STUDY OF THE EFFECT OF COMMERCIAL KINETIC INHIBITORS ON GAS-HYDRATE FORMATION BY DSC: NON-CLASSICAL STRUCTURES?

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ABSTRACT

A HP micro DSC-VII from SETARAM was used to study the efficiency and mechanism of action of commercial kinetic inhibitors for gas-hydrate formation in drilling fluids (OBM). The main objective was to find a suitable and reliable method of screening for these chemicals. The DSC technique consists in monitoring the heat exchanges, due to phase changes (here hydrate formation or dissociation), either versus time at constant temperature or versus temperature during a heating or cooling program. All products showed a gas hydrate dissociation temperature (at a given pressure) that matched with theoretical and previously published data. Nevertheless, for some additives two thermal signals were observed on the thermograms, one that corresponds to the theoretical value and another at a higher temperature (about +4°C). This second peak is insensitive to the heating rate applied for the dissociation, but the areas ratio (1st peak/2nd peak) changes with the additive concentration and with the driving force applied during the hydrate formation. Additionally, additive/water and additive/water/THF systems were tested. In each case, two dissociation peaks were also measured. The results allow us to disregard any kinetic effects bonded to this thermal phenomenon, and lead us to infer that some additives may induce non-classical crystalline structures of gas hydrates. To verify these results, crystallographic and spectroscopic experiments must be performed. The stabilities of these new compounds are under study.

Keywords: Non-Classical Gas Hydrate Structures, Differential Scanning Calorimetry (DSC), Kinetic Inhibitors.

NOMENCLATURE

P Pressure [MPa]
T_{eq} Gas hydrate equilibrium temperature [°C]
T_{form} Gas hydrate formation temperature [°C]

INTRODUCTION

Gas hydrates are crystalline water-based solids, physically resembling ice, in which low-molecular-weight gases (commonly known as guest molecules) are trapped inside "cages" of hydrogen-bonded water molecules. These substances are formed under high pressures and low temperatures. At present, three basic crystallographic forms are known for gas hydrates. The most common structures are structure I (sI) and structure II (sII).

The third one, structure H (sH), is rare in nature and only exists in the presence of larger molecules such as iso-pentane [1]. The type of hydrate structure formed depends on the trapped gas guest molecules. In general, small molecules, such as pure CH$_4$ and pure C$_2$H$_6$, form hydrates of structure sI. Larger molecules, such as pure C$_3$H$_8$, pure i-C$_4$H$_{10}$ or gas mixtures such as methane and ethane or natural gas, form structure sII hydrates.

Gas hydrates may cause problems in the petroleum industry since they can form inside pipelines. Hydrates often cause obstructions in the flow-line, valves and instrumentation, which results in anything from flow reduction to equipment damage. For the drilling industry, the formation of gas hydrates can also lead to serious operational and safety problems. In offshore drilling operations, as water depths increase, the potential for gas-hydrate formation during drilling...
operations also increases, due to the extreme conditions encountered at these water depths (down to -1°C and up to 40 MPa). To avoid gas-hydrate formation, specific adaptations of the drilling fluids are required [2]. Generally, the fluids to be used in deep-water drilling are of two types, namely water-based mud fluids (WBM) and oil-based mud fluids (OBM) [3]. Therefore, the key is to prevent the formation of gas hydrates in the drilling fluids by adding chemicals. These chemicals can act either by shifting the hydrate-equilibrium conditions towards lower temperatures and higher pressures (thermodynamic inhibitors) or by delaying hydrate formation (kinetic inhibitors). Salts and low-molecular-weight glycols are classic thermodynamic inhibitors which may cause extensive corrosion and toxicity problems. As they are used at high concentration, it can result in a very expensive fluid [4]. Kinetic hydrate inhibitors (KHIs) are polymer-based chemicals which do not prevent hydrate crystals from forming, but delay the formation of gas hydrates. They require much smaller concentrations than conventional thermodynamic inhibitors.

Gas-hydrate formation is a complex, multiphase crystallization process [1, 5, 6]. As high pressure and low temperature are required, it is difficult to observe experimentally, and various study approaches have been used to date. Differential Scanning Calorimetry (DSC) had been used extensively in studying the formation and melting mechanisms of ice in water-in-oil emulsions, and also in performing both kinetic and thermodynamic studies of gas-hydrate formation [7, 8].

Considering all of the experimental difficulties regarding the kinetics of hydrate formation, DSC was used for the study of the KHIs in the OBM. The work presented in this paper is devoted to the study of the effects of different commercial KHIs investigated in complex drilling fluids (such as OBM).

