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Investigation on the Synergistic Effect of Tetra Butyl Phosphonium Bromide with Poly(N-isopropylacrylamide) Based Kinetic Hydrate Inhibitor

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The problem of clathrate hydrate plugging in flow pipes has been the most important issue in the off-shore exploitation since hydrates were found in transport facilities. In recent years, low dosage hydrate inhibitors have attracted much interest among researchers in place of thermodynamic hydrate inhibitors such as methanol and mono ethylene glycol (MEG). Poly-vinyl caprolactam and poly-isopropylacrylamide (PNIPAM) are among the hydrate inhibitors that are typically used for polymers containing amide groups. Furthermore, various kinds of polymer inhibitors containing amide group including tetrabutylphosphonium bromide(TBPB), which is a quaternary salt, were synthesized and studied in a methane gas hydrate environment. In this experiment, the injection of 0.1 wt% inhibitor at 276 K and 5 MPa was followed by stirring the water to induce nucleation. From the result, when PNIPAM alone was used as a single KHI, PNIPAM exhibited worst performance among the KHIs tested in this study. But the mixing of TBPB with PNIPAM further extended the induction time and reduced the CH_4 hydrate growth rate. The real-time in situ Raman system used to understand the inhibition principle was recorded during CH_4 hydrate formation, as a result, PNIPAM showed that the large hydrate cage affected, while TBPB prevented the CH_4 molecule from occupying the small cage. TBPB was excellent synergist in blends with PNIPAM for kinetic hydrate inhibition of structure I forming CH_4 hydrate.

1. Introduction

The gas hydrate is a solid inclusion compound in which guest molecules of appropriate size and shape are integrated into a water-bonded water skeleton. This compound exists in sI, sII and sH, three different crystal structures organized in various cages of different sizes and shapes (Seo et al., 2013). Natural gas hydrate formation can cause blockages in the flow lines of gas and oil production, which can lead to serious economic losses and safety problems (Sloan, 1998). Consequently, there has been an increase in research into the development of new and effective inhibitors to prevent gas hydrates during natural gas and oil subsea production and transportation (Koh and Sloan, 2007). Methyl alcohol or monoethylene glycol (MEG), there are hydrogen bond between water, shifts hydrate-forming conditions to the zone of inhibition, preventing hydrates from occurring, which is called a thermodynamic hydrate inhibitor (THI) (Sloan et al., 2011). But large amount of THIs are usually required to prevent hydrate plugging of the flow lines, which increases costs too much for oil and gas production (Kinnari et al., 2011). A huge quantities of methanol, which is toxic, corrosive and flammable, are required for the inhibition of gas hydrates, and the use of methanol has raised environmental concerns because it is rarely used to regenerate continuously in condensate and gas fields (Zhao et al., 2015). Thus, other types of hydrate inhibitors suggesting low dose hydrate inhibitors (LDHIs) have been developed and used to reduce operating costs (Sloan et al., 2011). LDHIs, classified as a kinetic hydrate inhibitor (KHI) and an anti-agglomerate (AA), inhibited the induction time (nucleation time) and delays the rate of crystal growth of gas hydrates at low doses (0.1-2 wt%). Polymeric chemicals likewise poly-n vinyl

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caprolactam polymers are reported as representative KHI. Usually, the KHIs are polymeric materials that kinetically retard the nucleation and growth of hydrate crystals, while the AAs are surfactants that disrupt to hydrate particles prevent the hydrate growth/agglomeration. Most classes of KHI polymers contain amide groups. A group of KHIs based on the polymer of alkyl acrylamide was developed. It was also pointed out that poly (N-isopropylacrylamide) was recognized for its performance just as KHIs, especially when isopropyl serves as the alkyl group (Chua et al., 2012). Furthermore, quaternary ammonium salts have been used as synergists, particularly for N-vinylcaprolactam polymers.

Recently, a combination of KHI and THI has been investigated for more effective hydrate flow assurance (Tohidi et al., 2015). Among the various KHIs, polymer with amide group is used as a standard chemical to compare Inhibitor performance. This polymer KHI is known to exhibit better inhibition performance against sII (structure II) natural gas hydrates than sI (structure I) CH_4 hydrates, suggesting that the kinetic hydrate inhibition effect of polymer with amide group is crystal structure-dependent. Some fields contain a very large portion of CH_4 and form sI hydrates rather than sII. Therefore, there is a need to develop effective KHI for sI hydrate formation.

