Hydrate anti-agglomeration and synergy effect in normal octane at varying water cuts and salt concentrations

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Abstract

Anti-agglomeration is a promising approach to address hydrate risks in oil and gas flowlines from the deep sea. Salt concentration of the coproduced water with hydrocarbons is known to affect anti-agglomeration. Most studies report improvement in efficiency of anti-agglomeration but some authors report a decrease from salts. In this work, the effect of water cut (ratio of aqueous phase to total liquid) and NaCl concentration on the effectiveness of the cocamidopropyl dimethylamine anti-agglomerant (AA) are investigated in normal octane and methane systems. We also investigate the synergic effect of a cosurfactant (Span 80) in improving the performance of the AA at water cuts of 10%–30%. A likely mechanism of the synergism is suggested: the co-surfactant (Span 80) promotes the dispersion of water droplets in the oil phase and the AA prevents the agglomeration of the hydrate particles. We investigate emulsion formation and the phase behaviour of octane/brine/AA/Span 80 emulsion to shed light on the mechanisms at play. A solid-like fluid which hardly moves under gravity is observed when the normal octane and water/brine and the anti-agglomerant are mixed at a water cut of 95%. The solid-like behaviour which is attributed to flocculation can be remedied by the introduction of alcohols in the solution. There are similarities in emulsion formation and hydrate anti-agglomeration of normal octane and a condensate liquid which was investigated recently and there are also major differences.

1. Introduction

Gas hydrates are ice-like crystals composed of hydrogen bonded water molecules with light hydrocarbon species (e.g., methane) in the cages. Hydrates can form at low temperature and high pressure conditions in subsea flowlines [1]. The formation of gas hydrates often blocks the oil and gas flowlines, and may result in many safety and environmental concerns [2].

In hydrate mitigation, traditional thermodynamic inhibitors are expensive [2,3]. To reduce costs in deep water, low-dosage hydrate inhibitors (LDHIs), which are effective at low concentrations (0.1–1 wt%), have been developed to prevent hydrate blockage [4]. There are two types of LDHIs: kinetic hydrate inhibitors (KHis) and anti-agglomerants (AAs) [4–6]. KHis are water-soluble polymers that can inhibit nucleation and slow down the growth rate of hydrate crystals [7]. The performance of KHis may be weakened when sub-cooling is over 10 °C [8]. Therefore, inhibitors effective at higher sub-coolings are required. Anti-agglomerants (AAs) can be effective at high sub-cooling [4,9]. Quaternary ammonium salts (QAS), which have been in commercial use, are claimed to be effective at very high sub-cooling. Single-tail QAS containing a tail of 10–14 carbon atoms with an ammonium head group and an anion have been found to prevent hydrate agglomeration in saline conditions with a sub-cooling higher than 20 °C [4]. The main limitations of QAS are the toxicity and low biodegradability. They are also not effective at high water cuts.

AAs have been mainly investigated at low water cuts [4,9–11]. They have shown limitations at high water cuts [12–14]. They have shown limitations at high water cuts [12–14]. It is often stated that liquid hydrocarbon phase is required for AAs to function [1]. However, we have shown that the AA we used could be effective without the oil phase [15]. Most of the existing AAs are ineffective at high water cuts (over 50%) [9,16]. Recently, a limited number of studies have shown that AAs can effectively prevent hydrate agglomeration at high water cuts of 80–100% [14,15,17,18]. At 100% water cut a constant volume closed cell in a rocking apparatus was used to examine the performance of the AA [15]. At constant high pressure conditions, the AAs are mostly investigated in high pressure sapphire cells [10,19], autoclaves [8,18–21] and flow loops [22,23]. However, work on hydrate anti-agglomeration in rocking cells at constant high pressure conditions is limited [14,17,24]. The driving force for hydrate

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nucleation at constant pressure is higher than the conditions at constant volume.

