



## 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

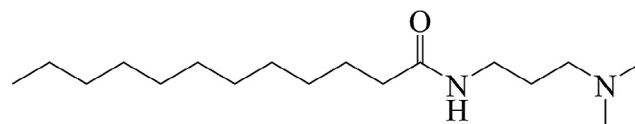


Fig. 1. Chemical structure of the effective component in the AA.

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/cm<sup>3</sup> 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

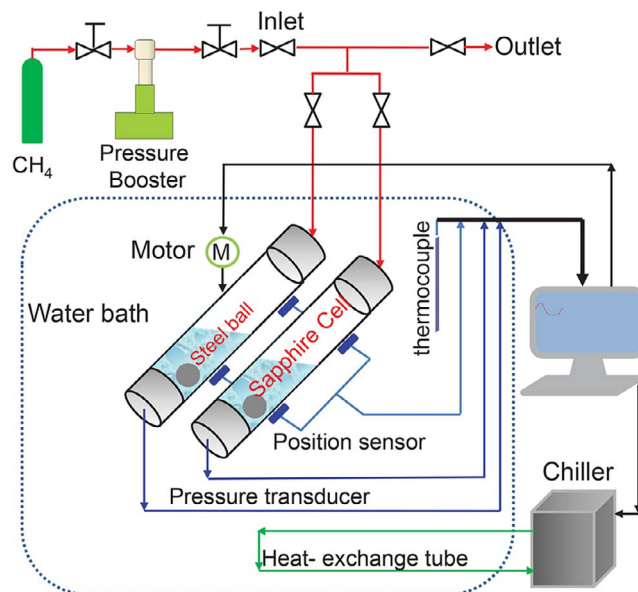


Fig. 2. Sapphire rocking cell setup.

at an angle of  $\sim 45^\circ$ . The bath temperature, cell pressure and the ball running time are recorded during the tests.

### 2.3. Emulsion formation and phase behavior

We visually examine the state of mixture, type of emulsion formation and effects of salts and alcohol. This part of the investigation is carried out at ambient temperature (20 °C) and pressure with AA, condensate liquid and the aqueous phase in 15-mL flat-bottomed vials or centrifuge tubes. The total liquid volume at atmospheric condition is 10 mL and the water cut varies from 10 to 95%. At these conditions, there is very little solubility of methane in the condensate. AA concentration (based on aqueous phase) is 1 wt% except in two tests where it is higher. The mixture of AA, condensate and the aqueous phase is homogenized by hand shaking for 10 min and then kept undisturbed. The phase distribution is recorded at 1 min, 10 min, one hour, and longer after mixing. Images provide qualitative emulsion droplets.

### 2.4. Concentration of AA in aqueous phase

We measure the equilibrium concentration of AA in the aqueous phase-condensate phase system as a function of salt by using UV–Vis (Perkin Elmer Lambda XLS UV–Vis Spectrophotometer) at a wavelength of 250 nm. As part of the process a standard calibration curve (see Fig. S1 in the Supporting Information) is obtained from a set of 5 AA solutions of known concentrations (0.01, 0.02, 0.04, 0.06 and 0.08 wt%). Emulsions with various salt concentrations were prepared and kept static under ambient conditions. After the phase separation of the emulsions in vials or centrifuge tubes, the AA aqueous solution is selected by removing the condensate layer using a pipette and the concentration of AA is measured by the UV–vis. In each test, the sample from water layer is diluted 10 times or higher with DI water to facilitate the concentration tests.

## 3. Results and discussion

### 3.1. AA performance

Performance of AA at various conditions is measured by visual observation and ball running time. A sudden pressure drop indicates hydrate formation. A long ball running time implies the high viscosity of the fluid in the cell. The effectiveness of hydrate anti-agglomeration is classified as “Yes”, “No” and “Yes<sup>P</sup>”. “Yes” represents a clear pass, “No” represents hydrate blockage as will be readily judged by the ball frozen in place. “Yes<sup>P</sup>” represents possible pass with deposition of hydrate particles at the end of the cell or (and) on the wall.

