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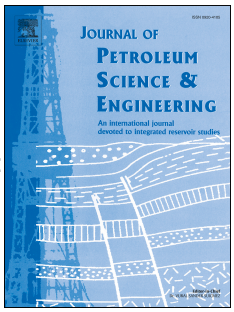

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Anomalous KHI-Induced Dissociation of Gas Hydrates Inside the Hydrate Stability Zone: Experimental Observations & Potential Mechanisms

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Keywords: Hydrate dissociation, KHIs, PVCap, Luvicap Bio

ABSTRACT:

In the past decade, the low dosage hydrate inhibitors (LDHIs) - which include kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs) - have seen increasing use for gas hydrate prevention in hydrocarbon production operations, offering significant CAPEX/OPEX advantages over traditional thermodynamic inhibitors (e.g. methanol, glycols). Typically dosed at < 2.5% in produced water, KHIs were historically considered primarily as hydrate nucleation inhibitors, although in recent years focus has shifted towards their powerful crystal growth inhibition properties. Beginning at low aqueous concentrations, KHI polymers induce a number of highly repeatable, well-defined, hydrate crystal growth inhibition (CGI) regions as a function of

subcooling, varying from complete inhibition, through long induction times and reduced growth rates, to final failure / uninhibited growth. This behaviour can be used to robustly assess KHIs for field use, as we have previously demonstrated through development of the KHI CGI evaluation method, which is now used as standard by a number of laboratories. During CGI testing, it is not uncommon to observe anomalous (should be stable thermodynamically) hydrate dissociation in the presence of KHIs, although very little is understood regarding this phenomenon. In this work, we present the initial findings of experimental studies aimed at investigating this anomalous dissociation for different commercial base polymers. Results demonstrate that, in addition to inhibiting hydrate growth/nucleation, low dosages (e.g. 0.5% and 0.25%) of KHI polymers can induce partial or complete hydrate dissociation, with this process largely generic to different KHIs. However, some KHI polymers cause catastrophic hydrate growth after nucleation begins and these polymers show no ability to dissociate hydrates, so this hydrate dissociation ability is not universal to all KHI Polymers. The cause of this dissociation is unclear, although it is postulated to result from interactions between the KHI and inherent hydrate morphological and/or structural changes. In addition to improving confidence in KHI field use, findings potentially have novel applications with respect to hydrate plug remediation and gas production from naturally occurring hydrates in oceanic/permafrost sediments.

1. Introduction

One of the most common used methods for hydrate prevention is the use of chemical inhibitors, which can be divided into two main categories; thermodynamic hydrate inhibitors (THIs), and low dosage hydrate inhibitors (LDHIs). THIs, e.g. methanol and mono-ethylene glycol (MEG), are ‘anti-freeze’ which shift hydrate phase boundary to lower temperatures / higher pressures by depressing the activity of water (Sloan and Koh, 2007). One of the problems

associated with the use of THIs is large quantities of inhibitor (e.g. 20-50 mass% aqueous) that may be required to prevent hydrate formation, which can cause both cost and logistical issues.

In contrast, LDHIs can inhibit hydrate formation at low dosages, e.g. 0.5-2.5 mass% aqueous. LDHIs are divided into two groups; anti-agglomerants (AAs) and kinetic hydrate inhibitors (KHIs). Both AAs and KHIs were first discovered in the early 1990s; while KHIs prevent hydrate nucleation and growth, AAs allow hydrates to form but prevent agglomeration (Kelland, 2006). However, some studies have shown the synergy effect of THIs and LDHIs(York and Firoozabadi, 2008; Heidaryan et al., 2010), i.e., KHIs can help reduce the amount of thermodynamic inhibitor required for high subcooling operations.

The active components of KHI formulations are typically low molecular weight polymer or copolymers (Kelland, 2006). Poly(vinylpyrrolidone) (PVP) and polyvinyl caprolactam (PVCap) were the first polymers found to have KHI properties (Kelland, 2006). Although KHIs are generally known as ‘anti-nucleators’, delaying the process of hydrate nucleation for extended time periods, they can also completely prevent or slow down hydrate crystal growth up to specific subcoolings within the hydrate region. KHIs can offer significant CAPEX and OPEX advantages over traditional thermodynamic inhibition methods, primarily due to much lower doses required.

Historically, the measurement of nucleation induction / hold times (time to nucleation at a specific subcooling inside the hydrate region) was used as the primary means to evaluate KHIs in terms of hydrate inhibition (Sloan and Koh, 2007; Kelland, 2006; Klomp, 2008). However, as nucleation is a stochastic phenomenon, KHI induction time data are often poorly repeatable / transferable. In recent years, to address this problem, a new crystal growth inhibition (CGI)

method for KHI evaluation has been developed at Heriot-Watt University (Anderson et al., 2011; Luna-Ortiz et al., 2014; Mozaffar et al., 2016). In the CGI method, nucleation stochasticity is removed by testing KHIs in the presence of viable hydrate crystals. Focusing on the ability of the KHI to inhibit the growth of these crystals, three main repeatable regions are measured as a function of subcooling, ranging from complete inhibition region (CIR), through slow growth region (SGR), to final rapid growth region (RGR) / no inhibition. The CGI method procedure is fully described in Section 2.3.

While KHI growth inhibition is increasingly well understood, there is much more limited data on the effect of KHIs on gas hydrate dissociation. There have been a number of reports of KHIs causing anomalously slow dissociation of hydrates outside the hydrate stability zone (Gulbrandsen and Svartås, 2017; Malaret et al., 2008). Gulbrandsen and Svartås in 2017 recently found that not only does PVCap increase apparent hydrate dissociation temperatures, but it also caused reduced cage filling typified by a lower large-to-small cage occupancy in hydrates formed from PVCap systems. Similar behaviour was consistently observed during CGI method development; KHIs, including PVCap, were found to readily reduce hydrate dissociation rates by one order of magnitude for ~5-7 °C just outside the hydrate stability zone (Anderson et al., 2011; Luna-Ortiz et al., 2014; Mozaffar et al., 2016; Glenat et al., 2011), leading to authors refer to this temperature / pressure range as the ‘slow dissociation region’ (SDR).