In addition to water cut effect, hydrate anti-agglomeration is also affected by salt concentration in the aqueous phase [9,13,15,23–25]. Cationic AAs such as QAS are more effective at higher salt concentrations [9,16]. Nagappayya et al. have reported that salts increase the solubility of ionic AAs in oil phase and promote the formation of water-in-oil emulsion, which facilitate the performance of QAS [25]. However, in a previous study we showed that the performance of QAS could be reduced by the divalent ions (e.g., Mg²⁺) [16]. For two non-ionic AAs (cocamidopropyl dimethylamine and rhamnolipid), we have reported that their performances may reduce by salts [15,16]. Sinquin et al. also report that salts can decrease the AA performance in an acidic crude oil, which contains natural surfactants [26]. In non-ionic surfactants as anti-agglomerants, Kelland et al. have studied the performance of alkylamide and found that the performance increases with increased salinity [23]. As a thermodynamic inhibitor, salts lower the hydrate conversion of water [27], which results in AA effectiveness at high water cuts when the hydrate fraction is lowered [17].

In a recent investigation [28], we have studied the effect of NaCl on hydrate anti-agglomeration over the whole range of water cuts (10–100)% in a condensate liquid/methane/brine system. At low water cut of 10%, NaCl lowered the efficiency of the AA. At 20% water cut, the AA performance was not affected by salt. From 30 to 90% and at 100% water cut, NaCl increased the effectiveness of the AA. At 95% water cut and 1 wt% AA, the mixture of water/brine/condensate turned into a very viscous fluid both in vials at ambient conditions and in the rocking cell apparatus at 100 bar (10 MPa). The solid-like behaviour was due to flocculation. The introduction of alcohol prevented formation of flocs. The combination of alcohol and NaCl was very effective in hydrate anti-agglomeration. These findings motivated us to use normal octane instead of a condensate liquid to investigate the effect of salt and water cut and provide further insight and to examine the differences between normal octane liquid and the condensate liquid. Additionally in this work, we investigate synergistic effect from Span 80 which is an anti-agglomerase in low water cuts at higher concentration than our AA. We find similarities between the mechanisms in condensate liquid and normal octane systems, especially at very high water cuts. We also find major differences in water cuts from 10 to 50%.

As stated above this investigation center on the effect of NaCl on the performance of the AA at high pressure (10 MPa) with water cuts in the range of 10–100% and synergic effect of a surfactant. We investigate the synergistic effect of AA and Span 80 on anti-agglomeration at low water cuts (10–30%). The phase behaviour and the emulsion formation are used to interpret the anti-agglomeration performance of the AA.

2. Experimental materials and methods

2.1. Materials

The AA used in this work is received from Lubrizol Corporation without further purification (AA composition: (80–89) wt% in glycerin, free amine and water). Span 80 (>99% Sorbitan Monoooleate) is from Tokyo Chemical Industry Ltd. (TCI). Fig. 1 provides the chemical structures of the AA and Span 80. Sodium chloride (99.8%) is from Fisher. Reagent alcohol (Ethanol 90 vol%, Methanol 5 vol%, Isopropanol 5 vol%, from Pharmco-Aaper) is used to prevent flocculation encountered at 95% water cut. Octane (97%, Acros Organics) and methane gas (99.99% ultrahigh purity, MADCO) are used as the liquid hydrocarbon and gas hydrate former, respectively.

Fig. 1. Chemical structures of AA (a) and Span 80 (b).

2.2. Test method in hydrate anti-agglomeration

The AA performance tests are conducted in a high-pressure rocking cell apparatus (RCS 2, PSL Systemtechnik, Germany) schematically shown in Fig. 2. It consists of two test cells with a maximum operating pressure of 20 MPa and a cell volume of 20 mL. Each cell contains a stainless steel ball that provides agitation and two proximity sensors which record the ball running time. A pressure transducer (accuracy 0.01 MPa) is connected to each cell to monitor the pressure inside the cell. The inner diameter of each cell and diameter of the steel ball are 0.5 in. (1.27 cm) and 0.4 in. (1.02 cm), respectively. During the rocking, the balls run back and forth and enhance mixing of the mixtures in the cells. Once the cell is blocked by hydrates, the ball will be prevented from moving. The temperature of the water bath is controlled by a chiller and checked by a thermocouple (accuracy 0.1 °C).

