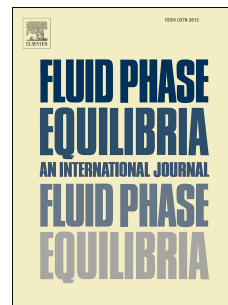# Accepted Manuscript

Effect of alcohols and diols on PVCap-induced hydrate crystal growth patterns in methane systems

Houra Mozaffar, Ross Anderson, Bahman Tohidi

EFFECT OF ALCOHOLS AND DIOLS ON PVCAP-INDUCED HYDRATE CRYSTAL GROWTH PATTERNS IN METHANE SYSTEMS

Houra Mozaffar[1,2*], Ross Anderson[1,2], and Bahman Tohidi[1,2]

1. Centre for Gas Hydrate Research, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland, United Kingdom & 2. HYDRAFACT Ltd., Heriot-Watt University Research Park, Edinburgh EH14 4AP, Scotland, United Kingdom

ABSTRACT

Methanol (MeOH), mono-ethylene-glycol (MEG) and ethanol (EtOH) are the most widely used thermodynamic hydrate inhibitors (THIs) for hydrate inhibition in hydrocarbon production operations. However, effective use of THIs often requires large quantities, which demands large storage, regeneration, and injection facilities which increase CAPEX/OPEX, in addition to environmental concerns. As a result, low dosage Kinetic Hydrate Inhibitors (KHIs) are seeing increasing use as a potential alternative for hydrate prevention, either partly or wholly replacing THIs. Combining KHIs with THIs offers a potential means to increase the sub-cooling to which KHIs can be used (THI acts as a 'top-up' inhibitor), while KHIs can be potentially used to reduce THI volumes. If the benefits of such combinations are to be realised, a better understanding of combined performance is required. Here, we report the results of experimental studies of combined KHI and THI methane hydrate inhibition performance using a Crystal Growth Inhibition (CGI) method previously developed at this laboratory. The KHI used for all tests is PVCap (poly-n-vinylcaprolactam) and the initial THIs investigated were MEG, MeOH and EtOH. For a more comprehensive understanding of the effect alcohols and diols (mainly the effect of the alkyl 'tail' carbon number of these chemicals) on PVCap performance, three other alcohols (n-propanol (n-POH), i-propanol (i-POH) and n-butanol (n-BOH)) and two other diols (1,3-propanediol (1'3-PDO) and 1,4-butanediol (1,4-BD)) have also been examined in the presence of this KHI. Results show that neither MeOH nor EtOH act as full 'top-up' thermodynamic inhibitors for PVCap: KHI-induced CGI regions are consistently reduced to lower sub-coolings as THI concentration is increased in both cases, although a negative effect is seen, which is more pronounced with EtOH than MeOH. Furthermore, n-POH and i-POH have slight negative effects on PVCap performance, while n-BOH has not shown this negative behaviour and has not reduced any of the CGI regions to lower sub-coolings. In contrast, MEG was found to consistently act as a full 'top-up' thermodynamic inhibitor to PVCap: CGI regions were larger or equal to those for PVCap alone, and were present on top of the thermodynamic inhibition offered by MEG up to concentrations of 50 mass%. Furthermore, MEG has an increasingly synergistic effect on PVCap as the concentration is increased, reducing hydrate growth rates in CGI regions where growth does occur. However, the findings indicate neither 1,3-PDO nor 1,4-BD seem to offer the same good synergism as MEG, and that the favourable properties of the latter are not ubiquitous to all diols: increasing central alkyl chain length of glycols progressively eliminates top-up properties.

Keywords: Gas Hydrates, Kinetic Hydrate Inhibitors, Alcohols, Diols, Crystal Growth Inhibition

1. INTRODUCTION

While Thermodynamic Hydrate Inhibitors (THIs) such as methanol and MEG are widely used for hydrate prevention in the oil and gas industry, the large quantities of inhibitor often required can result in significant CAPEX/OPEX. As a result, recently, the use of Kinetic Hydrate Inhibitors (KHIs) has become increasingly popular over traditional thermodynamic inhibitors as an alternative, more cost effective technology [1,2,3]. Furthermore, for high sub-cooling operations and/or high water-cut

* Corresponding author: Phone: +44 (0)131 449 7472 E-mail: houra.mozaffar@hydrafact.com

systems, KHIs offer a potential means to reduce the amount of thermodynamic inhibitor required [4]. Likewise, thermodynamic hydrate inhibitors such as methanol and ethylene glycol can potentially be used as a 'top-up' inhibitor to KHIs, increasing the total inhibition offered. To fully exploit KHI-THI combinations however, it is important to understand their interaction/compatibility with respect to hydrate inhibition.

Research has shown that although methanol is an effective thermodynamic hydrate inhibitor, it can actually enhance the rate of hydrate nucleation/formation when at low concentrations in water [5]. In addition, it has been found that, methanol (MeOH) has an unfavourable effect on the performance of PVCap; a well-known and one of the best performing KHI polymers [1]. The sub-cooling to hydrate formation decreases in linear proportion to the concentration of methanol, indicating that PVCap is less effective in the presence of methanol [6]. However, it has been found that the combination of thermodynamic inhibitors and kinetic inhibitors give better results [7].

While the above findings are useful for understanding the influence of THIs on KHIs, techniques used in the mentioned investigations are limited to the onset of hydrate formation. In this work, investigations have been undertaken using a new Crystal Growth Inhibition (CGI) technique, as developed by Anderson et al. [8]. This method has enabled us to avoid the problem of data stochasticity associated with nucleation / induction time (t_i) measurements and produce very reliable/repeatable results. This information is beneficial for gaining a more comprehensive understanding of the effects of THIs on KHIs which is essential for concluding how the combination of these chemicals perform in terms of hydrate inhibition. The new CGI method used in this study is increasingly becoming an industry standard method for KHI evaluation and is now being used by a number of companies in the oil and gas industry as test protocol [9,10].