While there are now a number of studies which show KHIs can affect the hydrate dissociation rate outside the hydrate stability zone, there is very little literature data on the effect of KHIs on hydrate dissociation *inside* the hydrate region. As noted, KHIs are known for preventing / slowing hydrate nucleation and growth. However, as they are not considered as having a thermodynamic THI-type effect (polymer aqueous concentration too low and molecular masses

too high to meaningfully depress water activity), it would not be expected that they could cause hydrate to dissociate. However, Anderson et al., 2011, first reported anomalous hydrate dissociation in PVCap + methane systems inside the hydrate stability zone; this occurring within the CGI method complete inhibition region (CIR). It was noted how 0.5 mass% PVCap results in a CIR of ~5.2 °C subcooling in methane systems, and that hydrates formed at higher subcoolings than this would partially or completely dissociate if warmed back into the CIR, even though they should theoretically be thermodynamically stable. Such behaviour has since been observed in the CIR for many KHIs, and as a result, anomalous hydrate dissociation was made one of the defining / identifying behaviours of the CIR region (Mozaffar et al., 2016). However, the process has mechanisms giving rise to it have not been investigated in depth.

In this work, we report the preliminary findings of an experimental investigation of anomalous hydrate dissociation in the presence of PVCap and Luvicap Bio KHI base polymers in s-I methane and s-II natural gas systems; the aim being to assess this process and its origins. Based on findings, we propose two simple mechanisms by which it may arise.

2. Materials and Methods

2.1. Materials

Three KHIs polymers were used in tests; ‘dry’ PVCap (poly-n-vinylcaprolactam) powder, PVCap as Luvicap-EG, and Luvicap Bio, all supplied by BASF. A brief description of these KHIs polymers is provided in Table 1. Luvicap-EG is PVCap (average MW = ~7000) at ~40 mass% in monoethylene glycol solvent (solvent concentration is too low to affect water activity measurably in aqueous solutions used). The dry PVCap polymer was the same Luvicap-EG with the ethylene glycol solvent removed by vacuum oven drying. Luvicap Bio was ~30 mass%

polymer in a water + MEG solvent mix. For all tests, a dosage of 0.5 or 0.25 mass% active polymer was used in aqueous phase, which made up 70% of cell volume. Distilled water was used in all tests. Methane, supplied by BOC, was 99.995% pure. The composition of the natural gas used (also supplied by BOC) is given in Table 2.

Table 1
A summary of properties of PVCap, Luvicap-EG, and Luvicap Bio. The structure of PVCap is taken from (Kelland, 2006).

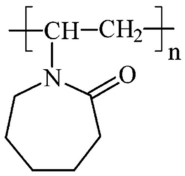
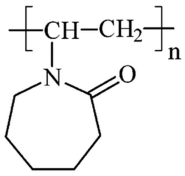
KHI	Structure	Solvent	average molecular weight
PVCap		powder	~7000
Luvicap-EG		40% polymer (PVCap) in MEG	~7000
Luvicap Bio	Commercially sensitive / confidential	30% polymer in MEG + water	Unknown

Table 2
Composition of the North Sea natural gas used in tests.

Component	Mole%
Methane	87.93
Ethane	6.00
Propane	2.04
i-Butane	0.20
n-Butane	0.30
CO2	2.03
Nitrogen	1.50

2.2. Equipment

All experiments were carried out using in-house high pressure stirred autoclaves (Fig. 1) of ~300 ml volume. Autoclave mixing rates were typically ~550 rpm. Autoclave temperature is controlled by circulating coolant from a programmable cryostat unit through a jacket surrounding the cell, with cell temperature measured by a PRT (platinum resistance thermometer) calibrated to give an accuracy of ± 0.1 °C. Cell pressure was measured by a Druck strain gauge (± 0.07 bar), calibrated using a Budenberg dead weight tester. Cell pressure and temperature are continuously recorded by PC, as is motor power, voltage, and rpm for some set-ups.

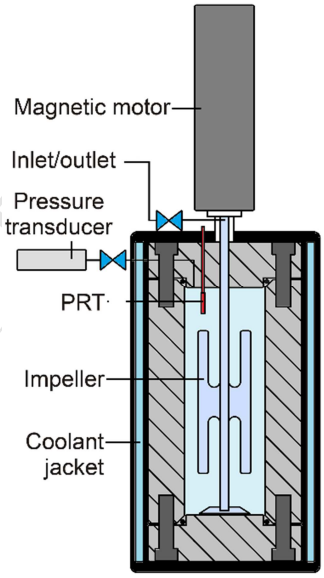


Fig. 1. Schematic illustration of a 280 ml high-pressure autoclave cell as used in experiments.

2.3. Crystal Growth Inhibition (CGI) Method

As described, the CGI method measures three main regions as a function of subcooling: complete inhibition region (CIR), slow growth region (SGR), and rapid growth region (RGR) (Anderson et al., 2011; Luna-Ortiz et al., 2014; Mozaffar et al., 2016; Glenat et al., 2011; Bourg et al., 2013). These regions are described in Table 3. In summary, to determine the CGI regions, different cooling/heating cycles are applied to the system at constant volume as follows.

(1) The system is first cooled rapidly into the hydrate region to form hydrates,

(2) The system is then heated to just outside the phase boundary to dissociate most of the hydrate crystals, leaving the system with viable hydrate crystals to have a 'seeded' system (history/nuclei)

(3) Following the first growth-dissociation cycle, the system is cooled down at different cooling rates (e.g. 1 °C / hour or 1 °C / 24 hours) to observe changes in growth rates/patterns as a function of subcooling. Steps 2 and 3 are repeated for a number of times to examine the repeatability of the reported results.