In each test, 10 mL-liquid samples containing hydrate anti-agglomerant (AA), octane and brine at various salt concentrations are prepared and charged to the cells. In synergic studies, we use Span 80 in combination with the main AA. Then the cells are placed on the platform axis of the motor in the bath and reconnected to the pressure transducers and methane gas supply. At the beginning of each test, the cells are flushed with methane three times to remove the residual air in the cells and pressurized to a pressure of around 10 MPa. The cells are first rocked at room temperature
Steel ball is trapped by hydrate plug, and cannot move. “Yes” rep- 

trely freely in the hydrate slurry. “No” implies hydrate blockage. The 

observation and ball running time. A sudden pressure drop in a cell 

dicates hydrate formation. A long ball running time indicates 

hydrate formation, the cells are maintained at constant pressure 

(~10 MPa) with additional methane intermittently charged by 

hand operation. In each test, the cells are rocked every 4 s at a rock-

ring frequency of 15 times per minute and an angle of ~45° on both 

sides. The bath temperature, cell pressure and the ball running 
time are recorded every 10 s to monitor hydrate formation and 

anti-agglomeration.

Effectiveness of AAs at various conditions is judged by visual 

observation and ball running time. A sudden pressure drop in a cell 

indicates hydrate formation. A long ball running time indicates 

high viscosity of the mixture in the cell. AA performance is classi-

fied as “Yes”, “YesP” and “No”, based on whether hydrate blockages 

are observed. “Yes” represents a clear pass. Hydrate particles adhere on the end or the 

wall of the cells. All rocking cell tests are repeated at least two 
times.

2.3. Emulsion preparation and phase behaviour tests

The mixtures of surfactants, water/brine, NaCl and n-octane are 

used to investigate formation of emulsions in clean glass vials (vol-

ume: 15 mL) in centrifuge tubes. Each vial and tube is filled with 

a 10-mL liquid mixture containing surfactants, octane and 

brine at various NaCl concentrations. Different experiments are 

conducted at different water cuts in the range of 10% – 95%. At 

100% water cut there is no n-octane. The mixture of n-octane, brine 

and surfactants is prepared by hand shaking for 10 min and then 

kept at static state. Images are taken 1 min, 10 min and longer after 

mixing at room temperature to facilitate the observation of phase 

behaviour and interpretation of the measurements.

3. Results and discussion

3.1. Hydrate anti-agglomeration performance

3.1.1. Water cut at 10%

We first investigate hydrate anti-agglomeration at 10% water 
cut at surfactant concentrations in the range of 1–3 wt% and salt 

concentration in the range of 0–10 wt%, both with reference to 

the aqueous phase. In Table 1, results show that 1 wt% AA is not 

effective at 10% water cut at salt concentrations in the range of 
0–10 wt%. Hydrate blockage occurs at the formation of hydrates, 

as seen in Fig. 3(a), in which steel balls are trapped in the hydrates. 

We increase the AA concentration to 1.4 wt%; no agglomeration is 

observed when there is no salt in the aqueous phase. However, 

when the salt concentration increases to 4 wt%, 1.6 wt% AA is 

required to prevent hydrate plugging. NaCl lowers the performance 

of AA. Fig. 4 shows the successful result of 1.4 wt% AA at 10% water 
cut without salt. Methane hydrates form at 6 °C at pressure of 
10.1 MPa as indicated by the sudden pressure drop and the fluctu-

ation of the ball running time. At this condition, the hydrate vol-

ume fraction in the liquid phase is about 7.5% (Table S2). The steel 

ball runs freely through the cell during the test. The ball running 
time is short throughout the test. In the condensate liquid at 
10% water cut [28], the effective concentration of the AA was 1 wt% 
without salt at the pressure of 10.0 MPa. There is a 40% increase in 
the effective concentration of AA in the n-octane system. We inter-
pret the difference to be due to the adsorption of various compo-

nents from the condensate liquid to the hydrate surface as 
compared to only adsorption from n-octane. In molecular dynam-

ics simulations of adsorption of hydrocarbons and surfactants onto 
hydrate surfaces we have observed adsorption of hydrocarbons 
and the AA [29].

