in September 2002 and is currently supported by 5 oil/gas and chemical companies and the Department of Trade and Industry (DTI). The research programme is focused on the investigation of the mechanisms of Low Dosage Hydrate Inhibitors (LDHI) and the evaluation of their performance under different conditions. The main objectives of the research include:

- Development and application of new techniques for studying the mechanisms of hydrate inhibition by LDHIs.
- Evaluation of the performance of current LDHIs at various conditions.
- Guidelines on effective design and deployment of LDHIs for deepwater applications
- Guidelines on screening of potential LDHIs using laboratory-based test procedures

In the last six months of the project, experiments have been conducted using the micromodel, and two conventional kinetics rigs to evaluate the performance of polyvinylcaprolactom (PVCAP) and a new kinetic inhibitor in methane and natural gas systems. The effect of hydrate structure on inhibitor performance was also studied in the rigs. A windowed kinetics rig used to study PVCAP performance in static conditions. The nucleation and growth of hydrate in with and without PVCAP in natural gas water system was investigated in an ultra sonic set up.

**Micromodel Experiments**

The blank tests for natural gas-water system were conducted to study the hydrate morphology at low and high degrees of subcooling and also to investigate the mechanism of hydrate formation. Experiments were conducted at two conditions; 14.5°C and 12°C subcooling. For high degree of subcooling the formation is in the both water and gas phases, whereas at low degree of subcooling it is only in continuous gas phase. However, there are no significant differences in hydrate morphology for low and high degree of subcooling. The still pictures in Figure 1 illustrate the hydrate formation sequence at high degree of subcooling (14°C). The hydrate crystal turned to white crystalline solid and more consolidated after about 20 hours due to crystal rearrangement to become more stable crystal. Only some traces
of hydrate crystal formed in the water phase due to low solubility of natural gas in the water phase to form hydrate.

Figure 1. Hydrate formation in Natural Gas-Water System at 1500 psia/103 bar, 4°C (14.5°C subcooling).

The tests carried out in the presence of 1 mass% of PVCAP showed that it significantly reduces the rate of hydrate growth in water phase for natural gas–water system. However, for methane–water system, PVCAP appeared to be less effective in reducing the hydrate growth and inhibiting hydrate formation in water phase as compared to natural gas–water system.

Several tests were conducted at different pressures (90 bar and 69 bar) to study and to compare the effect of a new inhibitor (HI03-22, composed of PVCAP, a synergist chemical, ethylene glycol and water) with PVCAP, on the hydrates formation and their morphologies. While hydrate morphologies are similar for the systems without inhibitor and the systems with PVCAP, it was observed that the size of hydrate crystals appeared to be smaller in the presence of HI03-22. In addition, the hydrate particles did not agglomerate or stick to each other in the presence of new inhibitor as shown in Figure 2.

Figure 2. Comparison of hydrate morphology (a) Without inhibitor (b) With 1 mass% PVCAP (c) With 2%vol HI03-22.
The morphology is mainly patches of very thin crystal flakes. The above observation may suggest that the synergist chemical in the new inhibitor could have affected the morphology of hydrate crystals. Visual observations also suggest that the rate of hydrate growth is faster in the presence of 2 vol.% HI03-22 in comparison with 1 mass% PVCAP.

Tests were conducted in HP micromodel for methane – water system in the presence of 2 vol % of HI03-22 to investigate and to compare the effect of new inhibitor on hydrate morphology. Figure 3 describes the progress of hydrate growth in this system. As shown in the pictures, hydrates started to form as black masses of hydrate particle, which appeared to consist many small particles following the profile of gas bubbles (Figure 3(a)). After 24 hours, some of the hydrate particles turned to white crystal with mainly at the edges of hydrate crystal structure. The growth of white crystal were obvious after 74 hours of hydrate formation where the hydrates formed shells inside the gas bubbles and water molecules appeared to be remained in the middle (Figure 3(b)). With time, the hydrate crystal developed a continuous thin hydrate crystal and appeared to be agglomerated to each other and not separated into small crystal flakes (Figure 3(c)).

![Figure 3. Changes in methane hydrate morphology in the presence of HI03-022 inhibitor with time at 1700 psia/117 bar and 4.3°C, 10.5°C subcooling.](image)

It appears that the new inhibitor affected the morphology of both hydrate structure I and II. It was also observed that some traces of gas hydrate formed in the water phase after 24 hours of hydrate formation. This might suggest that the new inhibitor, in the presence of methane, may not prevent hydrate formation in the water phase.
Kinetics Rig Experiments

Two series of experiments were conducted using the kinetics rigs. The first was to test a new formulation of kinetic inhibitors based on PVCAP (HI03-22, from Clariant) in order to find out the range of its applicability in different systems and conditions. The performance of the inhibitor in terms of induction time was tested at different degrees of subcooling. The effect of different hydrate structures on the performance of the inhibitor was studied by testing the inhibitor in natural gas-water and methane-water systems. The inhibitor was also assessed in two hydrodynamic conditions; shut-in and flowing (stirring) conditions.

From the results of the tests it appeared that for achieving the induction times longer than one day, the degree of subcooling should be less than 11°C for natural gas system and less than 9 °C for methane gas system. It was also confirmed that HI03-22 is more effective in structure II hydrate forming systems as expected for the PVCAP based KHIs. Furthermore, 2 vol% of HI03-22 is not as effective as 1 mass% of PVCAP in a natural gas system. At static conditions, with similar degree of subcooling as that at mixing conditions, longer induction times experienced in the presence of HI03-22 in a natural gas and methane systems. However it is interesting to note that for 1 mass% of PVCAP longer induction times were observed at mixing than that at static conditions. This perhaps was due to the presence of the synergist chemical in HI03-22, which can improve the gas-water interface property. Inhibitor performance could be mostly vulnerable to initial hydrate formation at the gas-water interface when the system is at a static condition.

The second series of experiments was designed and conducted in a kinetic rig to investigate the effect of hydrate structures on the performance of PVCAP. Two synthetic gas mixtures, which have the same hydrate phase boundaries but form different hydrate structures (sI and sII), were used in the experiments to exclude the effect of pressure or temperature. From tests results it appeared that at similar degrees of subcooling and pressures, the inhibitor performs much better in structure II hydrate forming systems.
**Experimental Measurements Made Using High Pressure Visual Rig**

During the initial phase of the project kinetic tests with the kinetic inhibitor PVCAP and natural gas showed that when the system was static, hydrate formation occurred (as indicated by a pressure reduction) earlier than in tests where the system was mixed. As this was contrary to what was expected it was decided to conduct some tests in a high pressure visual cell where observations of the way hydrates form could be conducted. Tests were carried out with natural gas without and with PVCAP with no mixing and a high degree of subcooling (14.7°C). In the tests the test fluids were equilibrated at a temperature close to 35°C and then cooled to around 4°C over 12 hours. The result of these tests showed that in a static situation when hydrates form the PVCAP significantly increases the amount of hydrates that formed. A plot of pressure with time for the tests without and with PVCAP is given in Figure 4. From a visual point of view there was also a significant difference. In the test with no PVCAP, hydrates formed on the cell walls in the vapour phase and at the gas/water interface, however there were few hydrates formed in the bulk of the water phase. In the test with PVCAP hydrate formation appeared to occur in an unusual sequence. Firstly hydrates formed at the gas water interface and on the cell walls in the gas phase. A picture of the hydrates formed at the gas/water interface is shown in Figure 5. The hydrates at the gas/water interface then appeared to dissociate and there was a movement of liquid water from the base of the cell to the upper part of the cell. Part of the sequence is shown in Figures 6a through 6c. Eventually all of the water was removed from the lower part of the cell and hydrates formed in the upper part of the cell.

Following these initial tests it was decided to investigate the effect of hydrate structure upon the way hydrates formed in static conditions. Tests were conducted following the same procedure but firstly with methane (structure I) and secondly with a mixture of methane and propane (5 mole% propane, structure II). In both suites of tests the same observation that the presence of PVCAP increased the amount of hydrates that formed was made. Comparisons for tests without and with PVCAP for both systems are presented in Figures 7 and 8. There was some difference from a visual point of view in the tests with PVCAP. In the test with methane, hydrates formed initially at the gas/water interface and on the cell walls in the gas phase and
then formation spread through the water phase. In the test with the methane/propane mixture, the pattern of hydrate formation was similar to that with natural gas described above, with all of the water being removed from the lower part of the cell. In all of the tests with distilled water there was no significant hydrate formation in the bulk of the water phase with only a few needle-like hydrate crystals growing down from the gas/water interface. An example of these crystals is shown in Figure 9.

Figure 4. Plot of pressure vs time data for two tests with natural gas hydrates in static conditions without and with PVCAP (1 mass%).
Figure 5. Picture of natural gas hydrates growing at the gas/water interface in the presence of PVCAP.

Figure 6a. 1 in a sequence of 3. Picture of natural gas hydrates formed in the presence of PVCAP, water phase being drawn from the lower part of the cell.

Figure 6b. 2 in a sequence of 3. Picture of natural gas hydrates formed in the presence of PVCAP, water phase being drawn from the lower part of the cell.
Figure 6c. 3 in a sequence of 3. Picture of natural gas hydrates formed in the presence of PVCAP, water phase being drawn from the lower part of the cell.

Figure 7  Plot of pressure vs time data for two tests with methane hydrates in static conditions without and with PVCAP (1 mass%).

T=34.3 C
T=4.1 C
Figure 8  Plot of pressure vs time data for two tests with methane/propane (5 mole% propane) hydrates in static conditions without and with PVCAP (1 mass%).

Figure 9. Picture of needle like methane/propane hydrate crystals growing into water phase from gas/water interface.
Hydrate Nucleation Tests Using Ultrasonic Waves

Hydrate formation as a crystallization process includes two phases, i.e., nucleation and growth. Based on simulation results an ideal kinetic inhibitor should have the ability to be adsorbed on both nucleation sites and growth sites. So it is essential to further understand the inhibition mechanism of LDHIs to improve the performance of existing LDHIs and/or designing new inhibitors. A series of tests using ultrasonic setup have been carried out to explore possibility of application of ultrasonic waves to detect hydrate nucleation and then to find out how the PVCAP as an example of LDHIs prolongs the induction time, by either slowing down nucleation or delaying catastrophic growth, or both of them.

The tests are divided into two phases. The first phase aims to initially find out if ultrasonic signals could be sensitive enough to detect hydrate nucleation. In the first phase a natural gas was used as hydrate former and glass beads, 0.1 mm in diameter, was packed in the test cell to act as nucleation sites to simulate mechanical stirring. The result shows two main advantages of ultrasonic test compared to conventional pressure analysis: (1) Higher sensitivity to gas hydrate crystallization makes it possible to detect hydrate nucleation or the very beginning of hydrate formation, and tiny amount of gas hydrate growth. (2) Prompt and significant response to the phase transition leads the identification of the onset point easier and more reliable. As can be seen in Figure 10, the FFT and the amplitude of the ultrasonic signal responded the initial hydrate formation at about 95 minutes and 73 minutes (respectively) earlier than the pressure signal. Furthermore, the pressure response was not as sharp and it is very difficult to identify the beginning of hydrate formation from the pressure change.
The FFT responded the start point about 95 minutes earlier than the pressure did, 73 minutes earlier than the amplitude did.

In the second phase the natural gas, tetrahydrofuran and carbon dioxide were used as typical hydrate formers. All the tests were carried out without glass beads to exclude the possibility of any effect of glass beads on the nucleation tests, for example, the adsorption of PVCAP on the surface of the glass beads. The objective is to find out how PVCAP as a kinetic inhibitor inhibits hydrate nucleation and growth. The test results suggest that PVCAP prolongs the induction time of hydrate formation through not only delaying the catastrophic growth but also slowing down hydrate nucleation. The presence of 1 mass% of PVCAP differentiated the various stages involved in hydrate crystallization process, i.e., nucleation----> slow formation ----> catastrophic growth. At a constant concentration of PVCAP (in this case 1 mass%) the delay in the induction time (due to the presence of PVCAP) depends on the amount of hydrate formers in the water phase. The lower the molar concentration of the hydrate former in the water phase, the longer the induction time, shown in Table 1.

Furthermore, at static conditions the presence of PVCAP resulted in more gas hydrates formation. It may be due to the fact that LDHIs makes gas hydrate more permeable, which warns that more attention must be paid to shut-in cases when LDHIs are applied. However, significantly more THF hydrates formed in the blank test than in the test with PVCAP, which directly supports the previous explanation and may also suggests that PVCAP is more effective to prevent hydrate growth from dissolved gas rather than from free gas.
Table 1  Induction delay and hydrate quantity

<table>
<thead>
<tr>
<th></th>
<th>Nucleation time</th>
<th>Delay catastrophic growth</th>
<th>Quantity of hydrates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>minutes</td>
<td>minutes</td>
<td>pressure drop</td>
</tr>
<tr>
<td>NG</td>
<td>undetectable</td>
<td>undetectable</td>
<td>undetectable</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>2300</td>
<td>32 bar in 4150 minutes</td>
</tr>
<tr>
<td>PVCAP</td>
<td>520</td>
<td>1050</td>
<td>20 bar in 180 minutes</td>
</tr>
<tr>
<td>CO₂</td>
<td>20</td>
<td>220</td>
<td>4 bar in 1500 minutes</td>
</tr>
<tr>
<td>PVCAP</td>
<td>80</td>
<td>300</td>
<td>3.4 bar in 240 minutes</td>
</tr>
<tr>
<td>THF</td>
<td>undetectable</td>
<td>60</td>
<td>0.8 bar in 600 minutes</td>
</tr>
<tr>
<td>PVCAP</td>
<td>80</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Development, Application And Testing of anti-agglomerant inhibitors

The study of AAs along with KHIs was included in the proposal of the current LDHI project. In the last Technical Steering Meeting, it was suggested that the testing of AAs should be scheduled in the experimental plan. In this report, a brief description and literature survey on the development, testing and field application of AA chemicals is presented. Some preliminary experiments have been carried out in our laboratory to develop the methodology for testing AAs using the Kinetics Rigs and the Glass Micromodels.

The development of AA LDHI chemicals can be traced over 30 years, started with commercial surfactants. There have been breakthroughs and a few successful field implementations in the last 10 years. The most powerful AAs up to date appeared to be the quaternary compounds, such as ammonium, phosphonium or amines. There are several commercial AAs available in the market from various companies. The current AAs need to operate in the presence of a liquid hydrocarbon phase, and has a limitation on the water cut.

There have been several successful field-testing and applications of AA LDHIs reported in the literature. Most of them were in the Gulf of Mexico. In most cases, AAs were deployed for treatments during shut-in and restart to replace methanol. There was also a case where excessive water was involved, and the use of methanol was impossible due to limited injection rate and cost. AAs are suitable for systems with limited water cut (less than 50% or 30%) in multiphase transportations. There is
no report on any potential adverse effect of AAs on other aspects of field operations. AA has been proven to be an economically viable alternative to conventional inhibitors for deepwater pipelines, due to its low dosage, fewer requirements on injection and storage.