Table 3
KHI Induced CGI Region Nomenclature and Typical Hydrate Growth Rates (Luna-Ortiz et al., 2014).

Region	Growth rate description	Typical growth rates order of magnitude (% water / hr)
CIR	complete inhibition region	0.00
SGR (VS)	slow growth rate (very slow)	0.01 (<0.05%/h)
SGR (S)	slow growth rate (slow)	0.1 (0.05 ≤ growth rate <0.5%/h)
SGR (M)	slow growth rate (medium)	1 (0.5 ≤ growth rate <5%/h)
RGR	rapid growth region	10 (≥5%/h)
SDR	slow dissociation region	dissociation rate 1 order of magnitude less than for no KHI

2.4. Shut-in Restart (SIR) Type Tests

To investigate the effect of KHIs on hydrate growth rates and abnormal hydrate dissociation inside the hydrate stability region, another 'Shut-in Restart' (SIR) type test was employed. In SIR type tests, the aim is to form hydrates at a set subcooling temperature without any nucleation barrier. The procedure therefore follows the CGI steps 1 and 2 initially to 'seed' the system with hydrate crystals / nuclei. However, before re-cooling, the autoclave stirrer motor is turned off, and the 'seeded' system cooled to a set subcooling temperature, with the lack of mixing preventing any measurable hydrate growth during cooling. At the set target subcooling, mixing is immediately restarted to initiate hydrate growth.

2.5. Hydrate Calculations

Hydrate phase boundaries for both s-I methane and s-II natural gas were predicted using HydraFLASH®, an in-house and commercial thermodynamic model by Hydrafact Ltd. / Heriot-Watt University. The sCPA (Simplified Cubic Plus Association) was used as the equation of state to predict phase equilibria and hydrate phase boundary. In addition, the theoretical s-II methane hydrate phase boundary was predicted by HydraFLASH; the software was forced to predict s-II methane phase boundary based on the assumption that s-I is not stable. The term of theoretical is due to the fact that there is no experimental data for the s-II methane phase boundary and the model uses tuning parameters for methane in s-II small and large cages to predict theoretical stability. The estimated percentage of water converted to hydrate was calculated based on the method of Aminnaji et al., 2017, from change in pressure / gas consumption data.

3. Result and Discussion

As noted, literature studies using the CGI method conclusively prove the existence of a complete inhibition region (CIR) inside the hydrate stability zone to a specific subcooling in the presence of KHIs. The subcooling extent of the CIR and hydrate fraction (of water converted) to which this applies are as a function of the polymer concentration and pressure. For the test conditions studied here, the CIR extent for 0.5% PVCap with methane is ~5.2 °C (Anderson et al., 2011). For Luvicap Bio, this is around ~3 °C and 8.5 °C in the methane and natural gas system respectively, as measured as part of this work (see Sections 3.3 and 3.4). Studies reported here focused on anomalous hydrate dissociation for these CIR conditions; while complete nucleation and growth inhibition has been well established, associated anomalous dissociation behaviour is not.

3.1. 1.4% PVCap Aqueous + Methane System

Fig. 2 presents experimental cooling / heating curve data for the 1.4 mass% PVCap aqueous with methane system. For these tests, the system was initially cooled down rapidly to form a large fraction of hydrates at high subcooling. Temperature was then increased to outside the hydrate region, allowing some dissociation at a constant temperature. Systems were subsequently cooled quickly again into the hydrate stability zone, then cooled slowly (1 °C / 24 hours, green datasets). Three runs with ~13, 21, and 30% water converted to hydrates (calculated from pressure drop) on re-cooling were carried out. In Fig. 2, the blue, red, and green datasets represent rapid cooling, hydrate dissociation at a constant temperature, then very slow cooling (1 °C / 24 hours) respectively. As can be seen, for all three experiments with different initial

hydrate fractions on re-cooling, significant anomalous hydrate dissociation inside the hydrate phase boundary was observed.

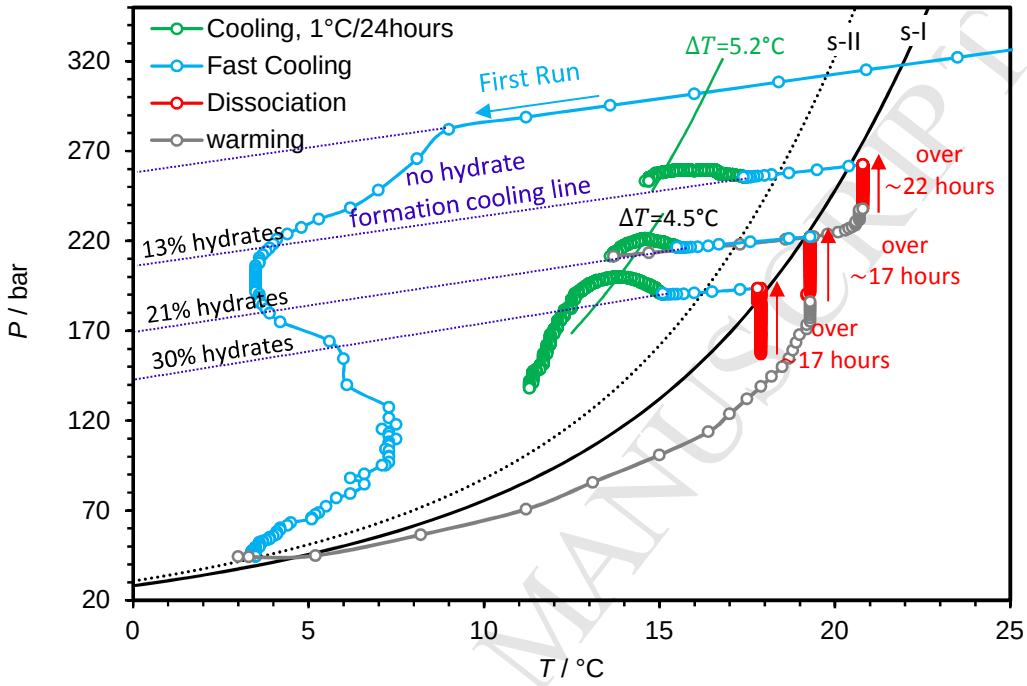


Fig. 2. Pressure-Temperature plot of cooling/heating curve data for the 1.4 mass% PVCap aqueous with methane gas system. The green line (e.g. 5.2 °C subcooling) is the standard extent of CGI CIR for the initial concentration of KHI. Data points are every 5 minutes.