In order to reduce the AA concentration, a commercial non-

ionic surfactant, Span 80, is used in combination with the AA to 

examine if there is synergy between the two surfactants. Span 80 
is an oil-soluble surfactant, which has a hydrophilic-lipophilic 
balance (HLB) value of 4.3 [30]. It is known that emulsifiers that have 
HLB values from 3 to 6 give rise to water-in-oil emulsions [30]. 

Span 80 has been used as a hydrate anti-agglomerant in the laborat-
ory [11,31,32]. In this study, we find that the performance of 
our AA could be significantly enhanced when used in combination 
with Span 80. Table 2 lists the synergistic effect from Span 80 and 
AA in hydrate anti-agglomeration. As shown in Table 2, the mini-

mum concentration of Span 80 for anti-agglomeration is 2 wt% at

Table 1

<p>| Aqueous/ Octane/ Water cut/ NaCl/ AA/ Effectiveness |</p>
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<th>(wt%)</th>
<th>(wt%)</th>
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<td>10</td>
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<tr>
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<td>8</td>
<td>20</td>
<td>4</td>
<td>0.8</td>
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</table>

Fig. 3. Visual observations of AA effectiveness: Water cut is 10%. In (a), the steel ball is frozen in the hydrate plug at the top of the cell.

Fig. 4. The cell pressure, bath temperature and ball running time at 1.4 wt% AA without salt: Water cut is 10%.
10% water cut without salt. At 4 wt% NaCl, Span 80 at 3 wt% leads to hydrate anti-agglomeration. A likely explanation for the adverse effect of NaCl on the performance of Span 80/AA is the reduced concentrations of Span 80/AA in the bulk water phase because of the charge of the salt ions in the aqueous phase. The strong interaction between salt ions and water would weaken the interaction between hydrophilic head group of Span 80/AA and water, which induces a further decrease in the concentration of Span80/AA in bulk water phase. Salt also destabilize the water-in-oil emulsion stabilized by Span 80 as will discuss later.

Interestingly, our measurements show that anti-agglomeration is achieved at 1 wt% concentration of the combined molecules of the AA and Span 80. A concentration ratio (weight basis) ranging from 1:2 to 1:3 of AA to Span 80 is effective to prevent hydrate agglomeration without the salt in the aqueous phase. At 4 wt% NaCl, a total concentration of 1 wt% of AA and Span 80 were less effective at the same conditions.

We suggest the following mechanism of synergistic effect of the AA and Span 80 in preventing hydrate agglomeration. Due to the oil-soluble nature of Span 80, the mixtures of Span 80 and our AA enhance water-in-oil emulsion stability before hydrate formation. When hydrate formation starts, another component of the combined surfactants, the AA, plays a main role in anti-agglomeration of hydrate particles in aqueous phase. The AA molecules have the advantage of stronger adsorption onto the surface of hydrate particles than Span 80, because the hydrogen bond between the hydrophilic group of AA and hydrate surface may be stronger than the hydrogen bond between Span 80 and hydrate surface. This interpretation is based on the enthalpy of hydrogen bond N–H–O (from the AA) and O–H–O (from Span 80), which are (29 and 21) kJ mol\(^{-1}\), respectively [33]. With the combined function of the dual surfactant system, the water-in-oil emulsions may be more stable and the hydrate anti-agglomeration may be enhanced. The mechanism will become clear when we present the effect of combined surfactants (AA and Span 80) on emulsion phase behaviour. Chen et al. [21] have also observed synergistic anti-agglomeration using AEO-3 and Span 20 as the compounded hydrate AAs in (diesel + water + natural gas) system. At 30% water cut, they observed a stable hydrate slurry with the addition of (3 wt% AEO-3 + 2 wt% Span 80) at 3.44 MPa and 274.2 K. Single applications of these surfactants at 3 wt% AEO-3, and 2 wt% Span 80 were less effective at the same conditions.

