Experimental Investigation of Natural Gas Components During Gas Hydrate Formation in Presence or Absence of the L-Tyrosine as a Kinetic Inhibitor in a Flow Mini-loop Apparatus

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Abstract

Hydrates are crystalline compounds similar to ice, with guest molecules like methane and ethane trapped inside cavities or cages formed by the hydrogen bounded framework of water molecules. These solid compounds give rise to problems in the natural gas oil industry because they can plug pipelines and process equipments. Low dosage hydrate inhibitors are a recently developed hydrate control technology, which can be more cost-effective than traditional practices such as methanol and glycols.

The main objective of the present work is to experimentally investigate simple gas hydrate formation with or without the presence of kinetic inhibitors in a flow mini-loop apparatus. For this purpose, a laboratory flow mini-loop apparatus was set up to measure the induction time and gas consumption rate during gas hydrate formation when a hydrate forming substance such as methane, ethane, propane, carbon dioxide and iso-butane is contacted with water in the absence or presence of dissolved inhibitor at various concentration under suitable temperature and pressure conditions. In each experiment, a water blend saturated with pure gas is circulated up to a required pressure. Pressure is maintained at a constant value during experimental runs by means of the required gas make-up. The effect of pressure on gas consumption during hydrate formation is investigated with or without the presence of PVP (polyvinylpyrrolidone) and L-tyrosine as kinetic inhibitors at various concentrations. The experimental results show that increasing the pressure of the system, causes to increase the experimental gas consumption and decrease the induction time. Also, the extent of gas hydrate formation at a given time is clearly less in the presence of the inhibitors. Moreover, when comparing the gas consumption during the hydrate formation for simple gas hydrate formation in presence of PVP and L-tyrosine inhibitors, it is seen that the gas consumption in presence of L-tyrosine is lower than that of PVP for all experiments.

Keywords: Simple gas hydrate formation, Kinetic inhibitor, Inhibition, L-tyrosine, PVP, Gas hydrate formation rate

Introduction

Hydrates are crystalline compounds similar to ice with guest molecules like methane, ethane, propane, etc. enclathered ("trapped") inside cavities or cages formed by the hydrogen bounded framework of water molecules. The van der Waals forces between the guest and the water molecules of the cavity help in stabilizing the hydrate structures. Davy [1] first observed clathrate hydrates in the chlorine and water system. There are three basic hydrate structures known to form from natural gases, structure I (sI), structure II (sII), and structure H (sH). The type of hydrate that forms depends on the size of the gas molecules included in the hydrate. As a rule of thumb, small molecules such as methane or ethane form sI hydrates as single guests, larger molecules such as propane and i-butane form sII hydrates. Larger molecules such as iso-pentane form sH hydrates in the presence of a “help” molecule such as methane. The type of hydrate depends on the composition, temperature, and pressure of the system. For example, it has been determined that natural gas hydrates can contain as much as 180 standard cubic feet of gas per cubic foot of the solid natural gas hydrates. Gas hydrates are reviewed in-depth by Sloan [2]. In petroleum exploration and production operations, clathrates pose a serious economic and safety concern. Gas hydrate crystals which grow inside a conduit such as a pipeline are
known to be able to block or even damage the conduit. Hydrates can block pipelines, subsea transfer lines, and in the event of a gas kick during drilling, form in the well bore, risers, BOPs (Blow-Out Preventers) and choke-lines [3]. Several methods are known to prevent hydrate formation and subsequent problems in pipeline, valves and other processing equipments. Physical methods have been used, e.g. increasing gas temperature in the pipeline, drying the gas before introduction into the pipeline, or lowering the gas pressure in the system. However, these techniques are either expensive or are undesirable due to loss of efficiency, and production. Chemical procedures have also been used. Electrolytes, for example, ammonia, brines and aqueous sugar solutions may be added to the system. Alternatively, the addition of methanol or other polar organic substances, for example, ethylene glycol or other glycols may be used. Methanol injection has been widely used to inhibit hydrate formation. However, for example, extremely large quantities of methanol (or various types’ alcohols) are needed to continuously treat a full wellstream fluid containing significant quantities of water. Because, it is only effective at high concentrations (such as 30% W/W) and there is a possibility for hydrate formation at low concentrations. Injecting thermodynamic chemical hydrate inhibitors into the pipeline will therefore usually be economically impractical because of the large quantity of chemicals required and the costs of transporting the chemicals to an offshore location. Today, attempts are being made to replace thermodynamic inhibitors by adding, at temperature and pressure ranges in which gas hydrates can form, additives in amounts of less than 2% which delay the gas hydrate formation. This new family of inhibitors, called Low Dosage Hydrate Inhibitors (LDHI). The kinetic hydrate inhibitors (KHI) used either prevents the nucleation and/or the growth of the gas hydrate particles or modify the hydrate growth in such a way that smaller hydrates particles result [4-15].