In this study, compared with inhibition performance of synthesized PNIPAM, which is evaluated with commercial inhibitor, TBPB and TBPB-PNIPAM mixture conditions.

2. Experimental

2.1 Materials

N-Isopropylacrylamide (Tokyo Kasei Kogyo Co.) was purified by recrystallization method using hexane–benzene mixture solution. Toluene was purified through washing with sulfuric acid, water, and 5% aqueous NaOH; this was followed by fractional distillation. Methanol (MeOH) and ethanol (EtOH) were distilled for 3 times before use. Tri-nbutylborane (n-Bu_3B) as a THF solution (1.0 M), tert-butyl alcohol (t-BuOH) (Aldrich Chemical Co.), hexamethylphosphoramide (HMPA) (Aldrich Chemical Co.), 3-methyl-3-pentanol (Aldrich Chemical Co.) and isopropyl alcohol (IPA) were used without further purification for polymerization. Tetrabutylphosphonium bromide(TBPB) and Luvicap EG were purchased from either Sigma-Aldrich or BASF Co., Ltd.

2.2 Synthesis of PNIPAM via free radical polymerization

Polymerization of Poly n-Isopropylacrylamide(NIPAM): 20 mL solution was prepared by dissolving NIPAM (1.062 g, 9.4 mmol) and 3-methyl-3-pentanol (3.835 g, 37.5 mmol) in toluene. A total of 16 mL of solution was transferred to a glass ampoule and cooled at 0 ° C. n-Bu3B solution (5.0 mL) (1.0 M) in tetrahydrofuran (THF) was added to the monomer solution to initiate the polymerization. The reaction was terminated after 24 h by addition of a small amount of 2,6-di-butyl-4-methyl phenol solution in THF at the polymerization temperature. The reaction mixture was poured into a large amount of diethyl ether, the precipitated polymer was collected by filtration and then dried in vacuo. Polymer yield was determined by gravimetric measurement.

2.3 Characterization

Analysis of 1H-nuclear magnetic resonance (NMR): The synthesized polymers were dissolved in D_2O, and then ^1H NMR spectra of the polymers were obtained using a Varian 400 (Varian, Palo Alto, CA, U.S.A.) spectrometer.

Analysis of fourier transform-infrared spectra (FT-IR): Infrared spectral data were collected on a PerkinElmer FRONTIER spectrometer using potassium bromide pellets and the ATR method.

Methane Gas Hydrate Experiment Apparatus and Procedure: The experimental apparatus shown in Figure 1, consists of stainless steel reactor (372.5mL), feed vessel (566.5mL), refrigeration system, water bath, data collection system and in-situ Raman system.

Before running each hydrate kinetics experiment, the reactor was filled with an aqueous test sample of 125 cm^{-1} (a liquid solution of pure or inhibitor), and then reactor was flushed more three times by methane gas to remove residual air.

Consequently, the all of system was kept at a desired temperature, and the reactor was filled with methane gas until the experimental pressure was obtained. Experimental conditions were conducted at 276.15 K (4.7 K subcooling) and 7.0 MPa. After the temperature had stabilized, the solution was stirred using a magnetically driven impeller with a rotational speed of 300 rpm, which was determined to be suitable for our experiment and was applied to all experimental runs.

During hydrate formation, the molar consumption data of the guest molecule (CH_4) can be obtained from the pressure deviation in the supply vessel. The gas consumption data was recorded every 5 s for the entire experiment, and Raman spectra were collected every 30 s for scattering data of the sample by a 532 nm laser source at 100 mW power.