### 3.1.2. Water cut at 20%

AA performance at 20% water cut is listed in Table 1. AA at 1.4 wt% is effective without salt. When 4 wt% NaCl is introduced into the aqueous phase, AA at 0.8 wt% is effective. Fig. S1 provides the results of 1 wt% AA and 1 wt% AA+4 wt% NaCl at 20% water cut. NaCl increases the performance of AA. The water-in-oil emulsions at 4 wt% NaCl is more stable (see Fig. S4) than with no salt (see Fig. S3). At salt concentration of 4 wt%, the water-in-oil emulsion fraction at 20% water cut is more than at water cut 10% as shown by Fig. S4. Table S2 shows that at 20% water cut and at 1.4 wt% AA in the aqueous phase, the hydrate volume fraction is about 15%; with NaCl at 4 wt% in the aqueous phase, the hydrate volume fraction decreases to about 11%.

Next the mixtures of the AA and Span 80 are examined for the synergistic effect. Tests are conducted by varying the concentration ratios of AA and Span 80 at a total concentration of 1 wt% (Table 3). Pure Span 80 concentration for anti-agglomeration is 3 wt% at 20% water cut (Table 3). The minimum dosage for the mixture of the AA and Span 80 is only 1 wt%. A concentration ratio ranging from 1:1 to 1:3 of AA to Span 80 is optimal for hydrate anti-agglomeration. The mechanism of the synergistic effect of AA and Span 80 was suggested above and will be further discussed when we present emulsion measurement.

### 3.1.3. Water cut of 30–80%

The results given in Table 4 show the performance of AA in systems with water cuts in the range of 30–80%. At 30% water cut, 1 wt% AA is effective without salt. When 4 wt% NaCl is introduced into the aqueous phase, AA at 0.8 wt% is effective. NaCl increases the performance of AA. AA and Span 80 mixtures are also examined for the synergistic effect. Tests are conducted by varying the concentration ratios of AA and Span 80 at different total concentrations, e.g., (0.4, 0.6, 0.8 and 1.0) wt%. We found pure Span 80 is not an effective anti-agglomeration at concentrations up to 6 wt% at 30% water cut (Table 5) with and without salt. The minimum effective dosage

<table>
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<th>AA/(wt%)</th>
<th>Span 80/(wt%)</th>
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<th>NaCl/(wt%)</th>
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<td>5/1</td>
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### Table 2

Synergistic effect of Span 80 and AA at different ratios (weight basis). Liquid (brine/octane) volume in Sapphire cell is 10 mL. 10% water cut.

<table>
<thead>
<tr>
<th>AA/(wt%)</th>
<th>Span 80/(wt%)</th>
<th>AA/Span 80 ratio</th>
<th>NaCl/(wt%)</th>
<th>Effectiveness</th>
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Synergistic effect of Span 80 with AA at different weight ratios. Liquid volume (brine and octane) in Sapphire cell is 10 mL; Water cut is 30%.

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</table>

3.1.4. Water cuts of 90 and 95%

Tests with AA and NaCl at water cuts of 90% and 95% are also conducted. Results of AA performance at 90 and 95% water cuts are shown in Table 6. Our measurements show that the salt concentration should be high at water cut of 90%; 11 wt% NaCl and 1 wt% AA provide anti-agglomeration. Agglomeration states of the hydrates with 1 wt% AA + 10 wt% NaCl and 1 wt% AA + 6 wt% NaCl at 90% water cut are shown in Fig. S2, which are designated by “Yes” and “No”, respectively. Addition of alcohol at 8 wt% (in relate to the aqueous phase) in combination with 4 wt% salt and 1 wt% AA can also prevent hydrate agglomeration.

At 95% water cut, the emulsions are easily formed at 1 wt% AA and severe flocculation of the emulsion is observed during rocking.
The flocs make the mixture very viscous and can completely block flow in the sapphire cell. Addition of alcohol can inhibit flocculation. Alcohol at 10 wt%, in a mixture of 4 wt% NaCl and 1 wt% AA prevents both flocculation and hydrate agglomeration (Fig. S2). The process of flocculation will be discussed later.

