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Recalcitrance of gas hydrate crystals formed in the presence of kinetic hydrate inhibitors

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ABSTRACT

Kinetic hydrate inhibitors (KHIs) are used to manage the risk of gas hydrate plug formation in oil and gas transmission pipelines and facilities. However, under severe conditions, hydrates can be formed in the presence of these additives. It is important to understand how these inhibitors would affect gas hydrate remediation. Here, the impact of different concentrations of polyvinylcaprolactam (PVCap), Luvicap® Bio and type III antifreeze proteins (AFP III) on the dissociation of propane hydrate formed in the presence of these additives has been evaluated using a high pressure micro differential scanning calorimeter. Remarkably, hydrates formed in the presence of these inhibitors were dissociated at different temperatures than those expected from hydrate equilibrium calculations as well as at higher temperatures. However, gas hydrates formed in KHI-free solution melted at the equilibrium temperature and multiple-melting points were not observed. Interestingly, an increase in inhibitor concentration decreased the amount of gas hydrate that dissociated at the equilibrium temperature. Consequently, larger amounts of hydrate were dissociated at higher temperatures. These results indicate that since remediation of hydrates in the presence of KHIs requires higher melting temperatures, more energy is required to remove hydrates under these conditions. Such an effect should be considered in the design of processes for flow assurance.

1. Introduction

Formation of gas hydrates in oil and gas production and transmission facilities has been realized as a main cause for flow blockage and often severe consequences. Gas hydrates are ice-like crystalline compounds consisting of proper size molecules entrapped in a network of hydrogen-bonded water molecules which are stable under proper thermodynamic conditions. Kinetic hydrate inhibitors (KHIs) have been employed to manage the risk of hydrate plug formation in oil and gas transmission pipelines for decades (Sloan et al., 2010; Creek, 2012; Englezos, 1996; Kelland, 2006). These low dosage additives (both chemical and biological ones) are able to prolong gas hydrate induction time and control post nucleation crystal growth. While it is of interest to hinder the formation of hydrate plugs, it is also important to assess the influence of these additives on the dissociation of a hydrate plug.

Kinetic inhibitors are known to interact in a complex manner with hydrates. Complex and multiple hydrate melting peaks were observed calorimetrically for hydrate prepared in the presence of the chemical inhibitors like polyvinylpyrrolidone (PVP) whereas a single hydrate peak at a lower melting temperature was observed for hydrate prepared in the presence of an antifreeze protein (biological inhibitor) (Daraboina et al., 2011a). For oil field operators, the existence of multiple melting peaks means the elevated stability with chemical inhibitors which renders their use more challenging. Observations in experiments in stirred vessels were consistent with the calorimetric observations showing a two-stage decomposition for hydrate prepared in the presence of chemical inhibitors (Daraboina et al., 2011b; Ohno et al., 2010) and 5 °C higher melting temperature compared to hydrate prepared in pure water (Makogon et al., 2000). It should be noted that the experiments reported in (Daraboina et al., 2011b) and (Daraboina et al., 2011a) were done with a methane/ethane/propane mixture and those in (Makogon et al., 2000) with a natural gas mixture. There was no explanation about the higher melting temperature in (Daraboina et al., 2011a) whereas the results reported in (Daraboina et al., 2011b; Makogon et al., 2000) were interpreted in terms of

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compositional and structural changes (Daraboina et al., 2011c; Ohno et al., 2012). More specifically, structure II hydrates dominated, as expected, but in the presence of the chemical inhibitors, structure I was also present. Hydrate cavities were found to be filled with more propane molecules than methane in the presence of KHIs. Only structure II was observed with biological inhibitors and almost 10% of the cavities were not filled. We note that ^{13}C NMR reports on the average composition of the sample, and the Raman spectra, taken from micron sized spots, showed that hydrates prepared in the presence of some of the inhibitors showed large changes in composition over the samples.

Two step dissociation of methane/ethane/propane hydrate formed in the presence of chemical kinetic inhibitors was also observed in saline systems (Sharifi et al., 2014a). In addition, hydrates formed in the presence of two antifreeze proteins (AFP I and III) were found to decompose at higher temperatures compared to the hydrates prepared in control solutions (Sharifi et al., 2014b; Walker et al., 2015). Finally, also a delay in the dissociation of a methane/ethane/propane hydrate formed in the presence of salinity, a liquid hydrocarbon phase and AFP III was observed (Sharifi et al., 2014c). Recently, delay in gas hydrate dissociation formed in the presence of different KHIs, was reported for natural gas hydrates(Daraboina et al., 2015b, 2013a).