**EXPERIMENTAL**

**Materials**

Four commercial KHIs were investigated against gas hydrate formation. They were identified as I-1, I-2, I-3 and I-4.

High purity methane (99.99% mol, N35® from Air Liquide) and a methane/propane mixture called C1-C3 (98% / 2% mol, from Air Liquide) were used to form respectively sl and sII gas hydrates. 99.9% Tetrahydrofuran (THF) from Carlo Erba SDS, was used to form THF hydrates. Ultra pure water was used for all the tests performed. This deionized water was produced by the Millipore Milli-Q 185 E system (resistivity of 18.10^6 Ω/cm).

The KHIs were tested against hydrate formation and dissociation in a simplified drilling fluid. This fluid was a water in oil emulsion prepared with a new environmentally-friendly low toxicity oil. This oil was used as the continuous phase in the Oil Based Mud (OBM). The oil phase composition is given in table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>642</td>
</tr>
<tr>
<td>Fluid Loss reducer</td>
<td>19.26</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>13.48</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>5.78</td>
</tr>
<tr>
<td>Lime</td>
<td>2.6</td>
</tr>
<tr>
<td>Lipophilic clay</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 1. Components of the oil phase of the OBM

**Oil Based Mud preparation**

The OBM used were water-in-oil emulsions. They were prepared at room temperature with 80% by weight of the oil system and 20% by weight of ultra pure water. Water was added drop by drop to the oil system while agitating the mixture using an Extrem Turrax® Ika T18 BASIC at 6000 rpm. When all the water had been added, the agitation rate was increased to 10000 rpm and was maintained for 10 minutes.

When testing the KHIs, aqueous solutions of these inhibitors were made and then the emulsions were prepared using the above procedure. Prior to emulsion preparation, the KHI solubilities in water at ambient and low temperature were investigated. Fresh emulsions were used for each experiment to avoid emulsion aging phenomena.

**Methods**

The DSC technique consists of monitoring the heat exchanges between the sample and a reference (thermogram), either versus time at constant
temperature, or versus temperature during a heating or cooling program. For this study two types of DSC calorimeters were used. The first calorimeter SETARAM DSC-131 was used to study the stability of the emulsions by investigating the formation/melting of ice at atmospheric pressure [9]. The second piece of equipment, a high pressure calorimeter SETARAM HP-micro DSC-VII, was used to study the formation and the dissociation of gas hydrates.

SETARAM DSC-131: this piece of equipment allows for the retrieval of thermograms at atmospheric pressure. It has little thermal inertia and the furnace operates in a temperature range between -170°C and +700°C. The sample cells used in this equipment are made of aluminum, with a capacity between 30 and 100 µL. It has a resolution of 0.4 µW with a time constant of 3s. This equipment requires liquid nitrogen for temperature control.

SETARAM HP-micro DSC-VII: this apparatus, based on the Calvet principle, was used for studying gas hydrate formation/dissociation. It uses the Peltier cooling and heating principle. Its working temperatures are comprised between -45°C and +120°C. The gas-tight high-pressure vessels, made of Hastelloy C276, are designed to work to up to 40 MPa with a usable volume of 0.5 mL. The screw top is equipped with a doughnut ring coupled to an anti extrusion ring, and is welded to a thermal line. The vessels are placed inside the calorimetric block and are connected to a high-pressure gas panel including a one-stage compressor (Figure 1).

An Olympus BX51 microscope connected to a digital camera CAMEDIA C-7070 Wide Zoom lens was used to investigate the droplet sizes distribution in the emulsions. It has a range of accessories that allows its connection with several image and video devices. It has a large field of vision of 22 mm which reduces exploration time. UIS2 Optics gives bright, acute and high contrast images. The photographs of the emulsions were obtained using the immersion objective x100.

Experimental Procedures

OBM characterization

DSC, coupled with microscopic images analyses, were the main analytical methods used in this work to characterize OBM emulsions. The calorimeter SETARAM DSC-131 was used to study the stability of the emulsion against the formation and melting of ice at atmospheric pressure.

In the field of emulsion characterization, DSC is the only available technique for distinguishing free water from emulsified water in any type of samples without any specific preparation. The sample is cooled at a constant scanning rate of 5°C/min until the water droplets in the emulsion crystallize. The crystallization temperature is correlated to the droplet sizes and decreases with them due to the supercooling phenomena: the smaller the volume, the lower the temperature [10]. Crystallization is a complicated process that requires three necessary steps: supercooling, nucleation and crystal growth. During the steady cooling of a population of droplets, a distribution of the crystallization temperatures is observed. Consequently, only a most probable temperature of crystallization can be experimentally determined, and this strongly depends on the volume of the sample. Re-heating the sample after crystallization allows for the study of melting temperature, which is independent of the aqueous solution state i.e. emulsified or free. The detailed principle of the technique applied to the characterization and stability of emulsions has been thoroughly described in previous publications [10, 11, 12].