As shown in Fig. 2, the anomalous hydrate dissociation behaviour inside the hydrate region stops, as expected, at the subcooling of the CIR boundary, i.e. in conjunction with the end of complete crystal growth inhibition. Furthermore, both the CIR subcooling extent – and therefore the extent of anomalous hydrate dissociation – reduce as the total fraction of water converted to hydrate increases; from ΔT = 5.2 °C (up to 13% hydrates) to 4.5 °C (to at least 30% hydrates) for the tests detailed here. This reduction in CIR extent with increasing water conversion is seemingly ubiquitous to KHI systems, and is most simply explained by a progressive reduction

in remaining KHI in solution. It can be envisaged that as the hydrate fraction increases, so more polymer is absorbed on crystal surfaces, reducing the remaining aqueous concentration, and so weakening further CGI inhibition.

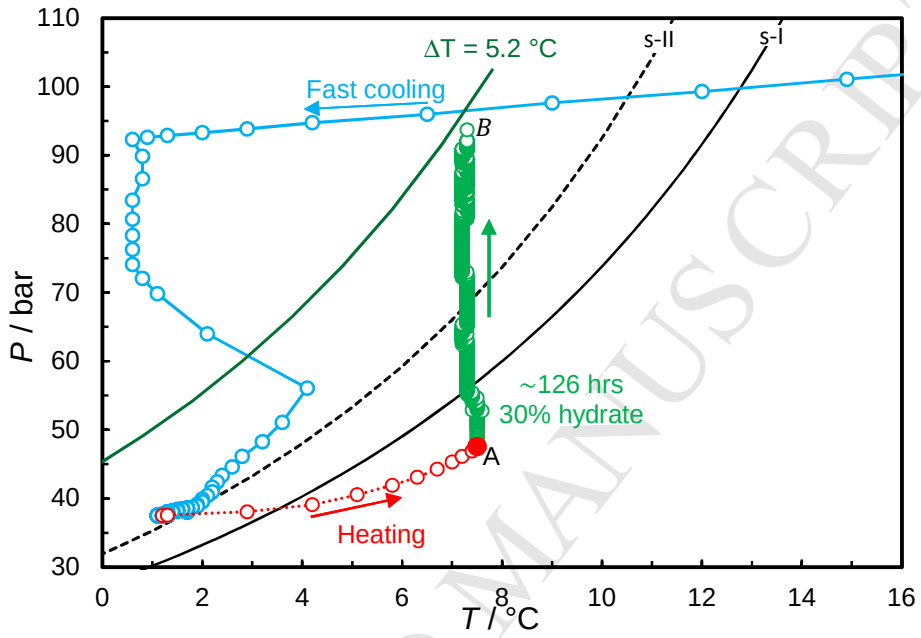


Fig. 3. Pressure-Temperature plot of cooling/heating curve data for the Luvicap-EG (0.5 mass% PVCap) + methane system. Green line (5.2 °C subcooling) is the standard extent of the CIR for the concentration of KHI present. Data points are every 5 minutes.

3.2. 0.5% Luvicap EG Aqueous + Methane System

To further assess anomalous KHI induced hydrate dissociation, tests were also undertaken on an aqueous Luvicap EG with methane system. The PVCap polymer concentration was the same as for tests in Section 3.1 at 0.5 mass% relative to water.

Fig. 3 shows experimental cooling/heating curves for the test. In a similar procedure to Section 3.1 experiments, temperature was first reduced rapidly to form hydrates at a high subcooling. Following this, temperature was likewise raised until PT conditions were outside the hydrate region and dissociation had begun at point A, where ~30% of water was converted to

hydrates. Unlike previous tests, however, instead of cooling again, system temperature was kept constant. As shown in Fig. 3, this resulted in the bulk of hydrates present in the system (~30% of water converted) dissociating over 126 hours, with most of this dissociation occurring within the hydrate region where hydrates should be thermodynamically stable. As for the PVCap tests in Section 3.1, this anomalous dissociation took place entirely within the complete inhibition region for KHI concentration tested.

3.3. 0.5% Luvicap Bio Aqueous + Methane System

In addition to experiments on PVCap, tests were also carried out on 0.5 mass% Luvicap Bio polymer aqueous with methane. As standard, the system was first cooled to a high subcooling to form hydrates before being then heated to dissociate hydrates. However, in tests here, rather than retaining a large hydrate fraction, almost all hydrates were dissociated, leaving only a minute fraction present or just hydrate 'history' (seeded system), as per the CGI method. Then, in contrast to previous tests, a shut-in / restart (SIR) procedure was carried out, as described in Section 2.4. As shown in Fig. 4, the SIR tests were carried out at three different subcoolings (~5 °C, ~7 °C, and ~9 °C) inside the hydrate region; subcooling being increased in steps of 2 °C beyond the CIR at ΔT = 3 °C.

