

## Performance evaluation of Luvicap EG and PVP as KHIs in methane, methane-THF and ethylene gas hydrate systems

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### Abstract

The performance of PVP and Luvicap EG, as commercial kinetic hydrate inhibitors (KHIs), in three different systems including methane, methane-terahydrofuran (THF) and ethylene were evaluated. A high-pressure rocking cell was applied to compare the effect of these two KHIs. The consumption of moles of gas versus time (hydrate growth rate) and the maximum subcooling in the presence of PVP and Luvicap EG were calculated. Results showed that the both polymers performed as inhibitors in methane and ethylene gas hydrate systems. However, in methane-THF system, the PVP was unable to reduce hydrate growth rate and the maximum subcooling temperature was lower than that of pure water, indicating poor inhibition performance of PVP in this system. The Luvicap EG polymer was superior to PVP in ethylene and methane-THF systems. However, in the methane gas hydrate system the PVP inhibition performance was better than Luvicap EG at a concentration of 0.1 wt%. While, at higher concentrations (0.3 and 0.5 wt%) the performance of Luvicap EG was excellent and completely prevented the formation of methane hydrate.

**Keywords:** Hydrate, Kinetic inhibitor, PVP, Luvicap EG, Ethylene, Methane.

### Research Highlights

- Inhibition performance in three different systems was evaluated.
- The effect of concentration on KHI performance was assessed.
- The performance of PVP with Luvicap EG was compared.

## 1. Introduction

Gas hydrate are crystalline compounds that water molecules forms a lattice by hydrogen bonds and encages guest molecules. Based on the size and the type of guest molecules, hydrate structure is divided into three types: structure I (sI), structure II (sII), structure H (sH). Gas hydrate can cause economic and safety problems in the oil and gas industry. Thus, how to prevent gas hydrate formation is very essential. Injecting thermodynamic hydrate inhibitors (THIs) into pipelines can hinder hydrate formation by shifting the pressure versus temperature hydrate equilibrium curve to lower temperature and higher pressure. However, since they are not environmentally friendly and dosed at high concentration which is not cost-effective, low dosage hydrate inhibitors (LDHIs) replaced THIs. LDHIs are effective at lower concentrations and include kinetic hydrate inhibitors and anti-agglomerants (AAs) [1-5]. Although plenty of hydrate restriction methods were proposed, kinetic hydrate inhibitors (KHIs) have seen increasing industry use since they delay hydrate nucleation and/or prevent rapid growth rate at low dosage. Several kinds of water-soluble polymers which can be used as KHIs are suggested, including polyvinyl pyrrolidone (PVP) and polyvinyl caprolactam (PVCap). Fig. 1 shows the chemical structure of PVP and PVCap [6,7].

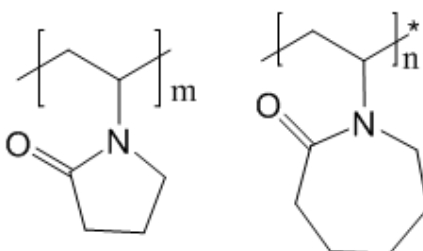


Fig. 1. The chemical structures of PVP and PVCap

PVP and PVCap are commercial products, which respectively containing 5 and 7 member ring of lactam. PVP is an effective inhibitor in high temperature and as the temperature decreases its effectiveness reduces and PVP loses its ability to prevent hydrate formation. PVCap is superior to PVP because its lactam ring size is larger [8]. In addition, their performance depends on pressure and temperature [9,10]. Although plenty of studies investigated the inhibition potential of PVP and PVCap, comparing their performance in different systems where various gases are present as hydrate formers has been less focused.

In this work, the effect of PVP with the molecular weight of 10,000 g/mol and Luvicap EG which is PVCap in ethylene glycol are investigated in three different system. A high-pressure rocking cell was applied to compare the KHI performance of both PVP and Luvicap EG. The impact of ring size of these two inhibitors on ethylene, methane and THF was also assessed.

## 2. Experimental section

## 2.1. Materials

PVP with the molecular weight of 10,000 g/mol and tetrahydrofuran (THF) were purchased from Merck. Luvicap EG supplied from BASF. Ethylene (with the purity of 99.9%) and methane (with the purity of 99.95%) were obtained from Technical gas service. Deionized water supplied by Abtin.