Laboratory testing of AAs involves three basic techniques: hydrate visualisation, rheological measurement of hydrate slurries, and assessment of hydrate plugging and deposition. Stirred tank reactors and simulated mini flow loops, with and without optical windows, are most popular laboratory equipment used for AAs selections.

In this project, a Kinetics Rig, with a specially designed stirring impeller for torque measurement, and Glass Micromodels will be used for AA testing. The Kinetics Rig is useful for rheological characterisation and blockage detection of the AA systems. Figure 11 shows the experimental result conducted for a water/condensate/gas system in the presence of 1 mass% phosphonium salt (an effective AA inhibitor). It is interesting to note that the marginal torque increase after hydrate formation was due to the use of the AA chemicals, which can disperse hydrate particles in the condensate phase. The size, morphology and distribution of hydrate particles in water/oil phases can be best viewed in the micromodels, as shown in Figure 12, in which a similar system (as described in Figure 11) was tested. The small hydrate particle sizes (less than 10 \( \mu m \)) and the appearance of hydrates in the condensate indicated the effectiveness of the AA chemical used. These preliminary experiments have demonstrated that the techniques developed at HW are suitable and effective for the testing of AA LDHIs.
Figure 11. Experimental results using Kinetics Rig-1 conducted for a system containing 33 vol% water solution (5% NaCl) in a North Sea condensate with 1 mass% of an AA chemical: Hydrate formation and torque increase. The chemical shows an excellent AA effect.

Figure 12. Particle sizes and distribution of hydrates in the micromodel in the fluid similar to the system described in Figure 11.
1.1. BACKGROUND
The economic risks involved in developing offshore and deepwater reservoirs demand cost effective methods and techniques for providing flow assurance solutions. The use of long tiebacks for transporting unprocessed well-stream could play an important role in the economical development of many deepwater and marginal fields.¹ A major concern with these subsea pipelines and production facilities is the possibility of flow restriction and blockage due to hydrate formation, which can lead to serious operational and safety problems. The cost of failure can be very high because of the high remediation cost and significant loss of revenues.²

Hydrates are crystalline, ice-like solids that form when gas molecules are trapped in hydrogen-bonded water cages under high pressure and low temperature conditions. These conditions are very typical for offshore operations. Conventional chemical treatments for preventing of hydrate formation are through one, or a combination, of methods such as: dehydration; insulation/heating; suitable operational practises; or injection of various chemical inhibitors (e.g. methanol or glycol). Conventional thermodynamic inhibitors are a major tool in current hydrate prevention strategies, but must be used in large volumes, e.g., up to 50 wt% methanol in the water-rich phase. This imposes severe capital and operational costs.³ Indeed, it is recognised that the cost of all the conventional hydrate prevention strategies can be prohibitively expensive for new deepwater developments and do shorten the economic life of mature assets.

In the past decade, a new group of non-thermodynamic chemical inhibitors has been developed which has received considerable attention form the industry. A number of laboratory studies and field trials have been reported in literature.³⁻⁷ These chemicals do not shift the thermodynamic phase boundary of hydrate formation, but interfere with the process of hydrate formation by means of a number of mechanisms proposed by several researchers.⁸⁻¹² Because the effective dosage for these new chemicals is much lower than those required for thermodynamic inhibitors, the new inhibitors are known as low dosage hydrate inhibitors (LDHI). LDHIs are typically divided by
different active mechanisms such as, anti-agglomerants (AA) and kinetic hydrate inhibitor (KHI). The anti-agglomerants are based on preventing the agglomeration and deposition of hydrate crystals so that a transportable hydrate slurry could be formed. Current anti-agglomerant inhibitors must be used in the presence of an oil phase.

Like many other crystallisation process, the formation of gas hydrate also involves two processes: nucleation and crystal growth. It is speculated that the effect of a kinetic inhibitor (long polymer chains) is to interfere the nucleation process and/or prevent the crystal growth after its nucleation. Therefore, effective kinetic inhibitors should either delay/prevent hydrate nucleation, and/or delay the catastrophic growth of hydrate volume and provide a hydrate induction time exceeding the water residence time in the pipeline. The induction time is defined as the duration beginning when the system falls into the hydrate-forming region until the onset of hydrate formation. It can be the most important parameter to evaluate the performance of a kinetic inhibitor. The LDHIs developed over the past decade have provided proof of concept, but still need considerable development before they can be adopted in many applications. The mechanism of LDHIs is still far from comprehensive apart from the adsorption theory. Three problems in particular arise: the extent of subcooling induced, the operating pressure, and the environmental acceptability. The current generation of LDHIs allow only 10–12 °C subcooling at medium pressure conditions whereas about 20 °C at high-pressure conditions is needed in many applications. There is still a need for the development of LDHIs suitable for high degree of subcooling and for high pressures. The performance of current LDHIs at various conditions has not been fully investigated. There has been rare information regarding hydrate formation and the mechanism and effect of LDHIs at micro-scales.

In response to the interests from the industry, the Centre for Gas Hydrate Research at Heriot-Watt University has extended its long-established hydrate research activities to the current project; **Flow Assurance: Micro and Macro-Scale Evaluation of Low Dosage Hydrate Inhibitors**. The objective of this study is to gain better understanding of gas hydrate formation and inhibition mechanisms using LDHIs both in micro and macro-scales, principally by the application of a glass micromodel set-up.
in combination with a conventional hydrate kinetic rig using a large stirred tank.\textsuperscript{14,15} The micromodel set-up will be used to gather data on hydrate crystal size and hydrate-fluid segregation. The kinetics rig is useful for evaluating the performance of inhibitor for industrial applications. Other analytical techniques, such as gas chromatograph, mass spectrometer and UV analysis will also be employed in the study. It is proposed to study various fluid systems, including, CO\textsubscript{2}, methane, natural gases, gas condensate and oil systems. The information generated in this work will be used to identify/design more effective low dosage hydrate inhibitors and/or deployment procedures for deepwater applications.

1.2. CENTRE FOR GAS HYDRATE RESEARCH-HW

In response to the interest indicated by the industry, the Department of Petroleum Engineering at Heriot-Watt University extended its research activity to hydrates in 1986. A number of research projects, mainly in addressing gas hydrate problems in subsea pipelines, have been conducted since then, resulting in the development of experimental equipment, novel test procedures, and prediction models. In June 2000, the research group was successful in securing a Research Development Grant from the Scottish Higher Education Funding Council to establish a Centre for Gas Hydrate Research at Heriot-Watt University.

The Centre was formally established in February 2001. The funding enabled us to refurbish the hydrate laboratory and extend our research activities to various applications of gas hydrates, by employing new staff and forming a multi-disciplinary research team with expertise in Chemical and Petroleum Engineering, Geology, Physics, and Microbiology.

The 17-person strong research group is active in a number of various aspects of gas hydrates, such as:

- Flow assurance, avoiding hydrate and wax problems in subsea transfer lines
- Kinetics of hydrate formation and dissociation
- Design and evaluation of low dosage hydrate inhibitors
- Storage and transportation of oil and gas using hydrate technology
- CO\textsubscript{2} separation and sequestration
Gas hydrates in marine sediments
Positive applications of gas hydrates

The results of the studies have been well documented in more than 100 publications.

The experimental equipment, in the two well-equipped hydrate laboratories, consists of; 7 versatile hydrate rigs for hydrate formation at various conditions, such as stirred tank, porous media and a rocking equilibrium cell. There are two novel high pressure glass micromodel facilities for visual investigation of gas hydrate formation and decomposition in simulated porous media. Another unique experimental equipment is an ultrasonic rig (which has been designed and built in our Workshop) for detecting and quantifying gas hydrates in subsea sediments (using physical techniques) and simulating various scenarios for gas hydrate dissociation or production. Recently, a very high pressure hydrate rig (up to 2000 bar) has been designed and commissioned for generating gas hydrate stability data at very high pressure conditions. The Centre is also well equipped for gas handling and analysis (GC/MS).

The hydrate theoretical studies have resulted in a reliable thermodynamic model, which is capable of predicting phase behaviour, including hydrate phase boundaries and flash calculations. Comparative studies with other commercially available packages have demonstrated the reliability of the developed thermodynamic model (Tohidi et al., 1997). For this reason, our gas hydrate prediction software (HWHYD) has been selected by a number of major companies for use in their operational and research activities.

The Centre provides support to the industry through 2 JIPs, technical studies, short courses, and supplying computer software. The main strength of the Centre is based on its dedicated multi-disciplinary research team, purposely built equipment in our workshop, and excellent laboratory facilities.

1.3. KINETIC HYDRATE INHIBITORS
The background to the development of kinetic hydrate inhibitors is well documented. Initially, alkylarylsulfonic acid and its salt, alkyl glycocides, tyrosine derivatives, and some surfactants have been patented as kinetic inhibitors. The finding of polymeric materials, such as polymers with an amide group (-N-C=O), has made the so-called
first generation of KHIs available for commercial applications.\textsuperscript{2,8} Polymers used in
the first generation KHIs include homopolymers, such as polyvinylpyrrolidone (PVP) and
polyvinylcaprolactom (PVCAP), and their copolymers. The performance of the
initial inhibitor formulation with single polymer component was not very satisfactory.
Therefore, the second-generation inhibitors have been formulated and commercialised
for industrial applications. These products are mainly new formulations based on
PVP and PVCAP and their derivatives to enhance product performance. Some
modifications on polymer structure, molecular weights, polymerisation process, and
adding good synergists have been made to increase the inhibitor performance.\textsuperscript{16,17}

Limited tests at our laboratory and other unpublished data have shown that the second
generation KHIs could handle subcooling up to 13 °C with at least 48 hours induction
time, but their performance could be greatly affected by the presence of other
compounds in the system, such as gas composition, liquid hydrocarbons, corrosion
inhibitors or other chemicals. They are also sensitive to pressure and temperature in
different circumstances.

1.4. MECHANISMS OF KINETIC INHIBITORS
Despite the technical achievements offered by the KHIs, the mechanism of inhibition
remains unclear. This has been argued whether the polymers act on the surfaces of an
already exiting hydrate crystal or whether they associate in some manner with
hydrate-forming constituents while still in solution. Common to all these polymers is
the presence of hydrophilic groups of structure that causes hydrogen bond to
(adsorption) hydrate crystals, thereby hindering the growth and agglomeration of
crystals. This adsorption theory was supported by studies using small-angle neutron
scattering (SANS) techniques and molecular simulations.\textsuperscript{9,11,12} However, whether and
how the polymers delay or enhance hydrate nucleation is still not clear.\textsuperscript{10} The effect
of synergists, and other compounds on the performance of these KHIs remains
unexplored.

In this project, the mechanisms of LDHIs, with particular emphasis on KHIs, will be
investigated using the high pressure glass micromodel combined with other
techniques such as GC analysis, mass spectrometer and UV spectrometer for gas and
inhibitor analysis.
1.5. RESEARCH OBJECTIVES
The research objectives could be summarised as:

- Gain better understanding of the process gas hydrate formation in gas and oil systems using the high pressure (400 bar) glass micromodels, and investigate the mechanism of gas hydrate inhibition by LDHIs using visual capabilities of glass micromodels and other analytical techniques.
- Upscale and repeat the micromodel tests using stirred tank type high pressure kinetics rig (up to 700 bar), and evaluate the performance of various LDHIs under different operating conditions.
- Study the effect of other factors on the LDHI performance, including presence of liquid hydrocarbon, gas compositions, gas/water ratio and gas hydrate structure.
- Use the information generated above in improving the design, formulation and/or deployment of LDHIs.
- Test new chemicals and new formulations to enhance the performance of current and new LDHIs supplied by the sponsors.

This project is supported and participated by sponsors from chemical manufacturers (chemical company), inhibitor providers (service company), inhibitor users (oil companies) and the DTI. This will provide a unique opportunity for the project to be steered corresponding to the industrial demand closely, and ensure a rapid materialisation of the research outputs.

1.6. PROGRESS REPORT
A technical steering meeting will be held twice a year to review the project work programme and progress. Every six months a project report will be produced and circulated to the sponsors prior to the six monthly meeting.

In the last six months, the continuation of the tests for investigation of the different parameters affecting the performance of PVCAP, were carried out in the kinetics rigs. Hydrate morphology of different systems with and without inhibitor was investigated by visual observation in high pressure micromodel. The application of ultrasonic waves in studying nucleation and growth of hydrate with and without inhibitor was examined. The literature survey for anti agglomerants completed and some preliminary experiments carried out.
Chapter 2 presents the results of the micromodel experiments carried out on two PVCAP based inhibitors in natural gas and methane systems. Chapter 3, presents the results of the experiments carried out on the mentioned kinetic inhibitors in the kinetics rigs to evaluate their performance in different bulk conditions and different hydrate structures. In this chapter the results of the tests conducted to study the effect of hydrate structure on the performance of the PVCAP in terms of induction time have also been presented. Visual observations of hydrate formation in different hydrate systems with and without PVCAP, using a windowed rig, at static conditions, are presented in chapter 4. Chapter 5 describes the application of ultrasonic set up to investigate hydrate nucleation and growth in the presence of PVCAP and with different hydrate formers. A brief description and literature survey on the development, testing and field application of anti agglomerants is presented in Chapter 6. In this chapter the results of some preliminary experiments in the Kinetics Rigs and the Glass Micromodels, are also presented.

REFERENCES:


7. Lovell D., Pakulski M., “Hydrate Inhibition in Gas Wells Treated with Two Low Dosage Hydrate Inhibitors”, SPE paper 75668, presented at the SPE Gas Technology Symposium held in Calgary, Canada, 40 April-2 May, 2002


CHAPTER 2
VISUAL OBSERVATION BY MICROMODEL EXPERIMENTS

2.1. INTRODUCTION
The main objectives of conducting experiments in micromodel are to provide visual observation of the hydrate crystal morphology and particle size to understand the basics of the gas hydrate formation and growth in various fluid systems and the mechanism of inhibition by low dosage hydrate inhibitors.

This section of report starts with the experimental results generated during March to June 2003 period and presented at the previous steering committee meeting on natural gas-water system with and without PVCAP (and not reported in the Previous Progress Report in March 2003). The experiments on the new kinetic inhibitor (HI03-22) provided by Clariant Company in natural gas–water and methane-water systems, which were conducted during this period, are also reported.

Prior to experiments on new inhibitor, some modifications were made on HP micromodel set-up to improve data acquisition and visual observation. These include the installation of switching valves and pressure transducers for inlet and outlet, and improvement in light source. Experimental procedure covering set-up and sample preparation have been described in previous progress report. In this report the test procedure adapted to the above-mentioned modifications are explained.