The observations reported above, we suggest to be a melting *recalcitrance* property of hydrate crystals formed in the presence of kinetic hydrate inhibitors. This property manifests itself as a delay in dissociation, dissociating at higher temperatures than expected and also possible compositional and structural complexities. The fact that hydrates formed from a gas mixture arguably provides a plausible explanation. Surprisingly, dissociation of methane hydrate (sI) formed in the presence of 0.2 and 1 wt % polyvinylcaprolactam (PVCap) (Lachance et al., 2009), and in the presence of Luvicap Bio (Daraboina et al., 2015a) also occurred in two distinct peaks. In addition methane hydrate formed in the presence of Luvicap EG and synergist polyethylene oxide (PEO) was found to decompose at about 4 °C higher temperature compared to water (Daraboina et al., 2013b). Finally, methane hydrate formed in the presence of the poly(VP/VC) inhibitor took longer to decompose completely, as compared to hydrate formed with water only (Bruusgaard et al., 2009). Thus, hydrates formed by a single component and thus preclude structural and compositional complexity also exhibit recalcitrance. Methane is known to form structure I hydrate whereas hydrates formed in the pipelines are typically structure II. It is, therefore, of interest to investigate a structure II hydrate formed by a single component.

In this work, propane was chosen as a gas hydrate former, which can only form sII in the presence of aqueous solutions. The effect of three different kinetic inhibitors both chemical and biological was studied using high pressure micro differential scanning calorimeter.

2. Materials and methods

2.1. Materials

Three kinetic inhibitors were used: a solution (40 wt % in ethanol) of poly vinylcaprolactam (PVCap; average molecular mass of about 23.3 kDa; BASF), a solution (28 wt % in water) of vinylcaprolactam copolymer specially prepared for biodegradation (Luvicap® Bio; BASF) and type III antifreeze protein (AFP III; globular protein with molecular mass of about 7 kDa; A/F protein Canada Inc., Swiss-Prot Database accession number P19414). Deionized water was used to dilute KHIs to prepare solutions in different concentrations of 0.02, 0.2 and 0.5 wt %. propane (UHP grade; Praxair Technology Inc.) was used as gas hydrate former to form structure II (sII) hydrates.

2.2. High pressure micro differential scanning calorimetry (HP-μDSC)

A calorimeter (μDSC 7 Evo; Setaram Inc.) was employed to evaluate the impact of KHIs on gas hydrate dissociation. The gas hydrate dissociation events were detected by endothermic peaks. The area under these peaks corresponds to the amount of the dissociated hydrates which were formed at the experimental conditions (Ohno et al., 2010). The uncertainty of the measured heat flow is 0.02 μW. The high pressure calorimeter and its use in hydrate dissociation is described in detail elsewhere (Sharifi et al., 2014a; Sharifi and Englezos, 2015). Briefly, the calorimeter uses double-stage temperature control with Peltier coolers allowing operation from 228 to 393 K with a programmable temperature heating and cooling rate of 0.001–2 K min^{-1}. The calorimeter is equipped with two 1 mL-high pressure cells (up to 40 MPa) referred to as sample and the reference cell. A customized stainless steel sample holder was used to hold the experimental solutions in the cells. The sample holder has a base with four pits (diameter of 1.5 mm, depth of 2.6 mm) drilled in it, and is supported with a rod (diameter of 1.6 mm, length of 7 mm) (Sharifi et al., 2014a)

2.3. Gas hydrate formation and dissociation in the calorimeter

4 μL of the desired solution were injected into the four allocated pits (1 μL in each) using a micro-syringe. Subsequently, the sample holder was placed in the high pressure sample cell. An empty sample holder was placed in the reference cell, too. Both sample and reference cells were pressurized with propane gas up to 400 kPa at ambient temperature (hydrate cannot form under this condition) and depressurized three times to remove air from the system.

