Kinetic Gas Hydrate Inhibitors and Synergy of the Inhibiting Molecules

Authors: Hua Guan
Corresponding author: Hua Guan, hguan@mishaco.com, M-I Production Chemicals, Minto Drive, Altens Industrial Estate, Aberdeen, UK, AB12 3LW

Abstract:

This paper investigates the application of kinetic hydrate inhibitors in three different gases and the synergy between different inhibiting molecules. Several commercially available kinetic hydrate inhibitors have been evaluated in the laboratory using rocking cell apparatus. Three different gas compositions have been used in the performance evaluation. The synergy of different inhibitor molecules has been studied through the evaluation of varies mixtures. The field requirement for low viscosity and high cloud point for kinetic hydrate inhibitors have also been studied and discussed. The hydrate dissociation curves for three gases have been modelled and the subcooling potential for each of the products has been calculated.

Following the review and optimisation of the different hydrate inhibiting molecules available in the market, it was found that one of the optimised mixtures has outperformed all the individual hydrate inhibiting molecules and mixtures for all three gases. This suggests the synergy between the different hydrate inhibiting molecules; the possible mechanisms were discussed in the paper.

Gas hydrates become an increasing problem to the oil and gas industry when the development entering deeper water encounters high-pressure and low-temperature regions. However, the mechanisms and applications of kinetic hydrate inhibitors are less well understood. This paper provides an overview of the performance of all different hydrate inhibiting molecules that currently available and discusses the mechanisms of hydrate inhibition and the synergy of different hydrate inhibiting molecules and therefore provides some guidance in future development on hydrate inhibiting molecules for different gases.
Introduction

Gas hydrate is a crystalline solid consisting of gas molecules (e.g., methane), each surrounded by a cage of water molecules. These ice-like crystals tend to form at high pressure and low temperatures when hydrocarbon molecules are trapped within cavities created by hydrogen bonding between water molecules. The hydrogen bonding allows the attachment between water molecules due to mutual acceptance and donation of hydrogen bonds, in such a way that the central water molecule is surrounded in a tetrahedral manner by the other four. Bonds that form in this way are relatively strong, and give the structure rigidity which means there is more space between molecules than there would be in the liquid state.

There are three different structures that gas hydrate can form, hydrate sI, sII and sH. This refers to the way in which the water cages are joined together, and held in place by van der Waals forces. At each vertex in the structure is one water molecule, which is then hydrogen bonded to others within the cage. A general illustration of hydrate is shown in FIG 1A, where a methane molecule is surrounded by a cage of water molecules.

A sII hydrate structure is illustrated in FIG 1B, it can be described as $A^n$, with $A$ being the number of sides that a face of the cage has, while $n$ is the number of faces in the cage holding this amount of sides. In a sII hydrate, it can be said there are eight $5^{12}6^4$ water cages and sixteen $5^{12}$ water cages per unit cell. In the oilfield environment, the most abundant hydrate form is sII, since it is stable whenever a natural gas mixture contains some propane or butanes besides methane. This is probably due to the presence of larger hydrocarbons such as pentane which can fill the larger $5^{12}6^4$ cages, while the smaller $5^{12}$ cages can be filled by the smaller hydrocarbons and other gases such as CO$_2$ and H$_2$S.

FIG 1: ILLUSTRATION OF HYDRATE (1A) AND SII GAS HYDRATE (1B)

The occurrence of gas hydrates in high pressure low temperature systems has caused significant problems to the oil and gas industry over the years. As the drilling and pumping of gas occurs from deeper parts of the ocean, the temperatures are getting lower while the pressures are getting higher. As a result, gas
hydrates becomes an increasing problem under these conditions, and a method of reducing their effect is critical to increase the efficiency of drilling and production.

Conventional chemical method for hydrate control is the use of thermodynamic inhibitors (e.g. methanol or glycols) which work by competing for hydrogen bonds with water molecules to decreasing the hydrate formation temperature. However, large quantity and storage space is required therefore high cost.