#### 3.1.1. AA performance at low water cut of 10 and 20%

We first investigate the effect of NaCl on hydrate anti-agglomeration at water cuts of 10 and 20% at AA concentration of 1 wt% in the aqueous phase. Results show that 1.0 wt% AA is effective at both water cuts without the salt in the aqueous phase. The hydrate particles remain dispersed in the fluid mixture as shown in Fig. 3(a); hydrate volume fraction in the liquid mixture is around 5% (Table S4). NaCl (e.g. 1 to 10 wt%) at 10% water cut makes the AA ineffective after hydrate formation as shown in Fig. 3(b), in which the steel ball becomes completely trapped by the hydrates. At 10% water cut and 4 wt% NaCl, a higher dosage of AA (e.g., 2 wt%) is required to prevent hydrate plug. In tests with NaCl, the aqueous phase is separated from condensate liquid in the high pressure cells.

At 20% water cut, there is no appreciable effect of NaCl on AA performance (Table 1). AA is effective without and with the salt. We have conducted tests to 6 wt% NaCl. Without salt, the hydrate volume fraction in the slurry is around 12% (See Table S4).

It has been reported that QAS become more effective at higher salt concentrations [5]. In this study, we find that at low water cut (e.g.,

10%) NaCl in the aqueous phase decreases the AA performance (Table 1). The mechanism will become clear when we present the effect of salt on emulsion phase behavior and AA partitioning in the aqueous and condensate liquid phase.

#### 3.1.2. AA performance at 30, 50, and 80% water cut

NaCl salt concentrations in the range of 3 to 4 wt% make the 1 wt% AA effective at a pressure of 10 MPa. Gao has also demonstrated that salinity of aqueous phase has a significant effect on AAs performance at high water cuts [12]. We introduce NaCl into the aqueous phase and determine the minimum NaCl concentration at various water cuts for effective anti-agglomeration. In all the tests 1 wt% AA is used. The minimum NaCl concentration is found to be 3 wt% at 30% water cut (Fig. S2). When the water cut increases from 30 to 50 and 80%, 4 wt% NaCl anti-agglomeration becomes effective (Table 2, Fig. S2). Fig. 4 shows the result at 50% water cut at 1 wt% AA and 4 wt% NaCl. Hydrate crystallization starts at 6.1 °C and 10.245 MPa. The ball running time increases quickly at the start of hydrate crystallizations. After the hydrate formation is fully developed at 2.0 °C, the pressure in the cell and the ball running time stay constant. The mixture in the cell turns into slurry and no blockage is observed during the test (Fig. S2). The hydrate volume fraction in the slurry is around 30% (see the Supporting Information). After hydrate dissociation, the pressure in the closed cell reaches 14.6 MPa at 14.5 °C.

At water cut of 80% there is significant increase in viscosity from the ball running time measurements (not shown). But the increase in viscosity at 50% water cut is not very pronounced (see ball running time in Fig. 4). Moradpour et al. [20] investigated viscosity of water/oil/hydrate mixtures. At water cuts of 50 and 70%, and hydrate volume fractions of 25 to 35%, there is significant increase in viscosity of the mixture [20]. It seems the AA used in this work does not show dramatic increase in viscosity at water cuts of 50% and lower. Due to strong adsorption of AA molecules of AA onto the surface of hydrate particles the size of hydrate particles may be small. This will facilitate the flowability of hydrate slurries. Lv et al. reported the high performance of AA in producing hydrate slurries of small hydrate particles in methane/water/diesel systems at low water cuts [21]. Salts reduce solubility of AA molecules in the aqueous phase and drive them to the hydrate surface. At water cuts of 90 and 95% to be described next, the ball running time is similar to the 80% water cut implying high viscosity of the slurry.

#### 3.1.3. AA performance at very high water cuts of 90 and 95%

We investigate our AA performance at very high water cuts of 90 and 95%. There is no report of AA effectiveness in this range of water cuts except the AA used in this work. Table 3 shows that NaCl at 11 wt% in combination with 1 wt% AA makes anti-agglomeration effective at 90% water cut. The effect of salt on stability of oil-in-water emulsion is often different than in water-in-oil emulsions. Fig. S2d shows the agglomeration states of hydrates with 10 wt% NaCl and 1 wt% AA at 90% water cut, designated by “Yes<sup>P</sup>”. At this condition, hydrate volume fraction in the liquid phase is around 33% (Table S4). When alcohol is introduced the concentration of salt could be reduced. We find that 8 wt% alcohol in combination with 4 wt% NaCl and 1 wt% AA can make the anti-agglomeration effective. Both alcohol and NaCl reduce the conversion of water to hydrates.

