THE MISSING POLY(N-VINYLLACTAM) KINETIC HYDRATE INHIBITOR – PART 2. HIGH PRESSURE KINETIC HYDRATE INHIBITION OF STRUCTURE II GAS HYDRATES WITH POLY(N-VINYLPIPERIDONE) AND OTHER POLY(N-VINYLLACTAM) HOMOPOLYMERS

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ABSTRACT
Poly (N-vinyl pyrrolidone) (PVP) containing the 5-ring lactam and poly(N-vinyl caprolactam) (PVCap) containing the 7-ring lactam are well-known kinetic hydrate inhibitors (KHIs). For the first time we have synthesized and studied the performance of poly(N-vinyl piperidone) (PVpip), containing the 6-ring lactam, as a kinetic hydrate inhibitor. In the second part of the study we have investigated the ability of PVpip to inhibit SII gas hydrate formation in a high pressure stirred autoclave. The results are compared to those of PVP and PVCap. Various polymer molecular weights have been investigated at varying subcoolings and with different test methods.

Keywords: gas hydrates, kinetic hydrate inhibitors, low dosage hydrate inhibitors

NOMENCLATURE
PVP – poly(N-vinyl pyrrolidone)
PVpip – poly(N-vinyl piperidone)
PVCap – poly(N-vinyl caprolactam)
$\Delta T$ – subcooling
To – detected onset temperature for hydrate formation
Ta – fast hydrate formation temperature
Mw = weight average molecular weight

INTRODUCTION
Kinetic Hydrate Inhibitors (KHIs) are now a well-known technology for preventing gas hydrate plugs in upstream oilfield operations.\(^\text{1-3}\) KHIs are water-soluble polymers, often with added synergists that improve their performance. KHIs delay the nucleation and usually also the crystal growth of gas hydrates. The nucleation delay time (induction time), which is the most critical factor for field operations, is dependent on the subcooling ($\Delta T$) in the system – the higher the
subcooling the lower the induction time. The absolute pressure is also an important factor.\textsuperscript{4,7}

The commonest classes of polymers, which are used in commercial KHI formulations, are homopolymers and copolymers of the N-vinyl lactams, N-vinyl pyrrolidone (VP) and N-vinyl caprolactam (VCap).\textsuperscript{8-15} The 6-ring N-vinyl lactam monomer, N-vinyl piperidone (VPip), is not commercially available and as a consequence polymers of VPip have not been investigated as KHIs. The structures of VP, VPip and VCap are given in Figure 1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structures.png}
\caption{The structures of poly(N-vinyl pyrrolidone) (PVP) (top left), poly(N-vinyl piperidone) (VPip) (bottom) and poly(N-vinyl caprolactam) (VCap) (top right).}
\end{figure}

In this paper we investigate the performance of VPip to prevent SII gas hydrate formation in high pressure autoclave tests. The results are compared to the known polymers PVP and PVCap. In an accompanying paper (Part 1) we report on the ability of VPip to prevent SII gas hydrate formation, again in comparison to PVP and PVCap.

**SYNTHESIS OF PVPIP**

A sample of VPip monomer was kindly donated by BASF, Germany. All other chemicals were obtained from commercial sources. Details of the polymerisation of VPip to give PVpip, together with characterisation data, have been published previously.\textsuperscript{16} As a representative example, in an inert atmosphere glovebox, VPip (1.82 g, 14.5 mmol), chain transfer agent (CTA) 2-(ethoxycarbonothioylthio)propanoate (54 mg, 0.243 mmol), and AIBN (0.1 mL of 2 mg/mL dioxane) were dissolved in 1,4-dioxane in a vial. The resulting solution was then introduced into a Schlenk tube equipped with a Young’s tap, sealed under nitrogen, and then taken out of the glovebox. The reaction mixture was then allowed to polymerize at 70°C for typically 10 h, after which an aliquot was taken from the mixture for 1H NMR conversion analysis. Conversions were calculated using 1H NMR spectroscopy by comparing the integrations of the heterocycle signals on the VPip monomer (δ = 3.57 and 2.45 ppm) with those of the corresponding signals of the polymer backbone (δ = 3.05 and 2.28 ppm). The light yellow solution was then quenched with liquid nitrogen. PVpip was recovered as an off-white powder (1.7 g, ca. 91% based on 62% conversion) after precipitation into diethyl ether multiple times until the residual monomer was less than 0.2%. Different homopolymer molecular weights were synthesized using different monomer:CTA ratios as determined by GPC:

- PVpip 4k, Mw = 4000
- PVpip 6k, Mw = 6000
- PVpip 25k, Mw = 25000
- PVpip 85k, Mw = 85000