Finally the droplet mean diameters and size distributions were determined using microscopy with image analysis (software ImageJ 1.37v of Wayne Rasband, National Institute of Health,
USA). The image analyses were performed on at least four pictures of 500 droplets for each sample.

**Gas hydrate procedures**

An aliquot mass of the prepared OBM - about 10 mg - was poured into the sample cell of the HP micro DSCVII. The gas was put in both the reference and sample cells (initial temperature 25°C) until the pressure reached 13.5 MPa. This pressure value was used for all the gas hydrate experiments. Afterwards, the systems were cooled from 25°C to the isotherm-formation temperature $T_{\text{form}}$ at a constant rate of 1°C/min. $T_{\text{form}}$ were lower than the hydrate equilibrium temperature $T_{\text{eq}}$ ($T_{\text{eq}} = 16.06 \pm 0.01$ °C at $P = 13.5$ MPa from CSMHYD software [13]). The sample was then maintained at the temperature $T_{\text{form}}$ for 5 hours to allow hydrate formation. Once hydrate formation was completely achieved, the emulsion was warmed up to 30 °C in order to dissociate the hydrates. Two heating rates were used in this work to study hydrate dissociation: 0.5 or 1 °C/min. For each experiment, heat flow per unit of mass (in W/g) and temperature (in °C) were recorded versus time.

Gas-hydrate formation was detected by an exothermic peak during the isotherm $T_{\text{form}}$. The gas-hydrate dissociation was detected by an endothermic peak during the sample heating from $T_{\text{form}}$ to 30°C. The dissociation temperature (equilibrium temperature) was defined for pure water as the onset temperature, and for aqueous solutions as the temperature of the apex, corrected by projecting the peak top on the base line, in a direction parallel to the linear portion of the pure-water melting peak. The enthalpies of formation and dissociation were determined by numeric integration of the exothermic and endothermic peak areas.

**RESULTS**

**KHI solubilities and OBM characterization**

The KHI solubilities in water were studied. All of the KHIs were soluble in water at concentrations between 0 and 2% by weight at room temperature as well as at 5 °C.

It was observed from the thermograms at atmospheric pressure (obtained with the SETARAM DSC-131) that the emulsions with and without KHIs were stable against the formation/melting of ice, since no significant differences were detected on the thermograms obtained after three consecutive ice formation/melting cycles.

<table>
<thead>
<tr>
<th>System</th>
<th>Ice Melting [± 0.1°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Water</td>
<td>-0.2</td>
</tr>
<tr>
<td>Emulsion without KHI</td>
<td>-1.7</td>
</tr>
<tr>
<td>I-1</td>
<td>-1.9</td>
</tr>
<tr>
<td>I-2</td>
<td>-1.3</td>
</tr>
<tr>
<td>I-3</td>
<td>-2.0</td>
</tr>
<tr>
<td>I-4</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

| £: emulsion with KHI at a concentration of 1% wt |

Table 2. Ice melting temperatures with the different systems at atmospheric pressure

Table 2 summarizes the information obtained regarding the melting of ice in the bulk water and in the different OBM emulsions. In bulk water, the ice melting was measured at a temperature close to 0 °C as expected. For the OBM without KHI, the melting temperature measured was -1.7 ± 0.1 °C. This drop in the freezing point (-1.5 ± 0.2 °C) was assigned to the partial solubility of some compounds present in the OBM emulsions. These compounds may act as thermodynamic inhibitors on the ice-phase formation.

The presence of KHIs slightly changes the ice melting temperature. Depending on the additive, the fusion temperature varies from -1.3 to -2.0°C. I-1 and I-3 Material Safety Data Sheets (MSDS) indicate that these additives contain Glycol. Glycol is a thermodynamic inhibitor of ice and hydrates, and this may explain the slight decrease in the ice melting temperature. It is also noteworthy that only one melting peak was observed for each of the emulsions.

From the analysis of the microscopic images, it was observed that the distribution of droplets size for the emulsion without KHI and the emulsions with KHI I-2 and KHI I-4 are rather mono-dispersed. For the emulsions containing the KHIs I-1 and I-3 a more poly-dispersed distribution was observed. The statistical parameters which describe the droplets size distribution are summarized in Table 3.
The KHI concentration tested was of 1% by weight.

