THE EFFECT OF PVCAP ON METHANE HYDRATE NUCLEATION AND GROWTH

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ABSTRACT

PVCap is a kinetic hydrate inhibitor which has recently attracted many researchers as it is an alternative method to the conventional thermodynamic inhibitors such as MeOH and MEG. Six different concentrations of PVCap in the range 20 to 2000 ppm (i.e. 0.002 to 0.2 wt %) were used to investigate the effect on both nucleation and growth of sI hydrate. The hydrates were formed at 90 bars from a pure methane gas (99.9995 %) and distilled water in an isochoric high pressure cell. The probability distribution function and the real gas equation have been used to investigate the effect on nucleation and growth during hydrate formation, respectively. The results show that PVCap has a clear effect on growth based on concentration. However, its effect on the nucleation was not found to be concentration dependent as promotional and inhibition effects were observed which were not as a function of concentration. This could possibly be due to the random phenomenon of newly born critical nuclei in the aqueous phase that could easily attract the PVCap during the nucleation process.

Keywords: gas hydrates, nucleation, growth, kinetic inhibitors, thermodynamic inhibitors

NOMENCLATURE

J nucleation rate [min⁻¹]
Δn amount of hydrates formed [mol]
p probability of nucleation
P pressure [bar]
ΔP pressure drop [bar]
T temperature [°C]
ΔT degree of subcooling [°C]
t₀ induction time [min]
τ lag time [min]

INTRODUCTION

Polyvinylcaprolactum (PVCap) is a water-soluble polymer which has been used as a kinetic hydrate inhibitor (KHI). KHIs belong to the class of low-dosage hydrate inhibitors (LDHIs) that have been in commercial use in the oil and gas industry for more than a decade [1]. KHIs work by delaying hydrate nucleation and crystal growth so that there will be plenty of time to transport the hydrate forming fluid to the process facilities before hydrates nucleate, grow and plug the pipeline. PVCap, as one of the most effective KHI, prevents hydrate growth by attaching to a growing crystal surface and preventing further growth. The pendant group of PVCap is very important in achieving strong adsorption [2]. Molecular dynamics simulation studies [3] on selection of kinetic hydrate inhibitors also indicated that the active inhibitor molecules of PVCap that attaches themselves to the hydrate surface are the double-bonded oxygens, the hydroxye groups, and the nitrogen. Figure 1 shows the chemical structure of PVCap possessing all the inhibitor molecules. A

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A seven-member lactam ring is attached to a carbon backbone. The lactam ring is characterized by an amide group (-N-C=O) which protrudes from the polymeric backbone. In another study [4] on the adsorption of KHIs on clathrate hydrates, PVCap was also reported as a more effective inhibitor by reducing the diffusion of hydrate formers (gases) from the bulk phase to the hydrate surface where the hydrate growth prefers to proceed.

![Chemical structure of PVCap](image)

Figure 1. Chemical structure of PVCap.

The inhibition effect of PVCap on hydrate growth has been reported extensively as discussed above, whereas the effect on nucleation was not addressed adequately. In this paper we address the effect of PVCap on the nucleation of methane hydrate. In addition to the major focus on nucleation, the effect of PVCap on the total growth of methane hydrates has been also investigated. The data on the effect of PVCap on the total growth of methane hydrate has been analysed by employing the real gas equation. From the real gas equation, one can easily derive the direct relationship between the amount of hydrates formed and the pressure drop in the system as

\[ \Delta n = \frac{V}{zRT} \Delta P \]  

(1)

where \( \Delta n \) is the amount of gas consumed when hydrates form, \( V \) is the gas volume, \( z \) is the compressibility factor, \( R \) is the universal gas constant, \( T \) is the experimental temperature, and \( \Delta P \) is the measured experimental pressure drop caused by hydrate formation. Equation (1) could be used to estimate the amount of hydrates formed in an isochoric system [5] by assuming that \( V/zRT \) is a constant of proportionality that does not vary much for all PVCap experiments. For the analysis of the data to investigate the effect of PVCap on the nucleation of sI hydrates, the classical theory of nucleation has been employed. According to this theory, the nucleation probability distribution function is given by [5-10]

\[ p(t) = 1 - e^{-J(t-\tau)} \]  