The cloud points (Tcl) in fresh water at 2 wt.% polymer were determined to range from 68-88°C with the lowest molecular weight polymer having the highest Tcl value.\textsuperscript{16}

**EXPERIMENTAL PROCEDURE KINETIC HYDRATE INHIBITOR TESTING**

KHI performance tests were carried out in the high pressure autoclave apparatus shown in Figure 4 and discussed previously.\textsuperscript{1,17} The autoclave consists of a stainless steel cell with volume 23 ml. The temperature was measured to an accuracy of ±0.1 °C and the pressure was measured with an accuracy of ±0.2 bars. Two kinds of test methods were carried out. The test method used was the “constant cooling” test method described in detail below.
In all the experiments we used the same synthetic natural gas (SNG) mixture that gives Structure II hydrates (Table 1). The aqueous phase was distilled water. No liquid hydrocarbon phases were used. At the onset of each “constant cooling” experiment the pressure was 78 bar. The equilibrium temperature at this pressure was calculated using Calsep’s PVTSim software to be 20.1 °C for distilled water and 90 bar, which was approximately 0.3 °C lower than our laboratory experiments in a larger 200ml titanium cell to determine the equilibrium temperature by standard slow hydrate dissociation (Figure 2). The cooling rate near the equilibrium temperature was 0.14 °C/hr. From our experience, the equilibrium temperature could have been up to 0.2 °C lower if we had used a cooling rate of 0.05 °C/hr, which would have given very good agreement with the predicted equilibrium temperature, but this makes the experiments considerably more time-consuming. For the rest of this paper we will assume that the equilibrium temperature for our SNG-water system at 78 bar is 20.1°C. At the onset of each “precursor constant cooling” experiment the pressure was 98 bar. The equilibrium temperature at this pressure was calculated using Calsep’s PVTSim software to be approximately 18.3°C (Figure 2).

Table 1. Composition of Synthetic Natural Gas (SNG).

<table>
<thead>
<tr>
<th>Component</th>
<th>mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>80.67</td>
</tr>
<tr>
<td>Ethane</td>
<td>10.20</td>
</tr>
<tr>
<td>Propane</td>
<td>4.90</td>
</tr>
<tr>
<td>Iso-butane</td>
<td>1.53</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.76</td>
</tr>
<tr>
<td>N₂</td>
<td>0.10</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.84</td>
</tr>
</tbody>
</table>

The same initial procedure for the preparation of the KHI experiment and filling of the cell was followed in all high pressure experiments in the steel cell:

1. The polymer to be tested was dissolved in distilled water to the desired concentration, either 2500 or 5000ppm (0.25 or 0.5 wt. % respectively).
2. The magnet housing of the cell was filled with the aqueous solution containing the additive to be tested. For standard constant cooling tests we used 8ml of aqueous solution. The magnet housing was then mounted in the bottom end piece of the
cell, which thereafter was attached to the steel tube and the cell holder.

3. The desired amount of the aqueous solution was filled in the cell (above the cell bottom) using a pipette, the top end piece was mounted, and the cell was placed into the cooling bath (plastic cylinder).

4. The temperature of the cooling bath was adjusted to 1-3 °C above the hydrate equilibrium temperature at the pressure conditions to be used in the experiment.

5. After purging the cell twice with the SNG, the cell was loaded with SNG to the desired pressure while stirring at 600 rpm.

The constant cooling test method was carried out as follows. After the initial procedure given above, the cell was charged with SNG gas at 78 bar and 20.5°C. The cell was stirred at 600rpm while cooling at a constant rate to 2°C over 18 hours. Due to the being a closed system, the pressure drops as the temperature decreases. Since the rate of cooling was slow we were able to determine the detectable start of hydrate formation as the first deviation from the constant decrease in the absolute pressure in the cell during cooling. This indicates that gas is being used to form gas hydrates. We also noted the temperature at which fast, catastrophic hydrate formation took place as the point when the pressure drop curve became almost vertical, i.e. when gas consumption for gas hydrate formation was very fast. This led to a hydrate plug forming in the cell and stopping of the stirrer. Typical plots of pressure and temperature versus time for the three different poly(N-vinyl lactams) are given in Figures 4-6. At least 6 constant cooling experiments were carried out with each polymer at each concentration (2500 or 5000ppm) in the aqueous phase. The average onset temperatures for first detectable hydrate formation (To) and the temperatures for fast, catastrophic hydrate formation began (Ta) are given in Tables 2-3.