The kinetics of gas hydrate crystallization is covered in a large number of studies in the literatures [16]. In the recent books, Makogon [17] and Sloan [2] provide an extensive review on the subject. Several models [18] have been published on the basis of the crystallization theory for the prediction of gas hydrate formation, but no one can predict gas hydrate formation very well because of the stochastic nature of the nucleation process. This in turn makes the prediction of the hydrate growth phase impossible. Several researchers [16, 18] have measured the rate of gas hydrate formation after nucleation, that is, the hydrate growth stage. The rate of formation is typically expressed in terms of the gas consumption rate. Several hydrate formation models have been published on the basis of experimental results from batch or semi-batch reactors. All the models require fitting of experimental data to obtain empirical constants. The semi-empirical model of Vysniauskas and Bishnoi [9] represents the first attempt to describe quantitatively the rate of gas hydrate formation. In their model, the rate of gas consumption is correlated against total gas-liquid interfacial area, temperature, sub-cooling and pressure. Englezos et al. [19] presented a growth model with a single adjustable parameter for the formation of methane and ethane hydrates. They included two steps for the growth: the diffusion of dissolved gas molecules from the liquid bulk to the crystal surface, and the integration of the gas molecules at the surface. Skovborg and Rasmussen [20] proposed a simplified model where the gas consumption rate only depends on the transport of gas from the gas phase to the liquid bulk phase. The consumption rate is a function of the gas-liquid mass transfer coefficient, the gas-liquid interfacial area and the mole fraction driving force.

Gailiard et al. [21] modeled nucleation, growth and agglomeration in their hydrate loop (with liquid hydrocarbons) applying
crystallization theory and methane gas consumption measurements. They proposed a population balance for the hydrate crystals in the system and expressed the nucleation, growth and agglomeration rates by empirical correlations. Experiments showed no induction time and the rate of heterogeneous nucleation.

In this work, a high pressure laboratory flow mini-loop apparatus was set up to measure the rate of hydrate formation for a pure gas natural gas component (such as C1, C2, C3, i-C4 and CO2) with or without the presence of kinetic hydrate inhibitors. The kinetic inhibitors are PVP and L-tyrosine. To our knowledge, no research paper is available on gas hydrate formation in a flow mini-loop apparatus for efficiency of L-tyrosine as a kinetic inhibitor.

Fig. 1: High pressure laboratory scale for flow mini-loop apparatus
T: Temperature gauge, P: Pressure gauge. MF: Magnetic Flow meter, DP: Pressure drop gauge

Fig. 2: Flow loop pressure and Temperature for methane during gas hydrate formation in a flow miniloo apparatus
Apparatus and Experimental Procedure

Apparatus
A laboratory flow mini-loop apparatus was set up to allow the study of simple gas hydrate formation with or without the presence of the kinetic inhibitors. The equipment is essentially composed of a pipe and a pump. The flow line is made of 316 stainless steel with an inner diameter of 10.6 mm and a pressure rating 10 MPa. The total length of mini-loop apparatus, shown in Fig. 1 is 12 m. Water is injected to the loop by means of an electromotor pump (Pump 2) and flow is implemented with a Kracht screw pump (Pump 1) with variable rates up to 0.75 m³/hr. Temperature control of the flow loop is implemented using pump fed water (Pump 3) circulation through insulated 15 and 32 mm diameter PVC pipes those encompasses the loop. Cooling is achieved by circulating of ethylene glycol as a coolant prepared in a cooling system operated as a refrigerator. The current temperature range is 2 to 4 °C with a maximum continuous cooling rate of about 100 °C / hr. The loop is monitored by three temperature sensors (platinum resistance thermometers or PT-100, T1-T3), two pressure sensors (P1and P2), one Endress-Hauser magnetic flowmeter (F) and one Rosemount pressure drop transmitter (DP1) arrayed around the flow mini-loop apparatus. Gas injection rate is monitored by the means of a Rosemount pressure drop transmitter and an orifice plate (DP2). The pressure of flow mini-loop maintained at a constant value during experimental runs by means of a regulator and gas make-up. All parameters and data are controlled and recorded every 90 sec. The accuracy of the pressure and temperature measurements is estimated to be +/- 0.05 bar and +/- 0.1 K, respectively.