At 95% water cut and 1 wt% AA, we observe that the liquid phase becomes very viscous, almost solid like by continuous agitation. Severe flocculation of the emulsion is observed during rocking of the cell. The flocculation makes the mixture very viscous and can completely prevent movement of the ball before hydrate formation. We can reproduce the flocculation of the emulsion in vials (15 mL) at room temperature and atmospheric pressure. The phase behavior including type of emulsion formation at 95% water cut will be discussed later. Addition of alcohol eliminates flocculation and makes AA effective. We will also discuss the process of flocculation later.

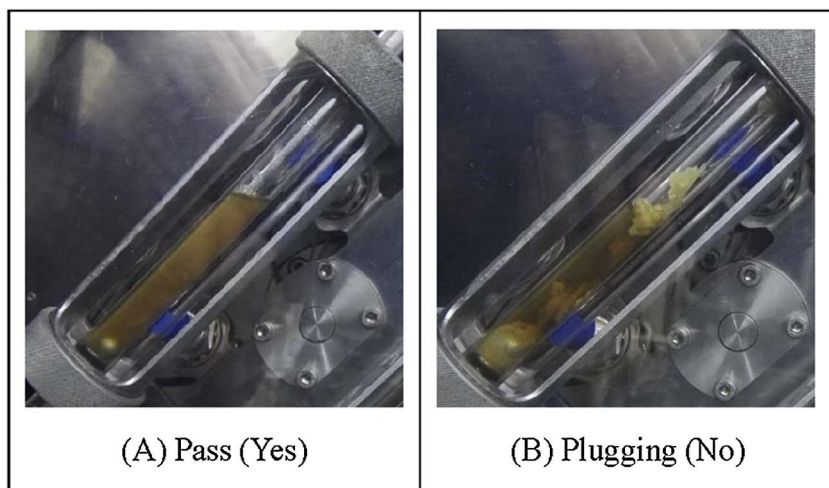


Fig. 3. Effectiveness of 1 wt% AA at 10% water cut (a) no NaCl (effective), and (b) 1 wt% NaCl (not effective).

**Table 1**  
Effectiveness of AA at various salt concentrations in methane/condensate/aqueous phase at 10 and 20% water cuts.

Aqueous (mL)	Condensate (mL)	Water cut (%)	NaCl (wt%)	AA (wt%)	Effectiveness
1	9	10	0	1	Yes
1	9	10	1	1	No
1	9	10	10	1	No
1	9	10	4	2	Yes
2	8	20	0	1	Yes
2	8	20	6	1	Yes

**Table 2**  
Effective dosages of AA and NaCl in methane/condensate/aqueous phase at 30, 50, and 80% water cuts.

Aqueous (mL)	Condensate (mL)	Water cut (%)	NaCl (wt%)	AA (wt%)	Effectiveness
3	7	30	3	1	Yes
5	5	50	4	1	Yes
8	2	80	4	1	Yes

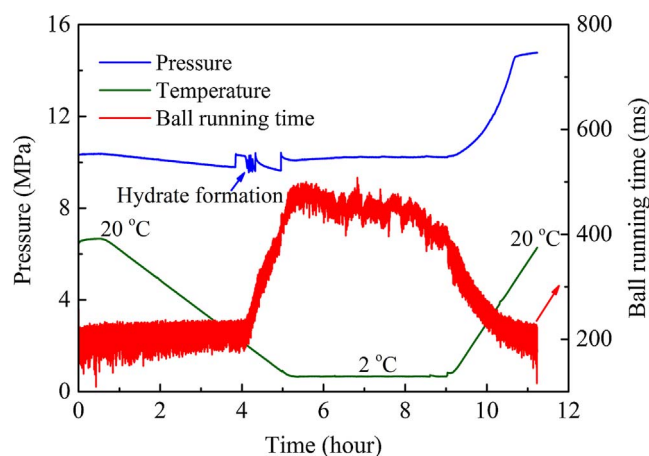


Fig. 4. The cell pressure, bath temperature and ball running time at 4 wt% NaCl and 50% water cut: 1 wt% AA.