## 2.2. Apparatus and methods

A high pressure stainless steel rocking cell which is shown in Fig. 2 is the main part of hydrate testing equipment. The volume of the cell is 100 mL and a cooling jacket was provided to adjust the temperature of the cell. A thermometer and a pressure transmitter were used to respectively measure the temperature and pressure of the cell. A data acquisition system was used to record the pressure and temperature of cell was washed by deionized water 4 times. Then the aqueous solution containing the mentioned above polymers or pure water was injected to the cell. When the temperature of the cell became stable at 2 °C, the specific amount of gas was charged into the cell. The Peng-Robinson equation was used to calculate the number of consumed moles in every moment of experiments in order to evaluate hydrate growth. A constant cooling method was used to measure the maximum subcooling which the solution of inhibitors can tolerate. In this method the temperature of the cell decreased and the temperature of the onset of hydrate formation was recorded and the difference of onset temperature and equilibrium temperature was reported as the maximum subcooling.

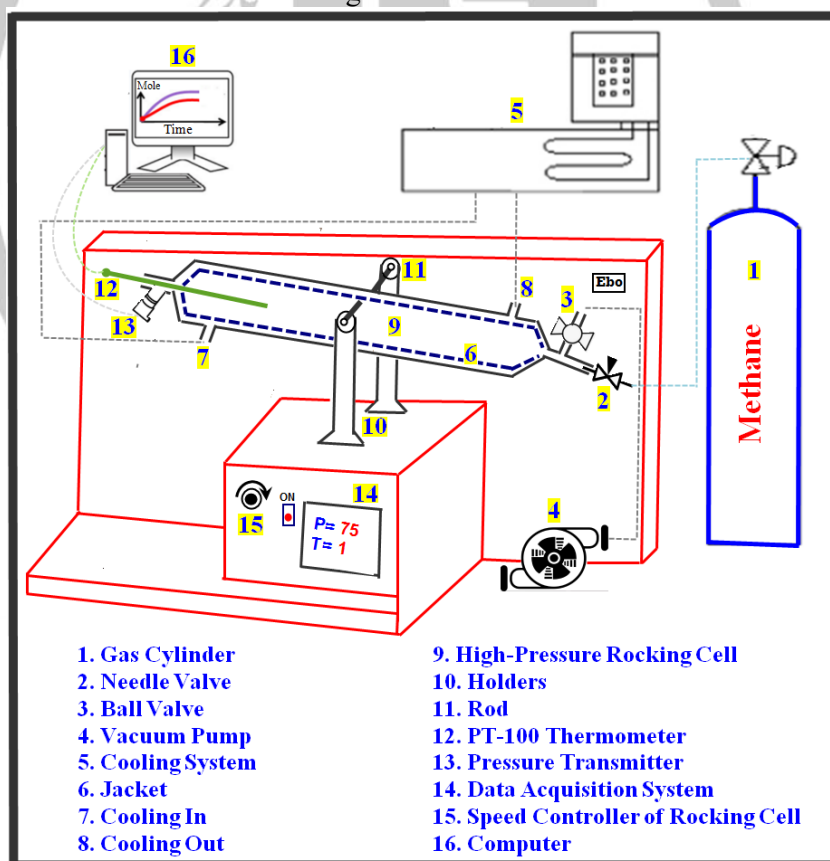


Fig. 2. Schematic of rocking cell for gas hydrate experiments

### 3. Results and discussion

#### 3.1. The effect of PVP and Luvicap EG in methane-THF system

With the aim of study the influence of PVP and Luvicap EG on sII hydrate, THF was used as a hydrate former. The gas consumption curves in Fig. 3 illustrate that PVP cannot be an inhibitor in methane-THF system. In terms of growth rate the performance of PVP was very similar to pure water, while Luvicap EG acted more effectively and could reduce the hydrate growth rate. The maximum subcoolings of these two inhibitors were also measured and the results are shown in Fig. 4. Based on results, PVP did not increase the subcooling. In other words, it acted as a promoter and the onset temperature of hydrate formation in the presence of PVP is even higher than pure water. It seems that PVP cannot be used to prevent methane-THF hydrate formation. Whereas, the maximum subcooling for Luvicap EG is the greatest and it can increased the maximum subcooling about 1.5 °C higher compared with pure water. To sum up, Luvicap EG is an effective inhibitor to decrease the growth rate and reduce the onset temperature of hydrate formation.

