

# Macroscopic and spectroscopic identifications of the synergetic inhibition of an ionic liquid on hydrate formations

Seong-Pil Kang<sup>a</sup>, Taesung Jung<sup>a</sup>, Jong-Won Lee<sup>b,\*</sup>

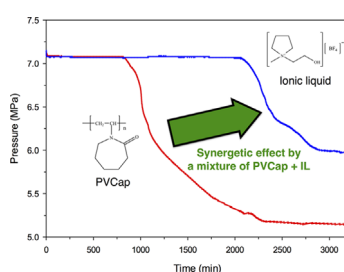
<sup>a</sup> Climate Change Research Division, Korea Institute of Energy Research, 152 Gajeongro-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

<sup>b</sup> Department of Environmental Engineering, Kongju National University, 1223-24 Cheonan-Daero, Cheonan-si, Chungnam 31080, Republic of Korea

## HIGHLIGHTS

- Synergetic inhibition of a ionic liquid on hydrate formation when mixed with PVCap.
- <sup>13</sup>C NMR spectra for both structures I and II hydrates with inhibitors.
- Time-resolved spectroscopic and macroscopic measurements are also performed.
- An ionic liquid shows the synergetic inhibition effect with a commercial inhibitor, PVCap.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 21 July 2015

Received in revised form

1 December 2015

Accepted 11 January 2016

Available online 15 January 2016

### Keywords:

Gas hydrates

Inhibition

Polyvinyl caprolactam

Ionic liquid

Mechanism

Synergetic effect

## ABSTRACT

In order to identify the synergetic inhibition of hydrate formation by a new pyrrolidinium cation-based ionic liquid with a commercial kinetic inhibitor, poly(N-vinylcaprolactam)(PVCap), pure CH<sub>4</sub> (structure I) and synthesized natural gas (structure II) hydrate samples are prepared and analyzed with solid-state <sup>13</sup>C NMR spectroscopy. In addition, the time-resolved macroscopic pressure changes and microscopic Raman spectra are also measured using the synthesized natural gas and two inhibitors. Hydrate formation or formed hydrate structure is found to be different for the PVCap-only and the PVCap + [HEMP][BF<sub>4</sub>] systems. Furthermore, the addition of [HEMP][BF<sub>4</sub>] is found to delay the induction time and hydrate growth further when added to the PVCap-only system although some deviations are observed for the induction time. Adding the ionic liquid to the PVCap system can have a synergetic effect on the hydrate formation (natural gas hydrate of the structure II, in particular), which may indicate different inhibition mechanisms of PVCap and [HEMP][BF<sub>4</sub>].

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Gas hydrates are nonstoichiometric crystalline solids which form due to a reaction between water and gases with a low molecular weight (Sloan and Koh, 2008). They require a specific temperature and pressure (generally, a low temperature and a high pressure) to form and exist stably (Carroll, 2009). Gas hydrate can be categorized as having three structures (structures I, II

and H) (Sloan and Koh, 2008; Ripmeester et al., 1987), mainly depending on the encaged gas species and their molecular size. While gas hydrate can be used in various fields due to its ability to store a large volume of gas per unit of volume in its solid structure (Kang and Lee, 2000; Seo and Lee, 2003), it is also known to be a hazardous material which can cause plugging problems in the oil and gas industries (Hammerschmidt, 1934). Thus, many studies have focused on the prevention or removal of unexpected hydrate formations for flow assurance purposes in oil and gas production facilities. Because it is impractical to operate pipelines always under non-hydrate forming conditions, hydrate inhibitors are commonly used to prevent hydrate formation. Inhibitors can be

\* Corresponding author.

E-mail address: [maruhill@kongju.ac.kr](mailto:maruhill@kongju.ac.kr) (J.-W. Lee).

divided into three types: thermodynamic inhibitors, anti-agglomerants (AA), and kinetic hydrate inhibitors (KHI) (Kelland, 2006). Thermodynamic inhibitors shift the thermodynamic equilibrium curves of the gas hydrates into the inhibition region (requiring a higher pressure at a given temperature or a lower temperature at a given pressure) such that the operational conditions can reside outside of the hydrate-forming region (Sloan and Koh, 2008). Methanol and monoethylene glycol (MEG) are well-known thermodynamic inhibitors. Although thermodynamic inhibitors can prevent hydrate formation by shifting the equilibrium curve, they have a number of disadvantages from the economic and environmental points of view because a high concentration (10–40 wt% to water) of the inhibitor must be added to be effective. AAs and KHIs, in the category of low-dosage hydrate inhibitors, can prevent hydrate plugging in pipelines when dosed at a concentration of ca. 0.1–2.0 wt% (active component) based on the water phase (Kelland, 2006). While AAs inhibit pipeline plugging by acting as a hydrate emulsifier (Perrin et al., 2013; Huo et al., 2001), KHIs are water-soluble polymers in general that prevent hydrate formation by delaying the nucleation and often the crystal growth of gas hydrates (Kelland, 2011). KHIs are often used together with synergists to enhance the inhibition effects. Tetraalkyl ammonium salts (Dahmann and Feustel, 2008; Sefidroodi et al., 2011; Chua and Kelland, 2012a), tetraphosphonium salts (Kelland et al., 2013a), hexaalkylguanidinium salts (Kelland et al., 2013b), alkyl glycols (Chua and Kelland, 2012b), or small surfactants (Rabony et al., 1998) have been studied as synergists for polymeric KHIs.