Table 3. OBM emulsions characteristics

<table>
<thead>
<tr>
<th>System</th>
<th>Droplets Counted</th>
<th>Mean Diameter [µm]</th>
<th>Standard Deviation [µm]</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>2.447</td>
<td>1.6</td>
<td>0.7</td>
<td>Mono-dispersed</td>
</tr>
<tr>
<td>I-1£</td>
<td>2.871</td>
<td>1.7</td>
<td>1.3</td>
<td>Poly-dispersed</td>
</tr>
<tr>
<td>I-2£</td>
<td>2.620</td>
<td>1.5</td>
<td>0.7</td>
<td>Mono-dispersed</td>
</tr>
<tr>
<td>I-3£</td>
<td>2.642</td>
<td>1.6</td>
<td>1.4</td>
<td>Poly-dispersed</td>
</tr>
<tr>
<td>I-4£</td>
<td>2.314</td>
<td>1.4</td>
<td>0.7</td>
<td>Mono-dispersed</td>
</tr>
</tbody>
</table>

£: emulsion with KHI at a concentration of 1% wt

Figures 2 presents respectively OBM/water emulsion and OBM/water/I-1 at 1% by wt emulsion.

Influence of KHI bond hydrate formation in the OBM

The results obtained for the methane gas hydrate formation with the different KHI at $T_{form} = -10 \degree C$ and 13.5MPa are shown in figure 3 and table 4.

Table 4. Effect of KHI on methane hydrate formation ($P = 13.5$ MPa, $T_{form} = -10\degree C$)

<table>
<thead>
<tr>
<th>System</th>
<th>Induction Time [s]</th>
<th>Peak Top [s]</th>
<th>Final Time [s]</th>
<th>Enthalpy [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>280</td>
<td>1250</td>
<td>2500</td>
<td>87.2</td>
</tr>
<tr>
<td>I-1£</td>
<td>400</td>
<td>2100</td>
<td>3500</td>
<td>35.5</td>
</tr>
<tr>
<td>I-2£</td>
<td>400</td>
<td>900</td>
<td>1900</td>
<td>82.3</td>
</tr>
<tr>
<td>I-3£</td>
<td>580</td>
<td>1200</td>
<td>2500</td>
<td>33.0</td>
</tr>
<tr>
<td>I-4£</td>
<td>500</td>
<td>1200</td>
<td>3000</td>
<td>85.0</td>
</tr>
</tbody>
</table>

£: emulsion with KHI at a concentration of 1% wt

In figure 3, it is observed that the induction times for the emulsions with KHI's are of the same order of magnitude as the reference (emulsion without KHI). This was not expected, since the main function of these substances is to delay the formation process. The time shift is very small (table 4) and the "Peak Top" measured for almost all the KHI's are smaller or similar to the one obtained for the reference indicating that if the hydrate crystallization is slightly delayed, the main crystal growth occurs more rapidly with the KHI's than without. From these results, it can be concluded that the KHI's are not effective in slowing down the formation of sI hydrates at a subcooling of approximately 24°C and a gas
pressure of 13.5MPa. The subcooling is defined as the difference between the equilibrium temperature of the hydrate and $T_{\text{form}}$. The formation conditions are too severe to allow KHIs to be effective. I-1 and I-3 inhibitors present smaller peaks than the reference and the two other KHIs tested. Their enthalpies of formation are drastically smaller which indicates that the quantities of hydrate formed are about 60% less than in the OBM without additives.

The corresponding dissociation thermograms are shown in Figure 4. The results are summarized in Table 5. For the reference without KHI, we observed an equilibrium temperature ($T_{\text{eq}}$) of 14.6 ± 0.2°C. As already mentioned, the theoretical equilibrium temperature of the methane hydrate formation under the working conditions is 16.06 ± 0.01 °C [13]. A difference of 1.5 ± 0.2 °C is found. This difference is similar in magnitude to the one measured for the depression of the melting point of water. As for ice, these thermodynamic inhibitors decrease the methane hydrate equilibrium temperature.

For all the experiments with KHIs, a peak at around 14.5 ± 0.2 °C is observed. It corresponds to the dissociation of the methane hydrate sl. The inhibitors I-1 and I-3 have the greater deviation from the referential value of the pure emulsion (table 5). As mentioned for ice melting, these KHIs contain glycol (mentioned in their MSDS). The glycol is a thermodynamic inhibitor of gas hydrates. The presence of glycol may displace the equilibrium temperatures to lower values.

Another thermal phenomenon was observed for some of these inhibitors (I-1, I-3 and I-4) – a second peak appears at higher temperature (Table 5). This peak, corresponding to another thermal exchange in the sample, can be due either to a kinetic effect (during the dissociation a part of the sample is meta-stable) or to a new species formed in the presence of these inhibitors. Further investigations are needed to conclude on this point.