2.2. EXPERIMENTAL PROCEDURE
Tests were conducted for natural gas-water system and methane-water system in the presence of 2 vol% HI03-22. The new kinetic inhibitor (HI03-22) is composed of PVCAP, a synergist chemical, water and ethylene glycol. In order to compare the morphology and performance of the new inhibitor with 1 mass% PVCAP, the same pressure set points as those of previous tests with PVCAP were used. The tests were conducted using the modified HP micromodel as shown by schematic diagram in Figure 2.1.
In the experiments 12 cc of solution containing 2 vol % of new inhibitor in deionised water (dyed with methyl blue) was charged into the inlet cylinder. The cylinder was connected to vacuum pump to remove trapped air. Subsequently natural gas or methane gas source was connected to the cylinder to saturate water with gas. The cylinder content was shaken several times to promote gas dissolution in the water. Then it was left overnight at about 1800 – 2000 psia (124 bar – 138 bar) depending on the gas cylinder pressure.

The saturated water and gas in the cylinder was pumped into the inlet side of micromodel. The gas sample was injected into the system from the outlet side to create gas bubbles in the system and to pressurise the system to the required test pressure. The system was then cooled down to 4°C. The formation of hydrate was visually observed and recorded accordingly. The induction time was measured from the time when the system pressure and temperature were stabilised. In some tests, the hydrate had formed before the system reached to the stable conditions (without induction time).
2.3. EXPERIMENTAL RESULTS AND DISCUSSION

2.3.1. Natural Gas – Water system

2.3.1.1. Without Inhibitor

The blank tests for natural gas-water system were conducted to study the hydrate morphology at low and high degrees of subcooling and also to investigate the mechanism of hydrate formation. Experiments were conducted at two conditions; 14.5°C and 12°C subcooling at 1500 psia (103 bar) and 1000 psia (69 bar) respectively. The video footage of hydrate formation for the above system was presented in previous steering committee meeting. It was observed that hydrate mainly formed in the gas bubbles (from free gas) and traces of hydrate formed in water phase (from dissolved gas). The hydrate structure was being transported through the water phase to the adjacent free gas bubbles to form hydrate. The process was continuous until all gas bubbles were converted to hydrate. The induction time was approximately 10 minutes.

At low degree of subcooling, hydrates formed following gas bubble profiles and spread rapidly in a continuous gas phase in the model with approximately 20 minutes of induction time. Diffusion plays an important role during hydrate growth at low degree of subcooling. This phenomenon was also reported by Tohidi et al (2002) for natural gas–water system at about 10°C subcooling conducted using low-pressure micromodel set-up.

From the results, it can be concluded that the degree of subcooling has an important effect on the mechanism of hydrate formation for natural-gas system. After hydrate formation the hydrate morphologies were similar in both cases. The still pictures in Figure 2.2 illustrate the hydrate formation sequence at high degree of subcooling (14°C). The hydrate crystal turned to white crystalline solid and more consolidated after about 20 hours due to crystal rearrangement to become more stable crystal. Only some traces of hydrate crystal formed in the water phase due to low solubility of natural gas in the water phase to form hydrate.
Figure 2.2. Hydrate formation in Natural Gas-Water System at 1500 psia/103 bar, 4°C (14.5°C subcooling).
2.3.1.2. In the Presence of PVCAP

The test was conducted at 1300 psia (90 bar) and 4°C with 14°C subcooling to study the effect of 1 mass% PVCAP on the hydrates formation and their morphology. The induction time of the system in the presence of PVCAP was 8 hours, which was, as expected, longer than the blank test carried out earlier at the same conditions. Similar to the system without PVCAP, hydrate initially formed dark solid masses then turned to lighter white crystalline as a function of time as they became more dense and solid crystals (Figure 2.3).

Figure 2.4 shows the still pictures comparing the hydrate growth rate with and without PVCAP. It is indicated that without PVCAP, more oriented and perfect hydrate crystalline was observed and the edges were changed to white crystalline after 20 hours (Figure 2.4(a)). On the other hand in the presence of PVCAP hydrate growth was still continuing but at a slower rate after 72 hours which can be seen from the dark solid masses of hydrate (Figure 2.4(b)). This evidence suggests that the PVCAP significantly reduces rate of hydrate growth in natural gas-water system. In the presence of PVCAP, the spread of hydrates through the model did not seem to occur via hydrates forming from dissolved gas, which suggest that PVCAP inhibit hydrate formation from dissolved gas in water phase.

(a) Before hydrate formation.
2.6

(b) 72 hours after hydrate formation -

Figure 2.3. Hydrate formation in Natural Gas-Water System in the presence of PVCAP at 1300 psia/90 bar, 4°C (14°C subcooling).

(a) 20 hours after initial hydrate formation without PVCAP.

(b) 72 hours after initial hydrate formation with PVCAP

Figure 2.4. Natural Gas Hydrate formation (a) without PVCAP (1500 psia / 103 bar, 4°C, 14.5°C subcooling) and (b) with PVCAP (1300 psia / 90 bar, 4°C, 14°C subcooling).
An interesting observation from the video footage (refer to July 2003 presentation material) during hydrate growth was that some of the gas bubbles were expelled from the hydrate structure. This could be due to fractionation of components in the natural gas. The gas bubbles are possibly consisting of light component such as methane. With time these gas bubbles turned to hydrate crystal. The explanation to this phenomenon is that larger size gas molecules will have more tendency to fill-up or fit into water cavity to make the structure of hydrate more stable as compared to the smaller size gas molecules such as methane.

For natural gas – water system, the effect of foaming that caused the formation of small and discrete gas bubbles and hydrate particle was not observed as reported earlier for methane-water system and carbon dioxide-water system. However, the interfacial tension study on different systems, planned to be conducted in the visual rig, could provide some clues to this observed phenomenon.

In another experiment with similar conditions, the effect of high gas to water ratio on the hydrate formation mechanism for the same system was investigated. In this experiment, hydrate began to form approximately 7 hours of induction time. Once the formation initiated, hydrates spread throughout model rapidly within 30 minutes. Hydrates formed from discrete gas bubbles moving as a front through the gas utilising small amount of water in the model as shown in Figure 2.5. Video footage of these observations (presented in the previous steering committee meeting) showed that hydrate crystalline appearance was lighter and less dense compared to the earlier tests. This was possibly due to insufficient water molecules in the system to form more solid hydrate crystals.
2.3.1.3. In the Presence of New Inhibitor (HI03-22)

Several tests were conducted at different pressures (1300 psia/90 bar and 1000 psia/69 bar) to study and to compare the effect of new inhibitor (HI03-22) with PVCAP, on the hydrates formation and their morphologies. In the experiments, natural gas with the composition listed in Table 1 was charged into the micromodel in the presence of 2%vol of HI03-22. The hydrate phase boundary provided in Figure 3.1 of Chapter 3 was predicted using an in-house hydrate software to determine degree of subcooling at testing conditions. The system was allowed to equilibrate using high precision quizix pump by mixing gas and distilled water prior to setting the test conditions.

Table 1: Natural Gas Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3.24</td>
</tr>
<tr>
<td>C₁</td>
<td>87.32</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.36</td>
</tr>
<tr>
<td>C₂</td>
<td>5.67</td>
</tr>
<tr>
<td>C₃</td>
<td>1.68</td>
</tr>
<tr>
<td>iC₄</td>
<td>0.23</td>
</tr>
<tr>
<td>nC₄</td>
<td>0.40</td>
</tr>
<tr>
<td>iC₅</td>
<td>0.10</td>
</tr>
</tbody>
</table>
The results show that new inhibitor formed hydrate at 1300 psia/90 bar (11.6°C subcooling) without induction time. This was due to the testing condition, which was beyond the strength of the new inhibitor to delay hydrate formation and growth. In comparison, the induction time of natural gas-water system in the presence of 1 mass% PVCAP at 1300 psia/90 bar and higher degree of subcooling of 14°C was 8 hours longer than that of above system.

Visual observations also suggest that the rate of hydrate growth is faster in the presence of 2 vol.% HI03-22 in comparison with 1 mass% PVCAP based on the still pictures shown in Figure 2.6. As seen, in the presence of PVCAP (Fig.2.6 (a)) and at 14°C subcooling, after passing 72 hours from the first hydrate particles formation, the hydrate crystals have not turned to white (more perfect structure), however in the presence of HI03-22, and at lower degree of subcooling than former (11.6°C), after 30 hours all hydrate crystals turned into white (their final stage in structural formation). This suggests that 2 vol% HI03-22 is weaker than 1 mass% PVCAP in delaying hydrate formation and growth probably due to low concentration of active polymer (PVCAP) which reduce its performance and effectiveness.

The above experiment was repeated at the same conditions after heating up the system to 35°C for about 24 hours. After cooling down the system, a little amount of hydrate formed earlier than the first test, at 6.3°C (~10°C subcooling). It formed in the gas phase in some part of the micromodel and most of the gas phase and water phase remained in the system without conversion to hydrate. However, the rate of growth appeared to be slower than the earlier tests possibly due to the lower degree of subcooling. Reducing the temperature by another 2°C (or 12°C subcooling) caused hydrate to form throughout the model while the earlier hydrate crystals formed at 10°C subcooling remained unchanged. All gas phase was converted to hydrate at 12°C subcooling. The video footage captured will be presented at the steering committee meeting.

2.3.1.4. Effect of Inhibitors on the Hydrate Morphology
While hydrate morphologies for the systems without inhibitor and the systems with PVCAP are not significantly different, it was observed that the size of hydrate crystals appeared to be smaller in the presence of HI03-22. In addition, the hydrate particles did not agglomerate or stick to each other in the presence of new inhibitor as shown in Figure 2.7. The morphology is mainly patches of very thin crystal flakes. The above observation may suggest that the synergist chemical in the new inhibitor could have affected the morphology of hydrate crystals. However, more tests is required to answer the question of whether synergist alters hydrate morphology and particle size for different systems.

(a) 72 hours after hydrate formation with PVCAP

(b) 30 hours after hydrate formation with HI03-22

Figure 2.6. Comparison of Natural Gas Hydrate growth at 1300 psia/90 bar, (a) with 1 mass% PVCAP at 14°C subcooling (b) with 2 vol%HI03-22 and at 11.6°C subcooling.
Figure 2.7. Comparison of hydrate morphology (a) Without inhibitor (b) With 1 mass% PVCAP (c) With 2%vol HI03-22
2.3.1.5. Other Phenomena Observed

Two interesting phenomena were observed during the experiments. The first observation was the dynamic growth of hydrate in gas phase shown in Figure 2.8. This observed phenomenon was described earlier by Makagon (1997) based on his experiments on kinetics and morphology of gas hydrates using a bathyscaphe chamber. His study on the locations of formation and growth of hydrate nuclei has shown that with large volumes of water in the presence of a free gas-water interface, nucleation proceeds at the surface of a gas-water interface. Once the hydrate film formation covers the whole gas-water interface, the surface contact process becomes a diffusive one. Massive crystal grows in the gas phase because of different molecular sizes of gas and water and different diffusion coefficients through a previously formed hydrate film at the gas-water interface. The growth rate of massive hydrates is determined by diffusive and sorption influx of gas and water molecules and intensity of heat removal from the forming crystal surface. This phenomenon supports the role of diffusion in hydrate formation.

The second observation was the dissociation of hydrate molecules within the hydrate structure following the profile of gas phase as a function of time illustrated in Figure 2.9. This phenomenon was observed in both inhibitors tested with natural gas-water system. However, it is unclear at this stage what caused the dissociation of hydrate. Further analysis is suggested to study this phenomenon.
Figure 2.8. Dynamics of Natural Gas hydrate formation/growth in the present of new inhibitor within 6 minutes of initial growth (1300 psia/90 bar and 6.4°C, 11.6°C subcooling). Hydrate begins to form at the gas-water interface and grow toward the middle of gas bubble with another layer of hydrate grow due to the diffusion and sorption influx of gas and water molecules from the forming crystal surface.
2 hrs after initial hydrate formation (continuous growth)

15 hrs after initial hydrate formation (slow growth)

120 hrs after initial hydrate formation (Termination of growth)

Figure 2.9. Changes in natural gas hydrate morphology in the presence of HI03-022 inhibitor with time at 1300 psia/90 bar and 6.4°C, 11.6°C subcooling. Observed hydrate dissociate within hydrate structure.
Chapter 2 Micromodel Experiments

2.3.2. Methane – Water System

Several tests were conducted with and without PVCAP for methane-water systems, which was presented at the previous steering committee meeting and also reported in the earlier progress report. At higher degree of subcooling (13°C), the system without PVCAP showed that hydrate remains largely around the gas bubble profile and became solid with hydrate crystals also growing from dissolved gas. In the presence of PVCAP hydrates formed dark masses and more dispersed (smaller hydrate particles) with less growth from dissolved gas as compared to without PVCAP. Tests repeated at lower degree of subcooling (10.5°C) with the presence of PVCAP showed that the morphology was similar to the earlier test with large plugs following profiles of gas bubbles and dark in appearance and less hydrates growth in water phase. It suggests that PVCAP, in the presence of methane, does not totally prevent the growth of hydrate in water phase.

2.3.2.1. Effect of New Inhibitor (HI03-22) on Methane Hydrate Morphology

Similar test at lower degree of subcooling, as above, was conducted for methane – water system in the presence of 2 vol % of HI03-22 to investigate and to compare the effect of new inhibitor on hydrate morphology. After charging the micromodel with test fluids and cooling down the system, hydrate formed immediately at 4.3°C and 1700 psia/117 bar, 10.5°C subcooling with no induction time as compared to the system in the present of PVCAP where the induction was about 13 hours.

Figure 2.10 described the progress of hydrate growth in this system with time. As shown in the pictures, hydrate started to form as black masses of hydrate particle, which appeared to consist of many small particles following the profile of gas bubbles (Figure 2.10(a)). After 24 hours, some of the hydrate particles turned to white crystal with mainly at the edges of hydrate crystal structure. The growth of white crystal were obvious after 74 hours of hydrate formation where the hydrates formed shells inside the gas bubbles and water molecules appeared to be remained in the middle (Figure 2.10(b)). With time, the hydrate crystal developed a continuous thin hydrate crystal and appeared to be agglomerated to each other and not separated into small crystal flakes (Figure 2.10(c)). From the still picture shown in Figure 2.11,
it was observed that some traces of gas hydrate formed in the water phase after 24 hours of hydrate formation. This might suggest that the new inhibitor, in the presence of methane, may not prevent hydrate formation in water phase.