The use of LDHI (Low Dosage Hydrate Inhibitor) which are typically dosed between 0.1-1.0 weight % (ref xv.) based on the water phase becomes popular due to its low dosage required, this provides a cost effective solution for hydrate control. Research into the gas hydrate field has been vast over the past decade, and several low dosage type gas hydrate inhibitors have been discovered during this time which has been reviewed by Kelland ⁴. LDHI’s can be further split into kinetic hydrate inhibitors (KHI’s) and anti-agglomerants (AA’s), which work in different ways, although neither mechanism is fully understood yet. Initial theory of Lederhos et al ⁵, which has to date not yet been proved suggest the mechanisms of LDHI as such: KHI works similar as scale inhibitors which is locked into the growing crystals, deforms the crystal, increase the crystallization energy so the crystallization process stops. AA works more similar as corrosion inhibitors, it stops the crystal growth by attaching onto the existing crystal surfaces causing the dispersion of small crystals without agglomeration. One of the key features for chemicals that working as KHI is to be able to fit the growing hydrate structure e.g. sII, a number of chemicals are found to do this ⁴,⁶,⁷,⁸ including polymers / co-polymers based on polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) polymers. The structure of PVP and PVCap is shown in FIG 2. These polymers can key into hydrate cage with H bond to distort hydrate crystallization process. The maximum sub-cooling that this polymer can achieve is 8-14°C. The other limitations of these polymers is that they are not inherently biodegradable therefore may have restricted application in certain geographical regions.

![FIG 2: STRUCTURES OF VP (A) AND VCAP (B) POLYMERS](image)

The evaluation methods of LDHI have been developed over the years; two types of equipment are used. Rocking cell type is found to be good to evaluate KHI while autoclave fitted with camera is found to be suitable for AA evaluation. In this paper, the LDHI evaluated are all believed to be KHI type of inhibitors, therefore rocking cell type is adopted in the experiment. Prediction software e.g. Multiflash® ⁹ is usually used to model the hydrate formation temperature in a given system, there are some modeling results shown in this paper.
The aim of this work is to investigate the application and associated mechanisms of all types of KHI that currently available in the market. This is done by evaluation of these inhibition molecules and their synergy in three different gas systems, using a rocking cell apparatus. This would allow the performance comparison of different type of molecules and synergy effects when different molecules are mixed together. We hope that this can shed some lights into the inhibition mechanism of different molecules and point out the key features of a good hydrate inhibitor. This knowledge would be of interests to the field, and would allow for other inhibitors to be synthesized specific to the gas type and the mechanism, which may be more successful than those currently available.

Methodologies

One of industrial standard protocols in evaluation of KHI is the use of rocking cell apparatus. FIG 3 shows the photo of the rocking cell apparatus used in this paper, while a close look of the sapphire cell encased in stainless steel with flexible tubing is shown in FIG 4. Up to four individual sapphire cells can be run in parallel for comparison purpose.

During the test, the cells were filled with 10ml of testing liquid (either DI – distilled water or 0.25% KHI solution) and pressurized with the target gas mixture, subsequently they were lowered into the bath containing mainly water with a small amount of monoethylene glycol (MEG). The rocking motor was then switched on. The bath was cooled using a constant cooling rate by setting the chiller ramp to -4°C in 300 minutes. Throughout the experiment pressure and temperature were extensively measured in order to closely examine the conditions required for hydrate formation to occur, with visual observations also be carried out. As hydrate formation is associated with a pressure drop in the system due to the gas being trapped within the ice-like cavities, measurements of pressure and temperature were taken very regularly. Hydrate formation temperature can be determined by the point at which the pressure drops significantly.

FIG 3: PHOTOGRAPH OF ROCKING CELL APPARATUS USED IN THIS PAPER

FIG 4: PHOTOGRAPH OF A SAPPHIRE CRYSTAL HYDRATE CELL
As illustrated in FIG 5 above, subcooling obtained from a test run is determined by the difference between the hydrate formation of the blank (uninhibited sample) and of the inhibited sample (denoted as x °C in FIG 5). Hence a good KHI will show a large subcooling i.e. bigger x °C, with hydrates forming at much lower temperatures.

Total of nine KHIIs have been evaluated by the rocking cell apparatus. The products evaluated are listed in TABLE 1. Product H and I are benchmarking chemicals which have defined chemical structures and do not contain any solvents, they were included in the testing for comparison. Product A, B, C, D, E, F and G are commercial available KHIIs of different polymer compositions in different solvents. Also listed in TABLE 1 is their physical properties viscosity and cloud point, it is clear that Product A posses the lowest viscosity and highest cloud point which is of benefit to field applications. During field application, high viscosity of a product can cause pumpability problem while low cloud point product cannot be injected from an injection point at higher temperature than that of its cloud point temperature. Other products in TABLE 1 may not be suitable for application in certain systems where the temperature of the injection point is too high.