As was expected, no hydrates formed within the complete inhibition region (CIR). At subcoolings higher than this, hydrate growth at different rates were initially observed in all SIR tests, as shown in Fig. 4. As the gas to water ratio used, and with the polymer not depressing the water activity measurably, hydrate growth was expected to result in pressure falling until equilibrium was reached on the s-I phase boundary for the system, as illustrated. This seemed to be the pattern, at least initially.

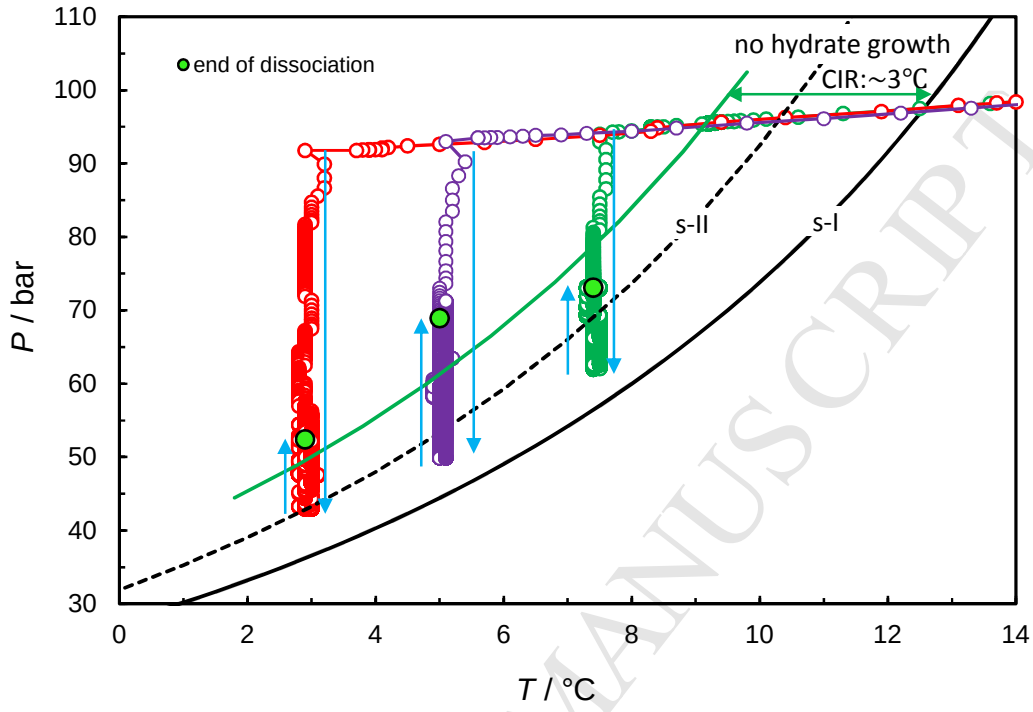


Fig. 4. Pressure-Temperature plot of data for multiple growth pattern measurement runs at different subcoolings for the 0.5 mass% Luvicap Bio + methane system. Aqueous phase was 70% of cell volume. Data points are every 5 minutes.

As shown in Fig. 4, initial hydrate growth was rapid in all cases, as would be expected for these well mixed systems at higher subcoolings where the KHI has only weak inhibition. Growth rates then reduced as pressure fell and PT conditions approached the expected equilibrium on the hydrate phase boundary. However, in all three cases this equilibrium was not reached, and instead, anomalous hydrate dissociation began within the hydrate stability zone.

Fig. 5 shows an example plot of pressure and temperature as a function of time for the Luvicap Bio SIR run initiated at 7.5 °C (ΔT=~5 °C). As can be seen, after initial rapid growth, PT conditions fall toward the phase boundary at lower subcoolings where the KHI can start to

inhibit hydrate growth. This causes growth to slow markedly, although it continues up to around 75 hours, beyond which it appears to stop for ~ 25 hours. At this condition, it is calculated that ~9% water was present as hydrates, although the pressure had not fallen to the phase boundary as would be expected. After this period, hydrates unexpectedly started to abnormally dissociate without any change in system conditions. While the process was very slow, over the course of the next 350 hours, the water fraction as hydrate reduced by nearly half from 9% to 5%, i.e. nearly half the hydrate initially formed subsequently dissociated anomalously. Following this, pressure stabilised with no obvious further dissociation or growth taking place.

A similar pattern was observed for all 3 SIR run tests, with substantial fractions of the hydrate initially formed at constant temperature subsequently proceeding to dissociate, even though no system parameters had been changed. Such behaviour is very much at odds with what would be expected; methane hydrate being thermodynamically stable at test conditions. This anomalous dissociation is similar in nature to that seen for PVCap (and other KHI polymers) and some possible explanations for its origins are discussed in Section 3.5.