Figure 2.10. Changes in methane hydrate morphology in the presence of HI03-022 inhibitor with time at 1700 psia/117 bar and 4.3°C, 10.5°C subcooling.
Comparison was made between methane hydrate system with PVCAP and new inhibitor (HI03-022) in term of rate of hydrate growth after about 50 hours of initial hydrate formation. Based on the still pictures taken for both cases at the same condition shown in Figure 2.12, the rate of hydrate growth in the present of new inhibitor is faster than PVCAP. It was observed that, at about 50 hours after hydrate formation, the growth of hydrate had reduced significantly indicated by white coloured hydrate crystal, whereas at the same time the system with PVCAP showed slow growth of hydrate based on the presence of black coloured hydrate particles. This observation suggests that new inhibitor is weaker than PVCAP in delaying growth of hydrate for methane-water system.
2.3.3. Effect of New Inhibitor on Morphology of Different Hydrates
A comparison between natural gas-water and methane-water systems were made to observed different morphologies of hydrates in the presence of new inhibitor. With this information, it appears that the new inhibitor affected morphology of both methane (structure I) and natural gas (structure II) gases as shown in Figure 2.13. It was observed that natural gas was in the form of crystal flakes while methane was in the form of continuous thin hydrate crystal.
2.4. SUMMARY OF RESULTS

The hydrates crystal morphology and their particle size were investigated by visual observations in high pressure Micromodel set-up. This information will assist in better understanding of gas hydrate formation and growth in various fluid systems and also the mechanism of inhibition by Low Dosage Hydrate Inhibitors (LDHI).
In this report experiments on two systems were reported: natural gas–water and methane-water systems. The study was focused on investigating the effect of degree of subcooling on morphology and mechanism of hydrate formation, effect of different inhibitors on hydrate morphology and rate of hydrate growth for the two systems.

Based on the results of the study, it is concluded that the degree of subcooling has an important effect on the mechanism of hydrate formation for natural-gas system. For high degree of subcooling the formation is in the both water and gas phases, whereas at low degree of subcooling it is only in continuous gas phase. However, there are no significant differences in hydrate morphology for low and high degree of subcooling. Some traces of hydrate formed in water phase due to low solubility of gas into water phase.

Several evidences from observation of hydrate growth showed that gas diffusion plays a major role in gas hydrate growth particularly at low degree of subcooling due to reduction in gas solubility as a result of hydrate formation.

PVCAP significantly reduces the rate of hydrate growth in water phase for natural gas–water system. However, for methane-water system, PVCAP appears to be less effective in reducing the hydrate growth and inhibiting hydrate formation in water phase as compared to natural gas-water system. It can be concluded that PVCAP appears to be more effective for structure II hydrates compared to structure I hydrates.

Experiments conducted to study the effect of new inhibitor (HI03-22) indicate that 2 vol% HI03-22 is weaker than 1 mass% PVCAP in delaying hydrate formation and growth in both systems of methane and natural gas. This is possibly due to low concentration of active polymer (PVCAP) in the inhibitor, which reduces its performance and effectiveness.

While hydrate morphologies for the systems with and without PVCAP are not significantly different, it was found that they are very different. In the presence of HI03-22. It appears that the new inhibitor affected morphology of bothhydrate structure I and II.
REFERENCES

Makagon Y.F. (1997), Hydrates of Hydrocarbons, Pennwell, Tulsa

CHAPTER 3

KINETICS RIG EXPERIMENTS

3.1. INTRODUCTION

Two series of experiments were conducted using the kinetics rigs. The first was to test a new formulation of kinetic inhibitors based on PVCAP (HI03-22, from Clariant) in order to find out the range of its applicability in different systems and conditions. The performance of the inhibitor in terms of induction time was tested in different degrees of subcooling. The effect of different hydrate structures on the performance of the inhibitor was studied by testing the inhibitor in natural gas-water and methane-water systems. The inhibitor was also assessed in two hydrodynamic conditions; shut-in and flowing (stirring) conditions.

The second series of experiments were designed and conducted in a kinetic rig to investigate the effect of hydrate structures on the performance of PVCAP. Two synthetic gas mixtures, which have the same hydrate phase boundaries but will form different hydrate structures (sI and sII), were used in the experiments to exclude the effect of pressure or temperature.

3.2. TESTING HI03-22

The new KHI (labelled as HI03-22) was supplied by Clariant, which is composed of PVCAP, a synergist chemical, water and ethylene glycol. The performance of the kinetic inhibitor was assessed in terms of induction time in different systems, by conducting experiments in a kinetic rig. In all the tests as suggested (by Clariant) a concentration of 2 vol% of the inhibitor in deionised water was used. The details of the tests and results are presented below.

3.2.1. NATURAL GAS -WATER SYSTEM

A total of thirteen experiments were carried out using Kinetic Rig 1 to measure the induction times in a natural gas-water system with 2 vol% of HI03-22 at different conditions. The composition of the natural gas (LAB-NG) used in the tests has been shown in Table 3.1. The hydrate phase boundary for the system was predicted by the in-house hydrate software (HWHYD) (Figure 3.1) and used for the calculation of
degree of subcooling at the testing conditions. The experimental results are summarised in Table 3.2 and the corresponding pressure and temperature profiles measured in the experiments are presented in the Appendix (Figures 1-13).

Table 3.1. Composition of the natural gas (LAB-NG) used in the experiments

<table>
<thead>
<tr>
<th>Component</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>i-Butane</th>
<th>n-Butane</th>
<th>i-Pentane</th>
<th>Nitrogen</th>
<th>Carbon dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol%</td>
<td>87.32</td>
<td>5.67</td>
<td>1.68</td>
<td>0.23</td>
<td>0.4</td>
<td>0.1</td>
<td>3.24</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Figure 3.1. Natural gas-water hydrate phase boundary predicted using the in-house model.

The first test was carried out at 4.5 °C and 93.5 bar, corresponding to 13.5 °C subcooling (Table 3.2 Test No. 1) and the induction time was short. To decrease the subcooling in the subsequent experiments the pressure was reduced to 65 bar. At subcooling from 12 °C to 11.7 °C, the induction times observed were between 3-7 hours (Test Nos. 2-8), however at 10.7-10.9 °C subcooling, the induction times were more than 24 hours. In Test No. 10, the system stabilised at 5 °C and 65.3 bar (Appendix, Figure 10) and there was no hydrate formation for 24 hours and after that during two days there was only 1 bar pressure drop, which means very little hydrate formation. From the above tests on 2 vol% of HI03-22 in water in the presence of the natural gas, it seems that in order to achieve longer induction times than one day the degree of subcooling in the system should be less than 11 °C.
At static conditions, 4 °C and 65.5 bar (11.7 °C subcooling), the induction times were between 15-20 hours (Tests No.11-13). As expected the induction time at static conditions was longer than that at flowing (mixing) conditions (compare with Tests No.7-8).

In previous tests on 1 mass% of PVCAP (2.5 mass% Luvicap®) in the natural gas-water system it appeared that it could prevent hydrate formation for more than two days at 12.8 °C subcooling (Appendix, Figures No.14-15). It seems that in the natural gas water system, 1 mass% of PVCAP is more effective than 2 vol% of HI03-22.

Table 3.2. Experimental results obtained from the kinetics rig for 2%vol kinetic inhibitor (HI03-22) solution in the presence of natural gas.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/ P</th>
<th>Subcooling / °C</th>
<th>Induction Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>4.5 / 93.5</td>
<td>13.5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>3.7/ 65</td>
<td>12</td>
<td>3.7</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>3.8 / 65</td>
<td>11.9</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>3.8 / 65</td>
<td>11.9</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>3.9 / 65</td>
<td>11.8</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>3.9 / 65</td>
<td>11.8</td>
<td>5.7</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>4.0 / 64.8</td>
<td>11.7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>4.0 / 64.8</td>
<td>11.7</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>600</td>
<td>4.8 / 65.2</td>
<td>10.9</td>
<td>&gt;60</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>5.0 / 65.3</td>
<td>10.7</td>
<td>24-60</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>4.0 / 65.5</td>
<td>11.7</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>4.0 / 65.5</td>
<td>11.7</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>4.0 / 65.5</td>
<td>11.7</td>
<td>16</td>
</tr>
</tbody>
</table>

3.2.2. METHANE-WATER SYSTEM

For comparison of the performance of the kinetic inhibitor (HI03-22) in a sI hydrate former system, experiments were carried out in a methane–water system in the presence of 2 vol% HI03-22. The summary of the experimental results is presented in Table 3.3 (Appendix, Figures No.16-23). At 9.2-10.4 °C subcooling, the induction times are very short. Longer induction time was observed only at low degree of subcooling (Test No.6). With comparison of the induction times at similar degrees of subcooling in the natural gas–water system (Table 3.2, Tests No.9-10), it seems that
this kinetic inhibitor performs better in a sII hydrate former system than that in a sI system. At no mixing conditions, the induction times were more than 1.5 days at 10.3 °C subcooling (Tests No.7-9).

Table 3.3. Experimental results obtained from the kinetics rig for 2%vol kinetic inhibitor (H0322) solution in the presence of methane.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction Time / hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600</td>
<td>4.6 / 120</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
<td>4.5 / 118</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>4.0 / 117.5</td>
<td>10.4</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>600</td>
<td>5.3 / 118.5</td>
<td>9.2</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>5.3 / 119.5</td>
<td>9.2</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>6.8 / 121</td>
<td>7.8</td>
<td>&gt;50</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>4.2 / 118</td>
<td>10.3</td>
<td>&gt;36</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>4.1 / 118</td>
<td>10.4</td>
<td>&gt;50</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>4.0 / 119</td>
<td>10.5</td>
<td>&gt;80</td>
</tr>
</tbody>
</table>

3.3. HYDRATES STRUCTURE EFFECT

In the previous report the effect of hydrates structures on the performance of different kinetic inhibitors was discussed and it appeared that, for the inhibitors tested, at same degrees of subcooling, the induction times in a natural gas system was longer than that in a methane system. This is also confirmed in the tests conducted for H103-22 (as shown section 3.2.2 above). However, in these tests, the effect of pressure was not excluded since at the same degree of subcooling in the two mentioned systems the pressures were different. The role of pressure on the performance of the kinetic inhibitors is not clear. In this study, two systems were designed in such a way that they have very similar hydrate phase boundaries while different hydrate structures will form at the same pressure and temperature conditions. Therefore the two systems can be tested at same degrees of subcooling and at same pressures. The mixtures of methane-ethane was selected as structure I hydrate former and methane-propane as structure II hydrate former. Using the in-house hydrate software, the composition of the gas mixtures were selected to be C₁(97 mol%)-C₃(3 mol%) for sII hydrate former and C₁(70 mol%)-C₂(30 mol%) for sI hydrate former. The phase boundaries of the
two gas mixtures are presented in Figure 3.2. At any pressure, the temperature differences between two phase boundaries are between 0.2-0.3 °C.

A solution of 1 mass% PVCAP in water was prepared and tested with the above gas mixtures to measure the induction times at similar conditions using Kinetics Rig 2. The results of the tests have been illustrated in Tables 3.4 and 3.5. (Appendix, Figures 24-30)

![Figure 3.2. Gas mixture-water hydrate phase boundary predicted by the in-house model.](image)

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>1.0 / 99</td>
<td>17.8</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>0.8 / 97</td>
<td>18</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>0.2 / 97</td>
<td>18.6</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 3.5. The results of the tests on 1 mass% PVCAP in water in the presence of 68.6 mole% methane and 31.4 mole% ethane.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RPM</th>
<th>Testing T/P</th>
<th>Subcooling</th>
<th>Induction Time/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>1.9 / 96.9</td>
<td>17.1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>3.8 / 97.2</td>
<td>15.2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>4.2 / 97.2</td>
<td>14.8</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>4.2 / 97.2</td>
<td>14.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The tests in both systems carried out at the pressure range close to 97 bar. From Table 3.4 it can be seen that for sII hydrate former system, at 17.8-18.6 °C subcooling the induction times is about 30-16 hours. However in sI hydrate former system (Table 3.5) at the same pressure range, the inhibitor was not able to prevent hydrate formation even at lower degrees of subcooling. The effect of gas composition or hydrate structures on the performance of PVCAP is very significant. It was speculated that the lactam ring of PVCAP has a better steric fit into the $5^{12}6^4$ cavity on the sII hydrate structure [Makogon, PhD Thesis, Colorado School of Mines, 1997]. More experiments are needed to confirm the results.

3.4. SUMMARY AND DISCUSSION

One of new formulations of PVCAP based kinetic inhibitors (HI03-22) from Clariant was tested in different gas system and at various conditions. From the results of the tests it appeared that for achieving the induction times longer than one day, the degree of subcooling should be less than 11 °C for natural gas system and less than 9 °C for methane gas system. It was also confirmed that HI03-22 is more effective in structure II hydrate forming systems as expected for the PVCAP based KHIs. Furthermore, 2 vol% of HI03-22 is not as effective as 1 mass% of PVCAP in a natural gas system. At static conditions, with similar degree of subcooling as that at mixing conditions, longer induction times experienced in the presence of HI03-22 in a natural gas and methane systems. However it is interesting to note that for 1 mass% of PVCAP longer induction times were observed during mixing than that at static conditions. The results of the tests with 1 mass% PVCAP in natural gas system with mixing and without mixing, at similar degrees of subcooling have been illustrated in the appendix.
(Figures 15, 31 and 32, 33). This perhaps was due to the presence of the synergist chemical in HI03-22, which can improve the gas-water interface property. Hydrate could be mostly vulnerable to initiated at the gas-water interface when the system is at a static condition.

The effect of hydrate structure on the performance of PVCAP based kinetic inhibitors was further studied by testing two different gas mixtures with similar hydrate phase boundaries, and it appeared that at similar degrees of subcooling and pressures, the kinetic inhibitor performs much better in structure II hydrate former systems.
CHAPTER 4
EXPERIMENTS IN HIGH PRESSURE VISUAL RIG

4.1. INTRODUCTION
Experimental measurements conducted to study the effect of the kinetic inhibitor PVCAP on natural gas hydrate formation showed that hydrate formation occurred earlier when the test fluids were not mixed (i.e., shut in conditions) by comparison with when they were mixed (i.e., flowing conditions). This is contrary to the usual trend in hydrate work which normally shows hydrate formation is both delayed, in terms of induction time, and less efficient, in terms of the time required to reach equilibrium, when the test fluids are not mixed. As the experimental rig used for these tests has no visual capabilities it was decided to utilise a high pressure visual rig to further investigate the observed behaviour. The high pressure visual rig allows observations and capturing of both still and moving pictures. Tests were initially conducted on gas hydrate formation from natural gas hydrates with and without PVCAP. These tests showed that when hydrate formation occurred with no mixing considerably more hydrates formed, in the same time period, when PVCAP was present by comparison with distilled water. In addition the pattern of hydrate formation in the presence of the PVCAP was markedly different to the case with distilled water. Further tests were conducted using the same kinetic inhibitor along the same lines with methane and with a mixture of methane and propane to investigate how formation in a cell with no mixing progressed with different hydrate structures.