In Figure 4, only one thermal signal was observed in the formation of gas hydrates with I-1 and I-3. If two species are formed, their formation occurs at the same time under the experimental conditions used. It is also observed for these inhibitors that the enthalpies of dissociation are approximately 70% of the dissociation enthalpy of the reference, implying less hydrate is formed with these systems. This is probably due to the presence of glycol.

The I-2 inhibitor does not have any effect on the equilibrium temperature or on the amount of hydrate formed.

In all of the tests performed, no thermal signal is observed around 0 °C. It is concluded that under the experimental conditions there is no ice formation in these systems.

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![Figure 4. Dissociation of methane hydrates, heating rate = 1 °C/min, P = 13.5 MPa (formation @ $T_{\text{form}}$ = -10 °C)](image)

Table 5. Results for the dissociation of methane hydrates. Heating rate = 1 °C/min, P = 13.5 MPa, (formation @ $T_{\text{form}}$ = -10°C)

<table>
<thead>
<tr>
<th>System</th>
<th>$1^{st}$ Peak Temperature [°C]</th>
<th>$2^{nd}$ Peak Temperature [°C]</th>
<th>Dissociation Enthalpy [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>14.6</td>
<td>-</td>
<td>97.7</td>
</tr>
<tr>
<td>I-1$^|$</td>
<td>14.3</td>
<td>18.5</td>
<td>66.5</td>
</tr>
<tr>
<td>I-2$^|$</td>
<td>14.7</td>
<td>-</td>
<td>97.1</td>
</tr>
<tr>
<td>I-3$^|$</td>
<td>14.3</td>
<td>18.7</td>
<td>57.0</td>
</tr>
<tr>
<td>I-4$^|$</td>
<td>14.5</td>
<td>15.5</td>
<td>70.0</td>
</tr>
</tbody>
</table>

$^\|$ : emulsion with KHI at a concentration of 1% wt

Similar experiments were performed with isotherm temperatures ($T_{\text{form}}$) of -5°C and 0°C. The dissociation thermograms at -5°C are similar to the one obtained at -10°C. At $T_{\text{form}}$= 0°C, a change in the proportion of the peak areas was observed, as
seen in Figure 5. These changes were studied in detail for the KHI I-1 (Figure 9).

Figures 5 presents one thermogram with the OBM emulsion without additive, one test with the KHI I-1 and KHI I-4. When the thermograms of I-4 and I-1 for a $T_{\text{form}} = 0 \, ^\circ\text{C}$ are compared to the ones obtained for a $T_{\text{form}} = -10 \, ^\circ\text{C}$ (Figure 4), the area increase of the second peak for each inhibitor is clearly seen.

In order to understand the nature of the second peak observed for I-1, I-3 and I-4, a series of tests were performed on the inhibitor I-1.

**Study of the I-1 Inhibitor**

*Methane hydrates*

On occasion meta-stable equilibria, which depend on the heating rate, can be observed in high sensitivity DSC equipment. In order to disregard any meta-stable equilibrium as being responsible for the second signal, the heating rate was diminished from 1 °C/min to 0.5 °C/min. Figure 6 shows the thermograms of hydrate dissociation for each heating rate.

Figure 6 shows that a decrease in the heating rate logically causes a better separation of the peaks. When the system reaches the second dissociation temperature, the first species is almost completely dissociated. As a result, the other tests were performed at a constant heating rate of 0.5 °C/min in order to facilitate the separation of the thermal signals and to obtain accurate energy measures associated to each thermal phenomenon. To obtain the area of each peak by deconvolution the software PeakFit 4.2 of Systat Software Inc. was used.

The dissociation-peak intensity diminishes with the decrease in the heating rate, whereas the enthalpies obtained by numerical integration for both cases are similar within the experimental error (~67 J/g). This fact can be reconciled since, when the heating rate decreases, the time of dissociation increases proportionally. As the energy is obtained from the integration of the power versus time, the area obtained remains constant under similar experimental conditions. The enthalpies obtained at the two heating rates are the same; the second peak does not depend on the heating rate or on the kinetic of dissociation. It is concluded that the second peak is not a consequence of a meta-stable equilibrium. The hypothesis of new species which are thermodynamically more stable than the methane hydrate seems to be highlighted. Its equilibrium temperature is higher than the equilibrium temperature of methane hydrates. It will be called sI*.

Figure 7 presents dissociation thermograms obtained at different concentrations of I-1. When the I-1 concentration increases, the peak areas assigned to sI decrease while the sI* peak areas increase. For both signals, the dissociation temperature moves slightly to lower values as the I-1 concentration increases. This is probably due to
the glycol contained in inhibitor I-1, as already mentioned. An analysis of this behavior shows that the sI species undergoes a greater displacement than the sI* species.