A sample of PVP 4k was obtained from International Specialty Products Corporation (ISP Corp.) and the PVCap 4k was obtained from BASF. No synergistic solvents were present in either sample.
RESULTS
Hydrate formation is known to be a stochastic process. Therefore at least 6 experiments were carried out at any one set of conditions with each polymer in the high pressure steel autoclave. This was to ensure that statistically significant results could be obtained when comparing To or Ta values between two polymers. Statistical significance was determined by carrying out t-tests. A t-test is any statistical hypothesis test in which the test statistic follows a t distribution if the null hypothesis is supported. The t-distribution is a continuous probability distribution that arises when estimating the mean of a normally distributed population in situations where the sample size is small. A null hypothesis is that there is no relationship between two measured phenomena, in this case between To (or Ta) values and different KHI polymers. It is most commonly applied when the test statistic would follow a normal distribution if the value of a scaling term in the test statistic were known. Once a t value is determined, a p-value can be calculated. If the calculated p-value is below the threshold chosen for statistical significance (usually the 0.05 level), then the null hypothesis is rejected in favor of the alternative hypothesis, in this case that there is a significant difference between the performance (measured as To or Ta values) for different KHI polymers.

Comparative study of poly(N-vinyl lactam)s of similar low molecular weight
The average To and Ta values for experiments with poly(N-vinyl lactam)s of similar low molecular weight are given in Table 2 and also summarized in Figure 7. The data are compared to experiments with no additive. Examples of graphs pressure and temperature versus time for all three poly(N-vinyl lactam)s are given in Figures 4-6.

In this 23ml steel cell we found that the To and Ta values for experiments with no additives were significantly lower than when using our four other autoclaves (sapphire, steel or titanium) with sizes of 23-200ml at the same experimental conditions. The observation of lower To and Ta values was also found to be true for PVP 4k and PVCap 4k which were also tested in two other autoclave equipments. The other polymers have not been investigated in other in-house equipments but the general trend seems to be that the autoclave used in this study gives lower To and Ta values. We are not sure what the reason is for this. The steel cell may be a little smoother than other metal autoclaves but probably not as smooth as the sapphire autoclave which is regularly polished. However, as the whole of this study was conducted in just the one autoclave, as is normal for our studies, we were able to compare the performance of the KHI polymers.

Table 2. Average onset (To) and fast hydrate formation (Ta) temperatures for poly(N-vinyl lactam)s in constant cooling experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conc./ppm</th>
<th>To</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additive</td>
<td>-</td>
<td>11.6</td>
<td>10.9</td>
</tr>
<tr>
<td>PVP 4k</td>
<td>2500</td>
<td>10.6</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>9.5</td>
<td>6.6*</td>
</tr>
<tr>
<td>PVPip 4k</td>
<td>2500</td>
<td>8.4</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>7.2</td>
<td>5.4</td>
</tr>
<tr>
<td>PVCap 4k</td>
<td>2500</td>
<td>8.0</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td>4.8</td>
<td>4.2</td>
</tr>
</tbody>
</table>

* Several Ta results were difficult to interpret. See text.

Figure 7. Average onset (To) and fast hydrate formation (Ta) temperatures for poly(N-vinyl lactam)s in constant cooling experiments.

In general we found greater variation in the To values for any one set of conditions, compared to the Ta values. To values varied by up to ca. 20% either side of the average taken from 6-8 experiments, whereas Ta values varied by up to...
15%. As a typical example, To values for PVPip 4k at 2500ppm were 5.9, 6.3, 7.2, 7.4, 7.9 and 8.4°C from six experiments. The average To value is 7.2°C and the scattering either side of this average is up to 18%. However, the Ta values for tests with PVPip 4k at 2500ppm were 4.5, 4.6, 5.6, 5.6, 5.9 and 5.9°C. The average Ta value is 5.35°C and the scattering either side of this average is a maximum 14%. Clearly, since Ta values are lower there will be less scattering either side of the average Ta value. However, there is a second possible reason for the closer values for Ta, which may be construed from understanding the nucleation and inhibition process with a KHI polymer. If nucleation begins at a relative high temperature there will be less super-critical particles formed which are inhibited from growing by the KHI. However, more particles will be nucleated as the temperature drops. At a low onset temperature hydrate particles will reach the supercritical size at a faster rate due to the higher subcooling (driving force) in the system. Thus, by the time one reaches Ta, when the KHI can no longer control hydrate formation, there could be fairly similar numbers of supercritical particles present irrespective of the onset temperature for hydrate formation. This can lead to quite similar values for Ta but a greater variation in To values. It should be pointed out that To is the temperature when hydrate formation is first observed by pressure drop. The temperature when nucleation actually starts and the first supercritical hydrate particle is formed may have occurred earlier at a higher temperature but is detected with the sensitivity of our instrumentation.