The visual cell has four ports allowing for the installation of a temperature probe a pressure transducer and two high pressure electric feed-throughs for measurements with a quartz crystal microbalance (QCM). It was proposed to utilise one of the electric feed-through ports to install a hypodermic needle allowing for interfacial tension (IFT) measurements by pendant drop technique. At the present time the pendant dropper has been installed and the system will be commissioned. It is anticipated that experimental measurements will be presented at the upcoming project steering committee meeting.

The following paragraphs describe the experimental equipment and the methods and results for the tests conducted using the high pressure visual rig.
4.2. EXPERIMENTAL EQUIPMENT AND METHODS

The experimental set-up is comprised of a high pressure cylinder fitted with sapphire windows at both ends. The cell can be used at pressures up to 517 bar and at temperatures between –30 and +50°C. The cell temperature is controlled by circulating water from a heater/chiller through an inbuilt jacket. A platinum resistance temperature probe monitors the cell temperature. The pressure of the cell is monitored by a strain gauge pressure transducer connected to the cell via a high pressure line. The accuracy of the temperature measurement is ±0.1°C and the pressure ±0.3 bar. A computer is used to log the cell pressure and temperature. A schematic of the experimental rig is shown in Figure 4.1. The cell is mounted on a rocking mechanism in order to give mixing when required.

For the tests reported here 50 ml of the water without or with inhibitor was injected into the cell and then gas was injected to the desired start point pressure. The cell was mixed to equilibrate the contents and then held in a horizontal position in order to make visual observations with the aid of a magnifying camera.

Distilled water was used in the tests with pure water and an aqueous solution composed of 1 mass% PVCAP was used for the tests with inhibitor present. The natural gas was used had the same composition as that given in Table 4.1. The methane used was 99.995% pure and the propane was 99.5% purity.
4.3. EXPERIMENTAL RESULTS AND OBSERVATIONS

4.3.1. Natural gas without and with PVCAP

Two tests were conducted with natural gas. In the first test distilled water was used and the initial pressure was set to 131 bar at 34.3°C. The temperature was then lowered at a constant rate to 4.1°C over a 12 hour period, and it was left at this temperature for the duration of the test. In the second test exactly the same procedure was followed but with PVCAP present, the starting pressure was 130 bar. For both of these tests the cell was held static. For both systems tests had been conducted with mixing and it was found that there was no induction time, hydrate formation was seen indicated by a pressure drop as soon as the temperature reduced to 4.1°C. At 4.1°C the pressure was close to 106 bar in both tests representing 14.7°C subcooling from the natural gas hydrate phase boundary. The initial conditions and the temperature to
which the cell was cooled were chosen to be close to conditions used in tests in the kinetic rigs.

The two tests showed significant differences both in terms of the pressure vs. time data and in terms of the visual observations. The pressure vs. time data for the two tests are shown in Figure 4.2. As can be seen the test with no PVCAP showed a slow pressure drop over time once the temperature was reduced to 4.1°C. This contrasts with the test with PVCAP where the pressure drop was much greater over time indicating that much more hydrates had formed. For the test with no PVCAP hydrates were seen to form on the vessel walls and at the gas/water interface. The bulk of the water phase remained hydrate free with only a few needle type hydrate crystals growing into it from the gas/water interface. In the test with the PVCAP hydrates initially were seen to form at the gas/water interface and on the cell walls in the vapour phase. Hydrates forming at the gas/water interface are shown in Figure 4.3. These hydrates then appeared to dissociate and hydrate formation was seen to take place in the upper part of the cell. The water phase appeared to be drawn upwards leaving no water in the lower part of the cell. Figures 4.4.1 through 4.4.3 show the sequence of events. This sequence of events was seen to happen over a period of around 20 minutes commencing at the time when the cell temperature was reduced to 4.1°C. There was no great pressure drop (about 3 bar) during this time indicating that the amount of gas bonded in hydrates was small although the mass appeared significant. Hydrate formation continued as seen by the pressure drop and more bulk and more solid looking masses of hydrate forming accompanying the continuous pressure drop. It can also be seen from the pressure vs. time data in Figure 4.2 that after about 30 hours the pressure dropped rapidly indicating an increase in the rate of hydrate formation at that point.
Figure 4.2. Plot of pressure vs. time data for two tests with natural gas hydrates in static conditions without and with PVCAP (1 mass%).

Figure 4.3. Picture of natural gas hydrates growing at the gas/water interface in the presence of PVCAP.
Figure 4.4.1. in a sequence of 3. Picture of natural gas hydrates formed in the presence of PVCAP, water phase being drawn from the lower part of the cell.

Figure 4.4.2. in a sequence of 3. Picture of natural gas hydrates formed in the presence of PVCAP, water phase being drawn from the lower part of the cell.
4.3.2. Methane without and with PVCAP

As with the tests on natural gas, tests were conducted without and with PVCAP in static conditions at a pressure and temperature close to those used in tests in the kinetic rigs. The temperature was cooled from 34.3 to 4.1°C over a 12 hour time period and then held for the duration of the test. The pressure prior to cooling was 142.3 bar and this reduced to 118 bar after cooling to 4.1°C. This represents 10.3°C subcooling from the methane hydrate phase boundary. Initially a test was conducted without PVCAP. The results from this test were similar to those with natural gas in that there was no delay in hydrate formation and that the pressure drop caused by hydrate formation was not rapid or large, around 1 bar over 110 hours. Visually the situation was similar with hydrates growing on the cell walls in the vapour phase and at the gas/water interface. There were some needle-like crystals growing into the water phase as shown in Figure 4.5. A second test was then carried out with PVCAP present to see what differences would be seen. No significant hydrate formation in terms of pressure reduction occurred until 19 hours after the temperature had been...
reduced to 4.1°C. At around this time there was a significant pressure drop after which the pressure stabilised until around 36 hours after 4.1°C had been reached. At this point the pressure dropped very rapidly and then stabilised until the test finished after 65 hours total running time. The pressure vs. time data for the tests without and with inhibitor are summarised in Figure 4.6. From a visual point of view the initial stages of hydrate formation were not captured, however it was seen that hydrates had formed throughout the water phase. Unlike the case with natural gas and PVCAP the water phase did not move from the lower part of the cell. Following this test hydrates were dissociated by raising the temperature to the initial starting temperature and mixing the cell for over 6 hours. The test was then repeated with continuous mixing to measure the induction time with mixing. Hydrate formation started 7 hours after the cell temperature had reached 4.1°C, compared to the 19 hours with no mixing.

Three further tests were conducted with methane and PVCAP. In all tests the same procedure was used. For the first test with a new sample of water/PVCAP the induction time for hydrate formation was 16 hours, which is similar to the 19 hours recorded in the previous test with a new sample (By new it is meant that no hydrates had been formed in the sample before). The reason to conduct the test was in order to try and capture the initial stages of hydrate formation on video. The hydrates were then dissociated by raising the temperature and mixing and the test repeated. In the second test the induction time increased from 16 hours to 52 hours and unfortunately the initial stage of hydrate formation was not captured on video. The pressure vs. time data for the two tests is shown in Figure 4.7. As can be seen the pattern of hydrate formation differed from the previous test with PVCAP in that the overall pressure drop was greater and appeared to be in two steps.

One further test was conducted to find out if the presence of particulate matter in the form of 1 mass% yeast would have any influence on the performance of the inhibitor and the pattern of hydrate growth. Yeast was chosen as an example of organic matter that might be present. Further tests could be conducted with different types of particulate material such as clay and sand particles. In this test with a new sample the induction time was increased to 69 hours. The pattern of pressure vs time was similar.
to that seen in the two previous tests. The data from all three tests is shown in Figure 4.8.

One final test with methane was conducted with distilled water and 1 mass% yeast to see if the particles may act as nucleation sites in the water phase and increase the amount of hydrates formed by comparison with the test with pure water. The result was that the pattern of hydrate growth was the same for the two cases with only a small amount of hydrates forming at the gas/water interface and on the cell walls in the gas phase.

Figure 4.5. Picture of needle like methane hydrate crystals growing into the water phase from the gas/water interface.
Figure 4.6. Plot of pressure vs time data for two tests with methane hydrates in static conditions without and with PVCAP (1 mass%).

Figure 4.7. Plot of pressure vs time data for two tests with methane hydrates in static conditions with PVCAP (1 mass%).
4.11

Figure 4.8. Plot of pressure vs time data for the three tests with methane hydrates in static conditions with PVCAP (1 mass%), in one test particulate matter in the form of 1 mass% yeast was present.

4.3.3 Methane/propane without and with PVCAP

Four tests have been done so far with a mixture of methane and propane composed of 5 mole% propane. First a test was conducted without PVCAP with the cell static. The temperature was decreased from 33°C to 0°C over 12 hours. The initial pressure was 57.5 bar and it decreased to 48.8 bar once the temperature reduced to 0°C representing 16°C sub-cooling compared to the hydrate phase boundary for this mixture. Hydrate formation started immediately the temperature had decreased to 0°C. The pressure drop associated with hydrate formation was not large. From a visual point of view the pattern of hydrate formation was similar to the previous static tests with natural gas and methane in that hydrates formed on the cell walls in the gas phase and at the gas/water hydrate phase boundary. Also needle like hydrate crystals grew down into the water phase from the gas/water interface, examples are shown in Figures 4.9. and 4.10. In the next test the same conditions and temperature cycle were used but with PVCAP present. In this test hydrate formation started less than 1 hour after the temperature reached 0°C, showing little induction time. Compared to the test without PVCAP the pressure drop on hydrate formation was much greater as shown in Figure 4.11 which gives the pressure vs. time data for the two tests. The pattern of
hydrate formation was similar to that seen in the test with natural gas and PVCAP in that the water was drawn to the upper part of the cell leaving no water in the lower part.

In the second two tests the starting pressure and temperature were kept the same but the temperature was reduced to 3.7°C over 12 hours in order to see what differences were seen with less subcooling. The subcooling in these tests was calculated to be 12.3°C. A test was run with PVCAP and no hydrate formation was seen 32 hours after the temperature had reached 3.7°C. The cell contents were then mixed and no hydrate formation was seen for a further 27 hours so the test was stopped. One further test was then run without PVCAP with mixing from the start. In this test hydrate formation started 2 hours after the temperature had reached 3.7°C. A plot of the pressure vs. time data for the two tests is given in Figure 4.12.

Figure 4.9. Picture of needle like methane/propane hydrate crystal growing into water phase from gas/water interface.
Figure 4.10. Picture of needle like methane/propane hydrate crystals growing into water phase from gas/water interface.

Figure 4.11. Plot of pressure vs. time data for two tests with methane/propane (5 mole% propane) hydrates in static conditions without and with PVCAP (1 mass%).
Figure 4.12. Plot of pressure vs time data for two tests with methane/propane (5 mole% propane) hydrates without and with PVCAP (1 mass%).

4.4. DISCUSSION

The tests conducted in the high pressure visual rig show some interesting observations in relation to the effect of PVCAP and hydrate structure on the formation of hydrates in a static cell. The three sets of tests showed the same effect of PVCAP on the amount of hydrate formation when compared to that formed in the absence of the inhibitor. This was that the amount of hydrate formation in the presence of the inhibitor was markedly greater and most of the available water was bonded in the hydrate structure. There was a difference in the way hydrates formed from methane (structure I) and those formed from natural gas and the methane/propane mixture (structure II) in the presence of the PVCAP. In the case of methane hydrates the hydrates formed at the gas/water interface on the cell walls and throughout the water phase. For the structure II hydrates the hydrates began to form at the gas water interface and on the cell walls and then some redistribution took place whereby most of the hydrates formed in the upper part of the cell leaving no water in the lower part of the cell. This difference may have been due to the fact that for the structure II tests where hydrates formed there was little or no induction time, whereas for the methane (structure I) hydrates there was a significant induction time.
In the methane hydrate tests it was observed that, for tests with PVCAP, the induction time increased after hydrates had been previously formed in the water. The longest induction time was seen with a test where particulate matter in the form of 1 mass% yeast had been added and no hydrate had been previously formed in the water. The two observations may be linked in that earlier tests with PVCAP showed that particulates formed in water containing PVCAP when hydrates were formed and dissociated in it. It was thought that the particles were comprised of PVCAP molecules joining together. It may be that the PVCAP particles and the yeast particles had a similar effect of prolonging the induction time in the static conditions. Clearly more repetitions would be required to prove the point. If it were proven it would be interesting to see if the same effect occurred in a mixed system.
CHAPTER 5

HYDRATE NUCLEATION TESTS USING ULTRASONIC WAVES

5.1. INTRODUCTION

Hydrate formation can be considered as a kind of crystallisation, which includes two phases, i.e., nucleation and growth. The nucleation is defined as a dynamic process during which crystalline clusters (crystalline nuclei) are generated in a supersaturated aqueous solution, but the size of the clusters is less than a critical size. During nucleation period lots of the clusters are growing, while some of them may be decomposed at the same time, so that nucleation is a dynamic and unstable process at micro-scale. Once the critical size has been reached hydrate nuclei will grow into solid hydrate crystals, which is the growth phase. Nucleation plays a prominent role in many phenomena in nature and technology such as hydrate formation, condensation, crystal growth, salt precipitation, etc. Simulation suggested that the best inhibition effectiveness could be gained using inhibitors that can be adsorbed on both nucleation sites and growth sites (Dimo Kashchiev and Abbas Firoozabadi, 2003). It has been widely accepted that kinetic hydrate inhibitors dramatically slow down hydrate growth. However, do kinetic inhibitors affect hydrate nucleation? How important can the effect on nucleation be by comparison with inhibition of hydrate growth? Only measuring induction time could not satisfy the requirement to further understand inhibition mechanism of hydrate inhibitors and to innovate the design of hydrate inhibitors.

However, conventional pressure analysis could hardly provide a reliable indication to identify nucleation process because the pressure change due to hydrate nucleation is so tiny that varying temperature always covers it. It is well known that ultrasonic waves can be applied for examination of characteristics of materials including gas, liquid and solid. Generally, there are four acoustic quantities that could be used as an indication of hydrate crystallization, i.e., velocity, amplitude, frequency spectrum and phase shift. Among them frequency spectrum and amplitude are proved to be quite stable for temperature and pressure changes to a certain extent, and sensitive to the appearance of any particles in solutions based on characteristic absorption and scattering of sound energy. Velocity is more sensitive to temperature than to
nucleation due to limited amount of hydrate nuclei. Figure 5.1a demonstrates the velocity and amplitude responses to hydrate formation. Figure 5.1b shows the significant difference of Fast Fourier Transform (FFT) before and after hydrate formation.

