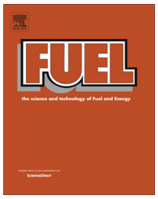
Fuel 180 (2016) 187–193

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Anti-agglomeration of natural gas hydrates in liquid condensate and crude oil at constant pressure conditions

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HIGHLIGHTS

- Anti-agglomeration in a wide water-cut range in real petroleum fluids is demonstrated.
- The effect of CO_2 in the petroleum fluid on anti-agglomeration is compensated by LiOH.
- The high gas volume to liquid volume (oil and water) ratio is demonstrated to require higher dosage of anti-agglomerant.

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form 7 March 2016
Accepted 10 March 2016
Available online 16 March 2016

Keywords:
Flow assurance
Natural gas hydrates
Anti-agglomerant
Gas condensate
Crude oil

ABSTRACT

An effective anti-agglomerant (AA) can reduce capillary force between hydrate particles to prevent them from sticking together, therefore preventing the blockage in pipelines. In recent studies, we have reported an AA formulation which shows high effectiveness at low dosage in methane/natural gas hydrates over the entire water-cut range. All our past work, however, was conducted in a closed rocking cell system with *n*-octane as the hydrocarbon liquid phase. In this work, we investigate the effectiveness of an improved formulation in various systems at constant high pressure (~100 bar natural gas) and high cooling rate (−8 °C/h) over the water-cut range of 30–80%. Condensate liquid and crude oil are used as the hydrocarbon liquid phase. Because of the impact of the acidic gases in natural gas, a small amount of lithium hydroxide is included in the new formulation. Lithium hydroxide is more efficient than sodium hydroxide which was used in our previous studies. The dosage is reduced by ~40% by mass. We demonstrate the effectiveness of improved AA formulation in an extensive set of measurements. The effect of salinity on the AA effectiveness is also investigated. It is found that increasing salinity can decrease the dosage of base chemical in the formulation significantly.

1. Introduction

Gas hydrates, also known as clathrate hydrates, are ice-like crystalline solids which are formed by host water molecules around small guest gas molecules, such as methane, ethane, propane, carbon dioxide, nitrogen and hydrogen sulfide, at relatively low temperature and elevated pressure conditions [1–3]. Formation of gas hydrates is a severe operational problem in gas and oil production and transportation. Gas hydrates deposit on pipe walls and agglomerate to form large plugs, which may result in blockages in pipelines and cause serious safety and environmental consequences.

Besides expensive and sometimes ineffective engineering means, such as removal of water prior to pipeline transportation and maintaining the pressure and temperature conditions outside the hydrate formation region, gas hydrate risks can be also reduced/eliminated by injecting hydrate inhibitors into pipelines [4]. There are three kinds of hydrate inhibitors available for gas and oil industries to manage gas hydrate risks. Thermodynamic inhibitors (TIs), such as methanol, ethylene glycol and triethylene glycol, can shift the equilibrium hydrate formation to a lower temperature and a higher pressure condition. However, in order to be effective, these traditional hydrate inhibitors have to be injected up to 100% of the weight of water. It is also known that TIs are not environmentally friendly [5]. Kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs), which are known as low dosage hydrate inhibitors (LDHIs), become more attractive in offshore

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http://dx.doi.org/10.1016/j.fuel.2016.03.029
0016-2361/

gas and oil production and transportation. LDHIs are dosed at a concentration of up to 3.0 wt.% based on the aqueous phase. KHIs are usually water-soluble polymers, which can significantly decrease the gas hydrate formation rate and allow to produce/-transport gas or/and oil fluid in a certain period of time [2]. The main drawback of KHIs is that they lose the effectiveness when the subcooling is over ~12 °C [4].

Unlike KHIs, AAs are effective at high subcooling. AAs may not slow down the hydrate growth, but they can prevent hydrate particles from sticking together to form large hydrate pieces, therefore holding back the blockage in pipelines. Quaternary ammonium salts (QAs), which were first developed by Shell in early 1990s, are the most well-known AAs [6]. Chua and Kelland have reported systematic study of gas hydrate anti-agglomerant performance of single-tail quaternary tributylammonium bromides at 33% water-cut (ratio of aqueous phase to total liquid phase, volume basis) [7]. Besides QAs, successful anti-agglomerant performance of commercial additives and new AAs have been published by several research groups [8–13]. However, most of AAs are only effective at low water-cut (e.g., less than 30%). Gao reported a proprietary Champion Technologies AA product, which can be effective at high water-cut (up to 80%) with 4 wt.% NaCl and 15 wt.% methanol or 7 + wt.% NaCl [4].

