Experimental validation of kinetic inhibitor strength on natural gas hydrate nucleation

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HIGHLIGHTS

- Chemical inhibitors were ranked based on the inhibition strength.
- The inhibition strength decreased significantly in the presence of reservoir fluid.
- The hydrate decomposition temperatures were not influenced by the presence of NaCl.
- The hydrate decomposition temperatures decreased slightly with liquid hydrocarbon.

ARTICLE INFO

ABSTRACT

The kinetics of natural gas hydrate formation in the presence of dissolved salts (NaCl) and crude oil (a middle east crude with density 851.5 kg/m^3) were investigated by using a standard rocking cell (RC-5) apparatus. The hydrate nucleation temperature was reduced in the presence of NaCl and oil in comparison with that in pure distilled water. The kinetic inhibition strength of various inhibitors (Luvicap Bio; Inhibex 505; Inhibex 501; Luvicap 55w; BIO inhibex-800; and Inhibex 301) was experimentally evaluated at complex conditions (in the presence of salts and crude oil) using the constant cooling temperature approach. These polymer-based chemicals were ranked based on the inhibition strength as follows: Luvicap Bio < Inhibex 505 < Luvicap 55w < Inhibex 501 < BIO-Inhibex-800 < Inhibex 301. The same trend was also observed in the presence of salts and liquid hydrocarbon phase. The KHIs' inhibition strength was not affected by NaCl but decreased significantly in the presence of crude oil. The hydrate decomposition temperatures were not influenced by the presence of NaCl, however, they decreased slightly in the presence of liquid hydrocarbon. The data presented here can contribute to appropriate hydrate risk management in oil and gas facilities.

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1. Introduction

Gas hydrates are crystalline formations where small gas components (guests) are enclosed by cages formed from water molecules (hosts) under suitable pressure/temperature conditions [1,2]. Gas hydrates attract scientific interest for reasons connected with flow assurance problems [3–6] in the oil and gas industry as well as environmental issues such as carbon capture and sequestration [7,8], natural gas storage and coal mine gas separation [9,10]. Additionally, gas hydrate formation in transmission pipelines is a serious economic and safety problem for the oil and gas industry. This is conventionally dealt with by shifting the thermodynamic equilibrium conditions to low pressures and high temperatures by using thermodynamic inhibitors such as methanol and glycols.

The increasing interest in hydrate research is due in part to the increasing water depth at which production occurs. Deep water increases the length and size of the pipeline, thereby increasing the risk of flow assurance problems as a result of hydrate formation (for example Fig. 1 shows a schematic of hydrate developing along the length of a pipeline, with snapshots of hydrates forming in time in laboratory experiments below). Thermodynamic inhibition (THI) is increasingly expensive because of the high chemical concentrations in the aqueous phase (>40% by weight) required to prevent hydrate formation in offshore production facilities [4]. The economic and environmental restrictions on this method resulted in the development of alternative solutions. Low dosage kinetic hydrate inhibition (KHIs) is one of the promising methods to reduce both operating and capital costs. Unlike THIs, KHIs do not prevent hydrate formation by shifting formation equilibrium, but interact with hydrate crystallization to delay hydrate nucleation in the pipeline fluids as they flow through pressure

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and temperature regimes where there is a risk of hydrate formation. If this nucleation delay time is greater than the retention time of the fluids in the risk zone, then hydrate formation can be effectively controlled. These KHIs are also known to alter crystal growth rates after nucleation [2,6,11–15]. Most KHIs are polymer based components while recent studies have shown that some antifreeze proteins and amino acids can also delay hydrate formation significantly [12,13,15–20]. The application of these KHIs in the field depends on many factors such as gas composition, flow rate, gas/oil ratio, oil composition, sub cooling, pipeline size, water cut, salinity, other chemical injections, cost etc. Although several laboratories are investigating new and existing kinetic inhibitors on hydrate formation in more realistic conditions (presence of salts and reservoir crude) [11,21–24], the direct transferability of these results to field applications still poses many challenges. It is necessary to obtain data for KHI performance at more complex field conditions to develop application based inhibitors. In the current study, we have implemented realistic field conditions by evaluating the performance of six different KHIs on natural gas hydrate formation in the presence of a saline aqueous phase and crude oil using a standard rocking cell apparatus. These six inhibitors chosen to work with are among the leading KHIs available commercially and used in field applications.

