Investigation of the performance of low-dosage hydrate inhibitors combined with wax inhibitors for a mixed CH$_4$-CO$_2$ gas hydrate formation

Xuemei Lang, Pingping Lv, Shurui Xu, Baoyao Li, Shuanshi Fan, and Yanhong Wang

Abstract: Within the oil and gas industry, low-dosage hydrate inhibitors (LDHIs) are a proven technology to control hydrates. Besides hydrate inhibitors, wax inhibitors (WIs) are frequently injected to prevent wax buildup in the crude oil pipeline. However, little attention has been focused on the effect of wax inhibitors on the performance of LDHIs. In this study, performance tests of 3 LDHIs in the presence of wax inhibitors were carried out for a 67% CH$_4$/33% CO$_2$ gas hydrate formation. Using the isothermal cooling method at pressures of 9 MPa and temperatures of 4 °C (subcooling is 9 °C), the results showed that the induction time of CH$_4$-CO$_2$ gas hydrate formation with LDHI/WI was shorter than the system with only LDHI. During the growth period, when the concentration of the WIs was 1 mass%, the growth time of the system with LDHI/WI was prolonged. Taking the induction time and the growth time into consideration, it was found that WIs had a more negative impact on the kinetic hydrate inhibitor performance at low dosage. The effect of WIs at high concentration could be negligible.

Key words: gas hydrate, low-dosage hydrate inhibitor, wax inhibitor, CO$_2$-rich gas, induction time.

Introduction

The crystalline structures of gas hydrates composed of small gas molecules trapped in water molecule cages always block oil and natural gas pipelines, and may result in serious safety and environmental problems.\(^1\)\(^-\)\(^3\) Generally, two kinds of chemical inhibitors are chosen to dissolve this hydrate formation problem. One is the addition of thermodynamic inhibitors (THIs), such as methanol or ethylene glycol in large quantities (20–50 mass% in the aqueous phase),\(^1\) which shift the phase boundary of gas hydrates so as to lower temperatures and higher pressures, preventing hydrate formation.\(^4\) The other approach is to add low-dosage (below 3 mass%) hydrate inhibitors (LDHIs), including kinetic inhibitors (KHIs) and anti-agglomerants (AAs).\(^1\)\(^,\)\(^5\) LDHIs have been used in many fields due to their cost-effectiveness and environmental friendliness. Moreover, the design of a new field development strategy with LDHI technology can provide large cost savings.\(^6\)\(^-\)\(^10\)

KHIs are water-soluble polymers that can delay either hydrate nucleation or hydrate growth.\(^1\)\(^)\) The interference slows down the kinetics and then extends the induction time for hydrate formation.\(^1\)\(^)\) Also, KHIs can be used in a wide variety of water ratios. Typical KHIs are poly (vinylpyrrolidone) (PVP) and polyvinylcaprolactan (PVCap). AAs are surfactant chemicals that contain a hydrophilic headgroup that absorbs to hydrate particle surfaces and a hydrophobic tail that prevents the aggregation of hydrate particles, resulting in a hydrate slurry.\(^1\)\(^)\)\(^3\) AAs produce water-in-oil emulsions that bind to hydrate particles.\(^1\)\(^)\(^)\)\(^1\)\(^)\(^1\)\(^)\(^3\) Typical AA chemicals are quaternary ammonium surfactants.\(^1\)\(^)\(^4\)

Wax deposition of crude oil in pipelines is also a serious plugging problem, which decreases their flow channel and reduces the flow rate, or even block the oil well.\(^1\)\(^)\(^5\) It is necessary to control wax deposition. Some technologies are currently used in the field, such as mechanical, thermal, and chemical methods.\(^5\)\(^6\)\(^-\)\(^8\) The widely used chemical methods are simple and accessible. There

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are different mechanisms of wax prevention by paraffin inhibitors. Possible ways of preventing deposition of paraffin are: increasing the wettability of the surface on which the wax are deposited and creating conditions unfavorable to deposition of wax on the pipe walls; prevention of growth of wax crystals by modifying their structure.\textsuperscript{19,20} Perhaps the most effective way of dealing with the problem of wax deposition in pipelines is to prevent it from occurring in the first place.

To solve the hydrate and wax problem simultaneously, both LDHIs and wax inhibitors are needed, which could possibly lead to incompatibilities. There have been a few studies on the interaction of these two kinds of inhibitors. Swanson et al. reported the successful use of both KHI and WI\textsuperscript{21} However, a problem exists because incompatibilities can emerge with different wax inhibitor and LDH combinations. Thus, our work studies the effect of wax inhibitors on the performance of selected LDHIs (KHI or AA).