### 3.1.4. AA performance at water cut of 100%

Fig. 5 presents the hydrate anti-agglomeration performance at 1 wt% AA and 11 wt% NaCl at 100% water cut. Hydrate crystallization starts at 2.7 °C and 10.1 MPa. Methane gas is added into the cell to

support the pressure due to gas consumption at 2 °C. The methane hydrate volume fraction is around 26% (Table S4). After hydrate dissociation from increase in temperature, the pressure increases to 13.82 MPa at 9.75 °C. The steel ball runs freely in the hydrate slurry during the whole test (Fig. S2) while the ball running time increases from 200 ms to around 1000 ms at the high hydrate content in the cell. It is interesting that the ball running time increases gradually before the hydrate formation, indicating that there is an increase in the viscosity of the AA solution. The increase in the viscosity of AA solution before hydrate formation is probably due to the formation of micelles at lower temperatures. The critical micelle concentration (CMC) of the AA in water is  $30 \pm 3$  ppm (0.003 wt%) [13], which is much lower than 1 wt%. The micelles can convert from spherical shape to ellipsoidal shape or other structures [22]. At this condition, the properties of the AA solution can be changed by the micelles. There is a sudden drop of ball running time at the beginning of hydrate crystallization. The sharp ball running time decrease indicates a sudden decrease in viscosity of the mixture, which is probably due to the dissociation of the micelles. In the aqueous phase, once hydrate particles appear, the AA molecules will preferably adsorb onto the hydrate crystal surface, resulting in the dissociation of micelles according to the sketch presented in Ref. 13. The adsorption of AA molecules on the surface of hydrate is due to the lower dielectric constant of hydrate (58 at 273 K) than that of water (88 at 273 K) [13]. This interpretation has been established by molecular dynamics (MD) simulations [23].

In a previous work we reported hydrate anti-agglomeration at 100% water cut in a closed system [24]. In this work, anti-agglomeration at 100% water cut is investigated at constant pressure of 10 MPa where the driving force is higher. In Fig. 6 we plot the effect of salt concentration on the equilibrium hydrate formation temperature for methane at 10 MPa. The hydrate equilibrium temperature ( $T_s$ ) in methane/brine system is calculated from [1]

$$\left[ \frac{1}{T_w} - \frac{1}{T_s} \right] = \frac{6008n}{\Delta H} \left[ \frac{1}{273.15} - \frac{1}{T_s} \right] \quad (1)$$

where  $T_w$  is the hydrate equilibrium temperature of water without salt,  $T_s$  is the freezing point of the NaCl solution [25],  $n$  is the hydration number,  $\Delta H$  is the heat of dissociation of hydrates. For methane, the value of the coefficient ( $6008n/\Delta H$ ) is 0.665 [1]. As shown in the hydrate plot in Fig. 6, 19 wt% NaCl (based on the water phase) will inhibit the formation of hydrates in methane/brine system at 10 MPa and 2 °C. The anti-agglomeration is observed at 1 wt% AA with 11 wt% NaCl.

Tests are also conducted to determine the effect of alcohol on hydrate anti-agglomeration. The measurements show that at 1 wt% AA and 4 wt% NaCl, 11 wt% alcohol results in anti-agglomeration. NaCl is more effective than the alcohol in hydrate anti-agglomeration when

**Table 3**  
Effectiveness of AA at various NaCl and alcohol concentration in the methane/condensate/aqueous phase at 90, 95, and 100% water cuts.

Aqueous (mL)	Condensate (mL)	Water cut (%)	NaCl (wt%)	AA (wt%)	Alcohol (wt%)	Effectiveness
9	1	90	11	1	0	Yes
9	1	90	10	1	0	Yes <sup>p</sup>
9	1	90	4	1	8	Yes
9.5	0.5	95	4	1	0	No
9.5	0.5	95	4	1	8	Yes
10	0	100	11	1	0	Yes
10	0	100	4	1	11	Yes