(2)

where \( p(t) \) is the probability to obtain an induction time equal with or less than the measured time, \( t_0 \), between time zero and time \( t \). \( J \) is nucleation rate per unit volume, and \( \tau \) is the lag time. For the nucleation stage of the process induction time was the major parameter, and for the growth the amount of gas consumed, measured from the pressure drop reading, was the main parameter studied. The following section discusses the experimental setup and procedure for measuring induction time and pressure drop in systems in the presence of PVCap as an additive.

**EXPERIMENTAL METHODS**

**Experimental setup and procedure:** The experimental setup we used for the investigation of PVCap on the nucleation and growth of sI hydrates is illustrated in Figure 2. The major components are the cylindrical cell, the cooling bath, PC, and gas supply cylinder. The cylindrical cell, with inner volume of 145 mL, was used in holding the hydrate forming fluid - distilled water (DIW) and PVCap. PVCap, dry powder with molecular weight 6000, was dissolved in DIW at concentrations of 0, 20, 50, 100, 500, 1000, and 2000 ppm. Pure DIW system without PVCap in solution was considered as the baseline for
comparison. In each experiment 50 mL of the cell volume was filled with the actual aqueous solution leaving 95 mL of the cell volume for pressurized methane gas (~90 bars).

The methane gas was accessed directly from the gas supply cylinder whose pressure was controlled by the pressure gauge on the gas cylinder and by another external pressure sensor. After mounting the cell as shown in Figure 2, the cell was charged with test solution and methane to the desired pressure and the system was cooled from an initial temperature of 13.7 °C down to 4 °C with a cooling rate of 10 °C/h. At 4 °C and 90 bar the sub-cooling, \( \Delta T \), with reference to hydrate equilibrium is approximately 8 °C. All experiments were initiated at this degree of sub-cooling. The temperature profile was controlled by the refrigerated and heating circulator with interfaced temperature control unit. Figure 3 shows the pressure versus temperature plot of the system during the cooling sequence. Point 1 of the figure represents the initial condition of the system. This initial temperature was about 1.7 °C outside the hydrate equilibrium region of the system at the experimental pressure. The system crosses hydrate equilibrium at point 2, and from point 2 to point 3, the system temperature is inside the hydrate forming region. Once the desired operating temperature at point 3 was attained by cooling, cell agitation was introduced by the start of stirring. The start of stirring was considered as the start of the experiment. A stirring rate of 750 rpm was used for all experiments of PVCap including the pure water baseline experiments.

At point 3, the system may take some time before onset for hydrate formation occurred. Path 3-4-5 shows the hydrate growth region after onset and between points 3 and 4 along this path, the system couldn’t restore the operating temperature of the cooling bath because hydrate formation is a fast exothermic reaction releasing heat energy in this section of the experiment. But the system recovers its operating temperature after a while as indicated by path 4-5. The pressure drop from point 3 to point 5 (49.2 bar in this specific graph) has been used to estimate the amount of hydrates formed in the presence of different concentrations of PVCap in accordance with Equation (1). The effect of the additive on the nucleation time was measured at point 3 prior to hydrate formation and growth.

Figure 4 shows the gas consumption and temperature as a function of time from the start of the experiment to the end. During the first step, the gas consumption plot shows a very fast gas intake because of methane gas molecules leaving the gas phase and entering into the liquid phase and filling sI hydrate cavities. This fast growth period is followed by a slow growth period where the system continues to build up gas hydrates slowly.

The gas consumption onset, or equivalently hydrate formation onset, is accompanied by a temperature pulse. Figure 5 shows the magnified section of Figure 4 during onset. The induction time, the time from the start of stirring at time zero to the onset of hydrate formation (28.12 min in
this specific figure), is determined from both the gas consumption plot and the temperature pulse that reflects the exothermic reaction of hydrate formation.