In this study, we used commercial inhibitor Inhibex501 (ISP), synthesized inhibitor HY-1,\textsuperscript{22} and anti-agglomerant KL-1 and two WIs, WJH-01 and BHFL-02, synthesized by CNOOC Energy Technology & Services, Oilfield Technology Services. The chemical structures of Inhibex501 and HY-1 are given in Figs. 1 and 2, respectively. The major component of KL-1 is a surfactant. WJH-01 mainly contains poly ether carboxylate (RO(CH\textsubscript{2}CH\textsubscript{2}O)nCH\textsubscript{2}COONa) and poly ether carboxylic acid esters (RCOO(CH\textsubscript{2}CH\textsubscript{2}O)nCH\textsubscript{2}CH\textsubscript{3}). BHFL-02 mainly contains alkyl poly ether carboxylate (RO(CH\textsubscript{2}CH\textsubscript{2}O)nCH\textsubscript{2}COONa) and poly ether alkyl amine. The molecular formula of poly ether alkyl amine is:

\[
\text{RO}(CH_2CH_2O)_nCH_2CH_3
\]

The testing gas was CH\textsubscript{4}CO\textsubscript{2} (33\%) mixture gas, which simulates the DongFang field gas in the South China Sea.

Experimental

Materials

The materials used in the experiments are shown in Table 1. The concentration of the mixture gas was analyzed by Gas Chromatography (GC). HY-1 was synthesized by free-radical polymerization of N-vinyl-2-pyrrolidone in diethylene glycol monobutyl ether.\textsuperscript{22} Inhibex501 (vinyl caprolactam/vinylpyrrolidone copolymer in butoxyethanol solution (w = 0.5)) is a commercial KHI. KL-1 is a type of AA supplied by China University of Petroleum. WJH-01 and BHFL-02 are common wax inhibitors. Distilled water used in this study was weighed on an electronic balance with an accuracy of ±0.1 mg and measuring range is 0–220 g.

Experimental apparatus

The schematic diagram of the experimental apparatus\textsuperscript{23} is shown in Fig. 3. We used it to evaluate the performance of LDHIs on the CO\textsubscript{2}-rich gas. The apparatus contains 6 identical magnetic-stirred steel cells, and the volume of each is 100 mL. The refrigeration chamber (Xutemp Temptech Co., Ltd. Hangzhou, China) provides a cold air bath, and the temperature is less than 0.5 °C. Thermocouples (type J) with an accuracy of ±0.1 °C were placed to measure the temperature. The pressure was measured by the transducer (Senex DG-1300) with an accuracy of ±0.01 MPa. All experimental data were recorded by a data logger (Agilent 34970A).

Experimental method

The induction time and growth time of gas hydrate with different LDHIs were tested using the isothermal cooling method.\textsuperscript{24} The deionized water with additives was prepared first. Then 40 g solutions were put in the pressure cells. The temperature of the chamber was raised to 30 °C and kept for 30 min. Then the CH\textsubscript{4}CO\textsubscript{2} gas was pumped into the cells to 9 MPa (phase equilibrium point of the mixture gas is 13 °C). Finally, the chamber was cooled continuously to around 4 °C (subcooling temperature is about 9 °C), which simulates the subsea temperature. Stirring was then started at 550 rpm.

Results and discussion

LDHI performance testing

Induction time is the most critical parameter to rank the performance of LDHIs. At least two parallel experiments were carried out to reduce deviation of results. The pressure and temperature data of the mixture gas + water versus time using the isothermal cooling method in an experiment are shown in Fig. 4.

In Fig. 4, we can see that the temperature drops at a constant rate until the expected 4 °C. During the cooling period, the pressure also drops at a constant rate. As the figure shows, we defined the start time of experiment as time zero, and \( t_0 \) is the start time of cooling; \( t_b \) is the time that nucleation starts, in which there is a sudden increase in temperature and a significant drop of pressure; \( t_a \) is the time when the catastrophic hydrate formation is finished. The induction time \( t_i \) is defined as the difference between \( t_a \) and \( t_b \): \( t_i = t_a - t_b \). The growth time \( t_g \) is defined as the difference between \( t_i \) and \( t_b \): \( t_g = t_i - t_b \).

The effect of wax inhibitors on the blank (without hydrate or wax inhibitors) system was summarized in Fig. 5. As Fig. 5 shows, the average induction time shows almost no difference between the system with 1% WJH-01 (3.95 h) and with deionized water.
(3.7 h), while the induction time of the system with 1% BHFL-02 (5.21 h) is a little longer, which means there is a weak influence on the CH$_4$-CO$_2$ gas hydrate formation. Additionally, both wax inhibitors can prolong the gas hydrate growth time. The 1% WJH-01 can prolong the growth time (5.89 h) longer than 1% BHFL-02 (3.94 h).