2.3.1. Protocol A: temperature ramping

A temperature ramping protocol was applied to form gas hydrates and consequently dissociate them. In this protocol, the system was pressurized up to 400 kPa with propane and the temperature was stabilized at 287 K for 10 min. Under these conditions, the system is located outside the hydrate stable zone (the calculated gas hydrate equilibrium temperature is about 277 K at the experimental pressure). The temperature was then cooled at a rate of 0.2 K min^{-1} from 287 to 248 K to provide enough driving force (sub-cooling of 29 K) to form gas hydrates. Subsequently, the temperature was ramped up at the same rate from 248 to 287 K to dissociate the gas hydrates formed. Each experiment was repeated at least three times to provide confidence in the data reproducibility, the list of the experiments and the dissociation temperatures are presented in a table. However, only the heat flow profiles of one experiment are presented. To evaluate the impact of heating rate on the hydrate dissociation process in the presence of inhibitors, another set of experiments was conducted at a rate of 0.1 K min^{-1} using 0.5 wt % of PVCap and KHI-free solutions.

2.3.2. Protocol B: temperature ramping containing an isothermal section

To test the potential significance of a kinetic effect in gas hydrate dissociation in the presence and absence of KHIs, protocol B was employed. After the stabilization of the temperature at 287 K for 10 min, the temperature was reduced to 249 with the rate of 0.2 K min^{-1} and then the temperature was kept constant for two hours. Subsequently, the temperature was ramped up to 279 K (about 2 K higher than equilibrium hydrate dissociation temperature) with the heating rate of 0.2 K min^{-1}. The temperature was

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kept constant at 279 K for five hours and then it was increased to 287 K with the same heating rate.

3. Results and discussion

The calorimeter detects phase changes that occur during the experiments by measuring the endo- or exothermic heat associated with the transitions. Gas hydrate dissociation and ice melting are both endothermic processes. Hence, a blank experiment was conducted to distinguish between hydrate dissociation and ice melting. The blank experiment was conducted with the same amount of inhibitor-free solution (4 μL) and under the same temperature ramping protocol but at atmospheric pressure. Fig. 1 illustrates the heat flow profile during the temperature ramping protocol for the KHI-free and blank experiment. Throughout the cooling process, a broad exothermic peak appears starting at about 268 K, which is not detected in the blank experiment (Fig. 1). This peak might be attributed to the propane liquefaction since the calculated saturation temperature at 400 kPa is 267.7 K (CSMGem). Four ice nucleation peaks (exothermic peaks) that corresponded to the four water droplets were detected in the vicinity of 252 K in both blank and KHI-free experiments.

During the heating period, a broad endothermic peak from about 255 to 267 K appears in the KHI-free experiment but not in the blank experiment. This peak might be attributed to propane vaporization. The ice melting peak was detected in the vicinity of 273 K for both blank and inhibitor-free experiments. The endothermic peaks corresponding to hydrate dissociation were distinguished from ice melting peak by a comparison with the peaks from the blank experiment. As it is shown in Fig. 1 (magnified section), the peak, which appeared at about 277 K in the KHI-free experiment and not in the blank experiment was attributed to propane hydrate dissociation at 400 kPa. The calculated equilibrium hydrate dissociation temperature is about 277.2 K at 400 kPa (CSMGem). The list of the propane hydrate formation/dissociation experiments and the detected dissociation temperature are presented in Table 1.

In the KHI-free experiment (Fig. 2, black solid line and Table 1), gas hydrate dissociation (endothermic peak) started at about 277 K, which is close to the expected gas hydrate equilibrium temperature (277.2 K) at 400 kPa. However, in PVCap (0.2 wt %) solution (Fig. 2, blue dotted line and Table 1), hydrate dissociation occurred in three

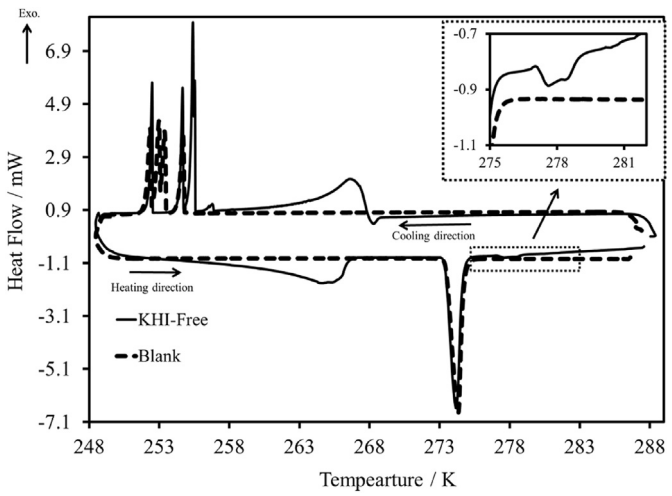

Fig. 1. The heat flow profiles for blank (dashed line) and KHI-free (solid line) experiments under protocol A (Temperature ramping). The inset shows the region in which gas hydrate dissociation occurred. Only a small amount of water was converted to hydrate in this experiment.