In addition to MeOH, ethanol (EtOH) is another alcohol which is seeing increasing use as a thermodynamic hydrate inhibitor due to its better environmental credentials. However, ethanol can in fact form clathrate hydrates at conditions pertinent to offshore operations [11]. Hence, carefully evaluating the effect of this thermodynamic inhibitor on KHI performance is also crucial for understanding the behaviour of the KHI-EtOH combinations.

Combinations of PVCap and two other alcohols –namely n-propanol and n-butanol, which have similar properties/molecular structures to MeOH and EtOH but different number of carbons in the alkyl 'tail'- also have been examined. Investigating the effect of these alcohols will help to understand the effect that the alkyl 'tail' carbon number of alcohols can have on PVCap performance. Furthermore, PVCap performance in the presence of i-propanol which has the same molecular formula but different structure to n-propanol has been examined to better distinguish the potential role of alcohol alkyl 'tail' and alcohol molecular weight on PVCap performance.

Mono Ethylene Glycol (MEG) is one of the most widely employed thermodynamic hydrate inhibitors and is a commonly used as carrier solvent / synergist chemical in KHI formulations. However, there is limited research on the performance of combinations of glycols and KHIs as hydrate inhibitors. In one study by Wu et al. (2006), the inhibition performance of mono-ethylene-glycol (MEG) and a kinetic hydrate inhibitor (VC-713) were tested individually and together. The study showed that the combination of MEG and the kinetic hydrate inhibitor had an overall better performance [7]. On the other hand, a study by Yousif, 1998 on the hydrate control process with MEG has shown that although mono-ethylene glycol is known to suppress hydrates when added in adequate amounts to water, it tends to enhance the rate and amount of hydrate formed when present in small concentrations [5]. Taking both these studies into consideration, further investigations on hydrate formation and growth behaviour in the presence of MEG + KHI is required to better understand the combined performance.

Furthermore, other diols − namely 1,3-propanediol (HO-[CH2]$_3$-OH) (1,3-PDO) and 1,4-butanediol (HO-[CH2]$_4$-OH) (1,4-BD), which have similar properties/molecular structures to MEG and only differ by additional carbons in the central alkyl chain − show similar performance to MEG in these

systems. Testing of these chemicals assist in gaining a better understanding of the effect of diol structure (mainly alkyl 'tail' carbon number) on PVCap performance and suggest a more reliable explanation for any behaviour observed.

2. EXPERIMENTAL

2.1. Materials and Methods

All the experiments were performed using constant volume methods, conducted on in-house (Hydrafact/ Heriot-Watt University) designed/built 280 ml volume high pressure (max 410 bar) stainless steel or titanium (salt compatible) autoclave cells, as illustrated in Figure 1. Cell temperature in this setup is controlled by circulating coolant from a programmable cryostat, which can maintain the cell temperature to within 0.1 °C, through a jacket surrounding the cell. The inside temperature of the cell is determined by a platinum resistance thermometer (PRT, ± 0.1 °C) which is connected to a computer for direct acquisition. Cell pressure is measured by either strain gauge pressure transducer (± 0.4 bar) or precision Quartzdyne (± 0.07 bar) transducer; these being regularly calibrated against a dead weight tester. The pressure transducer is mounted directly on the cell and connected to the same data acquisition unit as the temperature probe. This allows real time monitoring and recording of cell temperature and pressure throughout different temperature cycles.

To achieve a thermodynamic equilibrium quickly and create a state where all phases have as equal as possible ability to interact with each other, a stirrer with a magnetic motor was used to agitate the test fluid. Accordingly, to aid further mass transfer and maximise reaction rates, the impeller speed was normally set at ~750 rpm, giving good shearing/co-mingling of the aqueous and gaseous phases. Cell aqueous liquid volume fraction was typically 0.80-0.85.

The KHI polymer used in tests was poly-n-vinylcaprolactam (PVCap) which was Luvicap-EG base polymer (average molecular weight / AMW =~7000) supplied by BASF with the ethylene glycol solvent removed by vacuum oven drying. All five alcohols used in the tests were supplied by Fisher Scientific and the purity of each alcohol was as follows; Methanol 99.5%, Ethanol 99.5%, n-propanol 99.9%, i-propanol 99.0% and n-butanol 99.4%. also, mono-ethylene-glycol used was supplied from SIGMA ALDRICH with a purity of 99.5%, 1,3-propanediol 99.0% supplied by Fluka Analytical and 1,4-butanediol 99.0% supplied by SIGMA ALDRICH. Ultra-high purity grade methane gas (99.995% pure) supplied by BOC was used. Solutions were prepared using deionized water throughout the experimental work with aqueous PVCap solutions prepared gravimetrically.
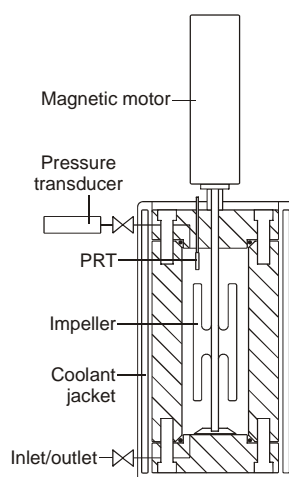

Figure 1 Schematic diagram of the 280 ml high pressure (max 410 bar) autoclave cells used in the experiments.

In all experiments, the thermodynamic hydrate phase boundary was predicted using the HydraFLASH® 2.2 model from Hydrafact / Heriot-Watt University [12] or determined experimentally as appropriate by the isochoric step-heating method of Tohidi et al. [13].

As noted, the method used for KHI evaluation was the Crystal Growth Inhibition (CGI) technique as fully described by Anderson et al. [8]. In summary, in this method the system is initially cooled to high sub-coolings from the hydrate phase boundary to induce hydrate formation. After this initial hydrate formation, the system is heated slowly outside the hydrate phase boundary leaving a small fraction of hydrate remaining (typically < 0.5% of water converted). Once only a small fraction of hydrate is left, temperature is again reduced but at a constant rate (e.g. 1.0 °C / hour) for detailed observation of growth rate changes as a function of sub-cooling. This is repeated a number of times for confirming repeatability. Finally, to confirm the extent of the complete inhibition and slow growth regions where appropriate, the system may be step-cooled with a small fraction of hydrate present [8]. Based on their studies, particularly the emerging close correlation between growth rates and exponential-type induction time trends, a simple logarithmic-type definition for CGI regions was defined by Anderson et al. [8] which is employed here (see Table 1).