Using the isothermal cooling method and the same experimental condition, the induction and growth time of HY-1, Inhibex501, and AA at different concentrations (1 mass%, 2 mass%, and 3 mass%) were tested and results are displayed in Fig. 6, Fig. 7 and Fig. 8, respectively. In Fig. 6, the average induction time $t_0$ of 1 mass%, 2 mass%, and 3 mass% HY-1 were 11.94, 8.58, and 4.34 h, respectively, and the average growth times were 9.37, 13.085, and 17.12 h, respectively. When the concentration of HY-1 increased, the induction time decreased, and the growth time was prolonged. In the case of KL-1, there is a clear statistical trend to shorten induction time when the concentration of KL-1 increases. It is noteworthy that the gas hydrate with KL-1 was growing all the time till the end of the experiment. Because KL-1 is a surfactant, it allows hydrates to form but prevents the hydrate crystals from agglomerating and subsequently accumulating into large masses. For the ISP-501 system, when the concentration of ISP-501 is 3 mass%, the average induction time is the longest, 7.32 h (Fig. 7). It is worth mentioning that ISP-501 can delay hydrate formation, but after the start of the formation, it will accelerate the dosage of the hydrate.

### Effect of wax inhibitor on LDHI performance

Figures 9, 10, and 11 show the effect of wax inhibitors (WJH-01 and BHFL-02) in different concentrations on the induction and growth time of CH$_4$-CO$_2$ gas with distilled water.

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**Table 1. Experiment materials used in this work.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Purity Description</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$-CO$_2$ gas</td>
<td>0.67 and 0.33 (mole fraction)</td>
<td>Guangzhou Zhuozheng Gas Industry Co., Ltd.</td>
</tr>
<tr>
<td>HY1</td>
<td>w$\geq$0.99</td>
<td>South China University of Technology</td>
</tr>
<tr>
<td>Inhibex501</td>
<td>w$\geq$0.99</td>
<td>ISP International Specialty Products Inc, USA</td>
</tr>
<tr>
<td>KL-1</td>
<td>w$\geq$0.99</td>
<td>China University of Petroleum</td>
</tr>
<tr>
<td>WJH-01</td>
<td>w$\geq$0.99</td>
<td>CNOOC Energy Technology &amp; Services-Oilfield Technology Services Co.</td>
</tr>
<tr>
<td>BHFL-02</td>
<td>w$\geq$0.99</td>
<td>CNOOC Energy Technology &amp; Services-Oilfield Technology Services Co.</td>
</tr>
<tr>
<td>Deionized water</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6. Induction and growth time at varying concentrations of HY-1.

Fig. 7. Induction and growth time at varying concentrations of ISP-501.

Fig. 8. Induction and growth time at varying concentrations of KL-1.

Fig. 9. Effect of WI on the induction and growth time of the system with HY-1.

Fig. 10. Effect of WI on the induction and growth time of the system with ISP-501.

Fig. 11. Effect of WI on the induction and growth time of the system with KL-1.
growth time of gas hydrate formation with HY-1, ISP-501, and KL-1, respectively.

To evaluate the effect of WI on LDHI performance, a “% Performance” scale of the LDHI was developed. In our work, “% Performance” was determined by induction time and growth time. We defined performance on the induction time as “%PI”, % Performance determined by the induction time as “%PI”, performance on the growth time as “%PG”, % Performance determined by the growth time as “%PG”. Then the “% Performance” is the mean value of %PI and %PG.

The concentrations of HY-1, ISP-501, and KL-1 in this study were 1 mass%, 3 mass%, and 1 mass%, which produce the longest average induction times of 11.94, 8.27, and 7.32 h, respectively. The %PI of HY-1, ISP-501, and KL-1 at that induction time was designated as 100%. In the same way, the percent performance without LDHI was designated as 0%. Using eq. (1), %PI of any WI + LDHI combination can be calculated by the induction time of the system with WI and LDHI.

\[
%\text{PI} = \frac{\text{Induction time of the system with WI + LDHI}}{\text{Induction time of the system with LDHI}} \times 100
\]

Using this equation, the impact of each WI on the LDHI performance determined by the induction time (%PI) can be calculated. For example, the induction time of the system with 1 mass% HY-1 was 11.94 h, with 0.1 mass% WJH-01 + 1 mass% HY-1 was 4.185 h. Applying eq. (1), the %PI of HY-1 in the presence of 0.1 mass% WJH-01 was 35%. Namely, adding 0.1 mass% WJH-01 to the 1 mass% HY-1 reduced the PI of HY-1 by 65%. This means that the lower the %PI of HY-1 in the presence of WI, the greater the effect on HY-1.