Table 1
List of the experiments and the detected dissociation temperatures.

Exp.#	Solution	Dissociation temperature (K)		
		First peak	Second peak	Third peak
1A	KHI-free	277.2	No Peak	No Peak
1B		277	No peak	No Peak
1C		277.3	No Peak	No Peak
Average[a]		*277.2 ± 0.5*	No Peak	No Peak
2A	PVCap (0.02 wt %)	277.3	No Peak	No Peak
2B		277.4	No peak	No peak
2C		277.3	No Peak	No Peak
Average[a]		*277.3 ± 0.2*	No Peak	No Peak
3A	PVCap (0.2 wt %)	277.2	279.8	283.4
3B		277.1	279.6	283.6
3C		277.3	279.5	283.3
Average[a]		*277.2 ± 0.3*	*279.6 ± 0.5*	*283.4 ± 0.5*
4A	PVCap (0.5 wt %)	277.1	279.4	283.9
4B		277.4	279.1	284.2
4C		277.3	278.9	284.3
Average[a]		*277.3 ± 0.5*	*279.1 ± 0.8*	*284.1 ± 0.7*
5A	AFP III (0.02 wt %)	277.3	No Peak	No Peak
5B		277.4	No peak	No peak
5C		277.4	No Peak	No Peak
Average[a]		*277.4 ± 0.2*	No Peak	No Peak
6A	AFP III (0.2 wt %)	280.1	281.5	No Peak
6B		279.8	281.7	No peak
6C		280.2	281.4	No Peak
Average[a]		*280.0 ± 0.7*	*281.5 ± 0.5*	No Peak
7A	Luvicap Bio (0.02 wt %)	277.2	278.5	No Peak
7B		277.1	278.6	No peak
7C		277.4	278.8	No Peak
Average[a]		*277.2 ± 0.5*	*278.6 ± 0.5*	No Peak
8A	Luvicap Bio (0.2 wt %)	282.9	No Peak	No Peak
8B		282.6	No peak	No peak
8C		282.7	No Peak	No Peak
Average[a]		*282.7 ± 0.5*	No Peak	No Peak

[a] Uncertainty values are calculated at 95% confidence for three experimental results.

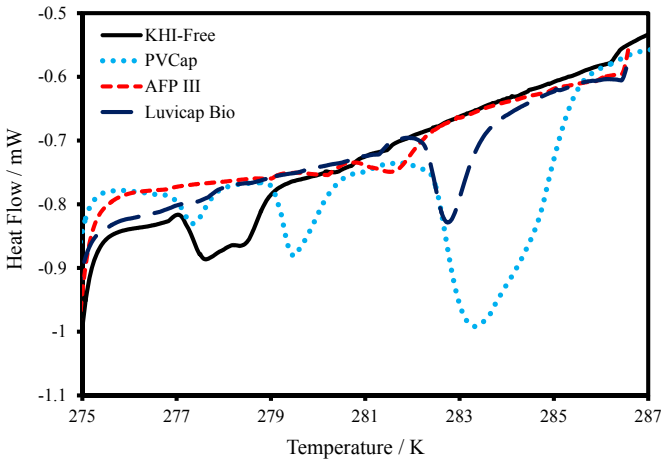

Fig. 2. The heat flow profiles during gas hydrate dissociation for different KHI solutions with a concentration of 0.2 wt % of KHI and KHI-free solution. The hydrate dissociation temperature at 400 kPa is 277.2 K (Protocol A: Temperature ramping). The endothermic peaks represent gas hydrate dissociation in each case.

separate events instead of one as observed in KHI-free sample. The first peak was observed at the expected hydrate equilibrium temperature (277.2 K). However, the other two peaks occurred at about 280 and 283 K, thus at a higher temperature than the expected equilibrium point. Interestingly, in the presence of 0.2 wt % of Luvicap Bio (Fig. 2, dashed blue line and Table 1) hydrate dissociation occurred in one event as the corresponding endotherm

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shifted to about 283 K (almost 5 K higher than the equilibrium point) and no peak was detected at the expected equilibrium temperature (about 277 K).