Regarding the methane-hydrate formation thermograms (not shown), no significant induction time variations were observed versus I-1 concentration. This lack of improvement is probably due to the very high driving force applied to the systems (subcooling around 24 °C and 13.5 MPa). Several cycles were carried out to evaluate the stability of this emulsion against gas-hydrate formation, demonstrating that it is stable against the hydrate formation/dissociation.

Figure 9 summarizes the evolution of the ratio sI*/sI measured during the dissociation for I-1 at 1% wt versus T_{form}. It is observed that for T_{form} of -10 and -5°C, the sI*/sI ratios are similar and close to 30%, and for T_{form} = 0°C the ratio increases to 50%. It can be concluded that the relative quantity of these two species depends on the conditions of hydrate formation. Increasing T_{form} leads to a decrease in the driving force for methane-hydrate formation and for the sI*. Apparently, when T_{form} is equal to or lower than -5°C, the conditions are so extreme (high subcooling) for both species that the ratio does not change considerably. When T_{form}=0°C, the ratio increases and more sI* is formed. I-1 is more efficient at lower subcooling and this corresponds to an increase of sI* species. We can conclude that the I-1 efficiency is probably linked to the formation of this particular species.

Hydrates sII: Methane 98% - Propane 2%

Although pure methane induces the formation of sI gas hydrate, it is necessary to determine if the sI* peak is exclusively formed with this sI gas former. The same experiments were performed with a methane and propane gas mixture (named C1-C3). This mixture promotes sII gas hydrates. The
equilibrium temperature for this system under the experimental conditions (P = 13.5 MPa) is $T_{eq}=20.38^\circ C$ calculated from CSMHYD software [13]. For this calculation, gas concentration in the bulk gas phase was used instead of the gas concentration in the oil-water interface.

Figure 10 presents the thermograms for hydrate dissociation obtained with the C1-C3 mixture. For the reference, only one dissociation peak is observed at 20.3 ± 0.2 °C. Surprisingly, this dissociation temperature is in good agreement with the theoretical equilibrium temperature; since a $T_{eq}$ decrease is measured for all the other systems studied. This is probably due to a level of uncertainty in the concentration of methane and propane, as explained above. Therefore, this lead. When the I-1 inhibitor is added at 1% and 2% wt., a second peak appears at higher temperatures. As for the sI hydrate, the second peak area increases when the concentration of I-1 increases. In this case, the temperature of this second peak is 26.1 ± 0.2 °C. This experiment confirms that the second peak sI* observed in thermograms for methane hydrates cannot be assigned to the structure sII, since, with a gas mixture that promotes the formation of sII, a second peak at a temperature higher than the theoretical $T_{eq}$ is also observed. With the C1-C3 gas, the second peak obtained will be called sII*.

The inhibitor I-2, which did not show any effect on the methane hydrates, was also tested. This inhibitor has no significant effect on sII-hydrate formation. The amount of hydrate formed (similar areas) and the equilibrium temperature are the same as for the reference (without inhibitor).

As in the case of sI hydrates, it is observed in Figure 11 that the total amount of hydrates formed in the presence of I-1 is lower than in the reference case. The ratio of the enthalpies associated to sII and sII* varies in the same way as the sI/sI* ratio.

![Figure 11. Effect of I-1 on C1-C3 hydrates and sII* species (P = 13.5MPa, $T_{form} = -10^\circ C$)](image)

It was observed that at the same KHI I-1 concentration, the amount of sII* formed was greater than the amount of sI* formed (Figure 8 and 11). The natural gas forms sII hydrates, but it was observed that the sII* species is formed in the presence of the KHI I-1 and that it has a greater dissociation temperature than sII. The formation of these sII* species could result in difficulties in the hydrocarbon industry. Finally, tests were carried out with bulk phase (not shown) to discard the influence of the emulsion and of the components of the oil system on the appearance of the sI* and sII* second peaks. Hydrate formation takes place at the gas/water or oil/water interface [14]. The emulsions have a water/oil-interfacial area thousands of times greater than the equivalent mass of bulk water. Consequently, the amount of hydrate formed with bulk water is much smaller, and it is difficult to make quantitative energy measurements.