Table 1 CGI regions and respective growth rates. Rates are based on the assumption the system is non-static and well mixed.

Region	Hydrate Growth Rate Description	% Aqueous Phase Conversion Rate / hr
CIR	Completely inhibited	0.00
SGR(VS)	Very slow growth (VS)	$\leq 0.1\%$
SGR(S)	Slow growth (S)	> 0.1% to $\leq 1.0\%$
SGR(M)	Moderate growth (M)	> 1.0% $\leq 10.0\%$
RGR	Rapid/fast	> 10.0% or as for no KHI present
SDR	Abnormally slow dissociation	One order of magnitude less than for no KHI

3. RESULTS AND DISCUSSION

CGI experiments have been carried out on a number of alcohols (MeOH, EtOH, n-POH, i-POH and n-BOH) and diols (MEG, 1,3-PDO and 1,4 BD) in PVCap-Water-Methane systems at various concentrations and pressures. Results of these tests are discussed in this section.

3.1. Effect of Alcohols on PVCap Performance

3.1.1 Methane with PVCap and Methanol

Methane hydrate crystal growth patterns in the presence 0.50 mass% PVCap aqueous with a range of concentrations of methanol from 2.5 to 50 mass% (MeOH relative to water + PVCap) at pressures up to ~300 bar have been investigated.

Figure 2 shows example CGI method cooling / heating curves and CGI boundary data for methane–PVCap–methanol (2.5 mass% MeOH). Similar curves were obtained for all other methanol concentrations. The hydrate phase boundary is shown for comparison. As illustrated in this figure, CGI regions are clearly discernible from cooling curve data. Clearly the presence of 0.5 mass% PVCap induced the presence of characteristic 'apparent' complete inhibition (CIR – no detectable hydrate growth and/or hydrate dissociation), slow growth rate (SGR) and rapid growth/failure (RGR) regions. However, as will be explained, it is found that methanol overall had a detrimental effect on the sub-cooling extent of all regions at all concentrations tested compared to aqueous PVCap alone.

Previously in this lab, for methane-water-PVCap alone, it was found that the complete inhibition region extends to ΔT_{sub} = ~−5.2 °C. Also, it was found that ΔT_{sub} for the SGR(S) and RGR boundaries

were ~−7.2 °C and ~−9.6 °C respectively [8]. However, data for the 5 different concentrations of methanol tested show that this alcohol has a consistently negative effect on the performance of PVCap; the extent of CGI region sub-coolings reduce as methanol concentration increases. For example, the CIR region reduces from ΔT_{sub} = ~−5.2 °C to ~−4.1 °C, ~−2.4 °C, ~−2.8°C, ~−2.9°C and ~−1.8°C for 2.5 mass%, 5.0 mass%, 10.0 mass%, 20.0 mass% and 50.0 mass% MeOH, respectively in the pressure range of 50 bar to 300 bar. Similarly, the extents of the SGR region / sub-cooling of the RGR boundary are also reduced to lower sub-coolings as a function of increasing methanol concentration.

Figure 3 shows PVCap-induced inhibition regions as a function of aqueous (relative to water) methanol concentration. As evident from this figure, at low methanol concentrations (< 5 mass%), the SGR(S) region reduces rapidly as methanol is initially added to the system, before rising again slightly to a peak at ~5 mass% MeOH, beyond which it steadily reduces in sub-cooling extent again as methanol concentration rises. The reasons for this initial drop then recovery in performance are unknown, although it may be speculated that at lower concentrations methanol might be encouraging hydrate nucleation; methanol is known to form s-II hydrates and s-H hydrates at low temperatures [14].
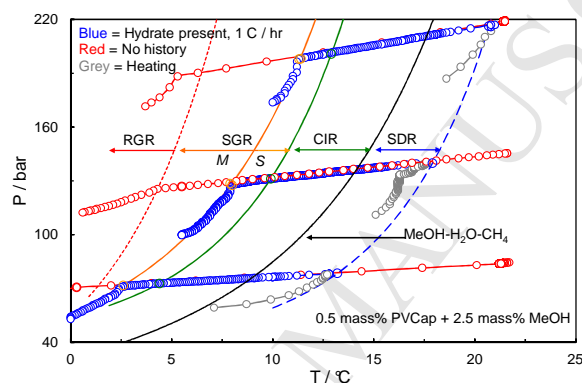

Figure 2 Example CGI cooling and heating curve data at three different pressures for 0.5 mass% PVCap / 2.5 mass% methanol aqueous solution with methane also showing CGI regions determined from changes in relative hydrate growth rates. CGI regions are explained in detail in Table 1. Points are every 5 minutes.
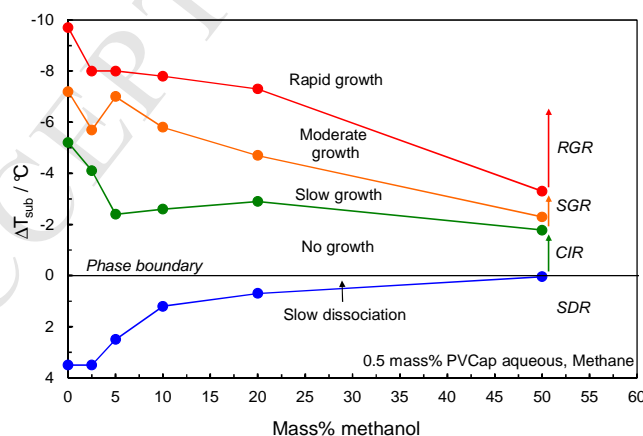

Figure 3 Average (50 to 300 bar) PVCap induced CGI regions for 0.5 mass% PVCap aqueous as a function of mass% methanol (relative to water + PVCap). CGI regions are explained in detail in Table 1.