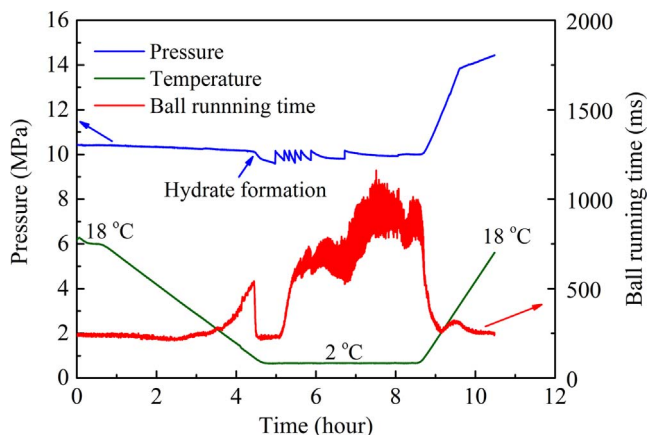


Fig. 5. The cell pressure, bath temperature and ball running time vs time: 1 wt% AA and 11 wt% NaCl at 100% water cut.

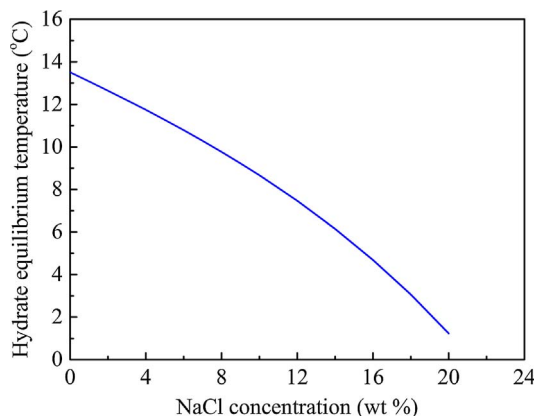


Fig. 6. Effect of NaCl concentration on methane hydrate equilibrium temperature at 10 MPa.

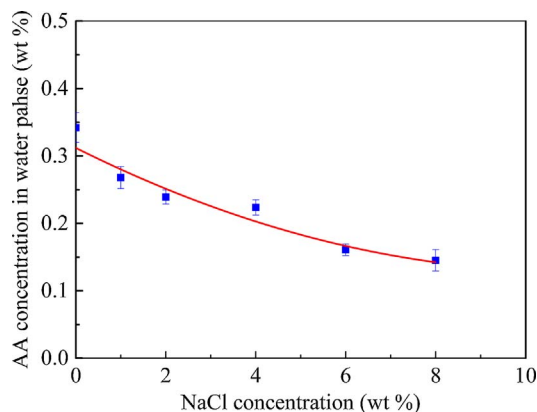


Fig. 8. AA concentration vs NaCl concentration in the aqueous phase separated from emulsions stabilized by 1 wt% AA: water cut is 10%.

only conversion of water to hydrates is considered.

### 3.2. AA partitioning in water and oil phase

We investigate the partitioning of AA in the hydrocarbon liquid and aqueous phases at 10% water cut. Images in Fig. 7 show that salt concentration has a significant effect on the stability of emulsion. All samples are unstable as phase separation occurs several minutes after mixing. The upper layer is oil phase, while bottom phase is water-in-oil emulsion after mixing. There is a significant effect of salt on breakup of the water-in-oil emulsions. The rate of separation is affected by the salt concentration. For the sample with 1 wt% NaCl, the water-in-oil emulsion in the bottom layer breaks one hour after mixing. For the sample with NaCl concentration higher than 2 wt%, the bottom phase converts into a clear water phase shortly after mixing, which indicates a complete separation. Only when there is no salt in water, the bottom emulsion layer stays stable after one hour of mixing. We verify W/O emulsions by testing the immiscibility of the emulsion droplets in water.

