

# Ranking of kinetic hydrate inhibitors using a high pressure differential scanning calorimeter



Nobuo Maeda<sup>a,b,\*</sup>, Malcolm A. Kelland<sup>c</sup>, Colin D. Wood<sup>d</sup>

<sup>a</sup> Department of Civil & Environmental Engineering, School of Mining and Petroleum Engineering, University of Alberta, 7-207 Donadeo ICE, 9211-116 Street NW, Edmonton, AB T6G1H9, Canada

<sup>b</sup> CSIRO, Ian Wark Laboratory, Bayview Avenue, Clayton, VIC 3168, Australia

<sup>c</sup> Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway

<sup>d</sup> CSIRO Australian Resources Research Centre, Kensington, WA 6152, Australia

## HIGHLIGHTS

- Performance of several kinetic hydrate inhibitors was tested using HP-DSC in up to 390 bar of analogue natural gas.
- A novel protocol was devised to increase the spread between effective inhibitors to obtain the efficacy ranking.
- HP-DSC is suitable for the testing of potential KHIs that can only be obtained in minute quantities.

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## ABSTRACT

A High Pressure Differential Scanning Calorimeter (HP- $\mu$ DSC) was used to characterize the kinetic inhibition performance of several kinetic hydrate inhibitors (KHIs) up to 390 bar (39 MPa) of model natural gas. A novel protocol was devised to increase the spread between effective KHIs to obtain their performance ranking. The natural gas used in the study was a mixture of 90 mol% methane and 10 mol% propane. Linear cooling ramps at a constant cooling rate of 0.5 K/min were used under isobaric conditions. Both the formation temperature of natural gas hydrate during a linear cooling ramp and the amount of hydrate formed were used for comprehensive analysis. The second method was based on the growth inhibition of natural gas hydrates and opened a new possibility that only several repeat measurements may be sufficient for fast screening of good KHIs. The results showed that HP- $\mu$ DSC is a promising tool for the evaluation of kinetic inhibition performance of KHIs that can only be obtained in minute quantities.

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## 1. Introduction

Gas hydrates are ice-like crystals that consist of typically non-polar guest molecules and host water (Sloan and Koh, 2008). Several crystalline structures have been identified which depend on the guest composition (Sloan and Koh, 2008). Gas hydrates typically consist of 85 mol% water and 15 mol% guest when all the cavities are occupied. On the one hand, gas hydrates provide a range of promising applications ranging from gas storage, carbon dioxide sequestration, gas separation to desalination (Englezos, 1993). On the other hand, gas hydrates are undesirable in oil and natural gas pipelines because their formation can lead to blockage of the

pipelines which, if not remedied in a timely manner, could lead to serious and very expensive consequences (Sloan and Koh, 2008).

Because of the risks gas hydrates pose to flow assurance, their inhibition has been a subject of scientific and industrial research for some time (Perrin et al., 2013; Kelland, 2006). It has been a common practice to use large quantities (up to 50 wt%) of thermodynamic hydrate inhibitors (THIs) such as methanol and mono ethylene glycol (MEG) in gas hydrate susceptible fields (Sloan and Koh, 2008). THIs preclude formation of gas hydrates by shifting the thermodynamic phase boundaries of gas hydrate formation to lower temperatures and/or higher pressures (Sloan and Koh, 2008). However, as the production fields move further offshore and deeper, and the concomitant tiebacks become ever longer, the costs of THIs increase rapidly.

As such, a relatively new group of chemicals, Kinetic Hydrate Inhibitors (KHIs) have been developed (Kelland, 2006; Tohidi et al., 2015). KHIs have hydrophilic polymers such as N-vinylpyrrolidone

\* Corresponding author at: Department of Civil & Environmental Engineering, School of Mining and Petroleum Engineering, University of Alberta, 7-207 Donadeo ICE, 9211-116 Street NW, Edmonton, AB T6G1H9, Canada.

E-mail address: [nobuo@ualberta.ca](mailto:nobuo@ualberta.ca) (N. Maeda).

(PVP) and N-vinyl caprolactam (PVCap) as the main active ingredient. They can be dosed at a much lower concentration than THIs (typically  $\sim 1$ – $3$  wt% when correctly formulated in solvents for field use) (Kelland, 2006). KHIs do not preclude the formation of gas hydrates but rather delay the nucleation of gas hydrates and/or slow the growth of gas hydrates while the production fluids are transported. Thus an effective, reliable, inexpensive and environmentally friendly KHI is highly desirable.

When a new KHI is developed, it has to be subjected to a range of rigorous testing before its field use. Conventional testing methods included autoclaves (Del Villano and Kelland, 2011; Duchateau et al., 2010), stirred batch reactors (Duchateau et al., 2012), rocking cells (Mady and Kelland, 2014), High Pressure-Automated Lag Time Apparatus (May et al., 2014), High Throughput Testing methods (Maeda et al., 2016) and others. A promising KHI that passes the initial tests by these techniques can then be subjected to more sophisticated and expensive testing methods such as flow loops (Di Lorenzo et al., 2014).