(a) Acoustic velocity and amplitude responses to hydrate formation

(b) FFT response to hydrate formation

Figure 5.1. Acoustic responses of ultrasonic waves to hydrate formation
Therefore, a series of tests have been conducted to explore the possibility of using ultrasonic waves to detect hydrate nucleation and then to find out how the PVCAP as an example of LDHIs works. The test results showed that it was at almost same time for pressure and ultrasonic signals to give their responses to the onset point of hydrate formation if there was not any hydrate inhibitor in the system, which may suggest that the nucleation process is very short in the absence of kinetic inhibitors. On the other hand, the acoustic signal indicated that there certainly was something happening before hydrate formation, a few tens of minutes gap between the first acoustic response and significant pressure change due to hydrate formation. The results also suggested that 1mass% of PVCAP delayed hydrate formation through not only blocking hydrate growth but also prolonging hydrate nucleation.

5.2. MATERIALS

Natural gas supplied by Air Product (Composition in Table 5.1)
Carbon dioxide supplied by Air Product
Tetrahydrofuran (THF, C₄H₈, 99%) supplied by Prolabo
Luvicap® (40 mass% PVCAP and 60mass % ethylene glycol) supplied by Clariant
Distilled water
Glass beads, 0.1 mm in diameter supplied by Biospec Products

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol%</th>
<th>Component</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3.86</td>
<td>i-C₄</td>
<td>0.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.5</td>
<td>n-C₄</td>
<td>0.35</td>
</tr>
<tr>
<td>C₁</td>
<td>86.49</td>
<td>i-C₅</td>
<td>0.08</td>
</tr>
<tr>
<td>C₂</td>
<td>5.71</td>
<td>n-C₅</td>
<td>0.08</td>
</tr>
<tr>
<td>C₃</td>
<td>1.63</td>
<td>C₆⁺</td>
<td>0.1</td>
</tr>
</tbody>
</table>

5.3. EXPERIMENTAL

The tests are divided into two phases. During the first phase a natural gas was used as hydrate former and glass beads, 0.1 mm in diameter, was packed in the test cell to act as nucleation sites and to simulate mechanical steering. The composition of the natural gas is shown in Table 5.1. The objective is to initially find out if ultrasonic
signals could be sensitive enough to detect hydrate nucleation. In the second phase, all the tests were carried out without glass beads to exclude the possibility of any effect of glass beads on nucleation tests, for example, the adsorption of PVCAP on the surface of the glass beads. Three typical hydrate formers including natural gas, carbon dioxide and THF have been used in the tests to simulate low, moderate and high water soluble hydrate formers.

![Figure 5.2. The schematic of the ultrasonic set-up](image)

### 5.3.1 Test Set-up

The schematic of the ultrasonic set-up is shown in Figure 5.2. Its key part is the test cell. Two ultrasonic transducers are fitted at the two end of the cell, respectively. One works as a transmitting transducer that generates acoustic signals, driven by the Pulser/Receiver (P/R), another one as a receiver that receives the signals through the fluids inside the cell. The received signals are pre-processed by the Digital Storage Oscilloscope (DSO) and then sent to the Personal Computer (PC) to display the waveforms and save the data for further analysis. There is a piston connected to one
of the two ends, which is useful to adjust the volume of the test cell. A dial indicator is fitted to the bar of the piston for determination of the piston’s position. A hand pump and a piston vessel are used to inject fluids. The test temperature is controlled by means of the cooling system that consists of a cooling bath and a jacket. In the tests the system temperature and pressure can be automatically recorded by logging on the computer.

5.3.2 Test Procedures

Phase 1 The cell was initially filled with the glass beads. After applying vacuuming to the cell to remove air, the natural gas was introduced. Finally, distilled water or aqueous solution of 1 mass% PVCAP was injected into the cell to achieve the desired pressure. It was supposed that quite even distribution of the free gas could be achieved due to the strong wettability of water, as can be seen in Figure 5.3.

![Figure 5.3. Gas bubbles are likely to distribute evenly in the glass bead pack.](image)

Phase 2 Further tests without glass beads have been carried out. In these tests, for the natural gas and CO$_2$ tests, after vacuuming the test cell distilled water/ aqueous solution of 1 mass% PVCAP was sucked into the cell. The gas was finally injected into the cell until building up the pressure to a required value. The water level was same to keep a constant contact area of the gas phase with the liquid phase, 71 volume % of liquid phase and 29 volume% of gas phase, as shown in Figure 5.4, which ensured most of sound energy could be received through the body of liquid phase. For the THF tests a solution was made of water or water + PVCAP (1mass%) and
THF (14.4 mass%). The solution was injected into the cell until pre-pressurising the system to gain good acoustic coupling. The system temperature was reduced either directly to a target point if the target temperature was known or step by step until hydrates could form in a reasonable period.

Figure 5.4. 71 volume% of liquid phase and 29 volume% of gas phase in the test cell.

5.4. TEST RESULTS AND DISCUSSIONS

5.4.1 Initial Natural Gas Tests with Glass Beads

In the first phase two natural gas tests have been done in the presence of glass beads with and without PVCA, respectively, to initially explore the possibility of applying ultrasonic waves to identify hydrate nucleation. Figure 5.5 shows the results.
(b) Natural gas tests with 1 mass% of PVCAP in glass beads—The pressure profile failed to indicate the first hydrate formation.

(c) Natural gas tests with 1 mass% of PVCAP in glass beads in details—The FFT responded the start point about 95 minutes earlier than the pressure did, 73 minutes earlier than the amplitude did.

Figure 5.5. Initial natural gas tests with glass beads.

In the absence of PVCAP, as shown in Figure 5.5a, while the system temperature and pressure was almost constant, the magnitude of the FFT started continuously reducing at 104 bar and 16.4 ºC, which suggests that certain phase transition happened inside the system. Some time later the amplitude of the waveforms and the system pressure started significantly dropping to indicate the onset of gas hydrate formation.
Although it could not be accurately determined the time gap between the FFT response and the pressure and the amplitude indications due to too big time interval of the data, FFT certainly detected the phase transition behaviour before gas hydrate formation. It would be reasonable to consider the phase transition behaviour before gas hydrate formation as hydrate nucleation.

Figure 5.5b shows the profiles of the temperature and pressure in the natural gas test with 1 mass% of PVCAP. The second formation at 106.9 bar and 12.1 °C is clear as the pressure kept dropping while the temperature was constant. But only relying on conventional pressure analysis it was hard to know what happened at around 111 bar and 14 °C, shown in the red circle. However, as can be seen in Figure 5.5c, the FFT started continuously dropping at 111.4 bar and 14.4 °C, about 73 minutes later the amplitude of the waveforms started reducing, whilst the pressure slightly changed its decrease slope about 95 minutes behind the FFT. This may suggest that the natural gas hydrates started formation after about 95 minutes of their nucleation.

5.4.2 Further Tests in Bulk Liquid Phase

The tests have been carried out using three typical hydrate formers including a natural gas with typical composition in Table 1, THF and carbon dioxide. The natural gas is expected to be representative of natural gases transported through the pipelines with low water solubility, whilst carbon dioxide represents a system with medium solubility in water and THF acts as a water-soluble hydrate former. It was aimed to see how the PVCAP inhibits hydrate formation from the three particular hydrate formers by means of ultrasonic test.

5.4.2.1 Natural Gas Tests

As it can be seen in Figure 5.7 and Figure 5.8, the blank natural gas test in the absence of PVCAP was conducted at a pressure higher than that in the PVCAP test because there was not measurable hydrate formation at the same pressure under which the PVCAP test was performed. The injection conditions and hydrate formation points are indicated in Figure 5.6. The natural gas was injected at P/T condition that was very close to the hydrate phase boundary, 20.4 °C and 141.1 bar for the blank test, 20.4 °C and 118.0 bars for the PVCAP tests. In the two tests hydrates started to form under different degrees of subcooling, mention system temperature at 133.2 bar (7 °C
subcooling) for the blank test, and mention system temperature at 107 bar (12 °C subcooling) for the PVCAP test.

Figure 5.7 shows the test result of the blank test without PVCAP. Figure 5.7a gives the outlines of the temperature and pressure, whilst Figure 5.7b shows the responses of T/P and ultrasonic waves to hydrate formation in details. It is impossible to identify whether or not gas hydrates formed only according to the conventional pressure drop (in Figure 5.7a) that was covered by the temperature decrease. However, as can be clearly seen in Figure 5.7b, the amplitude and FFT continuously dropped, which indicates hydrates started forming at 133.2 bar and 13.1 °C, 58 minutes after reducing the system temperature, and hydrate formation lasted 120 minutes to finish its significant growth.

![Figure 5.6. Phase boundary of NG2002 and test conditions](image)

(a) The outlines of the temperature and pressure in the natural gas test in bulk water without PVCAP
5.10

(b) The ultrasonic signals clearly indicate hydrates was forming in the natural gas test in bulk water without PVCAP.

Figure 5.7. Natural gas test in bulk liquid phase without PVCAP.

It should be noted that it was almost at the same time when the amplitude and FFT gave their responses to hydrate formation, which means that there was no time gap between nucleation and formation that could be detected by the ultrasonic waves (in the absence of PVCAP).

In comparison with the previous test without PVCAP there are significant differences of nucleation and induction time in the presence of 1 mass% of PVCAP. Figure 5.8a shows that the catastrophic formation was delayed for 2300 minutes from the first formation that could not be clearly indicated by the pressure profile. The first formation happened between 900 minutes and 1200 minutes and is shown in details in Figure 5.8b. In Figure 5.8b the FFT and amplitude gave their responses to the hydrate nucleation 110 minutes and 20 minutes, respectively, before the first formation where the system pressure started to drop. In general, the presence of PVCAP divided the process of hydrate formation into three phases: nucleation from 970 minutes to 1080 minutes, slow formation controlled by PVCAP from 1080 minutes to 3400 minutes, and catastrophic growth after 3400 minutes. In Figure 5.8 another fact is that there was a big pressure drop during the catastrophic formation, which suggests much more gas hydrates formed in the presence of PVCAP at static conditions, compared to the test without PVCAP shown in Figure 5.7.
Chapter 5  Hydrate Nucleation Tests Using Ultrasonic Waves

5.11

(a) The outlines of the temperature and pressure in the natural gas test in bulk water with 1 mass% of Pvcap.

(b) Ultrasonic signals clearly show the nucleation time in the natural gas test in bulk water with 1 mass% of PVCAP.

Figure 5.8. The natural gas test with 1 mass% of PVCAP in bulk condition.

5.4.2.2 THF Tests

THF is a water-soluble hydrate former. 14.4 mass% of THF was used in the THF tests to see how PVCAP could affect its hydrate formation behaviour. Figure 5.9 represents the test results. In Figure 5.9a for the test without PVCAP according to FFT response THF hydrates started nucleation at 400 minutes and 3.7 °C. About 60 minutes later the pressure started continuously rising, which indicates THF started to
form hydrates. The amplitude started to drop 10 minutes after the pressure rise. The pressure increased by 3.4 bar in 240 minutes.

![Graph showing pressure, temperature, amplitude, and FFT over time for THF test without PVCAP](image)

(a) THF test without PVCAP

![Graph showing pressure, temperature, amplitude, and FFT over time for THF test with 1.0 mass% PVCAP](image)

(b) THF test with 1.0 mass% of PVCAP

Figure 5.9. THF tests without glass beads

In the test with 1 mass% of PVCAP, as can be seen in Figure 5.9b, THF hydrates started nucleation at 1.7 ºC, 2 ºC lower than that of the blank test. About 80 minutes later the first hydrate formation caused the system pressure rose a little, but due to the effect of PVCAP the catastrophic growth could not happen until 620 minutes, 300 minutes later after the first formation. In 600 minutes the pressure dropped only 0.8 bar, i.e., less THF hydrates formed in this test with PVCAP than in the blank test.
5.4.2.3 Carbon Dioxide Tests

Carbon dioxide was chosen as a hydrate former with high solubility in water. Figure 5.10 shows the result of the carbon dioxide test without PVCAP. As can be seen in Figure 5.10a, there is a sudden increase in the system pressure and temperature when hydrates started formation at 760 minutes, 3.0 ºC and 37 bar, which may be caused by rapid heat release due to hydrate formation. The catastrophic growth happened 220 minutes later, but only 4 bar of pressure drop in 1500 minutes. Figure 5.10b shows the detail of the hydrate formation. The amplitude and FFT started dropping at the same time to indicate hydrate nucleation, which was 20 minutes before the sudden hydrate formation.

![Pressure and temperature plot](image1)

(a) Pressure and temperature plot

![Nucleation and formation in detail](image2)

(b) Nucleation and formation in detail

Figure 5.10. Carbon dioxide tests without PVCAP
In the presence of 1 mass% of PVCAP, as can be seen in Figure 5.11, carbon dioxide hydrate started nucleation represented by an abnormal rise of the FFT as well as the amplitude. After 520 minutes the significant attenuation of the FFT and amplitude reflected hydrates started its first formation, whilst a very tiny jump in the system pressure and temperature suggested hydrate quantity was very limited so that the pressure and temperature burst was hard to be seen. The catastrophic growth was delayed for 1050 minutes from the first formation. During the catastrophic growth quite a lot of hydrates formed, which caused a pressure drop of 20 bar in 180 minutes.

![Figure 5.11. Carbon dioxide test with 1 mass% of PVCAP](image)

**5.4.3 Helium Tests**

Two more tests with helium have been carried out to find out if any structure change of water and aqueous PVCAP solution could affect the ultrasonic signal. As the molecular size of helium is too small to stabilize hydrate cages, it was assumed that helium could not form hydrates at all. Figure 5.12a and Figure 5.12b show the results of helium-water test and helium-aqueous PVCAP solution test, respectively. In Figure 5.12 there are some points that can be pointed out:

- No anomalous acoustic response appeared during the temperature reduction from 20 °C to nearly 0 °C.
- In both water and aqueous PVCAP tests there was a smooth reduction of the amplitude and FFT at around 12 °C. After that the amplitude and FFT became stable even though the temperature kept decreasing.
It was assumed that temperature would dominate the interaction between gas phase (helium) and liquid phase (water or aqueous PVCAP solution), so that the pressure difference between the nucleation tests and the helium tests may be neglected.
5.5. CONCLUSIONS

(1) By comparison with conventional pressure analysis ultrasonic tests presents two main advantages: (1) Higher sensitivity to gas hydrate crystallization makes it possible to detect hydrate nucleation or the very beginning of hydrate formation, and tiny amount of gas hydrate growth. (2) Prompt and significant response to the phase transition leads to easier and more reliable identification of hydrate onset point. The helium tests prove that the FFT and amplitude changes most likely respond to hydrate phase transition rather than the change in structure of the aqueous PVCAP solution. Scientifically, it could not be clearly identified if the first acoustic response was resulted from unknown structure change of water/solution, or nucleation, or very beginning of hydrate formation. In general, based on the classification of crystallisation phases, it may be reasonable to consider it as nucleation that happened just before significant growth of hydrates. To complete the ultrasonic test method, there are some questions to be answered, especially about the theoretical mechanism.