A novel hydrate inhibitor, which is an ionic liquid, was reported by Xiao and Adidharma (2009), and they claimed that some imidazolium-based ionic liquids worked as KHIs. Although their experimental conditions were strange and impractical, they found that imidazolium-based ionic liquids were not good KHIs when used alone with structure II hydrates, but fairly good synergists for KHIs based on vinyl lactam polymers (Villano and Kelland, 2010). Dialkylimidazolium halide ionic liquids were also reported as potential KHIs in the CH<sub>4</sub> hydrate (Xiao et al., 2010). Several researchers have investigated the inhibition effect of some ionic liquids on CH<sub>4</sub> and CO<sub>2</sub> hydrates, but most of them focused on the thermodynamic inhibition effect of ionic liquids when dosed at high concentrations (Tumba et al., 2011; Li et al., 2011; Nazari et al., 2013; Richard and Adidharma, 2013; Zare et al., 2013). It was also reported that dialkylimidazolium tetrafluoroborates raised the rate of gas consumption and acted as a kinetic promoter of CO<sub>2</sub> hydrate (Chen et al., 2008; Makino et al., 2011). In this regard, some researchers have synthesized specific ionic liquids for a particular purpose because the physical properties of ionic liquids are strongly dependent on the length of the alkyl chain of the cation or on a specifically designed cation and anion. They then used these liquids as additional molecules that acted as synergists to enhance the inhibition performance with commercial inhibitors. Kim et al. (2011) compared the inhibition effect of a new pyrrolidinium-based ionic liquid, N-(2-hydroxyethyl)-N-methylpyrrolidinium tetrafluoroborate ([HEMP][BF<sub>4</sub>]), with other inhibitors including an imidazolium-based ionic liquid. In addition, Kang et al. (2013) reported that [HEMP][BF<sub>4</sub>] can be used as a synergist for inhibiting the CH<sub>4</sub> hydrate when mixed with a commercial polymer inhibitor, poly(N-vinylcaprolactam)(PVCap).

Although some ionic liquids have been reported as novel hydrate inhibitors, most of them did not exhibit a good kinetic inhibition effect when applied alone and a little thermodynamic effect when the dose was at high concentrations. Moreover, the inhibition effects by ionic liquids have been mainly investigated in macroscopic ways (e.g., shift of thermodynamic equilibrium curves or induction time during hydrate formation) or compared with a well-known KHI, PVCap. Therefore, in this study, we used an ionic

liquid [HEMP][BF<sub>4</sub>] as a synergist candidate for commercial KHI and investigated the inhibition behaviors with spectroscopic and macroscopic measurements. In addition, we also investigated the formation behaviors for both structure I and structure II hydrates and compared the results between the system using the PVCap alone and the one using the PVCap + ionic liquid. The experimental results obtained in this study will provide fundamental data for designing/optimizing ionic liquids as hydrate inhibitors as a synergist with commercial inhibitors.

## 2. Experimental methods

Pure methane and synthesized natural gas of an ultrahigh-purity (UHP) grade were manufactured and supplied by Rigas (Korea). The dry-based gas composition of the synthesized natural gas is summarized in Table 1. HPLC-grade water with a minimum purity level of 99.99 mol% was supplied by Sigma-Aldrich Chemical Co. and was used without further purification or treatment. Poly(N-vinylcaprolactam)(PVCap) was obtained from BASF under the product tradename Luviskol Plus™. It consists of PVCap as a 60 wt% solution in ethanol. Ethanol was eliminated by a rotary evaporator, and the remaining PVCap was further dried in an oven for more than 24 h. An analysis showed that the obtained PVCap had a purity of 98.0% and a MW of approximately 17,000. N-(2-hydroxyethyl)-N-methylpyrrolidinium tetrafluoroborate ([HEMP][BF<sub>4</sub>]) was synthesized using the same method described in our previous reports (Kim et al., 2011; Kang et al., 2013). The molecular structures of these two chemicals are shown in Fig. 1.

All of the hydrate samples were prepared with a specifically constructed high-pressure vessel. Approximately 200 cm<sup>3</sup> of water with and without inhibitors was charged in a high-pressure cell made of 316 stainless steel (with a maximum working pressure of 15.0 MPa and an internal volume of about 350 cm<sup>3</sup>). An external circulating chiller with accuracy of ±0.1 K (RW-40G, Jeio Tech, Korea) was used to cool and control the temperature. After the cell was purged by the synthesized natural gas to remove the remaining air in the system, it was pressurized to about 7.5 MPa at room temperature (296.6 K) with consideration of pressure reduction after subsequent cooling. Then, the reactor is cooled to 280.2 K with the external chiller and the pressure became 7.0 MPa with the pressure reduction due to the cooling. The isothermal measurements were started with agitation of a magnetic drive at 600 rpm. During this hydrate formation process, temperature and pressure of the reactor were collected using a data-acquisition system throughout the experiments at an interval of 0.25 min. When a sufficient pressure drop was observed due to hydrate formation, the high-pressure vessel was quenched in liquid nitrogen and the samples were collected for microscopic analysis. The isothermal hydrate inhibition experiments were repeated four to five times for each sample to verify reproducibility and reliability.

For microscopic measurements, the Bruker DSX400 NMR spectrometer at the Korea Basic Science Institute was used. Solid-state <sup>13</sup>C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were obtained at 240.0 K by packing the hydrate samples

**Table 1**  
Dry-based composition of the synthesized natural gas.

Component	Composition (%)	Component	Composition (%)
CH <sub>4</sub>	90.07	n-C <sub>4</sub> H <sub>10</sub>	0.65
C <sub>2</sub> H <sub>6</sub>	4.18	CO <sub>2</sub>	1.94
C <sub>3</sub> H <sub>8</sub>	2.11	N <sub>2</sub>	0.23
iso-C <sub>4</sub> H <sub>10</sub>	0.82	–	–

Download English Version:

<https://daneshyari.com/en/article/154517>

Download Persian Version:

<https://daneshyari.com/article/154517>

[Daneshyari.com](https://daneshyari.com)