<table>
<thead>
<tr>
<th>Product</th>
<th>Chemistry / Composition</th>
<th>Solvents</th>
<th>Viscosity (cp) @ 25 °C</th>
<th>Cloud point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To study the synergy between different KHI molecules, four mixtures were made and tested using the same procedure. The formulations of these mixtures are given in Table 2. Mixture 1 was designed to see the synergy between Product A and F; while Mixture 2 was specifically designed in order to confirm that the result shown for Mixture 1 is due to the synergy between Product A and F but not from the solvent used (i.e. EGMBE, MEG and water). Mixture 3 and 4 were formulated neat without any additional solvents. Mixture 3 was designed to see if there is additional synergy when Product B and E added; while Mixture 4 was to study the importance of Product F in the synergy effect.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Product A (wt%)</th>
<th>Product B (wt%)</th>
<th>Product E (wt%)</th>
<th>Product F (wt%)</th>
<th>EGMBE (wt%)</th>
<th>MEG (wt%)</th>
<th>H₂O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.5%</td>
<td>-</td>
<td>-</td>
<td>7.5%</td>
<td>14.5%</td>
<td>24.5%</td>
<td>15.0%</td>
</tr>
<tr>
<td>2</td>
<td>40.0%</td>
<td>-</td>
<td>-</td>
<td>7.5%</td>
<td>15.0%</td>
<td>25.0%</td>
<td>20.0%</td>
</tr>
<tr>
<td>3</td>
<td>82.0%</td>
<td>8.0%</td>
<td>2.5%</td>
<td>7.5%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>85.0%</td>
<td>1.5%</td>
<td>13.5%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The formation temperature of hydrates is also dependant on the gas used, total of three different gases are used in this paper to evaluate the effectiveness of KHI for different
gases. The composition of these gases is listed in TABLE 3. Theoretical hydrate formation temperatures for all three gases are predicted by industrial recognised software Multiflash®, the result is shown in the next section.

**TABLE 3: GAS COMPOSITIONS**

<table>
<thead>
<tr>
<th>Type of gas</th>
<th>N₂</th>
<th>CO₂</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>i-C₄</th>
<th>n-C₄</th>
<th>i-C₅</th>
<th>n-C₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.8</td>
<td>1.6</td>
<td>79.71</td>
<td>10.8</td>
<td>4.6</td>
<td>0.62</td>
<td>1.1</td>
<td>0.2</td>
<td>0.19</td>
</tr>
<tr>
<td>B</td>
<td>7.5</td>
<td>1.0</td>
<td>84.4</td>
<td>5.0</td>
<td>1.5</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.40</td>
<td>-</td>
<td>87.82</td>
<td>7.8</td>
<td>3.1</td>
<td>0.51</td>
<td>0.97</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Prediction Results and Discussions**

Based on these gas compositions in TABLE 3, the theoretical hydrate formation curves are modeled by Multiflash®.

The prediction results for gas A is shown in FIG 6 - gas A is expected to produce hydrates at 15.4°C when set up at 60 bars, and at 6.5°C when set at the lower pressure of 20 bars. Gas B which is pressurized at 20 bars is expected to form hydrates at 9.1°C (FIG 7). Gas C is expected to form hydrate at 8.9°C according to the curve in FIG 8.

By comparison, at a pressure of 20 bar without KHI, gas B is expected to produce hydrates the most easily at the highest temperature of 9.1°C, and gas A being the most resistant to the development of hydrates, forming at the lowest temperature of 6.5°C. This suggests that gas A can be transported from deeper, colder parts of the ocean without any inhibitor present as long as the system temperature is above 6.5 °C at 20bar; gas B and C are not going to form hydrate as long as the temperature is over 9.1 °C.

Looking at the gas compositions, this difference is probably caused by the relative amount of hydrocarbons with 4 or more carbon atoms in them within the gas. The amount of these in gas A is only 0.6%, compared with 2.11% for gas B and 1.88% for gas C. This would suggest that the bigger percentage of larger molecular weight hydrocarbons (> C₄) within the gas, the higher the hydrate formation temperature at constant pressure.

The hydrate formation temperatures derived from a prediction software is usually slightly (a couple of degrees) higher than those obtained from the experiment, but the trend obtained from prediction and experiment should be the same.

