Synergistic kinetic inhibition of natural gas hydrate formation

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HIGHLIGHTS

► Rocking cells allow us to get more reliable statistical data about hydrate inhibition.
► Luvicap lowered the nucleation temperature and delayed the nucleation time.
► PEO enhanced the nucleation inhibition strength of Luvicap.
► NaCl reduced the hydrate growth significantly.
► Hydrate formed in the presence of inhibitor took longer time to decompose completely.

ARTICLE INFO

ABSTRACT

Rocking cells were used to investigate the natural gas hydrate formation and decomposition in the presence of kinetic inhibitor, Luvicap. In addition, the influence of poly ethylene oxide (PEO) and NaCl on the performance of Luvicap was investigated using temperature ramping and isothermal experiments. Luvicap decreased the hydrate nucleation temperature in ramping and increased the hydrate nucleation time at fixed temperatures. The presence of PEO and NaCl enhanced the nucleation inhibition strength of Luvicap. However the addition of Luvicap promoted the hydrate growth after nucleation. PEO does not affect hydrate growth whereas NaCl reduced the hydrate growth both in the presence and absence of Luvicap. In addition complex two-stage hydrate growth was observed in the presence of Luvicap. Moreover, the hydrate formed in the presence of inhibitor took longer time/higher temperature to decompose completely. One should consider this complex inhibitor-mediated hydrate formation and decomposition kinetics when screening and designing kinetic inhibitors for field applications.

1. Introduction

Gas hydrates are crystalline compounds stabilized by the inclusion of gas molecules under suitable temperature and pressure conditions. These compounds are the major flow assurance problem in the oil and gas industry since they can form inside the pipeline and obstruct flow [1–4]. In the worst case scenario, the pipeline can explode and cause enormous economic and environmental damage. So the prevention or control of these compounds is necessary to avoid significant safety hazards in production facilities and prevent loss of production. Industry typically adds large amounts of methanol or glycols (so-called thermodynamic inhibitors) [4] during gas production to prevent hydrate formation. These chemicals shift the natural gas hydrate equilibrium conditions to low temperatures and high pressures. However, this method is increasingly expensive because of high concentrations in the aqueous phase (>40% by weight) required to prevent the hydrate

formation in offshore developments [5]. It is estimated that annually, the operating costs can be greater than $500,000,000 to prevent the hydrate formation via thermodynamic inhibitor (methanol) injection [6].

Therefore, over the last decade hydrate research has moved towards alternative low dosage (<1 wt%) kinetic inhibitors (LDHIs) to reduce costs (both operating and capital, since large equipment is required offshore to recover glycol, for example). Depending on the nature of the LDHI there is also great potential for reduced impact on the marine environment. A large number of different polymers have been explored as kinetic hydrate inhibitors (KHIs) [2,7]. These chemicals do not prevent ultimate hydrate formation but rather interfere with hydrate nucleation and/or growth to delay hydrate formation in pipelines as they pass through the hydrate risk zone. Newly discovered inhibitors need to be tested thoroughly in the laboratory and if successful can then be evaluated with field fluids at field conditions [8]. It is interesting to note that there are chemicals which do not themselves exhibit kinetic inhibition but may impact the performance of kinetic inhibitors [9]. Cohen et al. [10] reported that adding butoxy-ethanol to a kinetic

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inhibitor increased the induction time 30 times. Lee et al. [11,12] reported that addition of poly ethylene oxide (PEO) to starches enhances the performance of inhibition towards binary hydrate formation by an order of magnitude. Recently Talaghat, [13] reported that PEO and PPO enhance the performance of inhibitor towards binary hydrate formation in a flow-mini loop apparatus. However the mechanism of these polymers to enhance the performance of known inhibitors is not yet understood.

In addition to pressure, temperature and gas mixture composition, hydrate formation also depends on the salts dissolved in the water present in reservoir fluids. The presence of salts in produced water or sea water influences the hydrate formation equilibrium by affecting the water activity (the more saline the water, the lower the hydrate formation temperature). These salts have limited ability to shift the equilibrium and addition of more salts is generally not practical due to operational constraints [14]. Therefore it is necessary to evaluate the combined effect of kinetic inhibitors, synergists and salts on hydrate formation and decomposition. Moreover, there is evidence in the literature that hydrates formed in the presence of gas mixtures have a more complex behavior than those formed from single gases or liquid hydrate formers (THF) [15–22]. The addition of kinetic inhibitor to such systems complicates the mechanism even more. Because of the complex behavior associated with mixed gas hydrates is important to better understand the effect of kinetic inhibitors on these hydrates. However, few studies have been reported on kinetic inhibition of mixed gas hydrate [23–29]. Moreover, mixed gas hydrate decomposition behavior in the presence of inhibitors is poorly understood. Although it is possible to avoid hydrate formation under normal conditions using inhibitors, during long shut-in periods hydrate crystals will form and produce plugs even in the presence of inhibitors [23,29,30]. So understanding the nature of these plugs and the kinetic behavior of natural gas hydrate decomposition in the presence of inhibitors, synergists and salts is important for efficient hydrate plug removal in pipelines.