In the sample containing 0.2 wt % of AFP III (Fig. 2, red dashed line and Table 1) hydrate dissociation occurred in two endothermic events located at higher temperatures (about 280 and 282 K) than the propane hydrate equilibrium temperature. These results are in agreement with the previous published work indicating require higher temperature than equilibrium one for gas hydrate dissociation in the presence of KHIs (Daraboina et al., 2013b, 2011b; Gulbrandsen and Svartaas, 2008a; Lachance et al., 2009; Sharifi et al., 2014a, 2014b). However, in this work, we use a single gas hydrate former (propane), which forms structure II hydrate. Therefore, the higher temperature for gas hydrate dissociation cannot be only attributed to the impact of KHIs on the composition of gas hydrate formed as in the case the presence of a multi-component gas mixture.

The impact of different concentrations of KHI on gas hydrate dissociation is presented in Figs. 3, 5 and 6. Fig. 3 illustrates the influence of three different concentrations of PVCap on propane hydrate dissociation. As shown, at the lowest concentration, (0.02 wt % of PVCap) hydrate dissociation mainly occurred at the expected hydrate decomposition temperature (about 277 K the equilibrium temperature, Table 1). However, in the presence of higher concentration (0.2 and 0.5% wt of PVCap), smaller amounts of hydrate were dissociated in the vicinity of 277 K and the gas hydrate formed decomposed mainly at higher temperatures. Remarkably, comparing 0.2 and 0.5 wt % of PVCap (Fig. 3), in the former one (0.2 wt %, dashed-blue line) the first and the second peaks are larger than the first two peaks in the latter one (0.5 wt %, dotted-blue line). However, the third peak in the presence of 0.5 wt % of PVCap (with the area of 224.3 mJ) is larger than the third peak in the presence of 0.2 wt % of this inhibitor (with the area of 196.3 mJ). In addition, it is evident that by almost doubling the PVCap concentration (from 0.2 to 0.5 wt %) the position of the observed peaks did not change with the highest temperature at about 284 K (Table 1). These results demonstrate that the greater the concentration of KHI, the larger the amount of hydrate decomposed at higher temperatures. Perhaps, in the presence of a higher concentration of PVCap the first and the second peak might disappear and only one large peak would be detected at higher temperature. These results are in agreement with the previous work published to examine the influence of PVCap concentration on methane (Structure I), and methane/propane (Structure II) hydrates (Gulbrandsen and Svartaas, 2008b). It was reported that an increase in PVCap concentration increases gas hydrate

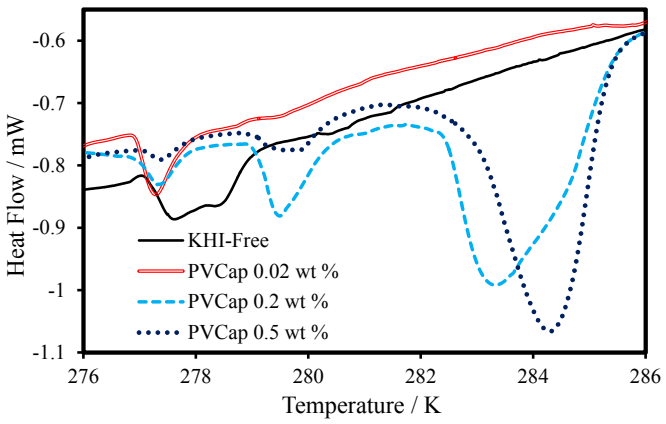

Fig. 3. Heat flow profiles during gas hydrate dissociation for KHI-free solution and different concentrations of PVCap uner Protocol A (Temperature ramping). The hydrate dissociation equilibrium temperature at 400 kPa is 277.2 K (Protocol A: Temperature ramping).