C1-C3 hydrates have been formed with pure bulk water at P = 13.5 MPa. Two dissociation peaks can be seen around 16 and 19.5 °C. They correspond to the equilibrium temperatures of sI and sII. In these conditions, both hydrates sI and sII are formed in
the aqueous phase, since there is an excess of methane. The solubility of C$_3$H$_8$ is lower than the solubility of CH$_4$. A hydrate layer is formed at the water/gas interface and, as methane is in excess in the bulk, the two structures are formed. When the emulsion is put under the same conditions only one peak is observed, corresponding to sII. In the emulsion, both gases are soluble in the oil phase that brings the two species to the water droplets' interface. This confirms the hypothesis that the as composition at the interface is different to the composition in the gas-bulk phase. When I-1 is added to the bulk water, a third peak appears at a higher temperature (around 29 °C). The energy of the thermal signal depends on the I-1 concentration. This new peak is assigned to sII*. These bulk-water results demonstrate that the sII* peak is not a consequence of interference between I-1 and the oil-system components, but of the presence of the inhibitor I-1 in the water. No sI* species has been detected, but it must be pointed out that in bulk water the equilibrium temperature of sI* is probably close to the T$_{eq}$ of sII. As the quantities of hydrates formed are low, and as it is difficult to measure the energies, it is not possible to conclude on the formation of sI* in these tests.

It was observed that for bulk water the induction time for the formation of the sII structure is lower than sI hydrates. This is because the sII hydrates have a higher equilibrium temperature than sI hydrates, so at the same formation temperature, the subcooling for sII hydrates is higher than for sI.

**Tetrahydrofuran Hydrates**

Water and tetrahydrofuran (THF) are able to form chlatratic structures similar to gas hydrates at atmospheric pressure. Stackelberg and Meuthen reported that 17 moles of water per mole of THF are present in the THF-hydrate structure with an equilibrium temperature of 5.1 °C [15]. The effect of KHIs on THF-hydrates have been investigated both in bulk phase and in OBM-emulsion phase.

Solubility tests were performed, and showed that THF was soluble in both water and oil system. A partition of the THF was then expected between these phases when working with the emulsion. An excess of 100% of the THF in the aqueous phase was therefore added. THF solutions at 32% by weight were used as the aqueous solution. The OBM-emulsions were prepared with a 20% water cut, as in the previous tests. The stability of THF-emulsions, with and without I-1, were verified by DSC. All the tested emulsions were stable against the ice formation/melting and hydrate formation/dissociation, since no significant changes in the peak positions and shapes were observed on the thermograms after 3 consecutive thermal cycles. THF-hydrate formation-dissociation tests were performed in the two pieces of DSC equipment. The results obtained are similar. Only the results from HP-micro DSC-VII are presented here.

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature [ ±0.2 °C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ice</td>
</tr>
<tr>
<td>Bulk THF 32%</td>
<td>no peak</td>
</tr>
<tr>
<td>I-1(1%) in Bulk</td>
<td>no peak</td>
</tr>
<tr>
<td>Emulsion</td>
<td>-1.8</td>
</tr>
<tr>
<td>I-1£</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

£: emulsion with KHI at a concentration of 1% wt

Table 6. Dissociation temperatures for the THF-hydrates

<table>
<thead>
<tr>
<th>System</th>
<th>Enthalpy [ ±0.5 J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ice</td>
</tr>
<tr>
<td>Bulk THF 32%</td>
<td>no peak</td>
</tr>
<tr>
<td>I-1 (1%) in Bulk</td>
<td>no peak</td>
</tr>
<tr>
<td>Emulsion</td>
<td>18.4</td>
</tr>
<tr>
<td>I-1£</td>
<td>11.1</td>
</tr>
</tbody>
</table>