(2) Based on the results of the ultrasonic tests PVCAP prolongs the induction time of hydrate formation through not only delaying the catastrophic growth but also slowing down hydrate nucleation. In gas hydrates tests using the natural gas and carbon dioxide in the absence of PVCAP there was slight or no time gap between hydrate nucleation and formation that could be detected. However, the presence of 1 mass% of PVCAP made the gap very clear and demonstrated hydrate crystallization process in three phases: nucleation, slow formation, and catastrophic growth. Furthermore, at the certain concentration of PVCAP, 1 mass%, the induction delay by PVCAP depends on the molecule concentration of hydrate formers in the water phase. The lower the molecule concentration, the longer the induction time, as can be seen in Table 5.2. In terms of concentration in water phase, the solubility of the natural gas is much smaller than that of carbon dioxide, whilst THF is totally water-soluble. This is in line with the micromodel tests, indicating that PVCAP reduces the amount of hydrates formed in the water phase.
Table 5.2. Induction delay and hydrate quantity*

<table>
<thead>
<tr>
<th></th>
<th>Nucleation time minutes</th>
<th>Delay catastrophic growth minutes</th>
<th>Quantity of hydrates pressure drop</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NG</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>Undetectable</td>
<td>Undetectable</td>
<td>Undetectable</td>
</tr>
<tr>
<td>PVCAP</td>
<td>110</td>
<td>2300</td>
<td>32 bar in 4150 minutes</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>20</td>
<td>220</td>
<td>4 bar in 1500 minutes</td>
</tr>
<tr>
<td>PVCAP</td>
<td>520</td>
<td>1050</td>
<td>20 bar in 180 minutes</td>
</tr>
<tr>
<td><strong>THF</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank</td>
<td>undetectable</td>
<td>60</td>
<td>3.4 bar in 240 minutes</td>
</tr>
<tr>
<td>PVCAP</td>
<td>80</td>
<td>300</td>
<td>0.8 bar in 600 minutes</td>
</tr>
</tbody>
</table>

*Note: Nucleation time is defined as a time interval between the FFT response and the first pressure drop. Delay of catastrophic growth is defined as a time interval between the first pressure drop and the catastrophic pressure drop.

(3) At static conditions the presence of PVCAP resulted in more gas hydrates formation. It may be attributed to the fact that LDHIs make gas hydrate more permeable, which warns that more attention must be paid to shut-in cases when LDHIs were applied. However, significantly more THF hydrates formed in the blank test than in the test with PVCAP, which directly supports the previous explanation and may also suggests that PVCAP is more effective to prevent hydrate growth from dissolved gas rather than from free gas.

Reference

6.1. INTRODUCTION
Anti-Agglomerants (AA) are another class of Low Dosage Hydrate Inhibitors (LDHI) developed over the last two decades, which are fundamentally polymeric surfactants, that prevent hydrates from agglomerating and depositing in pipelines.\(^1\) The action of AAs are based on having a “hydratephilic” head incorporated within the hydrate crystals and a “hydratephobic or oleophilic” tail that disperses the hydrates into a liquid hydrocarbon phase. AA LDHIs allow hydrates to form and have no intended effect on hydrate nucleation/growth kinetics. However, they keep the particles small and well dispersed in the hydrocarbon liquid, and the fluid viscosity remains low. This allows the hydrates to be transported along with the produced fluids. The main advantage of AAs over KHIs is that they are independent of subcooling and can be effective even at subcooling over 20 °C. Hence, they have a much wider range of pressure-temperature applications. However, known AAs only appear to work in the presence of a hydrocarbon phase and are limited to low water cut systems. Their effectiveness is also affected by the type of oil/condensate and the salinity of the water.\(^2\)

The study of AAs along with KHIs was included in the proposal of the current LDHI project. In the last Technical Steering Meeting, it was suggested that the testing of AAs should be scheduled into the experimental plan. In this report, a brief description and literature survey on the development, testing and field application of AA chemicals is presented. Some preliminary experiments have been carried out in our laboratory to develop the methodology for testing AAs using the Kinetics Rigs and the Glass Micromodels at the Centre for Gas Hydrate Research (HW).
6.2. AA CHIMICALS

The first mention of controlling hydrates with surfactants in the literature was by Yuliev in 1972. This publication (in Russian) existed much earlier than any other work in late 1980s, such as the research carried out in IFP (France) by Behar et al.4,5

In the late 1980s and early 1990s, many patents were filed for the use of surface-active agents as AAs. These include: organic phosphates, polyacrylamides and polyacrylates, non ionic diethanolamide, ethoxylated carboxylic acids and polyl esters, alkylarylsulphonic acids and their alkali metal/ammonium salts.6-9

Kelland et al tested several chemicals, including various polysaccharides and alkyl glycosides, but they were unsuccessful.2 Urdahl et al tested many of the commercially available surfactants including alkyl-phenylethoxylates.11 It was found that the efficiency of many of the available chemicals was inadequate, e.g. sodium dodecylsulphonate (SDS), polyacrylamides, and tyrosine.

In 1995, Klomp et al patented the use of highly branched quaternised alkyl ammonium or phosphonium compounds (usually with accompanying bromide/chloride ions).12 The compounds used to demonstrate the effectiveness of this system included, tetrapentyl-ammonium-bromide, tributyl-hexadecyl-phosphonium-bromide, and tributyl-decyl-ammonium-bromide. US Patents 5,648,575 (1997)13 and 5,879,561 (1999)14 were extensions of their work, in which other chemicals were tested using a flow loop, such as dibutyl-dicocoyl-ammonium bromide. Up to now, these have been the most powerful AAs available in the industry. Since then, there have been also many patents filed on new chemicals, including polyisobutane-polyethyleneglycol block copolymer, quaternised polyether amines, and novel quaternary amine polymers with increased solubility.15,16

Huo et al in 2001 tested the effectiveness of various commercially available AAs, and other potential compounds.18 They discovered a new effective AA; dodecyl-2-(2-caprolactamyl) ethanamide. The reason put forward to test the effectiveness of this type of chemicals was the nature of the caprolactam group. Polyvinylcaprolactam (PVCAP) was found to be an effective KHI, which is due to the steric fit of the lactam ring into the 51264 cavity on the s-II hydrate structure.19 This led to the idea of using...
the lactam ring as a surfactant head-group to adsorb onto the hydrate surface. Thus it was concluded that the main reason why most surfactants do not function as AA is because of their inability to attach to the hydrate surface. This theory can be used to explain why the quaternary ammonium and phosphonium salts with one or two short alkyls (such as methyl or butyl) and one or two long oleophilic hydrocarbon tails are effective AA inhibitors.

Figure 6.1 shows the chemical structure of tri-n-butyl-hexadecyl-phosphonium bromide, which is a good AA LDHI. The P atom (or N atom for an ammonium salt) at the centre of the quaternary compounds can form hydrogen bond with oxygen atoms in water molecules, and also the butyl branches may act as gas molecules to become internal parts of the hydrates. The long hydrocarbon tails, which are affinitive to oil/condensate, will pull the hydrate blocks formed into the liquid hydrocarbon phase. They will also prevent and slow the growth of hydrate crystals.

Figure 6.1. Chemical structure of tri-n-butyl-hexadecyl-phosphonium bromide, an effective Anti-Agglomerant hydrate inhibitor.

The AAs reported to date are mostly based on substituted quaternary compounds as described above, and in particular ammonium, phosphonium or amines. The products are often formulated as a synergetic mixture including other chemicals as carrier fluids. The commercial products available in the industry include Kostatech (from InSOL), HI-M-PACT (from Baker Petrolite) and Freeflow AA (from ONDEO Nalco).
6.3. FIELD APPLICATIONS

AAs have been found to be suitable for hydrate control in many situations encountered in offshore and onshore oil and gas productions. They are currently being tested and used in several field applications in deepwater and onshore systems. These AAs can be deployed with the existing methanol/glycol injection systems at much lower rates, thus requiring smaller pumps, small storage facilities, and less frequent supply trips.20

Some successful field/lab testing and implementations of AA LDHIs reported in the literature are summarised below:

1. There are some cases reported for the application of Baker Petrolite’s HI-M-PACT AA products.21 In a deepwater field in the Gulf of Mexico, the product offers subcooling of 22 °C (40 °F) in laboratory tests and 14 °C (26 °F) in the field application. Two wells in the said field were producing 4000 BOPD and 11,000 BOPD respectively and each made 500 BWPD. The GOR was 1100 SCF/STB. HI-M-PACT inhibitor was injected via capillary strings into the tubing just above SCSSV, which was continued until all the fluids in the tubing above the SCSSV were treated. Following a six-day shut-in, injection was resumed just prior to restarting the wells. Both wells were brought back on production without any hydrate problems, resulting in an additional 7500 bbls of accelerated oil production per shut-in.

Another deepwater well in the Gulf of Mexico was producing excessive water as well as appreciable volume of gas, and a maximum methanol injection rate of 7350 GPD was insufficient to control hydrates in the 24 miles condensate flowlines. Baker Petrolite reported treating this well with HI-M-PACT inhibitor at 0.35 gal/bbl of water, while phasing out methanol. After nine months of production there has been no hydrate problems. Production was increased by 20 MMSCFPD and the ultimate recoverable gas from the reservoir by 7.5 bcf.

2. Shell tested their AA LDHI in the Popeye field in the Gulf of Mexico’s Green Canyon blocks, located in 2000 ft of water.1,22 To inhibit hydrates during the initial years of production, methanol was injected. Before the AA field test, the production had reached 60 MSCFD, 3000 B/D of condensate and 430 BWD. The methanol
injection rate was 175 b/d. To replace methanol, AA LDHI was slowly injected over a 24-hour period until all methanol injection was stopped and the system was operating solely on LDHI. The volume of AA LDHI was 25 times less than methanol. As a part of the test, a shut in of 24 hour was conducted, and there was no problem in the restart. Thus eliminating the need for instantaneous corrective measures during the restart operation.

3. A LDHI qualification program was performed by BP and coworkers to select LDHIs for a field application in a Gulf of Mexico black oil tie-back pipeline (Troika to Bullwinkle, 14 miles), which is located in 2700 ft of water. The main hydrate concerns in this case were hydrate formation and plugging during extended shut-ins, and the subsequent cold restarts, in which 11 °C of subcooling is encountered at 156.8 bar (2300 psi). 10 LDHIs (6 AAs and 4 KIs) were prescreened in the laboratory using a stirred autoclave reactor and a wheel flow simulator. Three of the selected AA LDHIs passed all of the tests in the presence of the field oil with up to 40-60% water cut (3.5 mass% salt solution), and 1.5 to 2 mass% chemical dosages. The hydrates formed into a mobile slurry and no plugging tendency was observed. However, there has been no field test reported so far.

4. A gas well, Crimson Lake, located about 200 km northwest of Calgary, Alberta, was treated with a combined KI/AA product and an AA inhibitor by Conoco Canada and coworkers. The well was producing 6 scm/d condensate, 0.1 scm/d water and 0.5 MMscm/d gas. During the production, the well continuously formed hydrates at depths of 500 to 300 meters. Operators were pumping between 400 to 500L of methanol daily and could not sustain the production for more than 16-24 hours, and up to 2m³ of the solvent were used in one shot to dissolve hydrate plugs when they formed.

**KI/AA combination product:** the combined inhibitor was diluted with methanol in a stock tank to form a 20% KI/AA solution. The solution was pumped into the well through the spaghetti tubing at the rate of 30L/day for 30 days. This rate is equivalent to a loading 6L/day of the undiluted inhibitor. The well did not have any freeze-ups during the test period.
AA inhibitor: The AA (GHI-7183) consists of polyether polyamines and alcohol solvents. It is significantly less expensive than the KI/AA combination product. It was started at 30L/day as a 20% AA in methanol solution and a month later the treatment was lowered to 45L/day of a 10% AA in methanol. The dosage 45L/day is equal to 10% of the original ineffective methanol treatment rate and is equivalent to 4.5L/day loading of the undiluted inhibitor. A quaternary ammonium corrosion inhibitor was co-blended at 1% to compensate for oxygen introduced into the well with solvents. After about a month, this set-up was copied to six more wells in the area and operated without any hydrate problems.

There has been no unsuccessful field-testing of AAs reported in the literature. Field experience has indicated that the following factors in the design and application of an AA LDHI should be considered:

- Correct assessment of operating conditions and produced fluid composition
- Selection of an effective laboratory testing programme
- Capacity of the selected AA LDHI to prevent agglomeration and suitability at higher water cut
- Solubility of AA chemicals in water or oil phases and solvents
- Injection and economics
- Interaction with other chemicals used in the field, such as corrosion/scale inhibitors
- Effect on the field production: recycling/removal issues
- Environmental concern and safety

6.4. LABORATORY TESTING TECHNIQUES

Laboratory testing of AA LDHIs is designed to provide a high level of confidence that a selected product will perform effectively in the field. There are two important issues relevant to the testing of AAs for field application. Firstly, AA inhibitors will be used in large pipelines under various flow regimes and conditions, and it is difficult to recreate this type of system in a laboratory. Though it is not difficult to use similar fluid, it is difficult to simulate geometry and flow regimes in laboratory equipment. Subsequently, caution is required during the scaling-up of laboratory results. Secondly, similarly to Kinetic LDHIs, AA inhibitors are comparatively new, and test
protocols are not fully developed, or widely accepted in industry. Therefore, different testing methods and procedures should be considered. BP has observed on several occasions that LDHI performance can be a function of both process fluids and process conditions.\textsuperscript{23} It is recommended that, because of this fluid and process dependency, actual process fluids should be used in laboratory testing, and different testing methods should be used.

In this section, various laboratory equipment and techniques used in AA LDHI testing are reviewed and compared. In general, there are three criteria and methods that can be used for AA LDHI qualification; hydrate visualisation, rheological measurement of hydrate slurry, and assessment of hydrate plugging and deposition.

**Visualisation Techniques**
These techniques include the THF test at atmospheric pressure and optical cells at high pressures. The THF test simply involves the addition of tetrahydrofuran (THF) to water in a glass tube for hydrate observation, which is often used as a preliminary screening method for LDHIs. Optical cells are used with other equipment, such as stirred tank reactors and flow loops, for hydrate observation at high pressures. The visualisation window is usually made of sapphire for high pressure application.

Turbidimetry is also used, which measures the loss in intensity of light beams that pass through the solution of forming hydrate crystals. This type of work is very useful in identifying particle nucleation and growth, which is relevant to AA LDHIs. Herri \textit{et al} demonstrated this technique’s suitability for hydrate crystal systems.\textsuperscript{25}

In this project, the glass micromodel was proposed for hydrate visualisation in the AA testing. The details will be described in the next sections.

**Rheological Assessment Techniques**
Rheological measurement can be carried out in stirred tank type reactors, simulated flow loop equipment and other devices.