Material
The materials used for the experiments are ethylene glycol as a coolant, fresh water as an aqueous phase, analytical grade of methane gas with 99.95% purity, ethane gas with 99.95 purity, propane gas with 99.9% purity and iso-butane gas with 99.99% purity supplied by the Beijing Gas Industry Corporation were applied to prepare gas hydrate formation. The evaluated kinetic inhibitors, polyvinylpyrrolidone (PVP) with molecular weight of 10000 gr /grmole and L-tyrosine with molecular weight of 15000 gr /grmole, were supplied by the Sigma – Aldrich Company.

Experimental Procedure
The experimental procedures are given as follows. At the beginning of the operation, in the presence of kinetic inhibitors, the typical kinetic inhibitor (such as PVP) is added to the water in a mixing tank to produce the desired weight percent concentration of inhibitor in the aqueous solution. Then, the loop is filled with water containing KHI(such as PVP) and is circulated by means of a screw pump. Water is injected to the loop by an electromotor piston pump to increase the pressure to desired experimental value. At this pressure, aqueous phase (water containing kinetic inhibitors) is saturated by the gaseous formers (such as carbon dioxide, methane, ethane, propane and iso-butane) and is circulated through the flow loop. The fluid is circulated at a constant velocity. The stream temperature is adjusted by a cooling system operated as a refrigerator and stream pressure is adjusted by the injection of the gaseous formers from storage tank. The loop and its pump lay in a controlled temperature water bath for controlling the temperature of the fluid circulating in the loop.

The ethylene glycoloh from a bath is circulated through the external jacket of the pipe to ensure having uniform temperature. As the loop pressure changes or as hydrates form, the gas volume in the loop will accordingly change. Gas pressure drop is monitored while operating the system and abrupt change of the pressure drop in the loop is a measure for the pipe plugging by the hydrate crystals.
Results and discussion

The performance of kinetic inhibitors is usually evaluated in autoclaves and/or flow loops in terms of induction time. The induction time is defined as the elapsed time from the start of the experiments to the onset of hydrate formation. The induction time of gas hydrate nucleation is an important characteristic in evaluating the inhibition effect of kinetic hydrate inhibitors. A typical method is to measure the pressure of system with the elapsed time. The pressure in the hydrate formation system (such as in mini-loop apparatus) is expected to undergo three stages: the first rapid drop stage, representing the dissolving of gas in the liquid phase; the stable stage, denoting the induction of nucleation; and the second rapid drop stage, corresponding to the growth of hydrate crystals [22, 23].

The experiments are usually conducted at isothermal and/or isobaric conditions to simulate the field operating conditions. One method for investigating the rate of hydrate formation or evaluating the effectiveness of an inhibitor uses a bench-scale high pressure apparatus referred to as a mini-loop apparatus [24-27]. A typical plot of pressure and temperature data in the loop for a test carried out by only distilled water during the gas hydrate formation (including methane gas) process is shown in Fig. (2).

The mean value of experimental induction times for natural gas components (such as CO₂, methane, propane, and isobutane) at different pressures and temperatures in presence or absence of kinetic hydrate inhibitors such as PVP and L-tyrosine are reported in Table (1).