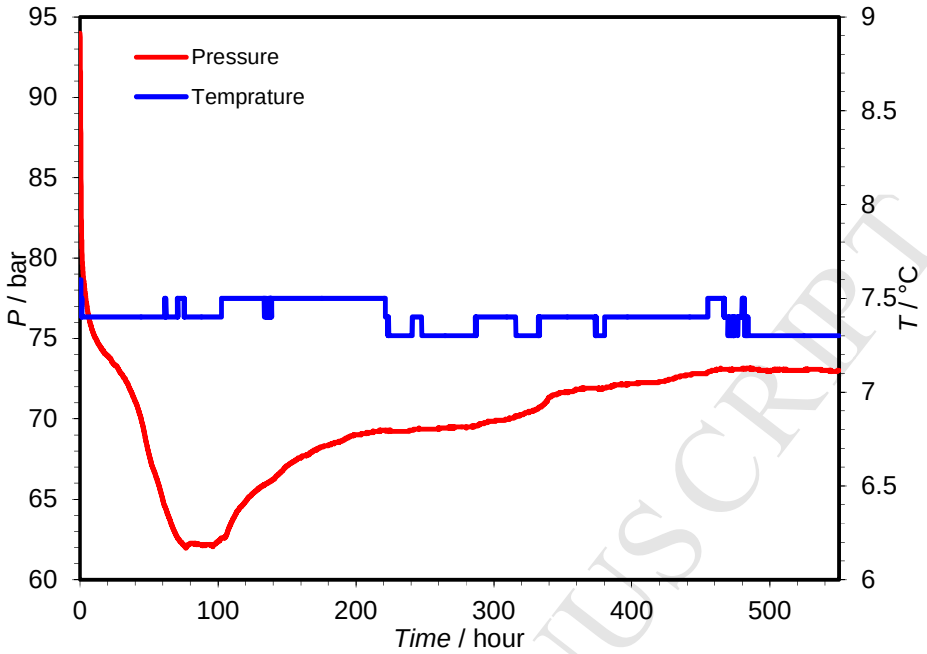


Fig. 5. Plot of pressure and temperature versus time for 0.5 mass% Luvicap Bio + methane SIR test initiated at 7.5 °C (ΔT=~5 °C) (Fig. 4).

3.4. 0.25% Luvicap Bio Aqueous + Natural Gas System

To further assess anomalous dissociation of hydrate in the presence of KHIs, work progressed onto the 0.25 mass% Luvicap Bio in a North Sea type natural gas system. Fig. 6 presents experimental cooling / heating curve data for this system. As part of measuring CGI regions initially, the system was first cooled down rapidly to form a large fraction of hydrates at high subcooling. Temperature was then increased to outside the hydrate region, allowing some dissociation at a constant temperature. CGI method instant cooling runs were then performed, followed by then by a standard step-cooled run (1 °C / 24 hours). As shown in Fig. 6, the CIR (complete inhibition region) extent for this system is ~8.5 °C subcooling temperature from the s-II phase boundary. This allows investigation of potential anomalous hydrate dissociation inside the hydrate phase boundary for a much wider range of subcooling temperature than is the case for methane systems, and findings have more specific relevance to real oil and gas systems.

Abnormal hydrate dissociation induced by Luvicap Bio was investigated at two subcoolings; 3.5 °C and 7 °C. As shown in Fig. 6, the green data points (points are 5 minutes) definitely confirm the ability of Luvicap Bio to induce hydrate dissociation in the CIR inside the hydrate phase boundary; hydrate actively dissociates on cooling into the hydrate region. In addition, results show that the hydrate dissociation rate using Luvicap Bio in the CIR decreases as subcooling temperature increases, i.e., while 30 psi (~ 2.1 bar) increased over 121 hours at 3.5 °C subcooling temperature (dissociation rate: 0.25 psi/hour), it took 196 hours to increase 20 psi (~ 1.4 bar) at 7 °C subcooling temperature (dissociation rate: 0.1 psi/hour).

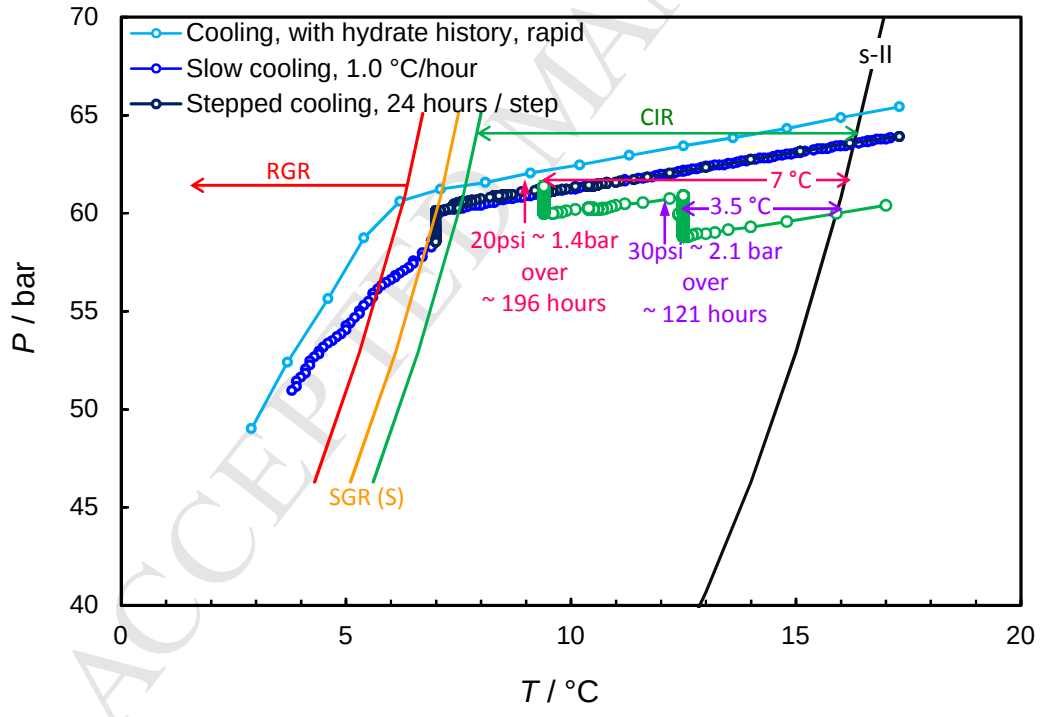


Fig. 6. Pressure-Temperature plot of cooling/heating curve data for the 0.25 mass% Luvicap Bio with natural gas system. The green line (8.5 °C subcooling) is the extent of CIR for the initial concentration of KHI. Heating / cooling curve points are every 5 minutes.