Hydrate formation is stochastic in nature and statistically significant number of experiments under the same experimental conditions is required in order to provide reliable information. While it is difficult to simulate pipeline conditions in the laboratory setup, rocking cells allow us to get more reliable statistical information about hydrate formation and decomposition under similar experimental conditions. The increasing use of identical rocking cells in different hydrate research laboratories also enables better comparison across laboratories. Using a rocking cell (RC-5) apparatus, we have successfully investigated the effect of Luvicap on natural gas hydrate nucleation, growth and decomposition using temperature ramping and isothermal methods. In addition, the influence of PEO and salinity (NaCl) on the performance of Luvicap on hydrate nucleation, growth and decomposition was also investigated.

2. Experimental section

2.1. Materials

The natural gas mixture (Table 1) used in the present work was supplied by Air Liquide. Deionized water was used to perform the experiments. A model sea water was prepared with 3.5 wt% NaCl (>99.5% purity) supplied from Merck. Luvicap-EG supplied from BASF was used as kinetic inhibitor. Poly ethylene oxide (PEO) of molecular mass of 100,000 was supplied in powder form by Sigma–Aldrich Chemicals.

2.2. Apparatus

The Rocking Cell (RC-5; has five test cells, PSL Systemtechnik, Germany) was used to test the inhibitor and synergist performance

Table 1
Natural gas composition.

Component	Mol%
Methane	87.81
Ethane	6.60
Propane	1.22
n-Butane	0.17
i-Butane	0.22
n-Pentane	0.02
i-Pentane	0.03
n-Hexane	0.01
Nitrogen	3.68
Oxygen	0.24

on natural gas hydrate nucleation, growth and decomposition (Fig. 1A). Each stainless steel test cell was made with stainless steel (AISI 316L) and has a volume of 40.13 cm^3 and is capable of operating up to 200 bar working pressure (Fig. 1B). The working temperature range of the cells was between −10 °C and 60 °C. A stainless steel ball (Dia: 17 mm) is placed inside and rolls back and forth along the length of the cell to agitate the solution inside it (Fig. 1C). The mixing in the cells was controlled by rocking the cells back and forth between angles of −45° and +45°. Once the cells are loaded with the desired solution, they were placed in a cooling bath controlled by an external refrigerator, which can be operated between −20 °C and +60 °C. The pressure and temperature of cells were monitored by data acquisition system throughout the experiment. Two different temperature programs used to study the hydrate formation and decomposition are presented in the following sections.

2.3. Temperature ramping experiment

Rocking cells are pressurized to 80 bar with natural gas and temperature ramping experiments were performed under constant ramping method, i.e. temperature decreased from 25 to 1 °C or increased from 1 to 25 °C at the rate of 0.02 °C/min. The rocking rate was held constant at 20 rocks/min throughout the rocking experiment. The typical pressure and temperature changes during the temperature ramping experiment with water are shown in Fig. 2a. In reference (typical pressure change inside the rocking cell during ramping test without rocking the cells: black solid line) experiment, a linear change in pressure was observed with decrease/increase in temperature due to thermal contraction/expansion. During a rocking experiment (hydrate formation, red[1] dashed line), initially the pressure decreased linearly in the cell due to thermal contraction. At hydrate nucleation (A) the gas is consumed due to hydrate formation and the pressure decreases more rapidly. The onset of hydrate nucleation is observed as a sudden deviation from the linear trend. The hydrates formed during cooling were decomposed by heating. The pressure increases linearly due to thermal expansion until the hydrate starts to decompose. Once the hydrate starts to decompose the pressure rises rapidly as the hydrate decomposes. After complete decomposition of the hydrate the pressure follows the linear trend again (B).

2.4. Isothermal experiment

Isothermal experiments provide information on the hydrate nucleation time for a given constant temperature (driving force). The experimental temperature is reached by adjusting the external chiller without rocking the cells. Once the desired temperature is reached, rocking commences at 20 rocks/min and is maintained

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[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.