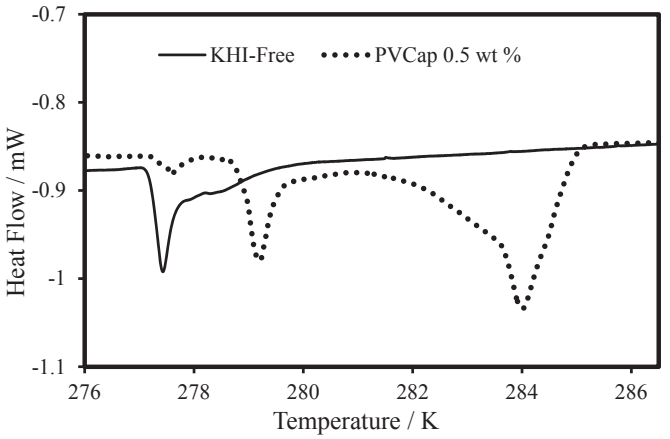

Fig. 4. Heat flow profiles during gas hydrate dissociation for KHI-free and PVCap (0.5 wt %) solutions with the heating rate of 0.1 K min^{-1} instead of 0.2 K min^{-1}uner Protocol A (Temperature ramping) The hydrate dissociation equilibrium temperature at 400 kPa is 277.2 K.

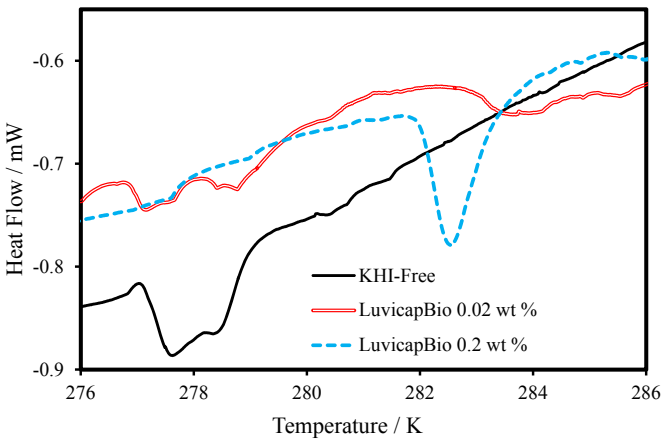

Fig. 5. Heat flow profiles during gas hydrate dissociation for KHI-free solution and different concentrations of Luvicap Bio under Protocol A (Temperature ramping). The hydrate dissociation equilibrium temperature at 400 kPa is 277.2 K.

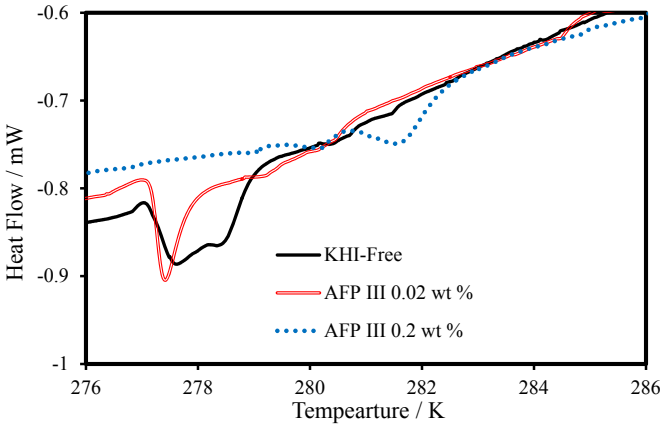

Fig. 6. Heat flow profiles during gas hydrate dissociation for KHI-free solution and different concentrations of AFP III under Protocol A (Temperature ramping). The hydrate dissociation equilibrium temperature at 400 kPa is 277.2 K.

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dissociation temperature. However, a threshold concentration level of inhibitor, above which the hydrate stabilizing effect of the PVCap was not further influenced, was reported.