Finally, the slow dissociation region (SDR) consistently reduces to lower sub-coolings as MeOH concentration increases, supporting CGI data in that MeOH is reducing PVCap effects on hydrate crystal growth and dissociation behaviour.

It should be noted that although the presence of MeOH has negative effect on PVCap performance, reducing the extent of all CGI regions, the combination of methanol and PVCap does still offer better total inhibition than methanol alone. Total inhibition is the sum of thermodynamic hydrate inhibition offered by MeOH and the kinetic hydrate inhibition offered by PVCap measured as CGI regions relative to the new MeOH present hydrate phase boundary. Figure 4 clearly demonstrates the total, thermodynamic and kinetic, methane hydrate inhibition offered by 0.5 mass% PVCap plus different concentrations of MeOH.
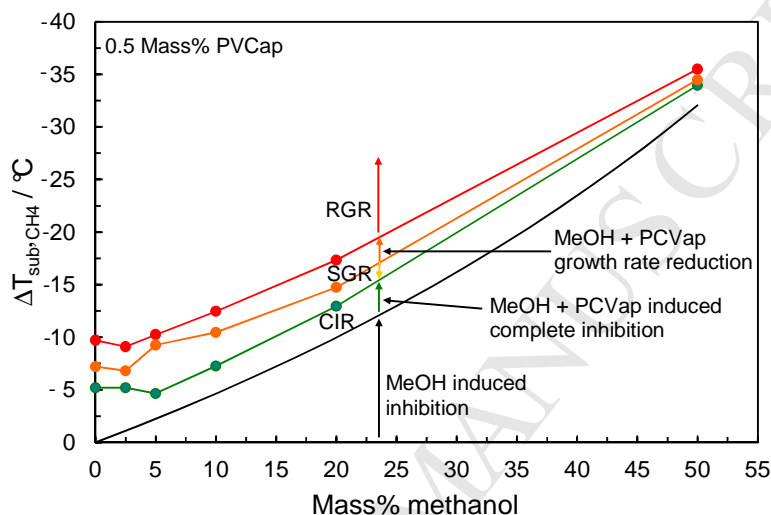

Figure 4 Total hydrate inhibition relative to methane hydrate phase boundary offered by combination of 0.5 mass% PVCap and different concentrations of methanol. CGI regions are explained in detail in Table 1.

Conclusively, the total kinetic plus thermodynamic hydrate inhibition offered by adding MeOH+PVCap to a methane system is more than the thermodynamic hydrate inhibition offered by only adding the similar amount of MeOH to that methane system.

3.1.2 Methane with PVCap and Ethanol

Methane hydrate CGI region data have been generated for 0.5 mass% PVCap aqueous with 2.5, 11.4 and 50 mass% ethanol (relative to water + PVCap) at pressures up to ~150 bar.

Example CGI method cooling / heating curves and CGI boundary data are illustrated in Figure 4 for methane–PVCap–ethanol (2.5 mass% ethanol) system. Figure 5 shows PVCap-induced CGI regions as a function of aqueous (relative to water) ethanol concentration.

As shown in Figure 5, CGI regions are clearly distinguishable from cooling curve data. For all ethanol concentrations tested, in a similar case to methanol, ethanol overall had a detrimental effect on the sub-cooling extent of all CGI regions at all concentrations tested, although was overall less negative than methanol.

As mentioned and illustrated in Figure 5, results for 0.5 mass% PVCap and 2.5 mass% ethanol with methane show that ethanol has a generally negative effect on the performance of PVCap. It is apparent that while the SGR(S) and RGR region boundaries (ΔT_{sub} = ~−7.5 °C and ~−9.3 °C respectively) remain at similar sub-coolings to those for water-PVCap (ΔT_{sub} = ~−7.3 °C and ~−9.6

°C respectively), the complete inhibition region reduces from ΔT_{sub} = ~−5.2 °C (for water−PVCap) to ~−3.9 °C (for water−ethanol−PVCap). Therefore, although the presence of ethanol does not notably affect the overall extent of CGI regions, the CIR is reduced in sub-cooling extent which results in an overall negative ethanol effect.

As ethanol concentration increases, the negative effect on PVCap becomes more pronounced. For example, at 11.4 mass% ethanol (Figure 6), the complete inhibition region has been reduced to only ΔT_{sub} = ~−1.2 °C. Similarly, the SGR(S) and RGR boundaries are reduced to lower sub-coolings of only ΔT_{sub} =~−5.1 °C and −7.3 °C, respectively.

Finally, tests with 50 mass% ethanol show that very high ethanol concentrations greatly reduce the performance of PVCap, so much so that the CIR has been completely lost, with only a small SGR region extending to ΔT_{sub} = ~−1.6 °C. This CGI reduction is reflected in there only being a very small SDR at higher ethanol concentrations (ΔT_{sub} = ~+0.8 °C for 11.4 mass% EtOH and ΔT_{sub} = ~+0.3 °C for 50 mass% EtOH), suggesting that polymer adsorption on crystal surfaces has weakened due to the ethanol.
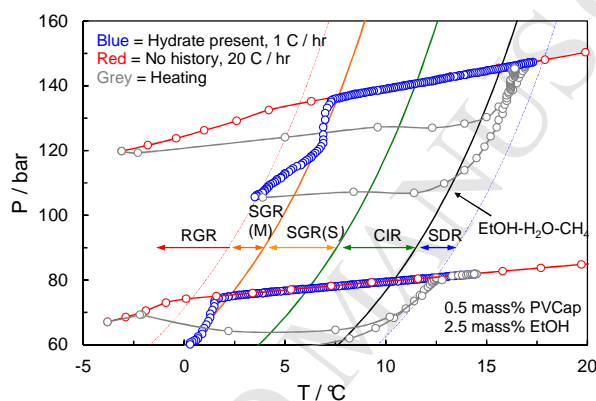