Figure 5. Measurement of induction time from gas consumption curve and temperature pulse at onset of hydrate formation.

RESULTS AND DISCUSSION

Equations (1) and (2) have been respectively used to calculate the amount of sI hydrate formation and the rate of nucleation for each concentration of PVCap. For the estimation of the amount of sI hydrates formation, average pressure drop of each concentration is calculated. This average pressure drop is assumed to be directly proportional with the average amount of gas consumed during the filling of hydrate cavities in the bulk liquid phase. The results are tabulated in the last column of Table 2. The amount of sI hydrates formed for 20 ppm PVCap is nearly the same as the amount of hydrates formed for the pure water system. This shows that PVCap at very low concentrations doesn’t affect hydrate growth. However, PVCap concentrations in the range 50-2000 ppm have shown significant differences in the amount of hydrate formation as compared to the 0 ppm PVCap average pressure drop. This indicates that PVCap at higher concentrations affect sI hydrate growth in some way. It is not known whether this effect of PVCap is due to morphological changes affecting the consistency (mechanical strength) leading to stirrer blockage or other factors affecting the conversion of water into hydrates.

However, the maximum effect on total gas consumption at 90 bars operating pressure was found at 100 ppm for the cell volume we used. According to the study [11] on effective inhibitors for natural gas hydrates, it was reported that optimal performance of PVCap depends on a certain concentration at a given pressure. The lactam rings of PVCap are believed to adsorb on the growing hydrate crystal. Hydrogen bonding by the amide group plays the major role in blocking further hydrate growth. But increasing the polymer network does not always provide better inhibiting performance though this may depend on system and cell sizes. It is difficult to suggest a reliable explanation of the pressure drop response based on “blind cell” PT studies only. PVCap is known to affect morphology as well as hydrate consistency and apparent hardness (mechanical strength) of the formed hydrates. During experiments with PVCap in another cell (1000 ppm) we observed that reduced pressure drop during hydrate formation could be correlated with stirrer blockage and stop of stirring. For the cell used in the present study there was no free insight into the stirring mechanism, but sensing the magnet field surrounding the stirrer from outside the cell at end of experiment showed that stirrer was blocked. It is therefore believed that the reduced pressure drop is due to formation of a hydrate of a consistency that is harder to crush and stir as compared to the baseline hydrate.

For investigating the effect of PVCap on sI hydrate nucleation, the classical nucleation probability distribution function given by Equation (2) has been employed to fit the experimental data points. Figure 6 shows the probability of nucleation versus induction time for all concentrations of PVCap used including the pure water baseline experiment. As shown in the figure, 20 and 1000 ppm PVCap nucleation probability distribution functions are shifted to the left of the pure water reference distribution curve. The 2000 ppm PVCap probability distribution function is comparable with the pure water baseline experiment. The rest 50, 100, and 500 ppm PVCap concentrations were found to the right of the reference distribution function. The estimated nucleation rate and lag time for all concentrations of PVCap are tabulated in Table 2. The 20, 1000, and 2000 ppm PVCap has increased the rate of nucleation as compared to the 0 ppm PVCap experiments. The 20 ppm PVCap nucleation rate
has shown a significant difference from the pure water baseline nucleation rate unlike the 1000 and 2000 ppm PVCap experiments. The 50, 100, and 500 PVCap experiments have reduced the rate of nucleation from which the 500 PVCap experiment has shown the significant reduction.