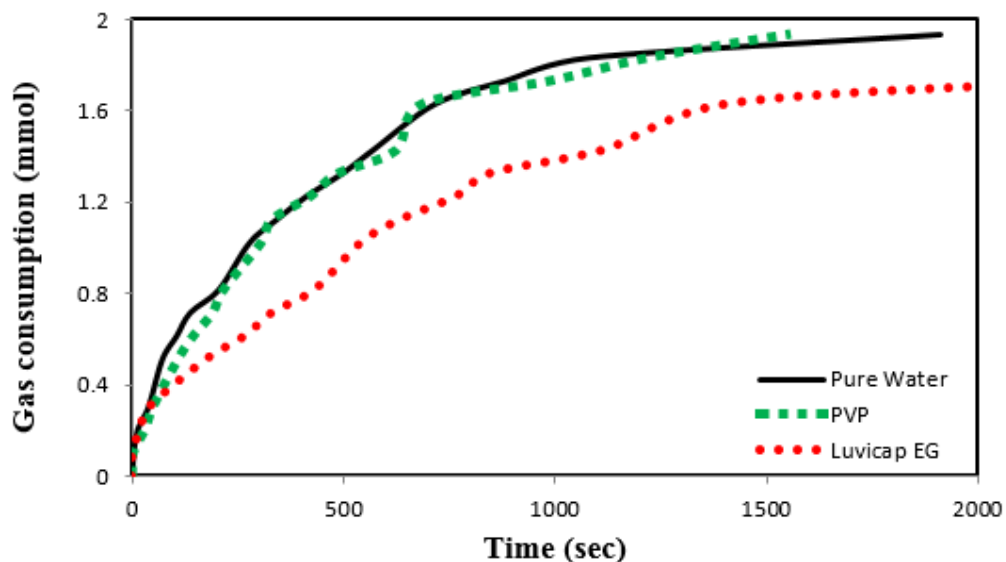


Fig. 3. The gas consumption curves in methane-THF system

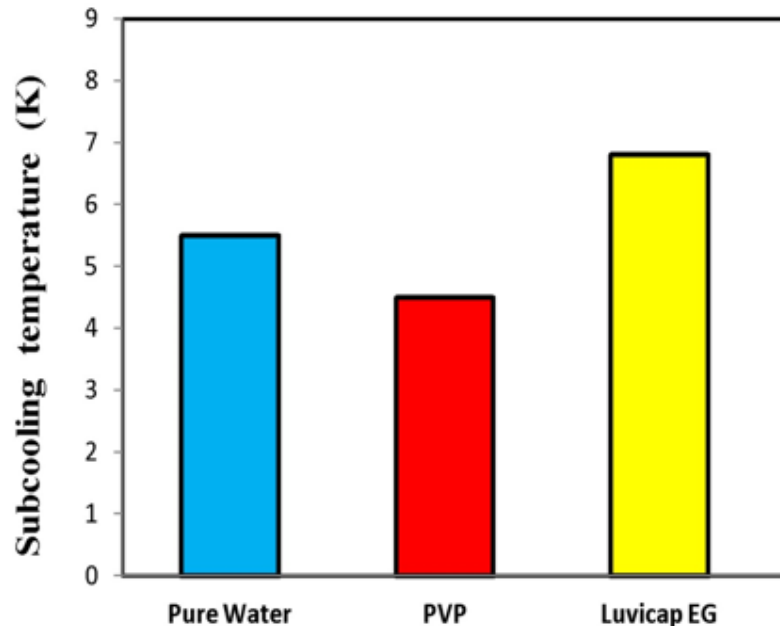


Fig. 4. The values of subcooling

### 3.2. The effect of PVP and Luvicap EG on ethylene hydrate

Ethylene forms hydrate structure I since it is not as large as propane and it should be mentioned that this gas occupies large cavities while methane occupies both small and large cages [11]. Fig. 5 illustrates the impact of PVP and Luvicap EG on growth rate of ethylene hydrate. Both polymers acted as inhibitors. The growth rate in the presence of these two polymers is lower than that of pure water. The inhibition potential of Luvicap EG is greater than PVP. Less gas was consumed in the presence of Luvicap EG. Furthermore, the slope of gas consumption curve is higher in the presence of PVP than that of Luvicap EG. It seems that Luvicap EG is a more appropriate KHI to prevent ethylene hydrate formation.