A \textbf{stirred tank reactor} usually equips with accurate thermocouples and pressure gauges and temperature control systems. Hydrate formation can be detected and quantified by pressure measurement. The stirred variety with a torque measurement is particularly useful in determining the rheological properties of hydrate slurry formed.
Various shapes of impeller can be used to facilitate the rheological characterisation and assessment of hydrate blockage. Hydrate formation can be also visualised in the reactor when an optical window is mounted on the reactor wall. These stirred tank reactors are used in many studies due to their relative simplicity, reproducibility, cost and versatility.

**Mini flow loop** is used to simulate the flow in pipelines. These apparatuses consist of a cooled high-pressure pipeline (usually ID>2in) with a pump used to pressurise and simulate the flow conditions encountered in field pipelines. Pressure drops across a section of the loop can be measured and used to assess the viscosity change of the fluid after hydrate formation.

**A rolling-ball** device can also be used to assess the rheological properties of hydrate slurries. The device consists of a stainless steel tube with a steel ball inside, attached to a rocking system to create rock and roll movement. The velocity of the rolling ball is measured to assess the viscosity change of the hydrate slurry.

**Plugging Assessment Techniques**

Hydrate plugging and blockage can be readily sensed in the stirred tank reactors and simulated flow loops. The other apparatus used for this purpose include rotating wheels and rotating tubes.

A high pressure **rotating wheel** has been used to assess the deposition of hydrate on the wall. The rotating wheel consists of a circular stainless steel tube attached to a motor gearbox system to create movement. The system has a torque measuring device to sense the imbalance (or torque fluctuation) of the wheel due to hydrate deposition. It also has a camera for visualisation purposes. The wheel is placed into a temperature-controlled chamber to maintain the required temperature. This system is useful in testing the effect of flow regimes and is much less resource and labour intensive than a flow loop. The system was used effectively by Lund et al and Urdahl et a, which demonstrated good reproducibility. However, it has several weak points, including limitation in simulating various flow regimes and poor mixing.

**A rocking tube** (such as the rolling-ball type) can be also used to detect blockage caused by hydrates. The test tube is charged with a hydrocarbon, water, and inhibitor mixture at required pressure and temperature. It then rocks back and forth until it is
plugged by a hydrate formation.

In the current JIP project, stirred tank reactors and glass micromodels will be used for the AA testing.

6.5. EXPERIMENTAL TECHNIQUES FOR AA TESTING
AT HERIOT-WATT UNIVERSITY

The schematic diagrams of the Kinetics Rigs and the Glass Micromodel in the Centre for Gas Hydrate Research (HW) were shown in the last report.

Kinetics Rig 1 used in the previous tests for KHIs was modified to facilitate the AA LDHI testing. A specially designed stirrer blade was used for mixing and torque measurement. The blade is a large and long U-shape impeller, which is fitted into the testing cell. The gap between the edges of the impeller to vessel walls is about 15 mm. During the experiments, the rheology of the hydrate slurry is monitored by measuring the torque applied on the stirrer shaft. After hydrate formation, torque will increase. However, if the hydrates formed are dispersed into oil/condensate phase as small particles as expected when an AA-LDHI is present, torque increase will be limited. Otherwise, large torque increase can be observed, which may lead to the blockage of the stirrer. The maximum torque, which can block the stirrer in the rig, is 55 N.cm. In the experiments, the required amount of water and oil/condensate are first loaded into the test cell, and then gas is charged into the cell up to the required pressure. The AA inhibitor can be pre-mixed with water phase or injected into the testing cell using a metric pump at high pressures.

Another category of experimental facilities used for testing AA are glass micromodels (medium and high pressure) set-up, which were used in KHI testing. The inclusion or injection of three-phase fluid (oil/water/gas) into the micromodel is the main concern in the experiment. Inducing a flowing condition in the micromodel is another important issue that should be considered. Stage injection of different phases (e.g. in the order of oil, water and then gas) and injection of a pre-mixed three-phase mixture will be tested. A micro pump will be used for fluid injection and creating flowing conditions in the micromodel. The size, morphology and location of hydrate particles formed in the presence of AA inhibitors will be visualised as well as,
the movement of hydrate particles between the oil and water phases.

**Preliminary Experimental Results: Kinetics Rig**

The effectiveness of the Kinetics Rig in sensing the rheological changes and stirrer blockage in different fluid systems with and without AA LDHI s was tested in a preliminary programme. A North Sea condensate was used in the tests as the oil phase.

Three aqueous systems were examined: 5% NaCl water solution (blank test), a 2.5% phosphonium salt with 4 short tails in 5% NaCl water solution (AA-1) and a 2.5% phosphonium salt with 3 short and one long tails in 5% NaCl water solution (AA-2). The water content used in the tests was 33% related to the water/oil mixture. A natural gas (Lab-NG) was used in the experiment.

Figure 6.2 shows the results obtained in a test with 5% NaCl water solution without AA chemicals. The profiles of pressure, temperature and torque measured in the test are illustrated. The stirring rate was maintained at 600 rpm during the test. Hydrates formed at around 155 bar and 7.5 °C (before reaching the set point of 4 °C). Large torque increase was observed after hydrate formation, and the stirrer was blocked 3 hours after hydrate formation, indicating large hydrate particles were formed.

A subsequent test was carried out after injecting 2.5 vol% of AA-1 into the system, and the results are shown in Figure 6.3. Hydrates formed at around 155 bar and 7 °C with a sharp torque increase, and the stirrer was blocked immediately. The data indicate that this chemical (AA-1) is not effective on dispersing hydrates; therefore it is not an effective AA inhibitor for the system under investigation. Similar tests were conducted for the system with AA-2, as shown in Figure 6.4. 2.5 vol% AA-2 was injected into the system. Hydrates formed at around 157 bar and 5 °C, with significant pressure drop. However, the torque increase was marginal during the whole process of hydrate formation and dissociation. The performance of AA-2 in torque reduction was excellent comparing to the blank test and the system containing AA-1. In fact, AA-2 is a proven and effective AA LDHI. The above test demonstrate the ability of the kinetic rig for screening AA-LDHIs.
Figure 6.2. Experimental results using Kinetics Rig-1 conducted for a system containing 33 vol% water solution (5% NaCl) in a North Sea condensate and natural gas without AAs: Hydrate formation and torque increase.

Figure 6.3. Experimental results using Kinetics Rig-1 conducted for a system containing 33 vol% water solution (5% NaCl) in a North Sea condensate and natural gas with 2.5 vol% AA-1: Hydrate formation and torque increase. The chemical seemed to be ineffective for the system under investigation.
Figure 6.4. Experimental results using Kinetics Rig-1 conducted on a system containing 33 vol% water solution (5% NaCl) in a North Sea condensate and natural gas with 2.5 vol% AA-2: Hydrate formation and minor torque increase. The chemical shows excellent AA effect.

**Micromodel Experiments**

Further evaluation of AA-2 was carried out using the glass micromodel in order to visualise the size, morphology and distribution of hydrate particles formed in a condensate/water/gas (three phase) mixture with the AA. In the micromodel test, 2.5 vol% AA-2 was dissolved in water phase (with 3% NaCl). To charge the micromodel with the testing fluids, water was first injected, followed by condensate, and then gas was charged to a required pressure- 73.8 bar (1070 psia). The system was then cooled to –1 °C for hydrate formation. Hydrate was formed overnight. Figures 6.5 to 6.7 show the micromodel images taken before and after hydrate formation.

The distribution of the three phases, water/oil/gas, in the micromodel are shown in different colours before hydrate formation in Figure 6.5, where water appears as bright white, oil as slightly red, and gas as bubbles. The images will be improved with a better colouring method in future experiments. Hydrate formation was taken place in static conditions, but local fluid movement was observed in the micromodel, probably induced by pressure change and gas consumption. The size and distributions of hydrate particles formed are shown in Figures 6.6 and 6.7. Small hydrate particles
formed all over the micromodel, most were around 5-10 μm and all were less than 20 μm. It is interesting to observe that, after hydrate formation, many hydrate particles were in the condensate, or being surrounded by condensate. It is not clear what has happened; whether hydrates were drawn into the condensate phase or condensate flowed over the hydrates, while both could be possible. Nevertheless, the hydrates formed have some affinities toward the condensate, and it would be readily dispersed into the oil phase under flowing conditions, as shown in the Kinetics Rig tests.

The experimental result obtained from the Kinetics Rig and the micromodel has clearly demonstrated the excellent performance of AA-2 as an effective AA inhibitor. It is also shown that the combination of the two methods can be effectively used to evaluate the AA LDHIs in both macro and micro scales. A new Kinetics Rig with a glass window will be built to facilitate the torque measurement and visualisation in the same rig for AA testing.

![Image of Water, Oil, and Gas in Micromodel](image.jpg)

Figure 6.5. Water, oil and gas in the micromodel before hydrate formation.
6.6. SUMMARY

In this section, the development of AA LDHI chemicals was briefly reviewed. The most powerful AAs up to date appeared to be the quaternary compounds, such as ammonium, phosphonium or amines. There are several commercial AAs available in the market from various companies. The current AAs need to operate in the presence of a liquid hydrocarbon phase, and has a limitation on the water cut.

There have been several successful field-testing and implementations of AA LDHIs reported in the literature. Most of them were in the Gulf of Mexico. In most cases,
AAs were deployed for treatments during shut-in and restart to replace methanol. There was also a case where excessive water was involved, and the use of methanol was impossible due to limited injection rate and cost. AAs are suitable for systems with limited water cut (less than 50% or 30%) in multiphase transportations. The use of AAs did not have any adverse effects on other aspects of field operations. AA has been proven to be an economically viable alternative to conventional inhibitors for deepwater pipelines, due to its low dosage, fewer requirements on injection and storage.

Laboratory testing of AAs involves three basic techniques: hydrate visualisation, rheological measurement of hydrate slurry, and assessment of hydrate plugging and deposition. Stirred tank reactors and simulated mini flow loops, with and without optical windows, are the most popular laboratory equipment used for AAs selections.

In this project, a Kinetics Rig, with a specially designed stirring impeller for torque measurement, and Glass Micromodels will be used for AA testing. The Kinetics Rig is useful for rheological characterisation and blockage detection of the AA systems. The size, morphology and distribution of hydrate particles in water/oil phases can be best viewed in the micromodels. Preliminary experiments, using a proven AA chemical in comparison with another similar compound and an un-inhibited system, have shown the techniques developed at HW are suitable and effective for the testing of AA LDHIs.

References:


10. Anselme et al, 1991, EPA. 0457375


APPENDIX

Pressure and Temperature Profiles of the Tests in the Kinetic Rigs
Figure 1. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4.5 °C and 93.5 bar, rpm=600

Figure 2. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 3.7 °C and 65 bar, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 3. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 3.8 °C and 65 bar, rpm=600

Figure 4. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 3.8 °C and 65 bar, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 5. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 3.9 °C and 65 bar, rpm=600

Figure 6. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 3.9 °C and 65 bar, rpm=600
Figure 7. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4 °C and 65 bar, rpm=600

Figure 8. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4 °C and 64.8 bar, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 9. Pressure and temperature profiles for NG-water $-2\text{vol}\%$ HI03-22. Testing conditions: $4.8 \, ^\circ\text{C}$ and $65.2 \, \text{bar}$, rpm=600

Figure 10. Pressure and temperature profiles for NG-water $-2\text{vol}\%$ HI03-22. Testing conditions: $5 \, ^\circ\text{C}$ and $65.3 \, \text{bar}$, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 11. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4 °C and 65.5 bar, no mixing

Figure 12. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4 °C and 65.5 bar, no mixing
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 13. Pressure and temperature profiles for NG-water –2vol% HI03-22. Testing conditions: 4 °C and 65.5 bar, no mixing

Figure 14. Pressure and temperature profiles for NG-water –1%mass pvcap. Testing conditions: 4.7 °C and 87.5 bar, rpm=600
Figure 15. Pressure and temperature profiles for NG-water –1% mass pvcap. Testing conditions: 4.7 °C and 86.9 bar, rpm=600, subcooling 12.8 °C

Figure 16. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 4.6 °C and 120 bar, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 17. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 4.5 °C and 118 bar, rpm=600

Figure 18. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 4.0°C and 117.5 bar, rpm=600
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 19. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 5.3 °C and 118.5 bar, rpm=600

Figure 20. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 5.3 °C and 119.5 bar, rpm=600
Figure 21. Pressure and temperature profiles for methane-water–2vol% HI03-22. Testing conditions: 6.8 °C and 121 bar, rpm=600

Figure 22. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 4.2 °C and 118 bar, no mixing
Figure 23. Pressure and temperature profiles for methane-water –2vol% HI03-22. Testing conditions: 4.1 °C and 118 bar, no mixing.

Figure 24. Pressure and temperature profiles for methane(97%mole)-propane(3%mole)-water –1mass% PVCAP. Testing conditions: 1 °C and 99 bar, rpm=1000
Appendix: Pressure and Temperature Profiles of the Experiments in the Kinetic Rigs

Figure 25. Pressure and temperature profiles for methane (97%mole)-propane (3%mole)-water –1mass% PVCAP. Testing conditions: 0.8 °C and 97 bar, rpm=1000

Figure 26. Pressure and temperature profiles for methane (97%mole)-propane (3%mole)-water –1mass% PVCAP. Testing conditions: 0.2 °C and 97 bar, rpm=1000
Figure 27 a. Pressure and temperature profiles for methane (68.6% mole)-ethane (31.4% mole)-water –1 mass% PVCAP. Hydrate formed at 1.9 °C and 96.9 bar, rpm=1000

Figure 27b. Hydrate formation conditions in the above test
Figure 28 a. Pressure and temperature profiles for methane (68.6%mole)-ethane (31.4%mole)-water –1mass% PVCAP. Hydrate formed at 3.8 °C and 97.2 bar, rpm=1000

Figure 28 b. Hydrate formation conditions in the above test
Figure 29. Pressure and temperature profiles for methane (68.6%mole)-ethane (31.4%mole)-water –1mass% PVCAP. Testing conditions: 4.2 °C and 97.2 bar, rpm=100

Figure 30. Pressure and temperature profiles for methane (68.6%mole)-ethane (31.4%mole)-water –1mass% PVCAP. Testing conditions: 4.2 °C and 97.2 bar, rpm=100
Figure 31. Pressure and temperature profiles for NG-water –1%mass PVCAP. Testing conditions: 4.8 °C and 87.5 bar, no mixing, Subcooling 12.7 °C

Figure 32. Pressure and temperature profiles for NG-water –1mass% PVCAP. Testing conditions: 4.5 °C and 94.8 bar, no mixing, Subcooling 13.6 °C
Figure 33. Pressure and temperature profiles for NG-water-1mass% PVCAP. Testing conditions: 3.9 °C and 93.5 bar, rpm=600, Subcooling 14.1 °C