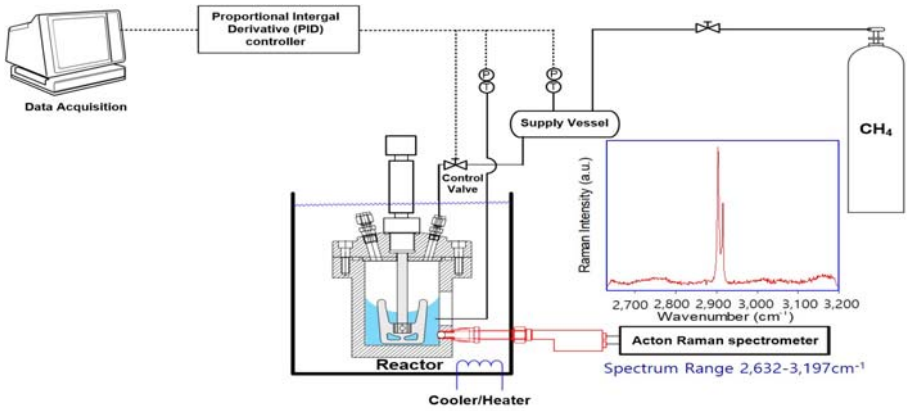

Figure 1: Schematic diagram of the gas hydrate experimental apparatus

As shown in Figure 2 shows the structures of the Inhibitors used for the present work. Among the three inhibitors for the CH_4 hydrate inhibition tests, Poly (N-isoacrylamide) (PNIPAM) was synthesized, and the other inhibitors were purchased.

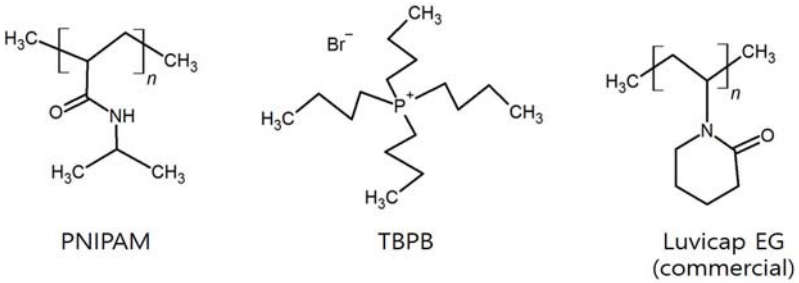

Figure 2: Chemical structures of PNIPAM, TBPB and Luvicap EG used for the experiments on kinetic inhibition of gas hydrate.

According to literature review, it was not significantly difference in gas consumption between the 0.1 and 1 wt% performance of the hydrate inhibitor (Houra and Tohidi, 2013). Based on this literature, the inhibition performance of PVCap was evaluated at an economic dose of 0.1 wt%. Methane gas in the reactor was consumed during gas hydrate formation and additional gas was automatically supplied from the feed vessel. The amount of gas uptake over time was calculated from the pressure drop profile in the feed vessel (>7.0 MPa) against the initial pressure. A more detailed description of the experimental procedure is available in a previous report (Lee and Englezos, 2005).

3. Results and discussion

3.1 ^{1}H NMR spectrum of PNIPAM

Figure 3a shows the ^{1}H NMR spectra of Poly (N-Isopropylacrylamide) via free radical polymerization. Moreover, the spectrum of the PNIPAM reveals the resonance of the repeat unit: CH_3, a (1.15 ppm), NCH_2 of isopropyl b (3.9 ppm), CH_2 backbone, c and d (1.55−2.35ppm). Finally, the peak of the solvent D_2O appears at 4.8 ppm.

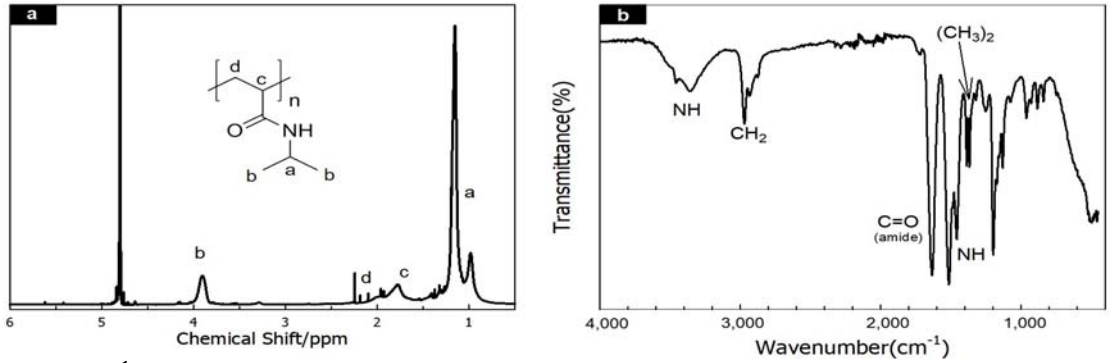

Figure 3: (a) ^{1}H NMR spectrum of PNIPAM, (b) FT-IR spectrum of PNIPAM.

