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Full Length Article

# In situ Raman investigation on mixed $CH_4$-$C_3H_8$ hydrate dissociation in the presence of polyvinylpyrrolidone

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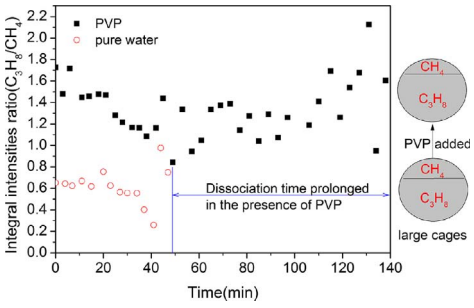
## GRAPHICAL ABSTRACT

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## ABSTRACT

The dissociation of hydrates containing kinetic inhibitors is important for the treatment of gas hydrate blockages in pipelines. In this work, the dissociation of natural gas hydrates in the presence of polyvinylpyrrolidone (PVP) was investigated by Raman spectroscopy and cryo-scanning electron microscope (SEM). The natural gas hydrates were formed from a synthetic natural gas mixture composed of $CH_4$ (95.0 vol%) and $C_3H_8$ (5.0 vol%). The results showed that the crystallographic structure of the formed hydrate was structure II (sII) with $CH_4$ encaged in both small and large cages and $C_3H_8$ in large cages. Raman spectra showed that PVP could not be captured by the sII hydrate cage and had no influence on the structural type of the hydrate. However, PVP inhibited the occupancy of $CH_4$ molecules in the large cages. The dissociation of hydrates in the presence of PVP was slower than without PVP. No other transient structure was observed during the dissociation and gas hydrate cages were suggested to collapse as an entity, without the interference of PVP. The microstructure of the gas hydrates appeared to change from close-to-spherical to scale-like when PVP was added.

## 1. Introduction

Gas hydrates are solid crystalline compounds, which consist of hydrogen-bonded polyhedral water cages stabilized by molecules with suitable size [1]. Natural gas hydrates formed from gas mixtures containing methane ($CH_4$), ethane ($C_2H_6$), and propane ($C_3H_8$) are renowned as potential energy resources due to their huge reserves and wide distribution around the globe [2]. At the same time, gas hydrates

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**Nomenclature**

| | |
|---|---|
| PVP | polyvinylpyrrolidone |
| PEtO | poly (2-ethyl-2-oxazoline) |
| THIs | thermodynamic hydrate inhibitors |
| LDHIs | low-dosage hydrate inhibitors |
| KHIs | kinetic hydrate inhibitors |
| AAs | anti-agglomerants |
| SEM | scanning electron microscope |
| PXRD | powder X-ray diffraction |
| NMR | nuclear magnetic resonance |
| wt% | mass fraction |
| vol% | volume fraction |

also pose a potential threat to gas/oil transportation as under suitable thermodynamic conditions, free water molecules in pipelines tend to form gas hydrates which may lead to a hydrate plug [3,4].

Depending on the gas species involved, gas hydrates with structures I and II can be found in pipelines. Structure I (sI) hydrates, having 2 small $5^{12}$ cages and 6 large $5^{12}6^2$ cages per unit cell, are often formed from $CH_4$, $C_2H_6$ or their mixtures. Structure II (sII) hydrates, having 16 small $5^{12}$ cages and 8 large $5^{12}6^4$ cages mainly include $C_1$–$C_4$ hydrocarbons (methane through butanes) [2]. However, the relationship between crystalline structure and guest molecule size is not strict, for example, in a $CH_4$ + $C_2H_6$ system, transitions of gas hydrate structure from sI to sII can be observed [3].

In response to the blockage of pipelines by hydrates, many methods for blockage prevention have been developed. The commonly used method is the addition of thermodynamic hydrate inhibitors (THIs) or low-dosage hydrate inhibitors (LDHIs) [5]. THIs are used to shift the hydrate-aqueous liquid-vapor equilibrium curve to a lower temperature or higher pressure, shifting the minimum hydrate formation conditions outside the boundaries of the environmental conditions. The effectiveness of THIs is well known, but the large concentrations, sometimes up to 60 wt% are required [6]. The primary advantage of LDHIs is stated in their name, as they are designed to be effective at low doses. Although LDHIs cannot change the equilibrium conditions of gas hydrates, they can prevent the supersaturated solution from crystallization and agglomeration for certain periods of time so that the risk of gas hydrate blockage is reduced to a minimum [7]. LDHIs can be further divided into two categories: kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) and their effective concentrations often range from 0.1 wt% to 2.0 wt% [8].

