



Full Length Article

Effect of salt and water cuts on hydrate anti-agglomeration in a gas condensate system at high pressure



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ABSTRACT

Anti-agglomerants (AAs) can be effective molecules in gas hydrate flow assurance in deep-water at high sub-cooling conditions. Salt and water cut (ratio of water volume to total liquid volume) may have a major effect on hydrate anti-agglomeration. The understanding of the effect of salt and water cut on hydrate anti-agglomeration is limited. There has been no systematic investigation of anti-agglomeration in water-cuts in the 10 to 100% range in rocking cell apparatus at high pressure. In this work, we conduct a systematic investigation of the effect of NaCl and water cut on the performance of a non-ionic anti-agglomerant which is effective at high water cuts (up to 100%). We use a condensate liquid as the liquid hydrocarbon phase and methane as hydrate former to conduct a systematic investigation of the effect of water cut and salt on anti-agglomeration at high pressure. At a low water cut of 10%, the salt makes the AA ineffective. At 20% water cut, NaCl does not have an appreciable effect on AA performance. In water cuts in the range of 30 to 100%, 1 wt% AA becomes effective when there is limited amount of NaCl in the aqueous phase. The effect of NaCl includes lowering of water to hydrate conversion and decreasing the solubility of AAs in water. At 95% water cut the mixtures of condensate, salt, water/brine, and AA form a very viscous emulsion. Addition of alcohol allows anti-agglomeration in this complex mixture. The measurements over a broad range of water cuts reveal formation of water-in-oil and oil-in-water emulsions as well as flocculation. To shed light on the mechanisms we perform emulsion studies and measure AA partitioning between the aqueous phase and the hydrocarbon phase. This study presents the mechanisms that their understanding may be essential in application of AA in a broad range of water cuts.

1. Introduction

Gas hydrates are ice-like crystalline compounds that are formed from water and guest molecules such as methane, ethane, propane and carbon dioxide at high pressure and low temperature [1–5]. Hydrates may form in flowlines at high pressure and sea-bed temperature conditions [5]. The precipitation and aggregation of gas hydrates in flowlines can lead to flow blockage causing severe safety concerns and environmental issues [1–3,5,6].

Traditional methods for hydrate mitigation such as temperature and pressure control and water removal prior to pipeline transportation may be expensive and not efficient. Gas hydrate inhibitors have been used to prevent hydrate blockage. These include: 1-thermodynamic inhibitors (TIs), and 2-low-dosage hydrate inhibitors (LDHIs) [3]. TIs change bulk phase properties and inhibit hydrate formation by shifting the equilibrium conditions to higher pressures and lower temperatures [3,7]. However, large amounts of TIs such as alcohols (e.g., triethylene glycol, monoethylene glycol and methanol) of some 20 to 60 wt%

(relative to the water phase) are normally required [5]. LDHIs, which can be effective at concentrations of 0.1 to 2 wt%, provide an attractive alternative to address hydrate flow assurance [2]. LDHIs can be divided into two categories: 1- kinetic hydrate inhibitors (KHIs), and 2- anti-agglomerants (AAs). KHIs are usually water-soluble polymers that delay the crystallization and lower growth of gas hydrates offering enough time to transport oil and gas fluids before hydrate build up in pipeline [5]. However, KHIs may become ineffective when subcooling (the difference between the hydrate equilibrium temperature and the operating temperature at a given pressure) exceeds 10 °C [5,6].

AAs are surfactants which are not primarily intended to delay the crystallization and growth of gas hydrates. They prevent the aggregation of small hydrate particles and keep them dispersed in the liquids. Compared to KHIs, AAs can be effective at high subcooling [1–3]. In deep-water, AAs may be potentially the method of choice [2,8]. Until recently, the main drawback of AAs has been ineffectiveness at high water cuts (e.g., > 50%) [9–11]. Recently, a number of papers report AAs which may be effective at water cuts of 80 to 100% in laboratory

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tests [12–14]. Gao [12] reported a new AA, which may be effective in a crude oil at various water cuts (30, 60 and 80%) in rocking cell tests. He presented results for a natural gas at 34°F (1.11 °C) and 1000 psi (6.89 MPa). In 4 wt% NaCl brine, the minimum effective concentrations of AA at 30, 60 and 80% water cuts were 1.5, 1, and 3 wt%, respectively. At 80% water cut and 4 wt% NaCl, when 15 wt% methanol was introduced into the aqueous phase, the effective concentration of AA was reduced to 0.5 wt%, indicating that methanol had a synergistic interaction with AA in anti-agglomeration. Gao also found that at 80% water cut, when the NaCl content in the aqueous phase was raised to 7 and 11 wt%, the minimum AA dosages would be 1, and 0.5 wt%, respectively. This demonstrated that NaCl can generate a step change in the performance of the AA. At a higher pressure of 2000 psi (13.79 MPa) and a high salinity of 15 wt% NaCl, the effective AA dosage was 1.5 wt%. No information on chemical structure and type of the AA was provided [12]. We have reported a new nonionic AA, cocamidopropyl dimethylamine, which can be effective at high water cuts in a closed system [13]. We have also reported an improved AA formulation, which can be effective in liquid condensate and crude oil at a pressure of 10 MPa and high water cut conditions (up to 80%) [14]. However, the performance of the improved AA formulation was not investigated at water cuts higher than 80% at constant high pressure. The AA was also not investigated at low water cuts. There has been no report in the literature on anti-agglomeration in the full range of water cuts from 10 to 100% in rocking cell apparatus at high pressure.