**FIG 6: PREDICTED HYDRATE FORMATION CURVE FOR GAS A**
Experimental Results and Discussions

All products listed in TABLE 1 and 2 were tested using the hydrate rocking cell apparatus at a dosage of 0.25 w/w%. Each test was repeated to ensure accuracy and repeatability of results. Blank samples without any KHI were tested in triplicates. The average hydrate formation temperature and formation time were recorded for each KHI and blank samples. The degree of subcooling archived by each product was calculated by the difference between the formation temperature of the inhibited sample and the formation temperature of the blank. Total three different gases were tested during the evaluation. Below are the test results for three different gases.

Test Result for Gas A @ 60bar

All products listed in TABLE 1 and 2 were tested at 0.25 w/w% using gas A at high set up pressure of 60bar. FIG 9 gives the subcooling results. Clearly, the inhibition
The performance of the benchmarking chemicals (Product I and H) is worst while Mixture 3 gives the best performance. The ranking of the products can be described as follows:


It is expected that Product I and H do not perform as well as other commercial available KHIs, due to their molecular structure which will be discussed later. Product G shows the worst performance among the commercial KHIs while Product A and D shows the best performance. Between the product mixtures, Mixture 3 and 4 has shown better performance than those of the individual KHIs which will be studied closely later on.

Comparing the performance of Mixture 1 (consists of both Product A and Product F) and Mixture 2 (consists of only Product A), Mixture 1 has outperformed Mixture 2 which indicate the possible synergy between Product F and Product A. More tests were carried out on Mixture 3 and 4 and the synergy effect between Product A and F will be discussed in details.

To reduce the experimental time, the subsequent tests at 20bar several products were excluded in the plan. Only Product A, B, C, D, E, F, I and Mixture 3 and Mixture 4 were included in the later tests.

Test Result for Gas A @ 20bar

Again, the dosage used was 0.25 w/w% for each product but gas A was at low set up pressure of 20bar. FIG 10 gives the test results. At this lower set up pressure, the degree of subcooling was reduced comparing with results at 60bar (FIG 9). This indicates that although the hydrate formation temperature decreases with decreased pressure, the subcooling achievable by a KHI decreases.
The performance ranking for various products remained the same:

Again Mixture 3 and Mixture 4 had showed better performance than each individual product which suggests the synergy effect between the product molecules. In particular, Mixture 3 which contains all four products (A, B, E and F) has by far outperformed Mixture 4 (only A, B, E without F); this indicates the importance of Product F in this synergy effect.

Test Result for Gas B @ 20bar
Again, the dosage used was 0.25 w/w% for each product but a different gas B was used at low setup pressure of 20bar. FIG 11 gives the test results. Comparing with Gas A (FIG 10), the subcooling achievable by each product is slightly higher than that of Gas A. This indicates that in certain systems, hydrate formed by Gas B is easier to be inhibited than that formed by Gas A. Again, the performance ranking for various products remained the same:

Mixture 3 and Mixture 4 had again showed better performance than each individual product which suggests the synergy effect between the product molecules. Mixture 3 has by far outperformed Mixture 4 which suggests the importance of Product F in the synergy effect.

FIG 11: SUBCOOLING RESULTS FOR GAS B @ 20BAR
Test Result for Gas C @ 20bar

Again, the dosage used was 0.25 w/w% for each product but a different gas C was used at low set up pressure of 20bar. FIG 12 gives the test results. Comparing with Gas A and B (FIG 10, 11), the subcooling achievable by each product is slightly higher than that of Gas A but similar as Gas B. This indicates that in certain systems, hydrate formed by Gas C is easier to be inhibited than that formed by Gas A. Again, the performance ranking for various products remained the same:


Mixture 3 and Mixture 4 had once more showed better performance than each individual product which suggests the synergy effect between the product molecules. Mixture 3 has by far outperformed Mixture 4 which suggests the importance of Product F in the synergy effect.

Overall Discussions

More discussions are made in the following headings:

Performance of Individual KHI Molecules

Although different gases and different pressures were tested, the ranking of each individual product is the same:

Product I molecule structure is shown in FIG 13, while all other products are of polymer or co-polymers of VP and VCap (see FIG 2). Clearly, Product I has terminal amine groups on a chain instead of the ringed structure of VP or VCap. This suggests that the amine groups in Product I does not inhibit hydrate formation very well, and that the PVP and PVCap monomers are good inhibitors probably due to their ring structure which have been able to key into the water cage better to blocking the formation of gas hydrate.