As the figures in Table 2 indicate, PVPip 4k has an intermediate performance between the two other poly(N-vinyl lactam)s, PVP 4k and PVCap 4k whether one considers the To or Ta values. The statistical significance of these results was confirmed by carrying out t-tests, which gave p values of < 0.05 for To or Ta data comparisons between the three polymers.

As far as we are aware, there has been only one modelling report of the interaction of PVPip with SII hydrate surfaces and no reports on nucleation inhibition with PVPip. This study predicted that PVPip would have an intermediate inhibition effect on inhibiting the growth of SII hydrates compared to PVP and PVCap. Assuming interactions with hydrate surfaces is the primary mechanism of hydrate inhibition, we can conclude that our gas hydrate studies correlate with the modelling prediction.

We have also carried out a related study on the growth inhibition of tetrahydrofuran (THF) SII hydrates with poly(N-vinyl lactam)s with 5-7 rings. This study showed that PVPip has intermediate performance at inhibiting the growth of THF hydrate crystals: PVCap performed best. These results also fit the results from the SII gas hydrate studies.

**Comparative study of poly(N-vinyl piperidone)s of varying molecular weight**

The second part of this study was to investigate the effect of varying the molecular weight of PVPip on the KHI performance on SII gas hydrates. Polymer molecular weight has been shown previously to be an important factor for other polymer classes, most notable poly(N-vinyl caprolactam), poly(N-alkyl(meth)acrylamide)s and poly(N,N-dialkyl(meth)acrylamide)s. For linear polyvinyl-based KHIs, the ideal molecular weight (Mw) for optimum performance appears to be around 1500-3000. At molecular weights below about 1000 the performance drops drastically and at increasing molecular weights above 3000-4000 the performance drops slowly but does not disappear. For example, ultra low molecular weight PVCap (oligomer with Mw < 2000), when dosed at 0.5 wt.% based on the water phase, has been shown to delay gas hydrate formation in a synthetic natural gas-water system at 13°C (23.4°F) subcooling for over 48 hours at 70 bar. This ultra low molecular weight PVCap polymer was also tested in a wheel loop in various fluid systems. Depending on the fluid type (gas only or with condensate or crude oil) the performance varied from 11-19°C (20-34°F) subcooling at constant pressure for a successful test that lasted 2-3 days. However, there is evidence that a bimodal distribution of molecular weights gives increased KHI performance. The polymer performs best when the majority of the polymer has low molecular weight and a minor proportion has a high molecular weight.

The results using four PVPip samples of varying molecular weights are summarised in Table 3 and plotted in Figure 8. Although, we would have expected a better performance for the lower
molecular weight versions, based on studies with other polymer classes of similar ranges of molecular weights, we did not observe a statistically significant difference in the performance of the four polymers as measured by $T_o$. However, for $T_a$ values there is a small but significant difference between the performance of the lowest and highest molecular weight PVPip samples. On average the PVPip 85k gave about $1^\circ C$ lower $T_a$ values than PVPip 4k. This suggests that the high molecular weight PVPip performs better at inhibiting SII gas hydrate crystal growth as it takes a higher subcooling before rapid gas hydrate formation occurs. This correlates well with the complementary studies on SII THF hydrates where we found that THF hydrate crystal growth inhibition improved as the polymer molecular weight increased from 4000 to 85000.\textsuperscript{22}

Table 3. Average onset ($T_o$) and fast hydrate formation ($T_a$) temperatures for poly(N-vinyl piperidone)s of varying molecular weight in constant cooling experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conc./ppm</th>
<th>$T_o / ^\circ C$</th>
<th>$T_a / ^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVPip 4k</td>
<td>5000</td>
<td>7.2</td>
<td>5.4</td>
</tr>
<tr>
<td>PVPip 6k</td>
<td>5000</td>
<td>6.8</td>
<td>4.8</td>
</tr>
<tr>
<td>PVPip 25k</td>
<td>5000</td>
<td>7.4</td>
<td>4.9</td>
</tr>
<tr>
<td>PVPip 85k</td>
<td>5000</td>
<td>6.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>

CONCLUSION

We have synthesized and investigated the ability of PVPip to inhibit SII gas hydrate crystals in a high pressure stirred steel autoclave. PVPip 4k with a molecular weight of 4000 performed better as a KHI than PVP 4k and worse than PVCap 4k, both of similar molecular weights.

We did not observe a statistically significant difference between the nucleation inhibition performance on SII gas hydrates with PVPip polymers with molecular weights ranging from 4000 to 85000. However, there was evidence that the highest molecular weight polymer gave longer delays in the growth of gas hydrate crystals before fast hydrate formation ensued. This correlates well with the complementary studies on SII THF hydrates where we found that THF hydrate crystal growth inhibition improved as the polymer molecular weight increased from 4000 to 85000.

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