Figure 5 Example CGI test data for 0.5 mass% PVCap / 2.5 mass% ethanol aqueous with methane at two different pressures. Also showing determined CGI regions which are explained in detail in Table 1. Points are every 5 minutes.
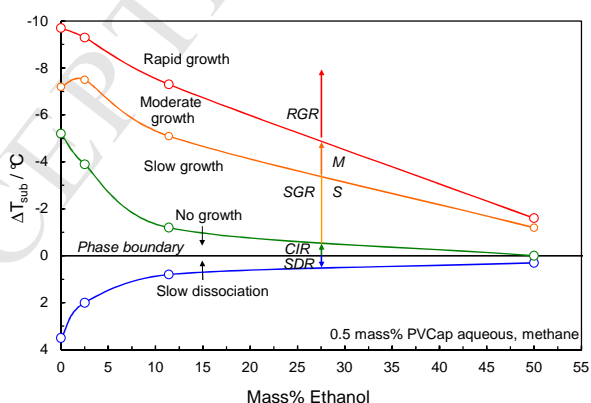

Figure 6 Average (40 to 120 bar) PVCap induced CGI regions for 0.5 mass% PVCap aqueous as a function of mass% ethanol (relative to water + PVCap). CGI regions are explained in detail in Table 1.

To summarise, similar to methanol, ethanol has a consistently negative effect on the performance of PVCap in methane systems; the extent of CGI region sub-coolings reduced as ethanol concentration increased. As illustrated in Figure 6, the higher the EtOH concentration the smaller the CIR region

becomes up to a point where it is completely lost at 50 mass% EtOH. Similarly, the SGR region is consistently reduced to lower sub-coolings as a function of increasing ethanol concentration.

Finally, as for methanol, although the presence of EtOH has negative effect on PVCap performance and reduces the extent of CGI regions, the combination of ethanol and PVCap does still offer better inhibition by mass of inhibitor than ethanol alone.

3.1.3 Methane with PVCap and n-Propanol

Methane hydrate CGI patterns in the presence of 0.5 mass% PVCap aqueous with 2.5 mass% n-propanol (relative to water + PVCap) with methane at two different pressures of ~70 bar and ~160 bar (2.5 mass% n-POH = 0.76 mole% n-POH) have been investigated. It should be noted that n-popanol is not a hydrate former and acts as a thermodynamic hydrate inhibitor at this concentration [15,16]. This has been taken into account when measuring PVCap hydrate inhibition properties.

Figure 7 shows example CGI method cooling curves and CGI boundary data points for the mentioned PVCap−n-propanol−methane system. As can be detected from this Figure, both 0.5 mass% PVCap and 2.5 mass% n-propanol show negative and positive effects on the performance of PVCap. Results illustrate that similar to ethanol, a water−n-propanol−PVCap system reduces the complete inhibition region by around ~1.0 °C. However, on the contrary, the slow growth region has been extended to higher sub-coolings, e.g. SGR has increased from ΔT_{sub} =~−7.3 °C (for water−PVCap) to ~−8.7 °C (for water−n-propanol−PVCap). Moreover, RGR has remained largely similar to that in a water−PVCap system. Consequently, while the presence of n-propanol has had a negative effect on CIR it has shifted both SGR conditions (S and M) to higher sub-coolings while RGR has remained unchanged.
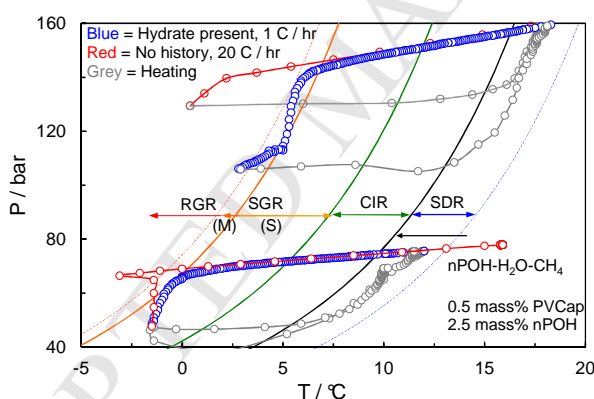

Figure 7 Example CGI cooling and heating curve data for 0.5 mass% PVCap / 2.5 mass% n-POH aqueous with methane at two different pressures. Points are every 5 minutes. CGI regions are explained in detail in Table 1.

3.1.4 Methane with PVCap and i-Propanol

Methane hydrate CGI patterns in the presence of 0.5 mass% PVCap aqueous with 2.5 mass% i-propanol (relative to water + PVCap) with methane at two different pressures of ~70 bar and ~160 bar (2.5 mass% i-POH = 0.76 mole% i-POH) have been investigated. It should be noted that similar to n-popanol, i-propanol is not a hydrate former and acts as a thermodynamic hydrate inhibitor at this concentration [15,16]. This has been taken into account when measuring PVCap hydrate inhibition properties.

Figure 8 shows example CGI method cooling curves and CGI boundary data points for the mentioned PVCap−i-propanol−methane system. As this Figure shows, in contrast to n-propanol, 2.5 mass% i-propanol has an overall negative effect on PVCap performance. Similar to the water−ethanol−PVCap system, in a water−i-propanol−PVCap system, although the performance of PVCap remains largely unchanged in the reduced growth rate region and rapid failure region, the complete inhibition region considerably reduces from ΔT_{sub}=~−5.2 °C (for water−PVCap) to ~−3.5 °C (for water−i-

propanol−PVCap). The smaller SDR region suggests the reduced performance of KHI (potentially weaker hydrate surface absorption of KHI) in this system.
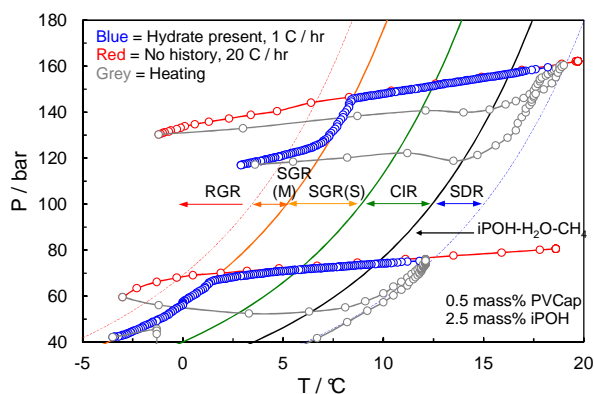

Figure 8 Example CGI cooling and heating curve data for 0.5 mass% PVCap / 2.5 mass% i-POH aqueous solution with methane at two different pressures. Points are every 5 minutes. CGI regions are explained in detail in Table 1.