We measure the AA concentration in the aqueous phase by using a

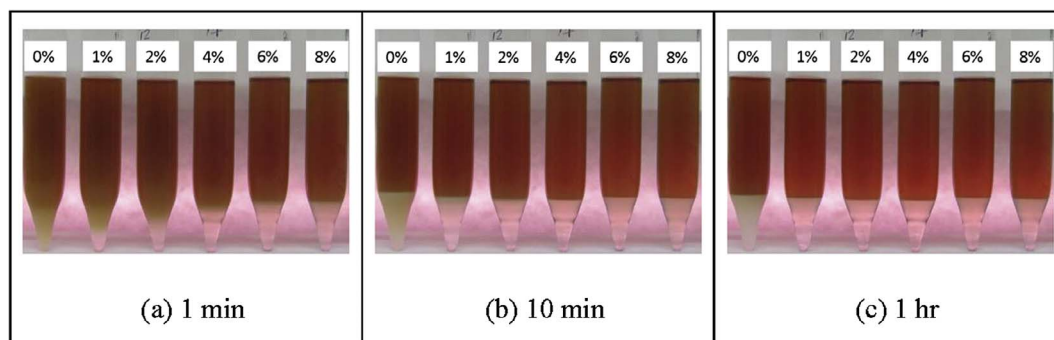


Fig. 7. Condensate and aqueous phase distribution at various salt concentrations at  $t = 1$  min (a),  $t = 10$  min (b), and  $t = 1$  hr (c) after mixing: water cut = 10%; AA = 1 wt%. Salt concentrations (wt%) are listed at the top of vials.