Salt in the aqueous phase may have a significant effect on the performance of AAs [5,13,15–19]. There are limited studies on salt effect but to the best of our knowledge there is no investigation on the salt effect as a function of water cuts. Cationic AAs such as quaternary ammonium salts (QAS) perform better at higher salinity and lower water cut [5]. Nagappayya et al. reported that QAS become more oil soluble at higher NaCl concentrations. Salts generally reduce solubility of ionic surfactants in water. The increase in oil solubility may lead to the formation of water-in-oil emulsion and enhancement of the hydrate anti-agglomeration performance of QAS [18]. We have investigated the effect of salts on tetrahydrofuran hydrates and AA performance; our results show that divalent cations like Mg^{2+} would decrease the performance of QAS and rhamnolipids [15]. There are limited published studies on effect of salts on the nonionic AA performance. Kelland et al. investigated the performance of a class of alkylamide surfactants, which were shown to be effective with synthetic sea water of 3.5 wt% salt concentration at the water cut range of 18 to 27%. The AA became ineffective at salt concentrations less than 0.5 wt% [19]. We have found that salt can reduce the effectiveness of the nonionic AA (cocoamidopropyl dimethylamine) [13]. On the other hand, due to the thermodynamic inhibiting effect of the salt, not all of the water molecules can convert to hydrates. The performance of AA improves at high water cut conditions when the salinity is high [5,14]. However there has been no systematic explanation for the improvement. The above reports have motivated us to investigate the improved understanding of the salt effect on AA performance.

In this work, we investigate the effect of NaCl on the AA performance at a pressure of 10 MPa at water cuts of 10 to 100%. The high pressure open cell (a cell with a valve connected to the gas cylinder to keep the pressure constant) at constant pressure is a severe test of AA performance. In order to interpret the results from AA we conduct emulsion measurements and partitioning of AA in the condensate hydrocarbon liquid and aqueous phases.

2. Materials and methods

2.1. Materials

The AA used in this study is from Lubrizol Corporation. It contains 80–89 wt% cocamidopropyl dimethylamine, which is the effective component (Fig. 1), 5–10 wt% glycerin, and a small amount of free

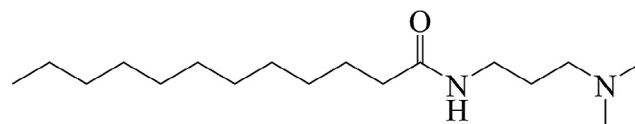


Fig. 1. Chemical structure of the effective component in the AA.

amine and water. The AA is used as received without further purification. Sodium chloride (99.8%) is from Fisher. Reagent alcohol (Ethanol (90 vol%)-Methanol (5 vol%)-Isopropanol (5 vol%), Pharmco-Aaper) is used to prevent flocculation encountered at the water cut of 95%. The condensate liquid, used as the liquid hydrocarbon phase is from Off-shore Mexico with a density of 0.757 g/cm³ at 20 °C (see composition listed in Table S1). The viscosity of the condensate liquid at 20 °C and 2 °C are 0.93 cP and 1.26 cP, respectively. Deionized water used in this study is from Thermo Fisher Scientific with pH in the range of 5.5–7.5 at 25 °C.

2.2. AA performance

AA performance is investigated at high pressure in a rocking cell equipment (PSL Systemtechnik, Germany). A schematic diagram of the rocking cell equipment is shown in Fig. 2. The rocking cell equipment contains 2 sapphire cells. Each cell has a volume of 20 mL equipped with a steel ball and two position sensors for the ball running time measurement. The steel ball runs back and forth in the cell during the tests and provides agitation. In each test, the cells are filled with 10 mL of liquid mixtures including surfactant, condensate and deionized water or brine. The cells are placed into a water bath connected to an external chiller. After the water bath is filled with water, the cells are flushed with methane three times to remove the residual air and then pressurized to a pressure of around 10 MPa. At the beginning of each test, the cells are rocked at ambient temperature for 30 min to reach equilibrium. After that the water bath is cooled from ambient temperature to 2 °C at the cooling rate of 4 °C/hr. This cooling rate was selected to provide several degrees of subcooling (e.g. about 7 °C at 4 wt% NaCl at 10 MPa pressure). The cells are rocked during the whole process. The temperature at 2 °C is kept constant for 4 hr allowing the hydrate to fully develop before it ramps back to the initial temperature. During the cooling and hydrate formation, additional methane is intermittently charged into the cells to maintain the pressure constant (~10 MPa). In each test, the cells are rocked with a frequency of 15 times per minute

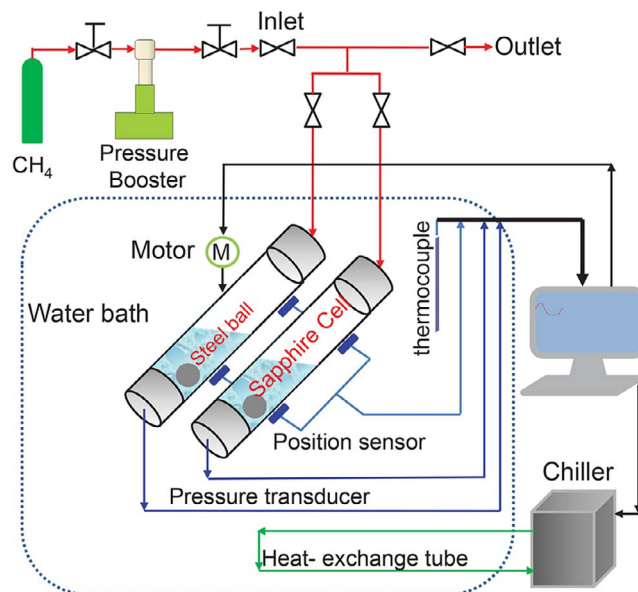


Fig. 2. Sapphire rocking cell setup.

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