Recently, our research group has reported the performance of a new AA synthetized by Lubrizol Corporation. We have demonstrated the effectiveness of newly developed AA formulation in methane hydrate over the entire water-cut range in the closed system by a sapphire rocking cell instrument, and proposed a new mechanism different from the well-known water-in-oil emulsion theory [14]. However, it is found that the AA loses effectiveness in natural gas which contains appreciable amounts of acidic gases, such as CO_2 and H_2S. To address the problem, we introduced NaOH to the new formulation to neutralize the effect of CO_2 [15]. We have reported hydrate powder formation in the anti-agglomeration of natural gas hydrates at high water-cut and high hydrate volume fractions [16]. The measurement of hydrate particle sizes by the focus beam reflectance measurement has been conducted. It is found that our AA formulation can reduce hydrate particle size significantly and eliminates large particles in an autoclave reactor [17].

All our published work was conducted in a closed system with *n*-octane as the oil phase, which may be simpler than the real situation in the gas and oil production. In this work, we investigate the effectiveness of our improved AA formulation in more challenging conditions which may be close to the conditions of offshore explorations in deeper and colder waters [18]. Experiments are conducted under constant high pressure (~100 bar natural gas) and high cooling rate (−8 °C/h) over the water-cut range of 30–80% in a rocking cell instrument. Condensate liquid and crude oil are used as the hydrocarbon liquid phase for the first time in the tests with the new AA, and deionized (DI) water and brine (NaCl in the range of 20,000–80,000 TDS (total dissolved solids)) as the aqueous phase. Because of the effect of acidic gases in natural gas on the AA performance [15], mainly CO_2 in this study, a small amount of LiOH is included in the new formulation. By using LiOH in this work, instead of NaOH which we have used in the past [15], the dosage of base chemical in the formulation is reduced by ~40% (mass basis). The new formulation is applied in various gas/brine/hydrocarbon liquid systems, and the effectiveness is judged by visual observations and the ball running time in rocking cells. We demonstrate the effectiveness of the improved AA formulation in the various testing systems. We also find that the increase in salt concentration in the aqueous phase can increase AA performance.

2. Experimental section

2.1. Materials

The AA used in this study is synthetized by Lubrizol Corporation. It contains 80–89% cocamidopropyl dimethylamine ($C_{17}H_{36}N_2O$), known as the effective component, 5–10% glycerin, small amount of free amine and water. Fig. 1 shows the chemical structure of cocamidopropyl dimethylamine. Condensate liquid (OS312464) and crude oil (OS312462) used as oil phases in the tests are supplied by Lubrizol Corporation. Condensate liquid has density of 0.726 g/ml and viscosity of 0.85 cP at 25 °C; it is slightly acidic. pH decreases from 7.2 to 6.9 when 2 mL of condensate liquid is added into 10 mL DI water. The density and viscosity of crude oil are 0.814 g/ml and 5.9 cP at 25 °C, respectively. Crude oil is more acidic than condensate liquid. pH decreases from 7.2 to 6.0 when 2 mL crude oil is added into 10 mL DI water. The composition of synthetic natural gas (Praxair Distribution Inc.) used in this study is shown in Table 1. Salinity of aqueous phase is controlled by adding NaCl (99.5%, Sigma–Aldrich). Base chemicals, such as NaOH (98.5%, Acros Organics) and LiOH (98%, Acros Organics), are used to improve the performance of AA.

2.2. Experimental set-up

The experiments are conducted in a high pressure sapphire rocking cell equipment (PSL Systemtechnik, Germany) shown in Fig. 2 [14–16]. Each cell has a volume of 20 mL equipped with a stainless steel ball and two sensor positions which record the ball running time. The diameter of the running ball is around 0.4 in., and the inner diameter of cell is around 0.5 in. When the cells are rocking, the balls provide agitation. In each test, the cells are filled with various amounts of aqueous solution, condensate liquid/crude oil and natural gas. The water bath is filled before the cells, which contain liquids, are pressurized with natural gas to the desired pressure of around 100 bar. During the tests, additional gas is added into the cells from time to time to keep the pressure in the range of 95–105 bar. The rocking frequency is set to 15 times/min at an angle of ~45°. The bath temperature, cell pressure and ball running time are recorded during the experiments. Fig. 3 shows an example of the bath temperature and cell pressure profiles.

At the beginning of each experiment, the testing cells are rocked at 20 °C for half an hour to reach equilibrium. The approximate equilibrium hydrate formation temperature based on hydrate dissociation in the tests is about 1–2 °C below the starting temperature. Then the water bath is cooled from 20 °C down to 4 °C at a cooling rate of −8 °C/h, while the cells are being

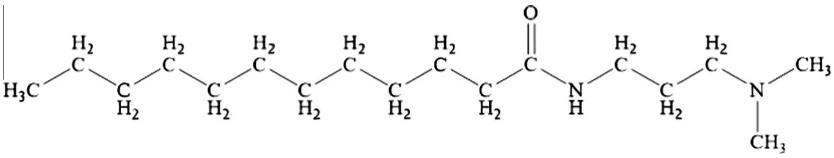

Fig. 1. Chemical structure of the effective component in the anti-agglomerant.