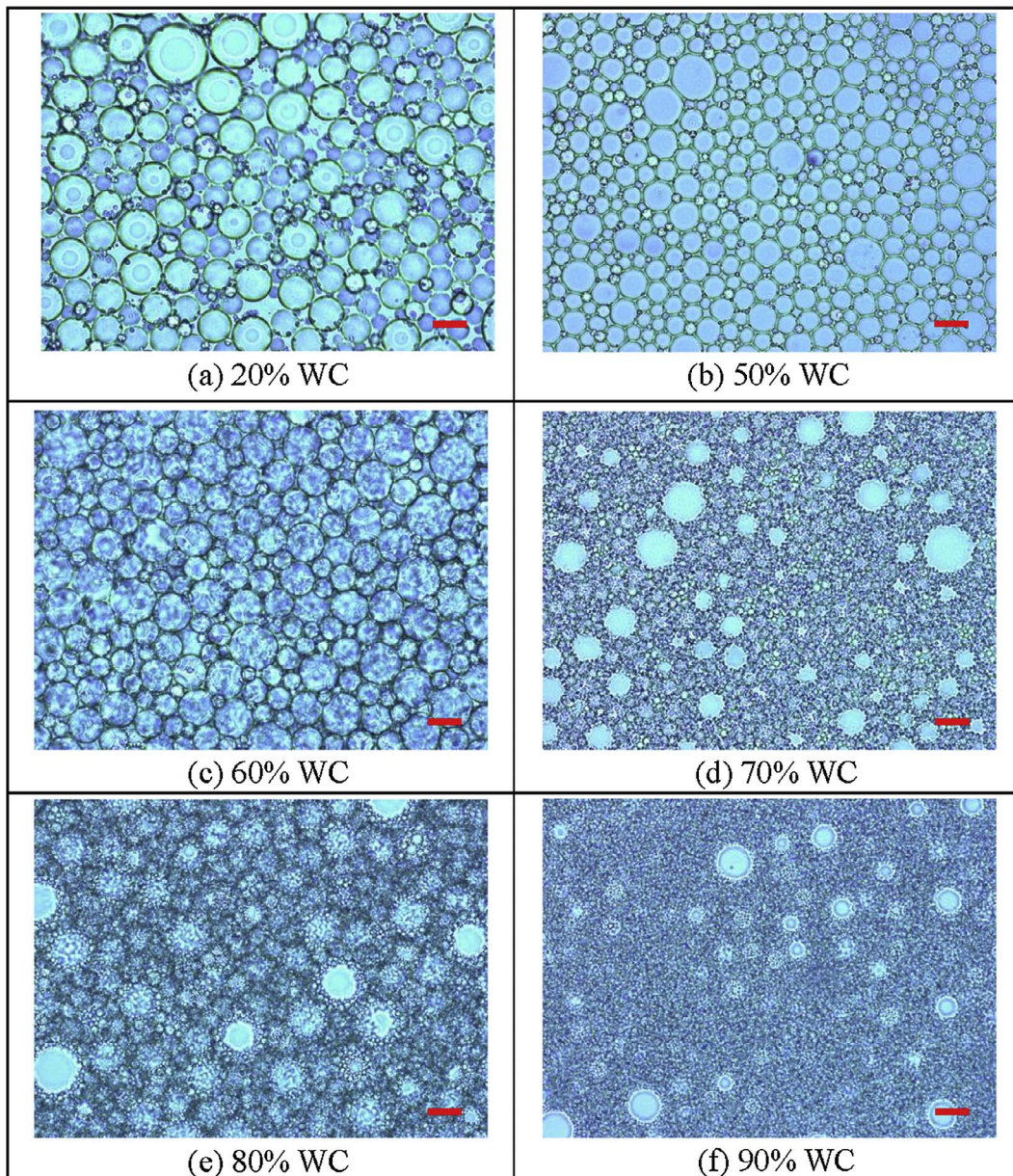


Fig. 9. Microscope images of fresh condensate/water emulsions at water cuts of: (a) 20%, (b) 50%, (c) 60%, (d) 70%, (e) 80% and (f) 90%. Each sample contains 1 wt% AA and 0 wt% NaCl. Scale bar in each micrograph is 100  $\mu$ m.

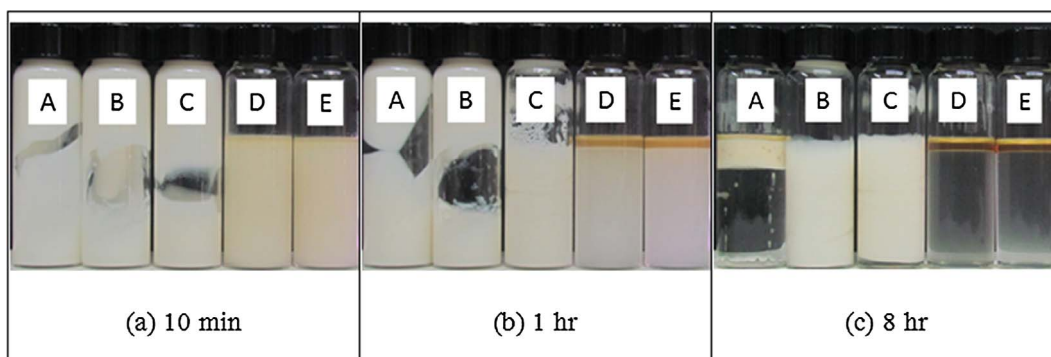


Fig. 10. Flocculation in mixtures of condensate, water and AA (water cut = 95%, AA = 1 wt%) at time: (a) 10 min, (b) 1 hr, and (c) 8 hr. (A. No salt; B. 4 wt% NaCl; C. 10 wt% NaCl; D. 8 wt% alcohol; E. 4 wt% NaCl + 8 wt% alcohol).

UV–Vis spectrophotometer to quantify the effect of NaCl on AA solubility in the aqueous phase. Fig. 8 shows that the AA concentration in the aqueous phase decreases by about 50% when the salt concentration increases from 0 to 8 wt%. The decreased AA solubility in the aqueous phase may increase the surfactant concentration in the hydrocarbon liquid phase. If the hydrates form in the aqueous phase and there are no emulsions, there may not be sufficient AAs to adsorb onto the hydrate crystals to achieve anti-agglomeration. This explains low efficiency of anti-agglomeration in low water cut from the salt effect. In a previous work, the adverse effect of salts on the performance of nonionic surfactants, rhamnolipids in the aqueous phase was observed [15]. We found that an increase in concentration of salts could result in a reduced efficiency of anti-agglomeration similar to what we observe at 10% water cut in this work. A similar mechanism was proposed to interpret salt effect [15].

### 3.3. Emulsion phase behavior

In mixing of water or brine with the condensate liquid and 1 wt% AA we observe W/O emulsions in water cuts range of 10 to 80%. At 90 and 95% water cuts, we observe oil-in-water (O/W) emulsions (see Figs. S3, S4). The stability of water-in-oil emulsions is significantly affected by water cut and NaCl. Emulsions at higher water cuts are more stable (Fig. S3) and form a network structure by droplets (Fig. 9). At water cuts < 50%, no aggregation of the water droplets is observed. When water cut is in the range of 50 to 60%, water droplets begin to contact each other. Once the water cut is above 70%, a network is formed due to the aggregation of the droplets (see Fig. 9). In general, water-in-oil emulsion increases the efficiency of anti-agglomeration. Fig. S4 presents the effect of NaCl on the stability of emulsions at various water cuts. NaCl can decrease the stability of the water-in-oil emulsions. Despite the adverse effect of NaCl on emulsion stability, NaCl improves the AA performance in water cut range of 30 to 80%. During the rocking cell tests with and without salt at the water cut of 30 to 80%, the liquid mixture turns to emulsions. These observations indicate that at 1 wt% AA the water phase is dispersed into the oil phase in the presence of salts at water cuts of 30–80% during rocking. Therefore, the enhancement in the performance of AA from NaCl may be mainly a result of the thermodynamic inhibition of NaCl, which lowers the conversion of water to the hydrates (Table S4). As shown in Table S4, at water cuts of 30, 50 and 80%, the water to hydrate conversions are 63%, 56% and 48%, respectively.