£: emulsion with KHI at a concentration of 1% wt

Table 7. Dissociation energies for the THF-hydrates

Tests were performed on the bulk solution containing 32% THF, with and without I-1, and on the 20% water cut OBM-emulsion prepared with the THF water solution. The results obtained from these tests are summarized in Table 6 (equilibrium temperatures) and in Table 7 (enthalpies). When the hydrate formation is carried out in the water bulk phase, the aqueous phase with THF presents only one peak of dissociation at 4.4 °C (Table 6). This peak corresponds to the THF-hydrate dissociation. In this case, it is not possible to observe the melting of ice since the THF has been added in excess. Water is the limiting reagent in hydrate formation, so it is completely consumed when hydrates form. When the inhibitor I-1 is added to the bulk, a second peak appears at a higher temperature (5.9 °C). This peak is assigned
to the THF hydrate*. With the emulsified system without I-1, two peaks appear (Table 6). The first one is assigned to the ice melting (-1.8 °C), and the second one is the product of the dissociation of the THF hydrates (+1.6 °C). The ice melting temperature depression is similar to the one measured during the OBM characterization (-1.7 °C in Table 2). The slight difference may be due to the high THF concentration in the sample. The $T_{eq}$ of THF hydrate is also naturally displaced towards a lower value. In the case of the emulsion with I-1, the same peaks are detected with an additional peak at a higher temperature (4.7 °C). This peak is assigned to structure* species and will be named THF hydrate*. It is observed that a concentration of I-1 of 1% generates a greater amount of the non-classical structure (THF hydrate*) in the bulk phase than in the emulsion (Table 7). The difference in the temperatures (Table 6), intensities (Table 7) and ice melting can be explained in terms of thermodynamic inhibitors (salts), THF and I-1 partition between the aqueous and oil phases. The experimental dissociation temperature in the bulk aqueous phase for the THF hydrate was 4.4 ± 0.2°C, which is lower than the reported value of 5.1°C [15]. Erva has reported that the dissociation points of these hydrates depend on the concentration of the solution with which they are in contact [16]. Thus, the equilibrium temperature decreases when the concentration of THF increases. Since an excess of 100% of THF hydrate stoichiometry amount for the formation of hydrates was added, to compensate for the THF loss due to its partition between the two phases, it is then expected that the equilibrium temperature will be smaller than the theoretical value. A new peak is detected at higher temperatures (more stable), both in bulk and in OBM emulsion, when the system contains the inhibitor I-1. It can be concluded that the structure* does not depend on the presence of high pressure gaseous hydrocarbon in the system. Pinder has demonstrated that the water and the THF form only one type of hydrate [17]. The observation of the non-classical structure with this system is very important, since THF hydrates form at atmospheric pressure. The study of their properties will be easier because high pressure gas will not be required. For example, X-ray diffraction or Raman spectroscopy could be used to observe structural changes in the crystalline network, and to confirm if the species* are indeed due to the presence of a new crystalline hydrate structure.

**CONCLUSIONS**

The very high driving force (temperature and pressure) used does not allow us to come to any clear conclusions regarding the KHI's efficiency on the methane-hydrates formation, the induction times measured being similar for all the KHI's as well as the OBM's without additives. All the thermograms present only one hydrate-formation peak. The hydrates formed above (with and without KHI's) were dissociated at the same pressure by increasing the temperature. A peak of methane-hydrate dissociation was detected on the thermograms of the OBM emulsion without additives. The dissociation was detected at a temperature slightly lower than the one predicted by the thermodynamic model. This variation has been assigned to the solubilisation of oil-system components in the aqueous phase. With the OBM emulsions containing the KHI's I-1, I-3 and I-4, two peaks were detected during the temperature increase: the first corresponding to the methane-hydrate dissociation and the second with a higher equilibrium temperature. This second peak has been named sl*. The sl* is not a meta-stable species as long as the ratio si*/si stays unchanged when the heating rate is changed. Further tests performed with the additive I-1 have led to the following conclusions:

- sl*/si increases when the additive concentration increases and when the temperature of methane hydrate formation is ≥ 0 °C,
- siII* is formed when a structure II gas methane + propane (98/2 % mol.) former is used.
- siII*/siII increases when the additive concentration increases,
- siII* appears also when bulk water with the additive is tested,
- THF hydrates* are formed at atmospheric pressure when THF is used with the additive,
- THF hydrates* have been observed in the two calorimeters used.

From all these experimental results, it can be concluded that I-1 forms a specific crystal species "s*" when hydrates form. The amount of "s*" species is related to the quantity of I-1, to the structure formed and to the kinetic of formation (subcooling). I-3 presents the same equilibrium temperature for the sl* species, probably because its active molecule is the same as in I-1 (same supplier). On the other hand, I-4 presents a sl* equilibrium temperature much closer to the $T_{eq}$
value of s1. The reason for this difference is still unknown. Additive I-2 does not present a "s*" dissociation peak: Is it because of the too-high subcooling? or because of the nature of the additive? Finally, what will be observed in gas-hydrate cases if the dissociation is performed at a constant temperature by varying the pressure? Other additives and other conditions must be tested in order to have a better view on these different points. It is commonly acknowledged that when hydrates form in the presence of KHI, the dissociation of these hydrates is much more difficult than without additives [18]. It was generally thought that this difficulty was due to a much slower kinetic of dissociation. With the existence of these "s*" species, these dissociation difficulties may be assigned to the "s*" higher stabilities and not to a change in the kinetic-dissociation rate. The existence of these "s*" species must be confirmed using other techniques, and the crystallographic definition of these species must be determined. For industrial applications, it may be very interesting to know the "s*" temperature of equilibrium, in order to be sure that the facilities will reach a high enough temperature to dissociate these new species if the KHI fails.

REFERENCES