3.5. Causes of Anomalous Dissociation in the Presence of KHIs

When first observing anomalous dissociation of hydrate in the presence of KHIs (Anderson et al., 2011), (Mozaffar et al., 2016), Anderson et al. briefly speculated that it possibly arose as a result of polymers interfering with the process of hydrate recrystallization to more stable crystals with a lower surface to volume ratio. For example, if the hydrates are formed at a very low temperature and high subcooling giving a high growth rate, it may result in hydrate crystals with high surface to volume ratio (e.g. dendrites, needles). Visual observation of gas hydrates (including methane hydrates) at the microscopic scale in synthetic porous media provides evidence for formation of high surface to volume ratio hydrate crystals at high subcooling which subsequently undergo significant post-growth recrystallization processes (Tohidi et al., 2001). In addition, for ice, various studies have shown that crystal growth morphologies and growth rates vary with subcooling considerably, e.g. needle like crystals could be formed at > 4.1 °C subcooling temperature (Shibkov et al., 2003). As a result, it was speculated the same is likely to be happening in hydrate systems and high surface to volume ratio crystals are formed at higher subcoolings. These hydrate crystals may not be thermodynamically favoured and need to recrystallize to lower surface to volume crystals if subcooling was subsequently reduced. However, the process of recrystallization involves both a dissociation and a re-growth component. KHIs are not known to stop dissociation (although they can slow it), but they can prevent hydrate growth. Therefore, should such recrystallization take place, KHIs could allow dissociation but prevent re-growth, resulting in net dissociation. This potential mechanism is illustrated in Fig. 7.

Kvamme et al. 2005 showed using molecular dynamic simulations that monomers of kinetic hydrate inhibitors like PVCap could potentially dissociate hydrates through such reformation /

dissociation processes (Kvamme et al., 2005). Results suggested that monomers could undergo hydrogen bonding with the hydrate at the water-hydrate interface and dissociate the hydrate in two steps; slow dissociation of half cages and then rapid dissociation of the other side of hydrate crystal. Similar processes could be occurring for the polymeric systems studied here.

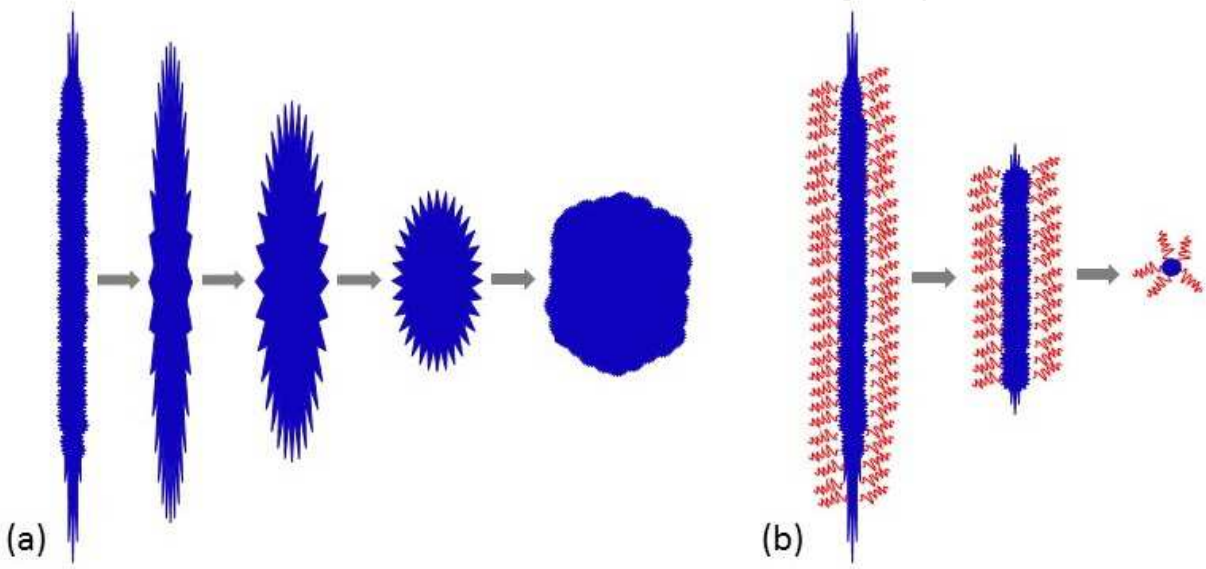


Fig. 7. Recrystallization of hydrates (a) without KHI polymer results in crystals with a lower surface to volume ratio forming, while for (b) KHIs interfere with this process resulting in net hydrate dissociation.

In addition to recrystallization to achieve lower surface to volume crystals, such processes might also occur in response to structural changes. Methane hydrate is generally understood to form simple s-I hydrates due to its small molecular diameter stabilising the large cavity of s-I better than it does s-II. This means at moderate temperatures and pressures, s-I is the more stable structure in terms of maximum upper temperature extent (at a given pressure) of the hydrate stability region. However, methane is known to stabilize structure-II at very low temperatures /

very high pressure (>1200 bar at room temperature) (Chou et al., 2000; Shimizu et al., 2002; Hirai et al., 2000; Loveday et al., 2001), but is generally not considered as doing so at the experimental conditions studies here (<300 bar).

In contrast to the above, Schicks and Ripmeester, 2004. reported the coexistence of s-I and s-II methane hydrates at low pressure conditions of 30-90 bar and 1.5-12 °C (Schicks and Ripmeester, 2004). Authors proposed the s-II hydrates formed to be metastable as they observed these to subsequently convert to s-I when temperature conditions were changed. However, results do support the temporary formation and coexistence of two structures, and that this may be a common feature of the growth process of hydrates in methane systems. However, Ohno et al. (2009) reported formation of both s-I and s-II hydrates and structural conversion from metastable to stable hydrate structures in methane-ethane gas mixtures of 65% or 93% CH4 and water, with and without PVCap. They reported that the degree of metastability depends on gas composition, i.e., structural conversion is much faster at higher methane concentration. Furthermore, in a study of the structural properties of methane (93%) + ethane (5%) + propane (2%) hydrates formed with and without KHIs, Ohno et al. (2012) reported that sI hydrates were less stable than sII crystals, and there was a conversion to the stable phase over time. Several inhibitors (poly-N-vinylpyrrolidone, a proprietary commercial product, as well as two biological inhibitors) were studied, and all retarded the structural transition from sI to sII hydrates. Similar structural recrystallization processes could very well explain the observed anomalous dissociation in the systems tested here. Fig. 8 shows an illustration of the suggested structural change from metastable s-II to s-I; this requires the (at least partial) dissociation of s-II hydrate crystals and regrowth as s-I. If as per our earlier example (Fig. 7) the KHI permits the

dissociation of s-II but completely inhibits the re-growth of this as s-I, then this could likewise result in net dissociation of gas hydrate observed.