3.1.5. Water cut of 100%

In a previous work, we have shown that our AA can be effective without the oil phase in a closed system [15]. In this work, we investigate the performance of the AA at a high pressure of 10 MPa where the driving force for hydrate formation is higher than at the constant volume. Results are presented in Table 6. Hydrate anti-agglomeration at high pressure of 10 MPa can realize by using 11 wt% NaCl and 1 wt% AA (Fig. S2). Fig. 6 presents the results at 11 wt% NaCl and 1 wt% AA at 100% water cut. Hydrate forms at 2.7 °C and 10.1 MPa. After the hydrate formation has completed at 2 °C, the ball running time ramps from 200 ms to 1000 ms, the volume fraction of the methane hydrate in the liquid slurry is around 26%, the salinity of the remaining water phase in the cell has increased to about 14% (Table S2). Interestingly, a gradual increase in the ball running time before hydrate formation is observed, indicating that there is an increase in the viscosity of the liquid mixture. The increase in the viscosity of the mixture may be due to the formation of AA micelles in the aqueous phase. The critical micelle concentration (CMC) of AA in water is reported to be around 30 ± 3 ppm (0.003 wt%) [15], which is much lower than 1 wt%. A sudden drop of the ball running time is also observed when the hydrate formation starts. The decrease in ball running time implies that there is a drop in viscosity which may be due to the dissociation of the AA micelles. In a previous study, Sun and Firoozabadi have proposed that, in water, the AA molecules may adsorb onto the surface of hydrate crystals once the formation of hydrate starts, and thus lead to the dissociation of the AA micelles [15]. Dissociation of micelles leads to a drop in the ball running time when hydrate formation starts.

Fig. 7 depicts the effect of salt concentration on hydrate equilibrium temperature at 10 MPa. The data of the methane hydrate equilibrium temperature (Ts) at 10 MPa where the driving force for hydrate formation is higher than at the constant volume. Results are presented in Table 6. Hydrate anti-agglomeration at high pressure of 10 MPa can realize by using 11 wt% NaCl and 1 wt% AA (Fig. S2). Fig. 6 presents the results at 11 wt% NaCl and 1 wt% AA at 100% water cut. Hydrate forms at 2.7 °C and 10.1 MPa. After the hydrate formation has completed at 2 °C, the ball running time ramps from 200 ms to 1000 ms, the volume fraction of the methane hydrate in the liquid slurry is around 26%, the salinity of the remaining water phase in the cell has increased to about 14% (Table S2). Interestingly, a gradual increase in the ball running time before hydrate formation is observed, indicating that there is an increase in the viscosity of the liquid mixture. The increase in the viscosity of the mixture may be due to the formation of AA micelles in the aqueous phase. The critical micelle concentration (CMC) of AA in water is reported to be around 30 ± 3 ppm (0.003 wt%) [15], which is much lower than 1 wt%. A sudden drop of the ball running time is also observed when the hydrate formation starts. The decrease in ball running time implies that there is a drop in viscosity which may be due to the dissociation of the AA micelles. In a previous study, Sun and Firoozabadi have proposed that, in water, the AA molecules may adsorb onto the surface of hydrate crystals once the formation of hydrate starts, and thus lead to the dissociation of the AA micelles [15]. Dissociation of micelles leads to a drop in the ball running time when hydrate formation starts.

\[
\left[ \frac{1}{T_w} - \frac{1}{T_s} \right] = 6008n \left[ \frac{1}{\Delta H} \right] \frac{1}{273.15} \frac{1}{T_p}
\]

(1)

where \( T_p \) is the equilibrium melting temperature of the NaCl solution [34], \( T_w \) is the hydrate equilibrium temperature in water without salt, \( n \) is the hydration number of methane molecules, and \( \Delta H \) is the heat of dissociation of methane hydrates. For methane, the value of \( (6008 n/\Delta H) \) is 0.665 [1]. The extent to which the NaCl can reduce the equilibrium temperature of methane hydrate at 10 MPa is shown in Fig. 7. At 19 wt% NaCl and 10 MPa, the hydrate equilibrium temperature is around 2 °C. At 100% water cut, 11 wt% NaCl combined with 1 wt% AA is sufficient to achieve anti-agglomeration, indicating that AA can significantly reduce the concentration of NaCl. At this condition, synergistic effect is observed when AA is combined with NaCl.