There is also an important concern about the influence of the temperature ramping rate on gas hydrate dissociation. Therefore, a series of experiments were conducted using PVCap solutions with a concentration of 0.5 wt % and KHI-free solutions under the same conditions as discussed above but with a lower heating rate (0.1 K min^{-1}), to address our concern of the impact of heating rate. Fig. 4 illustrates the results on the influence of the lower heating rate on propane hydrate dissociation. As shown, in the presence of PVCap (0.5 wt %) three dissociation peaks were observed as they were under the higher heating rate (0.2 K min^{-1}) (Fig. 3). However, for the KHI-free solution only one peak was observed at about 277 K, similar to the case for the higher temperature ramping rate (Fig. 3). These results clearly show that the heating rate is not the reason for the multi-peak-dissociation of propane hydrate in the presence of KHIs. The impact of heating rate on dissociation temperature of methane hydrate and mixture of methane/propane hydrate in the presence of PVCap was previously investigated (Gulbrandsen and Svartaas, 2008c), it was reported that hydrate formed in the presence of PVCap dissociated at higher temperature than expected one in different melting rates. Interestingly, the peaks observed for the lower heating rate (0.1 K min^{-1}) are sharper than the peaks detected at the higher temperature ramping rate (0.2 K min^{-1}) (Fig. 4). Nevertheless, the temperature at which the peaks occurred are quite similar to the case with the higher heating rate.

Fig. 5 presents the effect of different concentrations of Luvicap Bio on propane hydrate dissociation. Here, again, at a lower concentration (0.02 wt %), gas hydrate dissociation started at the expected hydrate equilibrium temperature (277.2 K). However, hydrate dissociated in a double-peak event. Interestingly, an increase in the concentration of Luvicap Bio (from 0.02 to 0.2 wt %) increased the propane hydrate dissociation temperature from about 277 to about 283 K (Table 1), and no peak was observed at the expected equilibrium dissociation temperature. The influence of different concentrations of AFP III is presented in Fig. 6 and Table 1. As shown, at a lower concentration of AFP III (0.02 wt %) the propane hydrate formed melted at the expected hydrate equilibrium temperature. Nevertheless, by increasing the concentration of AFP III to 0.2 wt %, the propane hydrate formed decomposed at a higher temperature (about 282 K) (Fig. 6). These results clearly show that an increase in propane hydrate dissociation temperature is related to the concentration of the KHIs, as observed in the presence of PVCap.

Fig. 7 illustrates the heat flow and temperature profiles for PVCap and KHI-free solution under protocol B described in the material and methods. The detected exothermic peaks appeared in the cooling part are attributed to gas hydrate and ice nucleation. The ice melting peak was detected at the vicinity of 273 K (Fig. 7).

Fig. 8 shows the heating section (from 273 to 287 K) of Fig. 7. As seen, in both KHI-free and PVCap experiments, an endothermic peak appeared at about 277 K representing gas hydrate dissociation in both experiments. Interestingly, and while keeping the temperature constant for five hours at 279 K, another endothermic peak was detected in the PVCap experiment, which was not seen in the KHI-free one. Throughout this experiment, the temperature was kept constant at about 2 K higher than the equilibrium temperature (about 277.2 K) for five hours to provide sufficient time for gas hydrate dissociation. However, as seen in Fig. 8, after this period and during temperature ramping up from 279 to 287 K an endothermic peak was observed in the PVCap solution at about 284 K. This peak is at a temperature that is in agreement with the temperature at which a third peak was observed for the PVCap solution

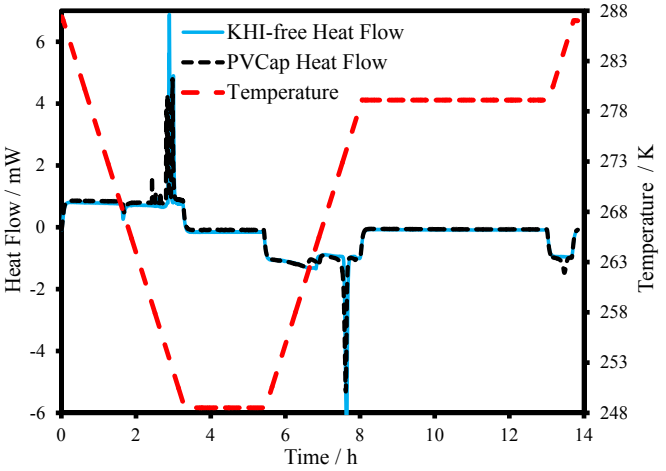

Fig. 7. Heat flow and temperature profiles under protocol B for PVCap and KHI-free solution.