3.1.5   Methane with PVCap and n-Butanol

Methane hydrate CGI patterns in the presence of 0.5 mass% PVCap aqueous with 1 and 3.1 mass% n-butanol (relative to water + PVCap) at pressure of ~90 bar (3.1 mass% n-BOH = 0.76 mole% n-BOH) have been investigated.

As evident from the example CGI method cooling / heating curves and CGI boundaries for methane−PVCap−n-BOH (3.1 mass% n-BOH) illustrated in Figure 9, in contrast to the other tested alcohols, n-butanol has an overall positive synergistic effect on PVCap hydrate crystal growth inhibition properties, at least at tested concentration and pressure.
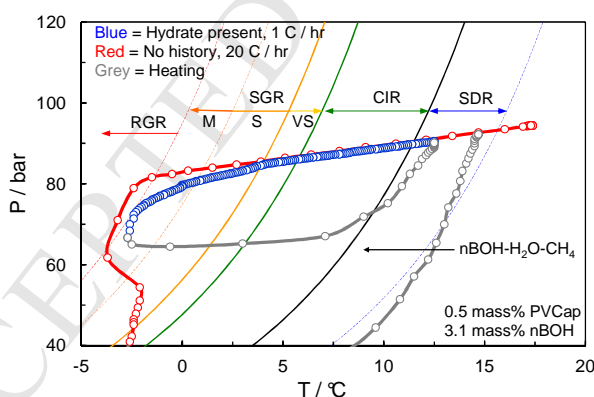

Figure 9 Example CGI cooling and heating curve data for 0.5 mass% PVCap / 3.1 mass% n-BOH aqueous with methane at ~90 bar pressure. Points are every 5 minutes. CGI regions are explained in detail in Table 1.

Results of the tested PVCap plus n-butanol system show that the complete inhibition region is very well preserved in this system remaining largely comparable to that of a water−PVCap system (ΔT_{sub} =~−5.3 °C). In addition to that, as illustrated in Figure 9, in this system as for propanol systems, both slow growth and rapid growth regions have been extended to higher sub-coolings. Furthermore, the RGR region is subdivided into three sub-regions. In the first region, RGR (VS), hydrate growth rate is incredibly slow in comparison to all other tested alcohol present systems and even an alcohol free water−PVCap system. The presence of this very slow growth region again supports the positive synergistic effect of n-BOH on PVCap performance.

Results of this section indicate that apparently the longer the alkyl 'tail' of an alcohol, the better PVCap hydrate crystal growth inhibition properties. However, it is clear that neither of these alcohols are 'top-up' inhibitors for a PVCap + water system; while the effect of n-butanol is very positive at low concentrations, it should be noted that it is insoluble in water at higher concentrations.

3.2. Effect of Diols on PVCap performance

3.2.1 Methane with PVCap and MEG

Methane hydrate CGI patterns in the presence of 1.0 mass% PVCap aqueous with a range of concentrations of MEG from 5.0 to 50.0 mass% (MEG relative to water + PVCap) at pressures up to ~300 bar have been investigated.

Since MEG tests have been performed with 1 mass% PVCap rather 0.5mass% PVcap it is important to indicate the effect of increased PVCap concentration to be able to distinguish between this effect and presence MEG in these tests. Previous studies have shown that while the CIR is the same for both 0.5 mass % and 1.0 mass %, increasing the concentration of PVCap to 1.0 mass% is very beneficial in that it greatly reduces growth rates in the SGR region compared to 0.5 mass % [17]. However, for a fair comparison in all MEG present tests analysis of all CGI regions and hydrate growth rates within those regions have been compared to 1 mass% PVCap alone.

Example CGI method cooling / heating curves and CGI boundaries for methane–PVCap–MEG (5.0 mass% MEG) are illustrated in Figure 10. Figure 11 shows PVCap induced CGI regions as a function of aqueous (relative to water) MEG concentration.

As shown in Figures 10 and 11, in contrast to MeOH and EtOH, MEG generally acts as a 'top-up' inhibitor for PVCap for the concentrations tested; MEG generally shifts the PVCap-induced hydrate crystal growth inhibition regions by a sub-cooling equivalent to the degree of thermodynamic inhibition offered by that MEG aqueous fraction.

For example, as shown in Figure 11, the CIR remains constant at $\Delta T_{sub} = \sim-5.2$ °C – which is the same as for water-PVCap alone – even up to concentrations as high as 50 mass% MEG. Likewise, the SGR (VS) region remains unchanged across the complete range of MEG concentrations tested. There is some variation in the SGR(S) and (M), although this is minimal and it is even larger in extent at 5.0 mass% MEG compared to PVCap alone.
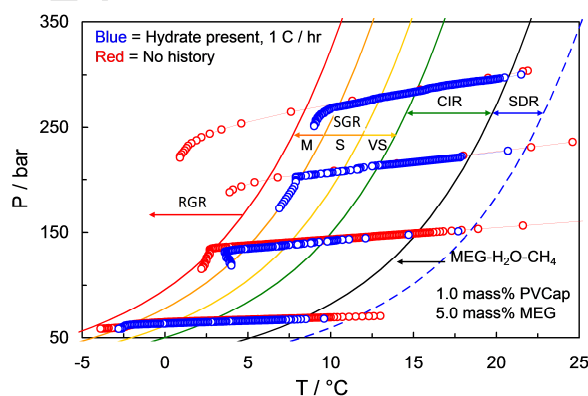

Figure 10 Example CGI cooling and heating curve data for 1.0 mass% PVCap / 5 mass% MEG aqueous with methane. Points are every 5 minutes. CGI regions are explained in detail in Table 1.
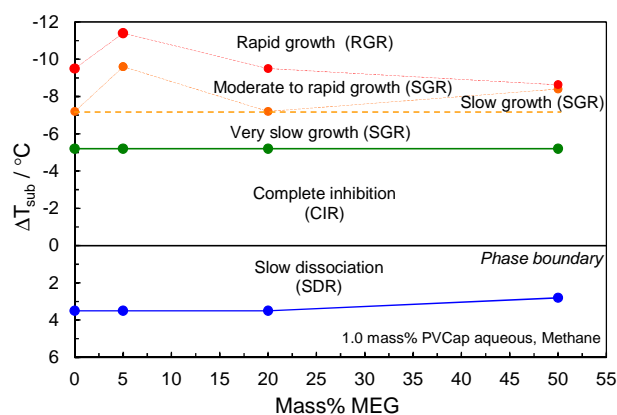
Figure 11 Average (50 to 300 bar) PVCap-induced CGI regions for 1.0 mass% PVCap aqueous as a function of mass% MEG (relative to water + PVCap). CGI regions are explained in detail in Table 1.

