Kinetic inhibition of natural gas hydrates in saline solutions and heptane

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HIGHLIGHTS

- PVP and PVCap prolonged induction time and reduced growth rate in saline solution.
- Addition of *n*-heptane delayed hydrate nucleation and reduced hydrate growth rate.
- In the presence of heptane, KI addition decreased nucleation time and hydrate growth.
- Gas hydrate dissociated in two steps either in the presence of heptane or without it.

ARTICLE INFO

ABSTRACT

The performance of polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) as kinetic gas hydrate inhibitors in saline solutions and with heptane was evaluated using high pressure microdifferential scanning calorimetry, as well as with a new apparatus, consisting of two high pressure stainless steel crystallizers. Although PVP and PVCap were found to prolong natural gas hydrate induction time in saline solutions, nucleation was followed by catastrophic hydrate crystal growth. PVP was found to be more effective in this case, since this hydrate growth was modestly slower. The addition of *n*-heptane to the natural gas in the system created a 4th phase. This resulted in increased induction time and a slowing of hydrate growth relative to the gas mixture. Unexpectedly, in the presence of *n*-heptane, addition of kinetic hydrate inhibitors (KHIs) decreased induction time, but catastrophic growth did not occur. Here PVCap was more effective than PVP in both prolonging the induction time and decreasing the rate of hydrate crystal growth. Once formed, however, hydrate decomposition took longer and proceeded in two steps in the presence of *n*-heptane. This observation has profound applications on the use these KHIs under ocean field conditions. In the case of hydrate blockages, our observations that hydrate dissociation started later with the KHIs and complete dissociation took longer could have far reaching economic implications for industry.

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1. Introduction

Natural gas hydrates are non-stoichiometric crystalline compounds formed by small size molecules trapped within hydrogen-bonded water cages under low temperature and high pressure conditions [1,2]. Formation of gas hydrates in hydrocarbon transmission pipelines has been identified as a major reason for pipeline blockage [3–5]. Traditionally, gas hydrate formation has been impeded by the injection of thermodynamic hydrate inhibitors (THIs) in order to shift the hydrate phase boundary to higher pressure and lower temperature conditions [6]. However, large amounts of THIs are required to prevent hydrate formation (at an annual estimated cost of $220,000,000) [7] and in addition,

safety, health, and environmental risks have pushed industry to seek other inhibitors. Low dosage hydrate inhibitors include kinetic hydrate inhibitors (KHIs) and anti-agglomerates [8–11].

Generally, KHIs are water-soluble polymers which are able to significantly prolong nucleation time and decrease post nucleation crystal growth rates [12]. The key ingredients of successful KHIs are polymers or copolymers containing vinyl-lactam monomers such as pyrrolidone in the form of polyvinylpyrrolidone (PVP) or caprolactam in the form of polyvinylcaprolactam (PVCap) [9]. Although extensive research has been devoted to evaluate the performance of potential KHIs using various techniques [1,13–18], with adsorption-inhibition mechanisms proposed to explain inhibitor action [19–21], their ability to alter gas hydrate crystal nucleation and/or growth is still not understood. In addition, the transferability of kinetic inhibition results between laboratory scale experiments and the field remains a significant challenge [22,23].

In this regard, more recently the performance of the KHIs in the presence of mixture of gases, rather than laboratory-preferred single gas components, have been assessed with a number of techniques (high pressure crystallizers [15,24–26], differential scanning calorimetery [13,16,17], Raman [18,27,28] and ¹H NMR spectroscopy [14]) in the hopes of more efficiently moving to field testing. Additional efforts to make such testing even more realistic and relevant for oil and gas reserves, particularly in deep waters, are required. Thus, the impact of parameters such as the salinity and the presence of a hydrocarbon liquid phase need to be assessed. Therefore, in this work a hydrate formation system that better simulates off-shore conditions was selected. These conditions were achieved by (a) employing a multi component (CH_4, C_2H_6, C_3H_8) gas mixture; (b) adding n-heptane to model a hydrocarbon liquid phase, and thus represent gas condensate; (c) applying high driving forces (in terms of over pressure or sub-cooling); and (d) increasing water salinity to simulate seawater conditions. In addition, the development of a novel high pressure crystallizer capable of mixing the gas and liquid components resulted in model pipeline conditions on a laboratory scale. A high pressure microdifferential scanning calorimeter (HP-μDSC) was used to evaluate how representative KHIs influence natural gas hydrate formation and dissociation process under these more realistic conditions.

2. Experimental section

2.1. Materials

NaCl (Fisher Scientific) was dissolved in distilled, deionised water to prepare a mass fraction of 3.5% solution. Two commercial KHIs were used: polyvinylpyrrolidone (PVP; average molecular weight of 3.5 kDa; Acros Organics) and a solution (40 wt% in ethanol) of polyvinylcaprolactam (PVCap; average molecular weight of ∼23.3 kDa; BASF). The KHIs were diluted to 0.1 mM in the saline solution. A natural gas mixture (UHP grade) consisting of methane (93%)/ethane (5%)/propane (2%) was supplied by Praxair Technology Inc. The liquid hydrocarbon phase was n-heptane (Fisher Scientific).