3.2 FT-IR spectrum of PNIPAM

As shown In the FT-IR spectrum presented in Figure 3b, the transmittance peaks at 1,381, 1,554 and 1,653 cm^{-1} can be assigned to the amide I band (mostly due to the C=O stretching vibration), amide II band (a combination of the N–H bending and C–N stretched vibration), and CH_3 bending vibration. Similarly, the peak shoulder at about 1,725 cm^{-1} might be due to the C=O stretching vibration of the monomer unit.

3.3 Inhibition effect of PNIPAM alone

To check the kinetic inhibition of gas hydrate, each KHIs (0.1 wt % dissolved in distilled water) were tested at 7 MPa, 276.15 K and 300 rpm in a semi-batch reactor. Figure 4a shows the kinetic behavior of hydrates containing KHIs and PNIPAM during hydrate formation. As the result of the experiments showed that the induction time was significantly delayed in the presence of inhibitors. In the absence of any KHIs, recorded induction time was only 2 min. In detail, when various KHIs or synthesized the PNIPAM were present in water, various induction times of 28-385 min were recorded. To obtain accurate results, the experiments were repeated 3 times and were shown in Figure 4.

The induction time for TBPB was the shortest among the inhibitors evaluated at less than 20 min, whereas the growth time was the longest. Induction time of Luvicap EG with amide group was about 385 min, which was the highest nucleation inhibition performance under the same conditions compared to other KHI. Luvicap EG and PNIPAM, which are used as KHI, are polymers having amide groups, which have the principle of adsorbing onto the particle surface of hydrate to inhibit formation and growth. (Kelland, 2006). In the case of TBPB, the kinetic inhibition test of gas hydrate resulted in induction time of about 30 min. TBPB leading to disrupt the water molecule with the intermolecular hydrogen bonding and hydroxyl groups of water in aqueous solutions, effectively inhibiting hydrate formation (Kim et al., 2011).

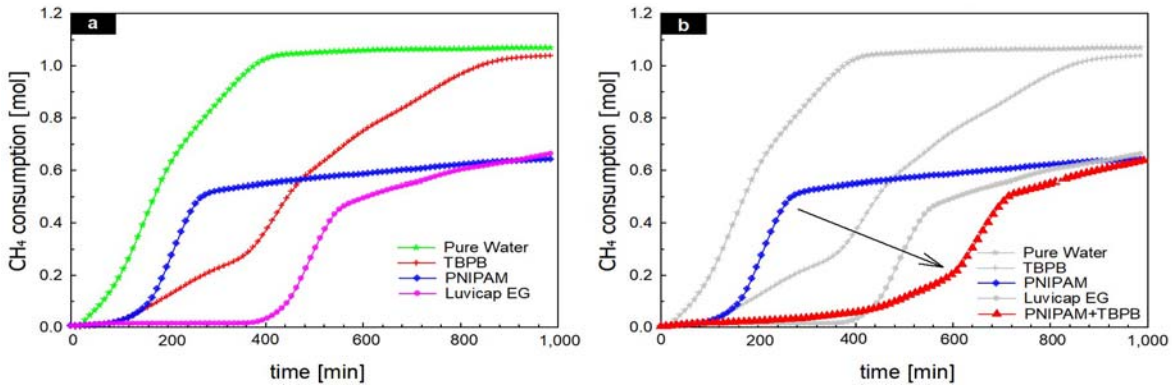

Figure 4: Consumption comparison of CH_4 hydrate (a) in the absence of TBPB-PNIPAM mixture (b) in the presence of TBPB-PNIPAM mixture

3.4 Inhibition effect of PNIPAM with TBPB

Figure 4b show that synergy effect of TBPB- PNIPAM mixtures on the CH_4 hydrate formation. Individual inhibition performance of TBPB or PNIPAM was very low with 28 and 40 min. In contrast, the mixture of TBPB and PNIPAM effectively extended the induction time to about 240 min compared to each single inhibitor. Also, the mixture of TBPB and PNIPAM shows the lowest low slope CH_4 consumption traces of the total inhibitors tested. Which results translated that the slowest growth rate of gas hydrates after nucleation. The inhibition performance of the TBPB inhibitor shown in Figure 4a shows the most of slow growth rate among the single inhibitors after induction time. The most remarkable result is that not only the TBPB-PNIPAM mixture increased the induction time, but also more than three times increase growth time dramatically, TBPB is expected that affect to the growth inhibition than nucleation.