A further observation in terms of the effect of MEG was that it greatly reduced growth rates, particularly in the SGR (VS). For example, in this region at 50 mass% MEG, growth rates were so slow that they were hardly detectable on the timescale of days. In that sense, the very slow growth region was almost an extension of the CIR and distinguishing the two regions was difficult.

Figure 12 illustrates the total, thermodynamic and kinetic, methane hydrate inhibition offered by 1.0 mass% PVCap plus different concentrations of MEG.
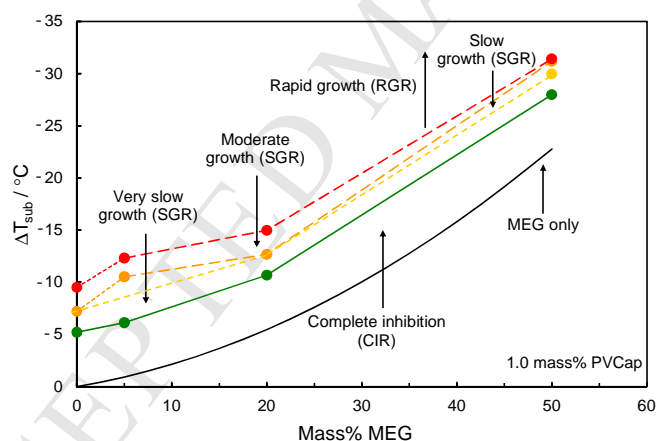
Figure 12 Total hydrate inhibition relative to methane hydrate phase boundary offered by combination of 1.0 mass% PVCap and different concentrations of MEG. CGI regions are explained in detail in Table 1.

Conclusively, as clearly shown in Figure 12 presence of MEG has a very positive effect on PVCap performance and the combination of MEG + PVCap offers far better inhibition by mass/volume inhibitor than MEG alone. As MEG acts to all extents and purposes as a full 'top-up' inhibitor to PVCap to at least 50 mass%, it could in theory be used to extend the sub-cooling of KHIs and/or significantly reduce MEG thermodynamic inhibitor volumes.

3.2.2   Methane with PVCap and 1,3-propanediol
Methane hydrate crystal growth inhibition region data have been generated for 0.5 mass% PVCap aqueous with 3.1 mass% 1,3-propanediol (1,3-PDO), equivalent to 0.76 mole % 1,3-propanediol, (relative to water + PVCap) at three different pressures up to ~250 bar.

Example CGI method cooling / heating curves and CGI boundaries for methane–PVCap–1,3-PDOl (3.1mass% 1,3-propanediol) are illustrated in Figure 13.
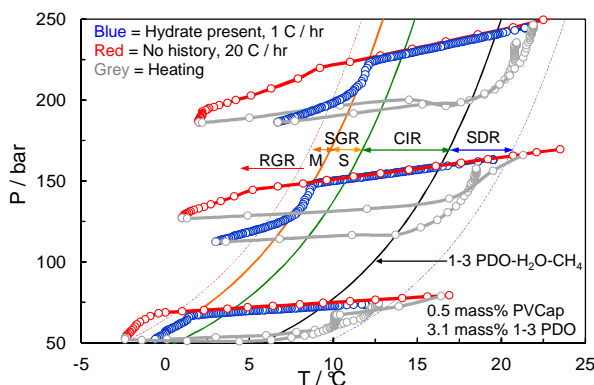

Figure 13 Example CGI cooling and heating curve data for 0.5 mass% PVCap / 3.1 mass% 1,3-propanediol aqueous with methane. Points are every 5 minutes. CGI regions are explained in detail in Table 1.

Results for 0.5 mass% PVCap and 3.1 mass% (0.76 mole%) 1,3-propanediol show that this diol has little impact on the performance of PVCap, at least at the tested concentration. Findings suggest that the complete inhibition region is preserved, remaining largely comparable to a water–PVCap system at ΔT_{sub} =~−5.1 °C. Likewise, the slow growth rate region/moderate growth rate initiation is largely unchanged at ΔT_{sub} =~−7.0 °C. Moreover, growth rates in each region seem quite similar to growth rates in a simple 0.5 mass% PVCap system. Thus, at this concentration, 1,3-propanediol generally seems to act as a 'top-up' inhibitor for PVCap but, unlike MEG, does not enhance its performance.

3.2.3 Methane with PVCap and 1,4-butanediol

Methane hydrate crystal growth inhibition region data have been generated for 0.5 mass% PVCap aqueous with 3.7 mass% 1,4-butanediol (1,4-BD), equivalent to 0.76 mole % 1,4-butanediol, (relative to water + PVCap) at two different pressures up to ~250 bar.