As there is almost no information on the PT stability extend of this metastable s-II hydrate, it is difficult to predict where the processes described might occur. Fig. 4 shows the HydraFLASH commercial model predictions for theoretical s-II methane hydrates (based on the assumption s-I is not stable, with the model using tuning parameters for methane in s-II small and large cages to predict theoretical stability). As can be seen, an s-II phase should apparently be stable, at least transiently, beyond around 2 °C subcooling inside the s-I phase boundary at the modest pressure conditions studied. Therefore, the formation of transient s-II – and subsequent interference by KHI polymer of in its attempted subsequent transition to s-I – could quite possibly offer a mechanism by which the observed anomalous dissociation could occur. Speculatively, looking at results in Fig. 4, it might be suggested that as pressure fell outside the s-II stability region during growth, so the s-II to s-I transition began in earnest. As Luvicap Bio allowed the dissociation of s-II but stopped s-I re-growing to replace it, so net dissociation anomalously occurred.

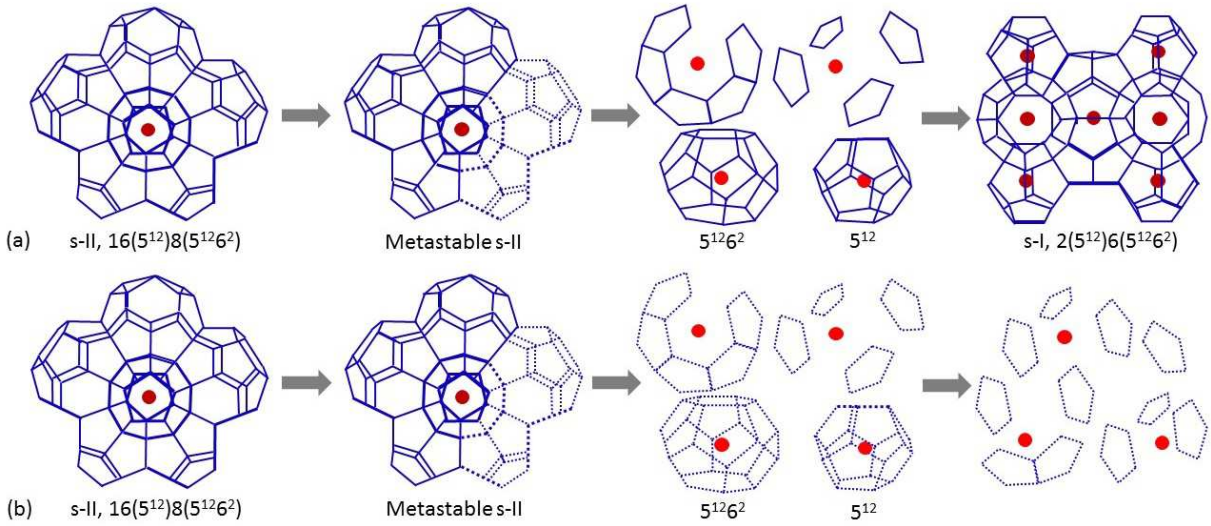


Fig. 8. Illustration of structural transitional mechanism of hydrate crystals from s-II to s-I without (a) and with (b) KHI polymers present. In the presence of KHI, regrowth as s-I is prevented, resulting in net hydrate dissociation.

4. Conclusion

The ability of different KHIs polymers to induce hydrate dissociation inside the hydrate stability region has been investigated experimentally. It was found that PVCap, Luvicap EG (PVCap in monoethylene glycol), and Luvicap Bio not only can prevent hydrate nucleation/growth in methane systems, but also induce abnormal hydrate dissociation inside hydrate stability region up to 3-5 °C subcooling, specifically within the KHI complete inhibition region (CIR) as described in the CGI evaluation method. In application real North Sea type natural gas system, results show that Luvicap Bio could induce hydrate dissociation inside natural gas hydrate stability region up to 8.5 °C subcooling temperature. This behaviour can result in the partial to almost complete dissociation of gas hydrates where thermodynamically

they should be stable. Anomalous dissociation commonly occurs when hydrate formed at high subcoolings is warmed to lower subcoolings, but can also occur apparently spontaneously at constant temperature, with hydrate growth suddenly reversing, causing the disappearance of large fractions of hydrate previously formed.

Two recrystallization processes are suggested as being the root of the anomalous dissociation: (1) reformation to reduce surface to volume ratios of needle-like / dendritic crystals formed initially and (2) the transition of initially formed metastable s-II hydrate structures to stable s-I. In both cases, KHIs polymers allow the dissociation but not the regrowth components of such recrystallization processes, causing a net hydrate loss.

Finding are of significance with respect to the traditional use of KHIs for hydrate prevention in oil and gas production pipelines, in addition to offering novel possibilities for plug removal using KHIs. Similarly, biodegradable polymer injection might present a means to induce the dissociation of naturally occurring gas hydrate in sediments for the purposes of methane gas production.

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Highlights

- Gas hydrate dissociation using kinetic hydrate inhibitors.
- PVCap, Luvicap-EG, and Luvicap Bio induce hydrate dissociation inside hydrate phase boundary
- The recrystallization is suggested as being the root of the anomalous dissociation