2.2. High pressure crystallizer apparatus

A new high pressure crystallizer was designed and fabricated to conduct gas uptake and dissociation experiments under constant pressure and volume, respectively (Fig. 1). Two 211 mL-stainless steel vessels surrounded by tubing were fitted with two circular polycarbonate viewing windows on the front and back. The vessels contained baffles to control vortex formation when stirred and were submerged in an insulated temperature-controlled circulating bath filled with a propylene glycol and water (1:1) solution. Two additional 300 mL-stainless steel vessels were also immersed in the water bath and acted as supply reservoirs to the crystallizers during hydrate formation. An external refrigerating/heating programmable circulator (VWR Scientific) was used to regulate the temperature of the circulating bath. The contents of the crystallizer were mixed by a gas induced impeller coupled with a hollow shaft which was rotated with a magnetic driven motor (Autoclave Engineers) and controlled by a universal motor controller (Autoclave Engineers). The shaft speed was measured with a universal tachometer display (rpm). Two rosemount smart pressure transmitters (model 3051, maximum uncertainty of 0.075 percent of span 0–15,000 kPa; Norpac controls) were used to measure the pressure of crystallizer and supply vessel and transmit signals to the computer in each unit. Three copper–constantan thermocouples (uncertainty of 0.1 K; Omega Engineering) were used to measure the gas, liquid and interface (liquid–gas, or liquid–liquid)

temperature. A high-pressure and low-flow control valve (Fisher, Baumann 5100, NPS ¼) with an actuator and coupled to a proportional, integral, derivative (PID) controller was installed between the crystallizer and the reservoir, and used to regulate crystallizer pressure. The data acquisition system (National Instruments) was connected to a computer to receive transmitted data from pressure transmitters and thermocouples. LabVIEW full development system software (National Instruments) was employed to communicate with the control valve and convert receiving signals for recording into Microsoft Excel.

2.2.1. Gas hydrate crystal formation

In order to simulate pipeline conditions a constant cooling rate method [29,30] using constant pressure was applied. In this procedure, the temperatures of the crystallizers were reduced from outside of the hydrate stability zone to a stable region under constant pressure. Since gas hydrate formation is an exothermic process [1], the onset of nucleation is marked by an abrupt temperature rise and pressure reduction. Two cooling rates (9 K/h and 1 K/h) were employed to simulate both start-up/low flow rate and high flow rate circumstances [31]. The crystallizer was loaded with 80 mL of desired aqueous solution (either saline solution or KHI in saline). Experiments with a liquid hydrocarbon also included n-heptane (40 mL) as these KHIs are water soluble polymers [12]; they will remain in aqueous phase in the presence of n-heptane. Therefore addition of n-heptane does not dilute KHIs solutions. The water bath temperature was adjusted at 293.15 K. The crystallizers were then pressurized so as to achieve conditions below the equilibrium hydrate formation point and subsequently depressurized three times to displace air from the system. After this, the crystallizers were pressurized with gas mixture to 7.0 MPa. The PID controller set point was adjusted at 7.0 MPa to maintain constant crystallizer pressures by the supply of gas from the supply vessels. The supply vessels were pressurized at 10 MPa with the gas mixture. Since the equilibrium hydrate formation temperature in 7.0 MPa is 288.8 K, as calculated by CSMGem [32], no hydrates could form at the initial condition (P = 7.0 MPa, T = 293.15 K). There was constant stirring (500 rpm) of the crystallizer contents and when pressure and temperature were stabilized in both crystallizers and supply vessels, a program of temperature reduction was initiated in order to reach a target temperature of 274.15 K. Refrigeration start time was considered as the zero time and data were recorded every 5 s. The number of moles of gas consumed to form hydrates or dissolved in solution (Δn_H) was calculated as described by Linga et al. [33]. The experiment was terminated when there was a considerable mass of gas hydrate crystals in the crystallizer such that stirring was practically impeded.

2.2.2. Gas hydrate crystal dissociation

Hydrate formation was considered complete when stirring was no longer possible, and thus simulate blocked pipeline conditions. Dissociation of the hydrate crystals was achieved by increasing the water bath temperature from 274.15 K to 301.15 K with similar heating profiles for all experiment. The beginning of the heating program represents time zero in the dissociation experiments. Crystallizer pressures (7.0 MPa at the beginning of hydrate decomposition) increased due to hydrate dissociation and consequent gas expansion. Data were recorded every 5 s. Gas hydrate crystal dissociation initiated once the temperature crossed the equilibrium boundary. The total number of moles of released gas at any given time, Δn_G, was calculated according to Linga et al. [34]. In order to more readily compare different experiments the normalized amount of the released gas was calculated as follows [15]:

$$\text{Normalized amount released gas} = \frac{\Delta n_G}{n_{total}}$$