The %PI of three LDHIs (HY-1, ISP-501, and KL-1) combined with two WIs (WJH-01 and BHFL-02) at 0.1 mass% and 1 mass% are summarized in Table 2. The effect of all WIs on the PI of the LDHIs is clearly negative. The results were not so consistent with Swanson et al. Overall, WI additives disadvantaged delay nucleation with KHIs (HY-1 and ISP-501) at 0.1 mass% than at 1 mass%, as shown in Table 2. Furthermore, increasing the concentration of WJH-01 decreased the PI of the AA (KL-1) to a greater degree. It is worth noting that when the concentration was 0.1 mass%, WJH-01 had almost no effect. BHFL-02 at a dosage of 0.1 mass% and 1 mass% had a same influence on the PI of KL-1, while the concentration of WJH-01 did not have a regular impact on PI. For instance, WJH-01 and BHFL-02 had different influences on the performance of the KL-1 at 0.1 mass% concentration. BHFL-02 had a significant effect on the PI of KL-1, bringing the %PI down to 40%, while WJH-01 had no impact. In general, WJH-01 had a more negative impact on the performance of HY-1 than BHFL-02, while the effect of BHFL-02 on the PI of ISP-501 and KL-1 was more adverse than WJH-01. The preliminary interpretation was that the WI surfactants may be aggregating on or around the active groups of KHI polymers, which could interfere with the polymer to prevent hydrates. And the interaction can be considered a combination of hydrophobic interactions between the alkyl chain of the WI surfactants and the methylene on the Inhibex501 or HY-1 ring, as it was deduced that the electrostatic interaction between the surfactant headgroup and the partial charges on the nitrogen and oxygen of the polymer ring. The interaction between KL-1 and WIs may be related to the chemical reaction between the cation (quaternary ammonium salt) of KL-1 and the anion (poly ether carboxylate) of WIs. Further experiments are required to determine this.

When the concentrations of HY-1, ISP-501, and KL-1 were 1 mass%, 3 mass%, and 1 mass%, respectively, the average growth times of the system were 9.37, 9.68, and 10.72 h, respectively. The %PG up to 165%. The PG of KL-1 with 0.1 mass% was still increased. The effect of two WIs (WJH-01 and BHFL-02) at 0.1 mass% and 1 mass% are summarized in Table 3. When the concentrations of the WIs was 1 mass%, they both can extend the growth time, especially BHFL-02, bringing the %PG up to 165%. The PG of KL-1 with 0.1 mass% was still increased. At low concentration, the effect of both WIs on the KHI was negative. This may be related to the excessive surfactants. As we know, the amount of adsorbed surfactants on the polymer is constant, which is known as the critical aggregation concentration (CAC). It appears that there is cooperative adsorption of surfactant and polymer at low surfactant concentration. When the concentration is high, the free surfactant micelles will be dominant, which may affect the growth process. This hypothesis warrants further study.

Finally, the “% Performance” is the mean value of “%PI” and “%PG”, which was calculated and listed in Table 4. The impact of WI at 1 mass% was less than that at 0.1 mass%. The Performance of LDHI in the presence of WI at high concentration was practically unaffected, however, in the presence of 0.1 mass%, the KHI’s performance was reduced to roughly half of its original value. Yet, the effect on the KL-1 at low concentration is negligible.

Table 3 shows the %PG of 3 LDHIs (HY-1, ISP-501, and KL-1) with 2 WIs (WJH-01 and BHFL-02) at 0.1 mass% and 1 mass%. As seen in Table 3, when the concentrations of the WIs was 1 mass%, they both can extend the growth time, especially BHFL-02, bringing the %PG up to 165%. The PG of KL-1 with 0.1 mass% was still increased. At low concentration, the effect of both WIs on the KHI was negative. This may be related to the excessive surfactants. As we know, the amount of adsorbed surfactants on the polymer is constant, which is known as the critical aggregation concentration (CAC). It appears that there is cooperative adsorption of surfactant and polymer at low surfactant concentration. When the concentration is high, the free surfactant micelles will be dominant, which may affect the growth process. This hypothesis warrants further study.

Conclusion

The effect of two WIs (WJH-01 and BHFL-02) on the performance of LDHIs (HY-1, ISP-501, and KL-1) for 67% CH₄/33% CO₂ gas hydrate formation has been studied using the isothermal cooling method in our work. The studies focused on the performance of HY-1, ISP-501, and KL-1 at different concentrations (1 mass%, 2 mass%, and 3 mass%) on the mixed gas hydrate inhibition and that of the
combination with WIs. The results showed that when the concentration of HY-1, ISP-501, and KL-1 was 1 mass%, 3 mass%, and 1 mass%, the average induction time of the gas system was the longest, at 11.94, 7.32, and 8.27 h, respectively. The performance of LDHIs was significantly reduced in the presence of WIs at low concentration. The effect of WIs at high concentration can be negligible. This may be related to the adsorption of WIs on the polymer. When the concentration is high, the surfactants will play a role, which will affect the growth process. However, further tests are required to verify the experiment mechanism.

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