3.5 Real-time *in-situ* Raman spectra of hydrate with inhibitors

The real-time Raman spectroscopy is suitable for observing the inclusion of gas molecules in gas hydrate cages and for verifying the structure of hydrates. In general, structure of CH_4 hydrate has the form of structure I and consists of a large ($5^{12}6^2$) cage and a small (5^{12}) cage. Pure CH_4 hydrate showed two Raman peaks at 2,904 and 2,914 cm^{-1}, indicated to the CH_4 molecule captured in large ($5^{12}6^2$) and small (5^{12}) cages (sI hydrates), individually. The Raman peaks show that large ($5^{12}6^2$) cages and small (5^{12}) cages of pure CH_4 hydrate result in concurrently rapid growth after nucleation of the hydrate. On the other hands, CH_4 hydrates with inhibitors showed significantly different enclathration of gas behavior during hydrate formation, as shown

in the Figure 5b – 5d. PNIPAM seems to be similar to that of pure CH_4 hydrate, but the large ($5^{12}6^2$) cage intensity of PNIPAM is slightly lower than pure CH_4 hydrate in the Figure 5b. The in-situ Raman spectra recorded during CH_4 hydrate formation showed that TBPB prevented CH_4 molecules from occupying small (5^{12}) cages, whereas PNIPAM, Luvicap EG had shown a strong influence on large ($5^{12}6^2$) cages of sI hydrates. As shown at Figure 5c, the kinetic growth patterns of the TBPB were different from that of pure CH_4 and PNIPAM hydrates For TBPB, the Raman peak associated with the CH_4 molecule in the large ($5^{12}6^2$) cage grew rapidly early after nucleation of the hydrate, while the intensity of the Raman peak for the small (5^{12}) cage increased slightly over 400 min. As mentioned above, the hydrate of pure CH_4 and PNIPAM grows simultaneously in the ($5^{12}6^2$) and small (5^{12}) cages after nucleation. In contrast, TBPB has a special effect on the inhibition of small (5^{12}) cages, preventing the CH_4 molecules from occupying small (5^{12}) cages. Figure 5(d) shows that the two inhibitors PNIPAM and TBPB, which have different inhibition mechanisms are mixed, show significantly better results than the each single inhibitor. The kinetic properties of the CH_4 hydrate added with the PNIPAM-TBPB mixture showed no change in Raman peak intensity values for large ($5^{12}6^2$) and small (5^{12}) cages until approximately 400 min after the start of the experiment. It means that both the large ($5^{12}6^2$) cage and the small (5^{12}) cage of hydrate are simultaneously inhibited in crystal growth due to the inhibition properties of PNIPAM and TBPB.