3.2. Emulsion phase behaviour

We investigate the complex phase behaviour at 1 wt% AA with water cuts ranging from 10% to 95% at two different NaCl concentrations in the aqueous phase (0 wt% and 4 wt%) and n-octane. Water-in-oil emulsions are observed at water cuts ranging from 10% to 70%, and oil-in-water emulsions when water cuts are higher than 80%. At low water cuts emulsions by 1 wt% AA are unstable as phase separation occurs in minutes, (Figs. S3 and S4). At 10% water cut, bulk water is separated quickly.

At 20% water cut, the water phase with 4 NaCl wt% in the vial in Fig. S4 is more cloudy than that of the corresponding water phase without salt in Fig. S3. Furthermore, the amount of phase separation in the middle layer is higher than that of the corresponding emulsion phase in Fig. S3. It seems that salt improves the stability of the emulsion at water cut of 20%. This may be the reason that NaCl increases the AA performance at 20% water cut as was mentioned above.

Compared with emulsions with 10 and 20% water cuts, the emulsions with higher water cuts (30–50%) exhibit higher stabilities (see Fig. S3a). This may be reason that 1 wt% AA is not effective at 10% and 20% water cuts without salt, while effective at 30% and 50% water cuts in hydrate anti-agglomeration as mentioned above. There is no significant effect of NaCl at water cuts of 30% and 50% on emulsion stability. There is also no appreciable effect of salt on AA performance at the water cut of 50%.

We also investigate the phase behaviour with combined surfactants (AA and Span 80) at water cuts ranging from 10% to 30% (see Figs. 8 and S5–S6). Fig. 8 shows the phase behaviours of the mixtures (10% water cut) stabilized by the mixtures of AA and Span 80 at a total concentration of 1 wt% (based on the aqueous phase). The ratio of AA to Span 80 in each sample is labelled on the tube. In each tube without salt, phase separation occurs within 10 min after the mixing. We observe the emulsions with 1 wt% AA sepa-
rates into three layers which are the octane phase in the upper layer, a bulk water phase in the bottom layer and a thin emulsion phase in the middle layer. The phase behaviours of the emulsions with 1 wt% AA are similar with the emulsions stabilized by 1 wt% AA in Figs. S3 and S4. In Fig. 8, emulsion with 1 wt% AA exhibit the weakest stability. Emulsion with AA and Span 80 exhibit higher stability. For each sample with AA and Span 80, a stable water-in-oil emulsion phase in the bottom layer and an octane phase in the upper layer are observed. Bulk water phase is not observed within 10 min, which may due to the enhanced emulsion stability by Span 80. This result is in line with the mechanism of synergistic effect of the AA and Span 80 in preventing hydrate aggregation we discussed in the AA performance tests. In the sample with 1 wt% Span 80, a larger amount of water-in-oil emulsion phase in the bottom layer is observed. We conclude that the emulsion stability of Span 80 is much higher than that of AA at the same conditions.

The stability of emulsion with 1 wt% Span 80 is significantly lowered by the introduction of 4 wt% NaCl in the aqueous phase. For the mixture with 1 wt% Span 80, the amount of emulsion phase significantly decreases by salt, indicating that the emulsion stability of Span 80 decreases by salt. This may be the reason that at 10% water cut, 2 wt% Span 80 is effective in fresh water while ineffective in brine (4 wt% NaCl).

For water cuts higher than 80%, we observe the flocculated emulsion network in optical microscopy images (Fig. S7). In pronounced flocculation at 95% water cut, we do not observe phase separations of emulsions.

We observe flocculation in emulsion at a water cut of 95% and AA concentration of 1 wt% at room temperature and atmospheric pressure in vials. 10-mL liquid samples containing AA, brine/water and n-octane are loaded into a clean flat-bottomed glass vials (15 mL) to produce mixtures of 5% octane, 1 wt% AA and two different concentrations of NaCl (0 and 4) wt%. The mixtures are homogenized by hand shaking. As shown in Fig. 9, the mixtures appear solid-like after vigorous mixing. Oil-in-water emulsions flocculated by non-ionic surfactants have been reported by several authors [35]. A sketch of flocculation of the oil droplets is shown in Fig. 10. This sketch shows the exclusion of surfactant micelles between approaching oil droplets which is the so-called “micelle depletion”. The result is flocculation of the emulsion.