KHIs take effect in the liquid water phase and delay hydrate crystallization while AAs interact with the liquid hydrocarbon phase rather than inhibiting nucleation in the aqueous phase. Most KHIs are water-soluble polymers and their molecules interact with the gas hydrate surface to inhibit gas hydrate nucleation and growth kinetically [9–15]. Therefore, a potential risk for hydrate formation exists if the operation conditions change. In order to comprehensively understand this process, studies on the dissociation of gas hydrates in the presence of KHIs are necessary.

To date, most studies on gas hydrate dissociation with inhibitors have been focused on thermodynamic inhibitors [16–20]. Thermodynamic inhibitors can promote gas hydrate dissociation and are used to remediate hydrate blockage. However, few works focus on gas hydrate dissociation with KHIs. Fan et al. [21] investigated the effect of poly (2-ethyl-2-oxazoline) (PEtO) on gas hydrate surfaces and noted that PEtO could adsorb to the surface of the gas hydrate crystal and form hydrogen bonds with the water molecules in gas hydrate cavities, causing the collapse of the gas hydrate structure. Daraboina et al. [22] carried out experiments of gas hydrate formation and dissociation with two KHIs and two antifreeze proteins in a stirred reactor and reported that the dissociation rate was significantly influenced by these chemicals. Bruusgaard et al. [23] reported that pure water droplets had the fastest dissociation rate followed by droplets containing type-I antifreeze protein and droplets containing poly(VP/VC), a lactam ring copolymer of PVP and polyvinylcaprolactam.

For microscopic measurements, powder X-ray diffraction (PXRD), $^{13}C$ nuclear magnetic resonance (NMR) and Raman spectroscopy are often used [24–26]. Traditionally, Raman spectroscopy is used to determine the hydrate structure and gas occupancies in different hydrate cages. Daraboina et al. [27] investigated the impact of KHI on gas hydrate formation using PXRD, Raman, and NMR and found that greater amount of $C_2H_6$ occupied large cages compared to $CH_4$ in the presence of chemical inhibitors of PVP and H1W85281, as a result of the preferential occupation of large cage by the heavier hydrocarbon. Komai et al. [28] investigated the dissociation kinetics of methane hydrates using in-situ Raman spectroscopy at temperatures below the melting point of ice. Liu et al. [29] performed in-situ Raman observations on the dissociation of $CH_4$ hydrates in synthesized silica sands. Zhou et al. [30] reported the characteristics of the melting processes of mixed $CH_4$–$CO_2$ hydrates using in-situ Raman spectroscopy and compared the results with those of pure $CH_4$ and $CO_2$ hydrates. These Raman spectroscopic researches were relevant with gas hydrate formation in the presence of KHIs or gas hydrate dissociation in the absence of KHIs. However, no in-situ Raman observations on gas hydrate dissociation with KHIs were reported.

Based on the above analyses, in-situ Raman spectroscopy is an effective method to learn about gas hydrate dissociation at the molecular level. Therefore, the dissociation of the mixed $CH_4$-$C_3H_8$ gas hydrates in the presence of PVP was investigated using in-situ Raman spectroscopy. The structure of the formed hydrates and the variations of gas concentrations in the hydrate phase, especially the $CH_4$ molecules in the large and small cages were measured and compared. The morphologies of the formed hydrates before dissociation were observed using a cryo-scanning electron microscope (cryo-SEM). The influence of PVP on the dissociation of the gas hydrates was discussed at the microscopic level.

## 2. Experimental section

### 2.1. Materials

A synthetic gas mixture consisting of $CH_4$ (95.0% in volume) and $C_3H_8$ (5.0% in volume) produced by Guangzhou Yigas Gases Co. Ltd was used in all experiments. The commercial kinetic inhibitor, PVP, was supplied by Tokyo Chemical Industry, Japan. The average molecular weight was about 360,000 and its purity is larger than 95%. Double distilled water was produced in the laboratory.

### 2.2. Sample preparation

The protocol for gas hydrate sample preparation was introduced in a previous study [30]. A 250 mL high-pressure vessel was connected to a 400 mL gas reservoir. Both the vessel and the reservoir were immersed in a thermostatic bath during the gas hydrate crystallization process. A custom designed sample holder was placed in the high-pressure vessel, which allowed the ice particles to evenly attach onto the inner wall of the holder. In this case, the conversion of ice to gas hydrates was fast, and was also convenient for removal of the formed gas hydrate samples for further study. A thermal resistor ( ± 0.1 K) and pressure sensor ( ± 0.0625 MPa) were used to measure the temperature and pressure in the vessel. The temperature and pressure data were collected using a data acquisition system (Agilent 7890, Santa Clara, CA) at 10-second intervals.

Before experiments, the distilled water or 0.5% PVP solution (in