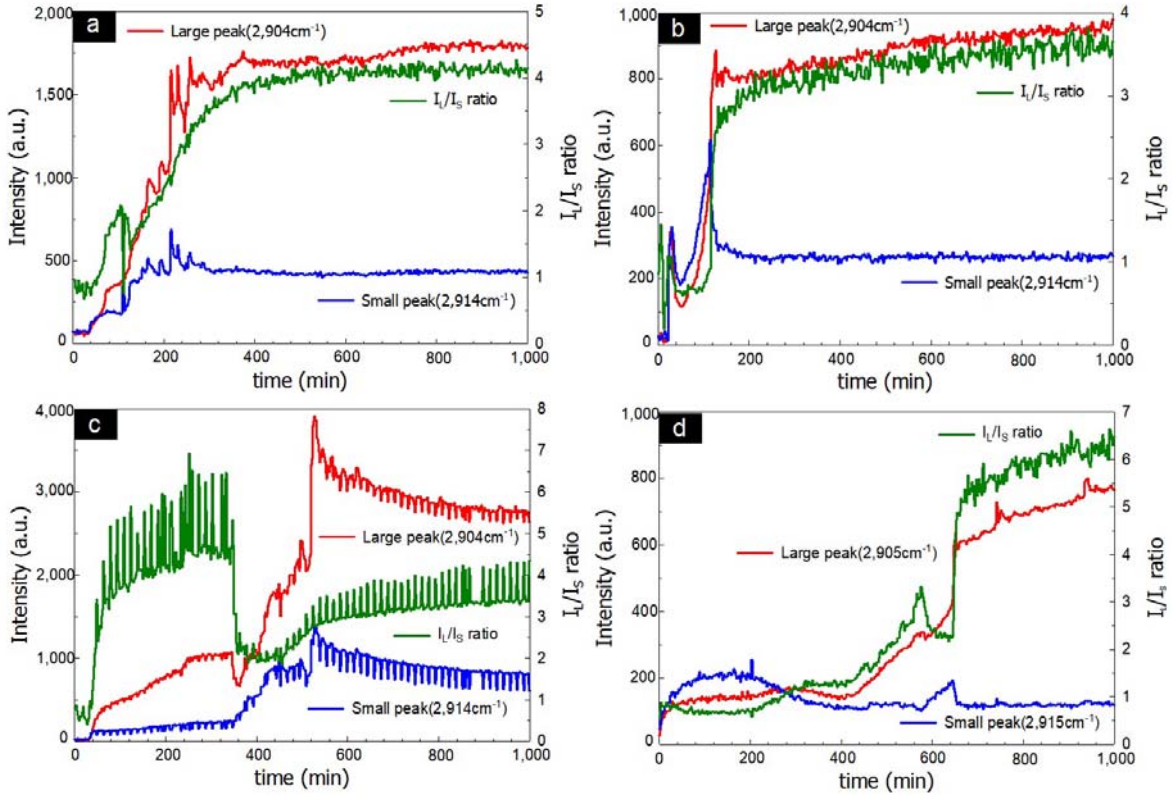

Figure 5: In-situ Raman spectra of (a) pure CH_4, and presence of (b) PNIPAM (c) TBPB (d) PNIPAM-TBPB mixture

In the case of pure CH_4 hydrates, the ratio IL / IS values of the intensity of peaks 2904 cm-1 and 2914 cm-1 corresponding to the CH_4 molecules occupied in the large ($5^{12}6^2$) cage and the small (5^{12}) cage, finally reached 4. This is slightly higher than the theoretical value of cage occupancy ratio (3.0) for CH_4 hydrate. The addition of PNIPAM resulted in a lower IL / IS value of around 3.7 than pure CH_4 hydrate (Figure 5b), which has been shown to affect growth inhibition of the Large ($5^{12}6^2$) cage. The IL / IS value of TBPB was 4.7 for about 380 min and was higher than pure CH_4 hydrate (4.1) and PNIPAM added hydrate (3.7). In Figure 5c, it is expected that TBPB is effective at inhibiting the occupancy of small (5^{12}) cages by CH_4 molecules and affects hydrate conversion and formation behavior.

Mixed inhibitor retarded the nucleation time about 5 times more than the single inhibitor concurrently delayed the crystal growth. The mixing inhibitor exhibited a synergistic effect by inhibiting nucleation time and at the same time retarding crystal growth by 3 times more than a single inhibitor.

4. Conclusion

Chapter 2 In this study, firstly it was synthesized that PNIPAM via free radical polymerization. The PNIPAM was confirmed to be successfully synthesized by ^{1}H-NMR and FT-IR analysis. Secondly, To evaluate the synrgistic effect, we conducted a kinetic inhibition experiment with TBPB-PNIPAM mixture or PVCap-based commercial KHI 'Luvicap EG' from gas hydrates in structure I form using a high pressure autoclave. Kinetic inhibition measurements of hydrates showed that the addition of Luvicap EG (PVCap) as a hydrate inhibitor delayed hydrate nucleation for the longest time among the inhibitors evaluated. Whereas, when PNIPAM or TBPB alone was used as KHI, the induction time, which indicators of the ability to inhibit nucleation, was short around 40 min. Mixture of PNIPAM and TBPB extended the induction time, resulted in a decrease in the rate of CH_4 hydrate growth, and demonstrated the expectation that TBPB is involved in crystal growth inhibition. TBPB was a good synergist PNIPAM for kinetic hydrate inhibition of CH_4 hydrate. As a final point, real-time in situ Raman spectra recorded during CH_4 hydrate formation provided evidence of specific inhibition mechanisms by which KHIs affect the hydrate cage occupancy of CH_4 molecules. PNIPAM has influence to large ($5^{12}6^2$) cages, but TBPB prevents CH_4 molecules from being captured in small (5^{12}) cage. The PNIPAM-TBPB mixtures showed best performance because the cages of the hydrates involved were large ($5^{12}6^2$) and small (5^{12}) cages, individually. The synergetic inhibition effect might be related to perturbation between water and hydrate particle. If it is possible to control to each cages inhibition of hydrates, such as PNIPAM-TBPB mixtures, it is expected to be selectively applicable depending on the oil production environment.

Acknowledgments

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