![Fig. 8](image_url)

**Fig. 8.** Phase and emulsion distributions of mixtures with AA and Span 80 at total concentration of 1 wt% (based on aqueous phase) and water cut of 10% at time $t = 10$ min (a, c) and $t = 8$ h (b, d) after mixing. Each sample contains 1 wt% (AA + Span 80) and 0 wt% NaCl (top, a and b) and 4 wt% NaCl (bottom, c and d). The mass ratio of AA to Span 80 is shown on the top of each tube.

![Fig. 9](image_url)

**Fig. 9.** Flocculation in mixtures of octane, water and AA (water cut = 95%, AA = 1 wt%) at: (a) 10 min, (b) 1 h, and (c) 8 h. (A. No salt; B. 4 wt% NaCl; C. 8 wt% alcohol; D. 4 wt% NaCl + 8 wt% alcohol).
As shown in Fig. 9(a), the mixtures A and B without alcohol appear solid-like, and block the vial after mixing. The addition of 8 wt% alcohol turns the mixtures C and D into homogenous oil-in-water emulsions. The alcohol can inhibit the flocculation of the emulsions. In our tests, the inhibition effect of 8 wt% alcohol on flocculation may be due to the enhanced solubility of AA in the aqueous phase. The addition of alcohol may render the aqueous phase a good solvent for AA, therefore the structure of the adsorbed layer on oil droplets, and the intermolecular hydrophobic interactions between AA molecules would be drastically affected. As a non-ionic surfactant, the formation of AA micelles in aqueous phase is highly likely to be driven by the hydrophobic interactions between AA molecules. The addition of alcohol will lead to the dissociation of AA micellar structures because of the reduced strength of hydrophobic interactions and therefore prevention of flocculation. A number of authors have confirmed that alcohols can enhance emulsion stability and inhibit the flocculation process [36,37].

4. Conclusions

We have investigated the effect of water cut and NaCl as well synergic effect from addition of Span 80 to a strong anti-agglomerant. NaCl affects the performance of the AA differently at different water cuts from 10 to 100%. Synergy effect from the introduction of surfactant of a weak anti-agglomerant combined with our strong anti-agglomerant can be achieved at low water cuts.

The main conclusions from this work are:

1. At 10% water cut, NaCl decreases effectiveness of both AA and Span 80 which may due to the decreased concentration in the bulk water phase and increase in the concentration of both in the oil phase.
2. At 20–30% water cut, NaCl increase the performance of AA. NaCl increases the stability of the water-in-oil emulsions and lowers water to hydrate conversion and consequently lowers hydrate volume fraction in the liquid mixtures. Salt may also promote the adsorption of AA on the hydrate surface.
3. At 10%–30% water cut, synergistic effect in different mixtures of AA and Span 80 is observed, which can be attributed to stability of water-in-oil emulsions by Span 80 allowing strong adsorption of AA at hydrate interface.
4. At 10% water cut, the minimum effective concentration of the AA/Span 80 is 1 wt%. At 20% water cut with and without salt, the minimum effective concentration of the mixtures of AA and Span 80 are 1 wt% and 0.6 wt%, respectively. At 30% water cut without salt, no synergistic effect is observed; while with salt, there is synergistic effect. The salt lowers water to hydrate conversion and increases adsorption of the AA on the hydrate surface.
5. At 50% water cut, no appreciable effect of NaCl on AA performance is observed.
6. At the water cuts of 80% and 90%, NaCl increases the performance of the AA. NaCl lowers water to hydrate conversion in the liquid mixtures and drives the AA to the hydrate interface. At 80%–90% water cut, water becomes the continuous phase and oil-in-water emulsions are formed. Higher salt concentration is required to have anti-agglomeration. The same effect is also observed at 95% and 100% water cut. Alcohol can be used to reduce the concentration of NaCl.
7. At 95% water cut, severe flocculation occurs in the system of octane/water/AA. The viscous flocculation can completely block the sapphire cells. Alcohol is used to alleviate 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.jct.2017.09.016.

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