A High Pressure Micro Differential Scanning Calorimeter (HP- $\mu$ DSC) is a tool that can be used to study thermodynamic properties as well as nucleation kinetics of gas hydrates (Davies et al., 2009; Lachance et al., 2008). It can apply a number of linear cooling ramps and measure heat flow profiles of a sample, which enable us to deduce the nucleation temperature of gas hydrates during a cooling ramp as well as the amount of gas hydrates formed. The amount of aqueous sample solution required for an HP- $\mu$ DSC measurement is only about 20 mg, or more than three orders of magnitude less than what is required for a conventional technique such as an autoclave. HP- $\mu$ DSC is therefore ideal for testing of novel inhibitors which are expensive and/or only minute amounts are available.

McNamee used water-in-oil (W/O) emulsions in conjunction with HP- $\mu$ DSC to assess the inhibition efficacy of KHIs (McNamee, 2011). The idea is that a large number of water droplets dispersed in an emulsion can offer sufficient statistics of nucleation events as long as the water cut is low and contagion of nucleation from one droplet to the next can be avoided. The underlying assumption is that the total oil-water interfacial area in the emulsion (which is proportional to the probability of nucleation) remains the same for all the KHIs to be tested and varies with temperature in a similar way.

In the current study, we did not adopt the W/O emulsion method. Instead, we used droplets of dilute KHI aqueous solutions in HP- $\mu$ DSC for the investigation of kinetic inhibition performance of four KHIs. We then compared the results from those of our earlier studies which used the same batch of materials (Mady and Kelland, 2014; Maeda et al., 2016).

## 2. Materials and methods

The four KHI we tested are; Luvicap 55W, Luvicap 21W, Poly(N-Isopropylacrylamide: PNIPAM) and Polyvinylpyrrolidone (PVP). The active polymer concentration of each KHI was 0.5 wt% for each sample in milli-Q water (18 M $\Omega$  resistivity). Between 20 mg and 70 mg of pure water or a sample KHI solution was introduced to the high pressure sample cell using a clean syringe. The actual amount used was measured each time by an analytical balance and recorded.

A high pressure micro differential scanning calorimeter from Setaram ( $\mu$ DSC7 evo, pressurized by an Ultra High Pressure Gas Panel) was used for the study. The high pressure cell has the maximum pressure rating of 400 bar (40 MPa). The guest gas used in the study was a mixture of 90 mol% methane and 10 mol% propane (C1/C3) which is a good analogue to natural gas. The guest gas pressures used were 100 bar (10 MPa), 200 bar (20 MPa), 300 bar

(30 MPa) and 390 bar (39 MPa) for each sample. All the measurements were isobarically carried out. The sample volume was much smaller than the guest gas volume and the guest gas pressure was held constant with a high pressure syringe pump of the Ultra High Pressure Gas Panel.

Instead of the induction time measurements at a constant sub-cooling which are known to be highly stochastic and also experimentally time consuming, we here used the constant cooling ramp method (temperature scan method). It has been shown that the cooling ramp method effectively compress the distribution width because continuous cooling keeps increasing the driving force for nucleation of subcooled samples until nucleation is forcibly induced (Maeda, 2015, 2016).

Each sample was subjected to a constant heating ramp from  $-33$  °C ( $\approx 240$  K) to  $45$  °C ( $\approx 318$  K) and then back for one cycle. This temperature scan range was selected to ensure that gas hydrate formation and complete dissociation take place in every cycle. Although the selection of this scan range resulted in formation of ice in every cycle, the ice formation and melting peaks were clearly identifiable in every cycle, as shown below. We note at this stage that even though these polymers can precipitate above around  $36$  °C, they are expected to dissolve again during the subsequent cooling at around the same temperature. The temperature scan rate used was  $0.5$  K/min for both heating and cooling in this study unless otherwise specified. Although we did not investigate the scanning rate effect of the KHI solutions, we note that the routine calibration of HP- $\mu$ DSC involves measurements of the melting points of pure water, decane and naphthalene using different scanning rates. The results did not show any variation beyond the ubiquitous random errors over the range of scanning rates which included  $0.5$  K/min. Minimum of five heating/cooling cycles were repeated at each guest gas pressure for each KHI sample.

As we did in our previous publications (May et al., 2014; Maeda, 2015, 2016), we denote the higher of the ice or the first gas hydrate formation temperature detected during a cooling ramp as  $T_f$ , and the thermodynamic equilibrium melting/dissociation temperature measured during a heating ramp as  $T_{eq}$ .

## 3. Results and discussion

First we show typical heat flow profiles from the HP- $\mu$ DSC in Fig. 1 for pure water. Here the cooling ramp is shown in blue and the subsequent heating ramp in red. It was observed that multiple peaks often appeared during a single cooling ramp, as was the case

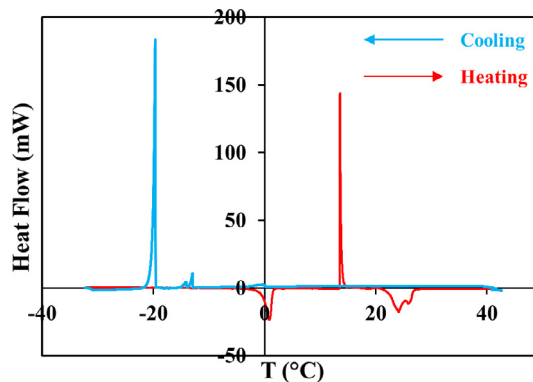


Fig. 1. Typical heat flow profile of pure water in 100 bar (10 MPa) of C1/C3 mixed gas. The blue profile is for the cooling ramp and the red profile is for the subsequent heating ramp. The exothermic heat flows are expressed in positives and the endothermic heat flows are expressed in negatives. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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