<table>
<thead>
<tr>
<th>Gas component</th>
<th>Temperature °C</th>
<th>Pressure MPa</th>
<th>Average Induction time (min.)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>fresh Water</td>
<td>pvp 100 ppm</td>
<td>pvp 200 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>4</td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>CO₂</td>
<td>4</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td>CO₂</td>
<td>4</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Methane</td>
<td>4</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Methane</td>
<td>4</td>
<td>7</td>
<td>50</td>
</tr>
<tr>
<td>Methane</td>
<td>4</td>
<td>8</td>
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<tr>
<td>Methane</td>
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<tr>
<td>Methane</td>
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<td>10</td>
<td>25</td>
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<tr>
<td>Ethane</td>
<td>4</td>
<td>1</td>
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<tr>
<td>Ethane</td>
<td>4</td>
<td>4</td>
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</tr>
<tr>
<td>Propane</td>
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<tr>
<td>Propane</td>
<td>4</td>
<td>2</td>
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<tr>
<td>Propane</td>
<td>4</td>
<td>4</td>
<td>10</td>
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<tr>
<td>iso-butane</td>
<td>2</td>
<td>1</td>
<td>90</td>
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<tr>
<td>iso-butane</td>
<td>2</td>
<td>2</td>
<td>60</td>
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<tr>
<td>iso-butane</td>
<td>2</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>iso-butane</td>
<td>2</td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>
As can be seen from this table, the presence of kinetic inhibitors in solution causes the induction time of gas hydrate formation to increase. Moreover, increasing the pressure of the system causes to decrease the induction time of gas hydrate formation. When hydrate crystallization occurs by progressive nucleation (hydrate crystallization proceeds by progressive nucleation when the hydrate crystallites are continuously nucleated during the process), inclusion the kinetic hydrate inhibitors into solution, from the macroscopic point of view, they delay the first appearance of stable hydrate crystal, and from the microscopic point of view, they adsorb on hydrate crystal faces to block crystal growth. This causes hydrate to remain as small crystals and sterically block guest diffusion. Thus, the required time for detectable volume of hydrate phase (or induction time) increases. In addition, as can be seen in Table 1, the induction time for methane in absence of kinetic hydrate inhibitors (pure fresh water) at temperature of 277 K and pressure of 8 MPa is 40 min. The addition of 100 and 200 ppm PVP to pure water delayed the induction time to 60 and 80 min, respectively. Whereas, the addition of 100 and 200 ppm L-tyrosine delayed the induction time to 250 and 320 min, respectively. Thus, the addition of 200 ppm L-tyrosine increases the induction time about 8 times. These results were shown that the fresh liquid water tends to have a shorter nucleation time during the gas hydrate formation. Furthermore, for example, the induction time for CO2 during the hydrate formation is displayed in Fig. 3. This figure shows that increasing the pressure of the system, the induction time of CO2 during the hydrate formation decrease.

The gas consumption results for carbon dioxide at a nominal temperature of 277 K and operating pressure range of 7 to 10 MPa, methane at a nominal temperature of 277 K and operating pressure range of 7 to 10 MPa, ethane at a nominal temperature of 277 K and operating pressure range of 7 to 10 MPa, propane at a nominal temperature of 275 K and operating pressure range of 1 to 4 MPa and iso-butane at a nominal temperature of 275.15 K and operating pressure range of 1 to 4 MPa during gas hydrate formation are shown in Figs. (4) to (8). The results show that the experimental rate of hydrate formation increase by increasing the pressure of the system.

![Graph](image-url)  
**Fig.3:** Effect of pressure on the induction time for CO2 during gas hydrate formation at 277 K in a flow mini-loop apparatus
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Fig. 4: Gas consumption for CO2 during gas hydrate formation at 277 K and various pressure in a flow mini-loop apparatus

Fig. 5: Gas consumption for methane during gas hydrate formation at 277 K and various pressure in a flow mini-loop apparatus

Fig. 6: Gas consumption for ethane during gas hydrate formation at 277 K and various pressure in a flow mini-loop apparatus
Fig 7: Gas consumption for propane during gas hydrate formation at 277 K and various pressure in a flow mini-loop apparatus

Fig 8: Gas consumption for iso-butane during gas hydrate formation at 275 K and various pressure in a flow mini-loop apparatus

Fig 9: CO2 consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 7 MPa and temperature of 277 K in a flow miniloop apparatus
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Fig. 10: CO2 consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 8 MPa and temperature of 277 K in a flow miniloop apparatus

Fig. 11: Methane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 9 MPa and temperature of 277 K in a flow miniloop apparatus

Fig. 12: Methane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 10 MPa and temperature of 277 K in a flow miniloop apparatus
Fig. 13: Ethane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 1 MPa and temperature of 277K in a flow miniloop apparatus.