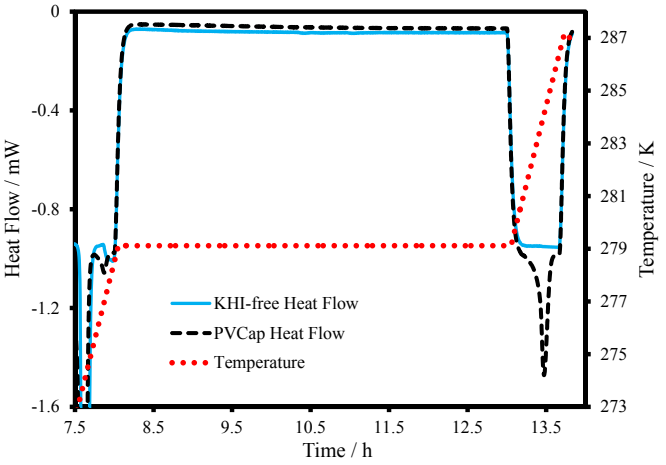

Fig. 8. Heat flow and temperature profiles during heating section (from 273 to 287 K) in protocol B for KHI-free and PVCap solution.

in the temperature ramping experiments (Table 1). The fact that the hydrate remained above the equilibrium temperature for about five hours leads us to believe that the peaks detected at higher temperatures in the presence of KHIs in the temperature ramping experiments could not be attributed to a kinetic effect.

Although an adsorption-inhibition mechanism has been proposed for the performance of KHIs (Anderson et al., 2005), the main mechanism is still not understood and it is not clear how these additives affect gas hydrate dissociation, either. Previously, in the presence of multi-component gas mixtures, it was shown that addition of inhibitors changed the degree of cavity filling and influenced the concentration of guest molecules in the hydrate structures. In spite of the expectation of the formation of sII hydrate in the presence of the tested multi-component gas mixture, the formation of sI hydrate was reported in the presence of KHIs (Daraboina et al., 2011c), too. Hence, gas hydrate dissociation at temperatures higher than expected, was attributed to the formation of unexpected sI hydrate and changes in the occupancy of the hydrate cavities by different guests. However, in this work a single component hydrate former which only forms sII was used to examine the proposed mechanism. As discussed above, the propane hydrate formed in the presence of inhibitors dissociated at

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higher temperatures than the expected equilibrium temperature. Our results show that, in the presence of KHIs, changes in the composition of gas hydrate may not be a reason for propane hydrate dissociation at higher temperatures than equilibrium one. Recently, using molecular dynamic simulation, it was shown that the CH_3 group of the threonine residue of type I AFP molecules was able to fill the methane hydrate cavities and, therefore, inhibit hydrate formation in the presence of AFP I molecules (Bagherzadeh et al., 2015). This proposed mechanism, filling the gas hydrate cavities with the CH_3 groups present in AFP molecules, can be implicated here to explain the impact of these additives on propane hydrate dissociation at higher temperatures. Therefore, at higher concentration of type III AFP more hydrate cavities might be filled with methyl group and then more hydrate will be dissociated at higher temperatures. However, there is no methyl group in PVCap structure and maybe in Luvicap Bio, neither. Perhaps, there are other chemical groups (such as pendant groups) in these two inhibitors which can fill the hydrate cavities (Sloan et al., 2010). Nevertheless, more studies, particularly applying NMR analysis, is crucial to measure the filling of hydrate cavities with chemical groups (such as CH_3) bonded to the KHI molecules. Interestingly, and based on the results presented above, in the presence of high concentrations of KHI, propane hydrate dissociated at higher temperature, this effect might be used to keep gas hydrates stable in an extended temperature region for energy transportation purposes.

4. Conclusions

The impact of three kinetic hydrate inhibitors (PVCap, AFP III and Luvicap Bio) on the dissociation of propane hydrate formed in the presence of these additives was determined using a high pressure micro differential scanning calorimeter. It was observed that higher temperatures were required to dissociate propane hydrate formed in the presence of these KHIs compared to the KHI-free solution. We call this effect a melting recalcitrance property of hydrate formed in the presence of kinetic hydrate inhibitors. In addition, propane hydrate dissociation occurred in more than one steps and was observed in the form of multi dissociation peaks. Interestingly, increasing the concentration of KHIs increased the amount of hydrate, which was dissociated at higher temperatures and, consequently, decreased the amount of hydrate dissociated at equilibrium temperature. In this work, propane was used to form single component sII gas hydrate. Therefore, delay in gas hydrate dissociation could not be attributed to the impact of KHIs on hydrate composition as it was previously reported in hydrates formed by multi-component gas mixtures.

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