

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



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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.

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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 [1–3]. Furthermore, for high sub-cooling operations and/or high water-cut 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'

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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 Fig. 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

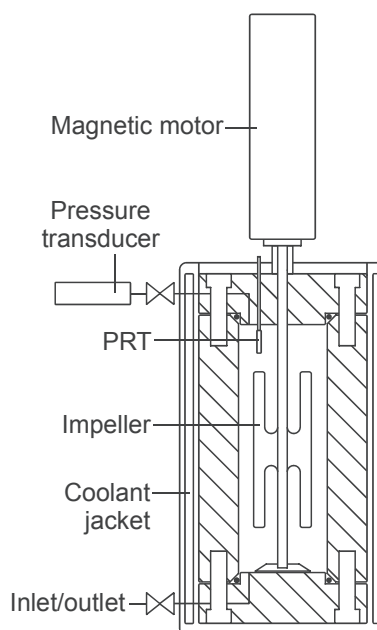


Fig. 1. Schematic diagram of the 280 ml high pressure (max 410 bar) autoclave cells used in the experiments.

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