Fig. 14: Ethane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 4 MPa and temperature of 277K in a flow miniloop apparatus.

Fig. 15: Propane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 1 MPa and temperature of 277 K in a flow miniloop apparatus.
Fig. 16: Propane consumed during gas hydrate formation in presence of PVP and L-Tyro sine at pressure of 2 MPa and temperature of 277 K in a flow miniloop apparatus

Fig. 17: Iso- butane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 3 MPa and temperature of 275 K in a flow miniloop apparatus

Fig. 18: Iso- butane consumed during gas hydrate formation in presence of PVP and L-Tyrosine at pressure of 4 MPa and temperature of 275 K in a flow miniloop apparatus
Finally, for measuring of the gas consumption rate during the gas hydrate formation in presence of the kinetic inhibitors in a flow mini-loop apparatus, the efficiency of two types of the kinetic additives such as PVP and L-tyrosine which is developed to avoid either nucleation or crystal growth of simple gas hydrates, is tested based on the proposed experimental procedure.

The time dependence of the experimental gas consumption during the gas hydrate formation in presence of PVP and L-tyrosine at specified temperatures, various pressures and inhibitor concentrations are tested. All experiments for various gas formers are run at above specified experimental conditions. Typically, the comparison results between the consumed gas during the gas hydrate formation in presence of 100, 200, 2500 ppm PVP and 100 and 200 ppm L-tyrosine at above specified experimental conditions are shown in Figs. (9) and (10) for CO2, (11) and (12) for methane, (13) and (14) for ethane, (15) and (16) for propane and (17) and (18) for iso-butane. As can be seen from figures ((8) - (18)), the comparison results measured values for the mentioned simple gas hydrate formation in presence of the kinetic inhibitors indicate that increasing the pressure of the system cause to increase the experimental gas consumption. In addition, the curves indicate that the amount of consumed gas is either slightly smaller (using the PVP as an inhibitor) or in the case of L-tyrosine clearly smaller than that for blank water.

Moreover, the extent of hydrate formation at a given time is obviously less than that in the presence of the inhibitors. Also, when comparing the gas consumption during the gas hydrate formation for the mentioned gas in presence of PVP and L-tyrosine inhibitors, it is seen that the amount of consumed gas in presence of L-tyrosine is lower than that of PVP for all the experiments. Also, in all the experiments, when comparing the induction time during the gas hydrate formation for the above pure gases in presence of PVP and L-tyrosine inhibitors, it is seen that the induction times in presence of L-tyrosine are higher than that of PVP. Although, the PVP as a kinetic inhibitor causes to increase the induction time and decrease the gas consumption rate, but this inhibitor also exhibits as a weak inhibiting effect on pure gases during gas hydrate formation. Whereas, the L-tyrosine exhibited as a strong inhibiting effect on pure gases during gas hydrate formation. On the other hand, the results show that the efficiency of L-tyrosine inhibitor is higher than that of PVP inhibitor due to having more induction time and lower gas consumption.

Conclusions

The performance of two kinetic hydrate inhibitors such as PVP and L-tyrosine at various pressures and temperatures conditions and different concentrations was evaluated for five pure gases including carbon dioxide, methane, ethane, propane and iso-butane at the specified experimental conditions using a flow mini-loop apparatus. The natural behavior of the experimental curves is similar for all isotherms. Observing the data at any particular isotherm, it is seen that there is a strong dependence of the rate of formation on the driving force which indicates that greater deviations from the three-phase equilibrium line causing higher consumption rates. The results shown, at higher driving forces the rate of gas hydrate formation is larger. Increasing the dosage of the inhibitors obviously delays the induction time for all two inhibitors assessed. Also, an increase in pressure of the system causes to decrease the induction time of gas hydrate formation. In addition, the results of the experiments show the rate of gas hydrate formation with presence of the kinetic inhibitors is always smaller than that without using any inhibitor. Moreover, the results show that the efficiency of L-tyrosine as a kinetic inhibitor is higher than that of PVP inhibitor due to having more induction time.
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