At 95% water cut, the process is different from the simple water-in-oil and oil-in-water emulsions. An added complication is from severe flocculation of the mixture. We conduct tests in vials (15 mL) at room temperature. AA, condensate, and brine/water are loaded into the vials to prepare a mixture with a concentration of 5 vol% (based on total liquid phase) condensate oil and 1 wt% AA, but different concentrations of NaCl (0, 4 and 10 wt%). Emulsions form from hand shaking. The oil-in-water emulsion easily forms under mild shaking, and breaks quickly under static conditions. Flocculation of the emulsions is observed from vigorous shaking. A variety of nonionic surfactants have been found to flocculate the oil-in-water emulsions [26]. A model based on micelle depletion may be used to rationalize the flocculation of oil-in-water emulsions stabilized by nonionic surfactants [26]. Strong flocs have been discussed in the theory of “micelle depletion” in the aqueous phase. Based on the theory of micelle exclusion, the flocculation is driven by exclusion of surfactant micelles between two approaching oil droplets.

As shown in Fig. 10(a), flocculation occurs at 95% water cut under room temperature and ambient pressure. The mixture of liquid condensate/water (brine)/AA turns to a viscous cream-like material. We find that flocs with salt exhibit higher stability (Fig. 10). Liu et al. have reported that Arquard 2HT-75 can form solid like emulsion at 75% water cut with NaCl [27].

In a previous study we demonstrated that alcohol cosurfactants can

improve the stability of oil-in-water emulsions with the nonionic rhamnolipids used as an anti-agglomerant [16]. In this work we found that 8 wt% alcohol can prevent the flocculation (Fig. 10). The addition of 8 wt% alcohol makes the aqueous phase a good solvent for AA. The inhibition effect of alcohol on emulsion flocculation may be due to the enhanced solubility of AA in aqueous phase. The introduction of an alcohol into the aqueous phase may increase the solvency of aqueous phase for AA. Flocculation which is believed to be due to formation of structures between neighboring emulsions through connections with micelles is affected by an alcohol. The alcohol addition will promote the dissociation of AA micelle structures due to the reduced strength of hydrophobic interactions and therefore inhibit the flocculation process. Ref [28] discussed the dissociation of micelles by alcohol would effectively prevent the flocculation of emulsions.

## 4. Conclusions

NaCl affects the AA performance in a condensate liquid at various water cuts from 10 to 100% due to different mechanisms.

1. At 10% water cut, NaCl decreases effectiveness of AA due to rapid destabilization of water-in-oil emulsions.
2. At 20% water cut, no appreciable effect of NaCl on AA performance is observed. The effect from water-in-oil emulsion and the effects from increase in salt concentration in the aqueous phase balance each other. The salt reduces AA dissolution in the aqueous phase which may increase the adsorption at the hydrate interface.
3. NaCl in the water cut range of 30 to 80% improves the performance of AA. NaCl lowers water to hydrate conversion and consequently lowers hydrate volume fraction in the liquid mixtures. NaCl also reduces the solubility of AA in the aqueous and drives the AA to the hydrate interface.
4. In the range of 30 to 80% water cuts, water-in-oil emulsions form.
5. At 90% water cut, oil-in-water emulsions are formed and water becomes the continuous phase. As a result, higher salt concentration will make the AA effective. The same effect is also observed at 100% water cut. The effect of salt is different in stability of water-in-oil and oil-in-water emulsions
6. At higher water cuts the effect of an alcohol in reduction of hydrate volume fraction is similar to salt. The salt is more effective in comparison to alcohol.
7. At 95% water cut, we observe pronounced flocculation with very high viscosity to the extent that the fluid system in vials moves hardly under gravity. The introduction of alcohol inhibits flocculation.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2017.08.096>.

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