![Figure 6. Probability of nucleation versus induction time for all concentrations of PVCap.](image)

Table 2: Estimated nucleation rate, induction time, and pressure drop for 0 – 2000 ppm PVCap.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Nucleation rate (1/min)</th>
<th>Lag time (min)</th>
<th>Average P drop (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.07</td>
<td>7.80</td>
<td>25.30</td>
</tr>
<tr>
<td>500</td>
<td>0.01</td>
<td>-44.1</td>
<td>29.20</td>
</tr>
<tr>
<td>1000</td>
<td>0.29</td>
<td>0.28</td>
<td>29.50</td>
</tr>
<tr>
<td>2000</td>
<td>0.19</td>
<td>2.74</td>
<td>28.06</td>
</tr>
</tbody>
</table>

The time the system takes to attain a constant rate of nucleation is called the lag time. This lag time is tabulated in Table 2 for all concentrations of PVCap used. For the 50 and 500 ppm solutions a negative lag time as suggested by the analysis means that nucleation has occurred and a constant rate of nucleation is reached before the start of stirring. During all experiments the system crosses the hydrate equilibrium curve approx. 82.5 minutes prior to start of stirring and at -44.1 minutes (i.e., lag time of 500 ppm experiments) the system is 6 °C inside the hydrate region. A negative lag time and a low nucleation rate as for the 50 and 500 ppm experiments means that the nucleation process may take place over a broad time span as indicated by the corresponding graphs.

The 100 ppm experiments have taken the longest time to attain a constant rate of nucleation. Both the lag time and the rate of nucleation have shown concentration independent effect of PVCap on the nucleation of the system. This could be due to the random nucleation phenomenon occurring in the liquid phase that could easily get the attention of PVCap upon molecule rearrangement for a cavity. Hawtin et. al. [12] observed from MD simulation that long-lived 5^{12}-like cage structure did not exist before the first 5^{12}-cavity was formed. Thus, it appears that formation of the 5^{12}-cavity is essential for the methane nucleation process. Increase in the rate of nucleation in the presence of additives has also been reported [13] from molecular dynamics simulation studies on methane hydrate systems. This study shows that LDHIs increase the rate of nucleation when crystals are observed. Once the crystal structures are observed in the bulk volume, they could easily get the attention of the additive and the additive starts promoting the nucleation process. Thus, the promotional effect of PVCap on the nucleation phase is primarily dependent on the random phenomenon of restructuring of water molecules for a crystal. When stable nuclei are formed, the inhibitor can block hydrate growth by adsorbing onto the surface. Thus, the effect on nucleation and growth is part of different mechanisms.

During our experiments no effect on growth rates were observed for PVCap concentrations of 100 ppm or below. At 500 ppm the initial growth rate was considerably reduced over the first 30 seconds from start of growth. At 1000 ppm the exothermic fast growth was delayed by 1 minute and at 2000 ppm the catastrophic growth process was delayed by 2 minutes. Thus the effect on the growth of sI hydrate was found to be concentration dependent. Unlike the nucleation phase, the growth phase of methane hydrates require fast transporting of methane molecules in the active site of the growing crystal. Such transporting of methane molecules to the growing crystal is a major
parameter for hydrate kinetics [14]. This major factor could easily be affected by the presence of PVCap in the crystal forming region. Subramanian and Sloan [15] showed the formation of the large $5^{12}6^2$ cavity of sI methane hydrate during the post nucleation growth stage is the time limiting step and that 200 ppm (i.e., 0.02 wt%) PVCap significantly reduced the formation of hydrate cavities, especially the large $5^{12}6^2$ cavity. So, on one hand PVCap may promote methane hydrate nucleation and on the other hand reduce growth probably blocking growth sites involved in the formation of the large $5^{12}6^2$ cavity.

CONCLUSION

Methane hydrates were produced in a stirred high pressure cell apparatus. Polyvinylcaprolactam (PVCap) has been used to study its effect on both nucleation and growth of sI hydrates. The real gas equation and the classical probability distribution functions have been employed to analyze the experimental data. The analysis showed that PVCap has a clear effect on the growth part of methane hydrate formation depending on concentration. However, on the nucleation phase of methane hydrate formation, the promotion or inhibition effects of PVCap were primarily dependent on the random nature of newly born critical nuclei that could make the PVCap start acting on the system. The latter result was also supported by molecular dynamics simulation studies.

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REFERENCES