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 5 wt% NaCl (>99.5% purity) supplied from Merck. 5% NaCl solution was used to mimic saline conditions at the lower end of those encountered in industry, which can vary from sea water (3.5%) up to 20%. Hydrate inhibitors tested in this work were Inhibex 301; Inhibex 501; Inhibex 505; Inhibex BIO 800 from Ashland (ISP) and Luvicap 55 W; Luvicap Bio from BASF. These chemicals were kindly supplied by M-I SWACO, A Schlumberger Company. The middle east crude had a density 851.5 kg/m^3 was used.

2.2. Apparatus and methodology

A Rocking Cell (RC-5; has 5 test cells, PSL Systemtechnik, Germany) was used to test the inhibitors on the natural gas hydrate formation. Each stainless steel test cell has a volume of 40.13 cm^3 and is capable of operating up to 200 bar working pressure. 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. The mixing in the cells was controlled by rocking the cells back and forth between an angle of −45° and +45°. Once the cells are loaded with the desired solution, they were placed in a cooling
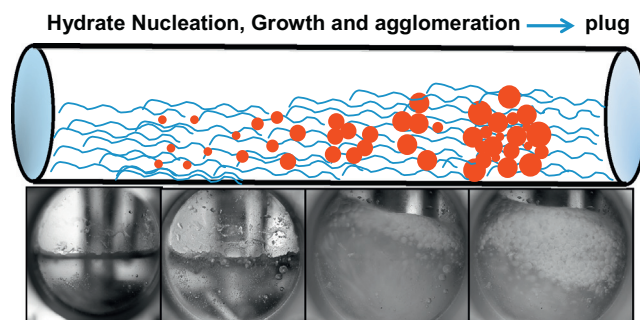
Table 1
Natural gas composition.

Component	Mol%
Methane	87.81
Ethane	6.60
Propane	1.22
n-Butane	0.17
i-Butane	0.22
n-Pentane	002
i-Pentane	0.03
n-Hexane	0.01
Nitrogen	3.68
Oxygen	0.24

Hydrate Nucleation, Growth and agglomeration ⟶ plug

Fig. 1. Schematic of hydrate plug formation (top) in oil and gas pipelines with sequential images of hydrate formation in lab experiment (bottom).

bath controlled by an external refrigerator, which can be operated between −20 °C and +60 °C. The pressure and temperature of the cells were monitored by the data acquisition system throughout the experiment. Temperature ramping experiments were performed using a constant ramping method, i.e. once the cell was loaded with solutions and pressurized (100 bar), temperature decreased from 25 to 1 °C or increased from 1 to 25 °C at the rate of 0.1 °C/min. The rocking rate was held constant at 20 rocks/min throughout the rocking experiment (Fig. 2). During a temperature ramping (cooling cycle) experiment, initially the pressure decreased linearly in the cell due to thermal contraction. At hydrate nucleation 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 (Fig. 2A). 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 (Fig. 2B). The details of the experimental setup and procedures were described elsewhere [22]. All experiments were repeated four times (4 * 5 = 20 data points) with fresh inhibitor solutions to ensure repeatability of results under the same experimental conditions and an average temperature was calculated. While some studies have suggested that several hundred replicates are necessary to obtain statistically significant data [25], the stochasticity (variance) of induction time is also a function of the hydrate formation driving force. Based on the scatter we obtained, we believe that 20 replicates was sufficient to generate useful induction time data.

3. Results and discussion

The effect of dissolved salts (5 wt% NaCl) on the natural gas hydrate formation was investigated and typical results are presented in Fig. 3. In constant cooling experiments, the hydrate nucleation temperature was identified by sudden consumption of gas due to hydrate formation. The average onset of hydrate nucleation temperature (T_w) in the presence of water (control) occurred at 15.5 °C. In solutions containing 5 wt% NaCl the hydrate nucleation temperature (T_{sw}) drops to 12.3 °C. These results are not surprising since salt solutions are known to shift the hydrate phase equilibrium to lower temperatures and higher pressures by lowering the water activity in the liquid phase. The ions resulting from dissolved NaCl form a strong columbic bond with dipoles of water molecules and attract water clusters around them, thereby reducing the availability of water molecules as hydrate building blocks.

The effect of six different KHIs on hydrate nucleation has been determined using a standard rocking cell apparatus. In the presence of 1 wt% inhibitors, the average hydrate nucleation