FIG 13: STRUCTURE ILLUSTRATION FOR PRODUCT I – BENCH MARKING PRODUCT

Among the other products, Product D (PVCap) and Product A (VP/VCap copolymer) performed the best, followed by Product B (PVCap) and Product F (VCap/VP copolymer), then Product E (VCap/DEAEMA copolymer) and Product C (VCap/PEG graft). It is difficult from these results to conclude whether PVP or PVCap or others is the best functional group until more is known of the exact structure of the molecule and the inhibition mechanism. Many factors can affect the inhibition such as the length of the chain, the number of pendant groups present, the spacing between them and the way in which these are attached to the chain. The pyrrolidone, and caprolactam rings are not small in size, and therefore how they fit onto a polymer chain may differ from one to another monomer with more carbon atoms in the chain between pendant groups. This may affect the inhibition if specific orientation is required. Without a clear picture of each individual molecule, it is therefore difficult to draw too specific conclusions as yet.

Synergy of Inhibitor Molecules
For all three different gases, Mixture 3 and 4 have outperformed the individual products. This has clearly suggested the synergy between the different inhibitor molecules. Mixture 3 is a mixture of Product A, B, E and F while Mixture 4 is a mixture of Product A, B and E only, Mixture 3 has shown much better performance than Mixture 4. This indicates the importance of Product F in this synergy effect.

It is clear from the results that mixing these different types of inhibitors increases the inhibition properties. This could be due to the different sizes of molecules within the inhibitor mix help to stopping the growth of different sized cavities: for example, the larger PVCap molecules fitting into the sII hydrate $5^{12}6^4$ cages, while the smaller PVP pendants fitting into the $5^{12}$ cages.

In particular, Mixture 4 (without Product F) has shown poorer performance than Mixture 3. This suggests that the addition of this specific polymeric chain in Product F has increased the inhibitor efficiency greatly.
The synergy between individual molecules is clear from the results of various mixtures.

Conclusions

Several commercial available KHIs based on PVP and/or PVCap molecules and several mixtures were evaluated through rocking cell apparatus using three different gases. Same performance ranking were obtained:


It is clear that PVP and PVCap hydrate inhibitor molecules have much better inhibition performance that of the benchmarking molecule, this is possibly due to their ring structures can key into the hydrate forming cavities and subsequently blocking the gas hydrate formation.

It is also clear from the results that mixtures of different molecules have shown better performance than each individual molecule. This suggests the synergy between these molecules. The synergy is possibly provided by the different sizes which help to stopping the growth of both small and big hydrate forming cavities.

Overall it is difficult to conclude whether PVP or PVCap is a better functional group until more is known of the exact structure and the inhibition mechanism. Depending on the arrangement of pendant groups on the polymer chain (e.g. pendent structures, numbers and spacing), the pendent groups may selectively key into the cavities (instead of hydrocarbon gas) to prevent gas hydrate formation. It is also possible that the pedant groups on the chain are acting as anti agglomerants, stopping any hydrate particles from joining together by taking up so much space around them.

Three different gases were used in this study. Although the rankings of the KHIs remained the same, there are differences in hydrate formation temperatures. Gas A has the lowest hydrate formation temperature followed by gas B and C, this difference is probably caused by the relative amount of hydrocarbons with 4 or more carbon atoms within the gas. The amount of these in gas A is only 0.6%, compared with 2.11% for gas B and 1.88% for gas C. This suggests that the bigger percentage of larger molecular weight hydrocarbons (> C4) within the gas, the higher the hydrate formation temperature at constant pressure.

Nomenclature

LDHI = Low Dosage Hydride Inhibitor
KHI = Kinetic Hydrate Inhibitor
AA = Anti Agglomerate
PVP = PolyVinylPyrrolidone
PVCap = PolyVinylCaprolactam
VP = 1-Vinyl-2-Pyrrolidone
VCap = VinylCaprolactam
PEG = PolyEthylene Glycol
DEAEMA = N,N-DiEthylAminoEthyl MethAcrylate
DMAEMA = N,N-DiMethylAminoEthyl MethAcrylate
DI = Distilled Ionised water
MEG = Mono Ethylene Glycol
EGMBE = Ethylene Glycol Mono-Butyl Ether

Reference

2 Kelland, M. A., Production Chemicals for the Oil and Gas Industry, p225, Boca Raton, CRC Press, Taylor & Francis Group, 2009
9 Multiflash® version 3.8; published 2009; Infochem.