Example CGI method cooling / heating curves and CGI boundaries for methane–PVCap–1,4-BD (3.7 mass% 1,4-butanediol) are illustrated in Figure 14.
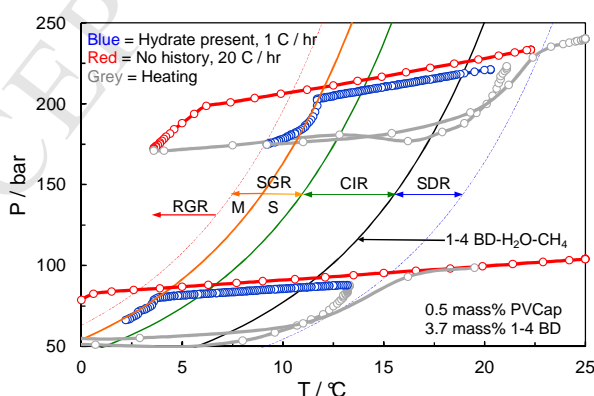

Figure 14 Example CGI cooling and heating curve data for 0.5 mass% PVCap / 3.7 mass% 1,4-butanediol aqueous with methane. Points are every 5 minutes. CGI regions are explained in detail in Table 1.

Results for 0.5 mass% PVCap with 3.7 mass% (0.76 mole%) 1,4-butanediol suggest that this diol has a generally negative effect on PVCap performance, with CGI regions apparently reduced, e.g. CIR and SGR(S)/SGR(M) are ~0.5 °C smaller each. Thus, unlike MEG and 1,3-propanediol, 1,4-

butanediol is not a top-up inhibitor at this concentration and has an overall negative effect on PVCap performance.

Conclusively, results so far show that neither 1,3-propanediol nor 1,4-butanediol seemingly offer the same good synergism as MEG, indicating that the favourable properties of the latter are not ubiquitous to all diols, and that increasing central alkyl chain length has progressively eliminated top-up properties.

4. CONCLUSIONS

In this work the effect of a number of alcohols and diols (some of which are well known thermodynamic inhibitors) on the performance of the kinetic hydrate inhibitor polymer PVCap was investigated using the crystal growth inhibition (CGI) technique which was developed by Anderson et al. (2011).

CGI region studies on alcohol (MeOH, EtOH, n-POH, i-POH and n-BOH)-PVCap-water systems at tested concentrations of alcohols with methane at 0.5 mass% PVCap showed that none of the tested alcohols act as a 'top-up' thermodynamic inhibitor; complete inhibition regions are consistently reduced to lower sub-coolings in the presence of methanol, ethanol, propanol and i-propanol, although this it is preserved in the presence of n-butanol.

The reasons why methanol, ethanol, i-propanol and n-propanol have negative effect on CIR are unclear, although it is known that MeOH can form clathrate hydrates at low temperatures and the other three alcohols can form clathrate hydrates at conditions pertinent to offshore operations, thus they may be encouraging growth by competing with polymer pendant amide groups for partial enclathration into open cages.

Although four of the alcohols (MeOH, EtOH, n-POH and i-POH) clearly deteriorate the performance of PVCap, the combination of alcohol plus PVCap does still offer better inhibition by mass of inhibitor than any of the alcohols alone. Hence, it can be concluded that KHIs offer a potential means to reduce the amount of thermodynamic inhibitor required for high subcooling operations, in particular for MeOH and EtOH which are being used as hydrate inhibitors.

Furthermore, results of n-propanol and i-propanol experiments suggest that, molecular weight of alcohol alone is not apparently the controlling factor on the influence of alcohol on PVCap performance. In addition to that, alcohol alkyl 'tail' length apparently plays a role in PVCap hydrate crystal growth inhibition properties which could potentially be related to solubility parameters; the longer the alkyl tail, the higher sub-cooling obtained for SGR and RGR, with increasing preservation of the CIR (e.g. n-butanol).

In contrast, data demonstrate that MEG generally acts as a full 'top-up' thermodynamic inhibitor for PVCap for the range of concentrations tested (up to 50 mass%). Furthermore, MEG can greatly reduce hydrate growth rates (potentially due to an increase in MEG concentration due to hydrate formation).

On the other hand, studies on the other two tested diols show that neither 1,3-propanediol nor 1,4-butanediol seemingly offer the same good synergism as MEG. While 1,3-PDO has little observable impact on PVCap performance and acts as 'top-up' thermodynamic inhibitor, with crystal growth inhibition regions generally equal to those for PVCap alone, 1,4-BD does not act as 'top-up' thermodynamic inhibitor and reduces CGI regions to lower subcoolings. Conclusively, findings indicate that the favourable properties of MEG are not ubiquitous to all diols, and that increasing the central alkyl chain length of diols progressively eliminates top-up properties.

While each of the findings greatly enhance the understanding of the effect of different alcohols and diols on PVCap performance, further investigation is required to gain better understanding on the actual reasons and causes behind these synergist or antagonistic behaviours.

NOMENCLATURE

ΔT_{sub}	Sub-cooling [°C]
AMW	Average Molecular Weight
BD	Butanediol
CAPEX	Capital Expenditure
CIR	Complete (hydrate) Inhibition Region
CGI	Crystal Growth Inhibition
EtOH	Ethanol
i-POH	iso-Propanol
JIP	Joint Industry Project
KHI	Kinetic Hydrate Inhibitor
M	Moderate (growth)
MEG	Mono-ethylene glycol
MeOH	Methanol
n-BOH	Normal butanol
n-POH	Normal propanol
OPEX	Operational Expenditure
PDO	Propanediol
PRT	Platinum Resistance Thermometer
PVCap	Poly-n-vinylcaprolactam
RGR	Rapid (hydrate) Growth (rate) Region
S	Slow (growth)
SDR	Slow (abnormally, hydrate) Dissociation Region
SGR	Slow (hydrate) Growth (rate) Region
THI	Thermodynamic hydrate inhibitor
t_i	Hydrate nucleation induction time [hrs]
VS	Very Slow (growth)

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Highlights: EFFECT OF ALCOHOLS AND DIOLS ON PVCAP-INDUCED HYDRATE CRYSTAL GROWTH PATTERNS IN METHANE SYSTEMS

- None of the tested alcohols act as a 'top-up' thermodynamic inhibitor with PVCap.
- Alcohol plus PVCap offers far better inhibition than any of the alcohols alone.
- Alcohol molecular weight alone is not the controlling factor on its effect on PVCap
- MEG is a full 'top-up' thermodynamic inhibitor for PVCap at tested concentrations.
- Increasing diols central alkyl chain length gradually eliminates top-up properties.