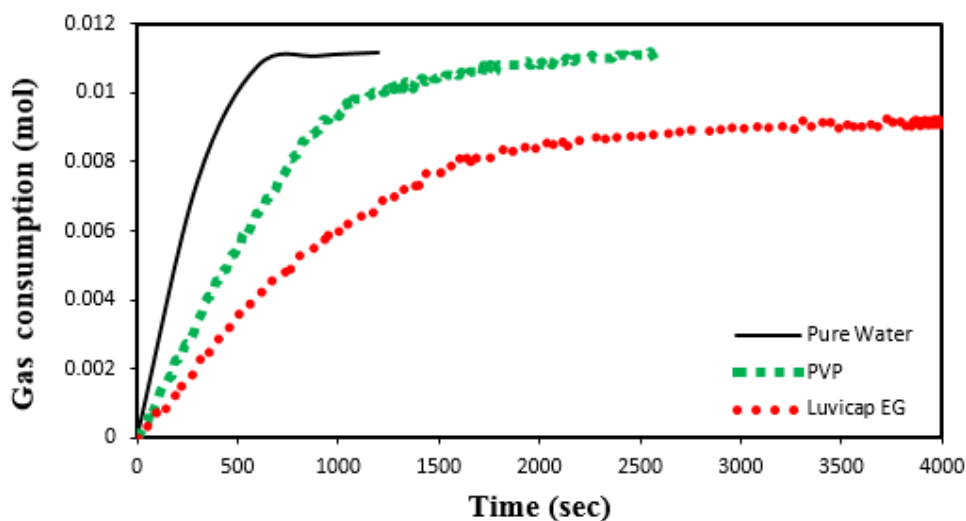


Fig. 5. The growth rate of ethylene hydrate in the presence of PVP and Luvicap EG compared with pure water

### 3.3. The effect of PVP and Luvicap EG on methane hydrate growth rate

The methane hydrate formation rate is also calculated in the presence of PVP and Luvicap EG. Methane gas forms hydrate structure I because of its small size and it occupied both large and small cavities of hydrate structure I. Table 1 shows the average growth rate of hydrate to the moment that the half of total moles of gas were consumed in the presence of PVP and Luvicap EG at different concentrations compared with pure water. Although at the concentration of 0.1 wt% Luvicap EG did not act as effectively as PVP, at higher concentration no hydrate was formed. It means that Luvicap EG performed better than PVP at higher concentration. As it shown in Fig. 6 both PVP and Luvicap EG could decrease the hydrate growth rate at the concentration of 0.1 wt%. However, Luvicap EG was not as effective as PVP. The possible explanation for better performance of PVP might be related to low concentration of PVCap in Luvicap EG. In other words, the amount of KHI in Luvicap EG is less than PVP and as methane is able to occupy both small and large cages the amount of Luvicap EG was not sufficient to restrict methane formation at the concentration of 0.1 wt%. Therefore, Luvicap EG at the lowest concentration was not as suitable as PVP to reduce methane hydrate growth rate, in contrast at higher concentrations it gave significant inhibition effect and perfectly inhibit hydrate formation so no hydrate was formed.

**Table 1. The average growth rate of methane hydrate (at half time of total moles of gas were consumed)**

Aqueous solution	Concentration (wt%)	Average growth rate (mmol/min)
Water	---	1.76
PVP	0.1	0.13
PVP	0.5	0.04
Luvicap EG	0.1	1.03
Luvicap EG	0.3	No Hydrate
Luvicap EG	0.5	No Hydrate

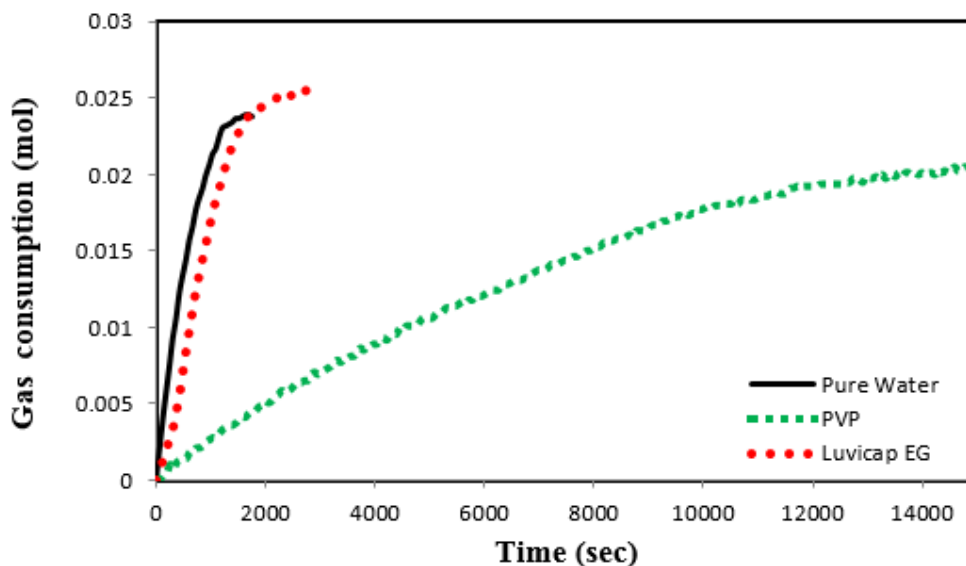


Fig. 6. The growth rate of methane hydrate in the presence of Luvicap EG and PVP

#### 4. Conclusions

The KHI performance of two commercial kinetic hydrate inhibitors, namely PVP and PVCap was evaluated in the high-pressure rocking cell. Based on the results, both polymers can inhibit the hydrate formation in all three systems and the growth rate in the presence of PVP and Luvicap EG was lower than that of pure water. In terms of decreasing the growth rate Luvicap EG was superior to PVP in ethylene system and methane-THF system, while in methane system Luvicap EG did not work efficiently at the low concentration. Based on the results of maximum subcooling, PVP was not effective in the methane-THF system and the onset temperature of hydrate formation was also greater than that of pure water, whereas Luvicap EG can shift the onset temperature of hydrate formation to lower temperature. It could be deduced from the results that Luvicap EG had superior effect to prevent hydrate formation specially hydrate structure II.

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## ارزیابی عملکرد Luvicap EG و PVP به عنوان بازدارنده هیدرات گازی در سیستم های

### هیدرات گازی متان، متان-تتراهیدروفوران و اتیلن

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### چکیده

عملکرد پلیمرهای تجاری PVP و Luvicap EG به عنوان بازدارنده رایج سینتیکی هیدرات (KHIs) در سه سیستم مختلف هیدرات گازی متان، متان-تتراهیدروفوران و اتیلن ارزیابی شد. یک راکتور الاکلنگی برای مقایسه این دو بازدارنده سینتیکی استفاده گردید. مقدار مول گاز مصرف شده بر حسب زمان (سرعت رشد هیدرات) و حداکثر دمای ابرسرمایش در حضور PVP و Luvicap EG محاسبه شد. نتایج نشان داد هر دو پلیمر در سیستم هیدرات گازهای متان و اتیلن به عنوان بازدارنده عمل می کنند. در سیستم هیدرات متان-تتراهیدروفوران، PVP قادر به کاهش سرعت رشد هیدرات نبود و حداکثر دمای ابرسرمایش PVP در این سیستم کمتر از آب خالص بود که بیانگر عملکرد ضعیف این پلیمر در سیستم متان-تتراهیدروفوران می باشد. پلیمر Luvicap EG در سیستم های اتیلن و متان-تتراهیدروفوران بهتر از PVP عمل می کند. با این حال، در سیستم هیدرات گازی متان عملکرد بازدارندگی PVP در غلظت ۰/۱ درصد وزنی بهتر از Luvicap EG بود. در حالی که در غلظت های بالاتر (۰/۳ و ۰/۵ درصد وزنی) عملکرد Luvicap EG عالی بود و به طور کامل از تشکیل هیدرات متان جلوگیری کرد.

واژه های کلیدی: هیدرات، بازدارنده سینتیکی، PVP، Luvicap EG، اتیلن، متان.