

# Effectiveness of Alcohol Cosurfactants in Hydrate Antiagglomeration

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**ABSTRACT:** Hydrates are crystalline inclusion compounds where hydrogen bonded water molecules form cages to trap small hydrocarbon and nonhydrocarbon molecules. Under high subcooling conditions, these crystals grow rapidly into large pieces and may cause enormous problems in transport and deepwater oil capture. One of the most effective methods to address gas hydrate problems is through the formation of small hydrate particles in the nanometer or micrometer range dispersed in the fluid phase. In this approach, special surfactants are required, which are called antiagglomerants (AAs). However, there are major limitations when salt is present in water and when volume ratio of water in fluid (i.e., watercut) is high. In this work, we investigate a wide range of alcohols as cosurfactants along with the rhamnolipid as AA in a multiple screening-tube rocking apparatus by monitoring the temperature of vials and morphology of mixtures. The results show medium-sized alcohols, such as isopropanol (IPA), are effective cosurfactants. Small quantities of IPA reduce the effective dosage of surfactant in the formation of hydrate particles in both water and brines. Our emulsion size measurements, by dynamic light scattering, and interfacial tension measurements reveal the effectiveness of alcohol cosurfactants in stabilizing oil-in-water emulsions, therefore enhancing the hydrate antiagglomeration effect.

## 1. INTRODUCTION

Gas hydrates are clathrate compounds in which the host molecule is water. During oil and gas production and transportation, especially in the deep sea, formation of gas hydrates may plug flowlines.<sup>1</sup> There are significant safety issues and high costs associated with hydrate formation. The failure of the attempts to capture the runaway oil using a dome in the recent Gulf of Mexico spill was due to gas hydrate formation at a temperature of around 4 °C and high pressure.<sup>2</sup>

Thermodynamic inhibitors (THIs), such as methanol, and monoethylene glycol have been used to prevent hydrate formation for over half a century.<sup>3,4</sup> Such inhibitors are required at high concentrations (e.g., 10–60 wt % in the aqueous phase). Consequences are high cost, salt precipitation, and environmental issues. Kinetic inhibitors (KIs) have been extensively investigated since middle 1980s. These chemicals either inhibit hydrate formation<sup>5</sup> or reduce the rate of growth<sup>6</sup> at much lower dosage (e.g., 0.1 to 2.0 wt %). However, KIs are not effective at high subcoolings of 15–25 °C often encountered in deep sea. Antiagglomerants (AAs) become an attractive option because they can maintain hydrates in small particles and allow flow in hydrate slurries. AAs are surface active chemicals (surfactants) that contain a hydrophilic headgroup binding with water droplets and a hydrophobic tail keeping aqueous emulsions in the oil phase.<sup>3</sup> These surfactants prevent hydrates from growing into large particles, thus preventing agglomeration. We like to point out that, in principle, there is no need for the presence of the oil phase to achieve antiagglomeration. However, to the best of our knowledge, there is no reported published work on hydrate antiagglomeration in the absence of the oil phase.

Quaternary ammonium salts (QAs) are perhaps among the most effective AAs. They were first developed by Shell in 1993.<sup>3</sup> These chemicals are also effective corrosion inhibitors and provide protection to metal facilities. QAs are toxic; as a result,

their use is hindered. Recently, there have been interests in biosurfactants as antiagglomerants for ice<sup>7</sup> and hydrates.<sup>8</sup> We have shown that the biosurfactant rhamnolipid is an effective AA. The biosurfactants are generally environmentally friendly.<sup>9,10</sup>

Alcohols are well-known as cosurfactants in surfactant–solution polymorphism and emulsion stability.<sup>11–13</sup> They are also reported as lipotropes in oil/water systems by increasing the solubility of water in apolar systems without forming reverse micelle (no surfactant).<sup>14</sup> However, a large quantity is required in this application. Since alcohols reduce the interfacial tension between water and oil and accumulate at the interface in various degrees, the combined effect of surfactants and cosurfactants has the potential to provide the most desired formulation in very small quantities in formation of hydrate slurries with a broad range of oil to water ratios. Recently, for the first time, we reported that a small amount of methanol could enhance the effectiveness of AAs significantly.<sup>15</sup> Methanol has a strong dual nature; it is both a cosurfactant and a strong solvent in aqueous solutions. By adding methanol as a cosurfactant, the dosage of AAs can be reduced below the conventional limit (i.e., 0.5 wt % in water) for effective antiagglomeration. There is much economical benefit due to the substantially lower price of methanol compared to the price of AAs. Unlike methanol, alcohols of medium chain length have stronger affinity for the interface between water and oil bulk phases and might be more effective cosurfactants. Various authors have demonstrated that medium-chain alcohols can be effective cosurfactants.<sup>12,16</sup>

In some hydrate systems, usually both brine and oil are present. York and Firoozabadi reported previously that the

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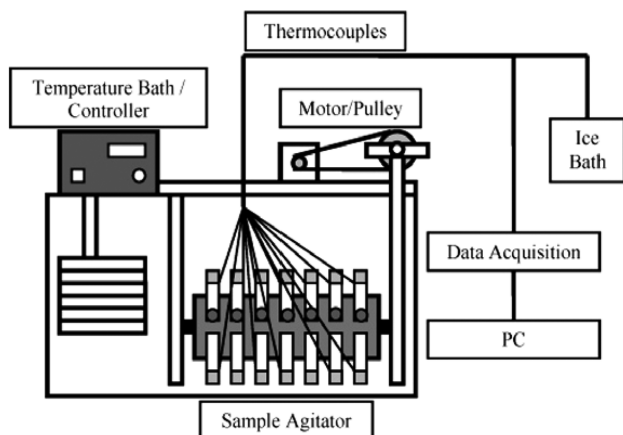
presence of salt reduces the effectiveness of rhamnolipids, thus rendering it an ineffective antiagglomerant in tetrahydrofuran (THF) hydrates.<sup>17</sup> It is known that the addition of salt raises the interfacial tension between oil and aqueous phases, which is opposite to the effect of an alcohol. We investigate the effect of various alcohols in the oil/brine systems

## 2. EXPERIMENTAL SECTION

The main objective of this work is to examine the effectiveness of different alcohols as cosurfactants in hydrate antiagglomeration in view of the promising results from methanol<sup>15</sup> with and without salt.<sup>17</sup>

In this work, we use the biosurfactant rhamnolipid as the AA. Cyclopentane is employed as both model oil and hydrate former. Cyclopentane hydrates may be closer to methane hydrates than to THF hydrates; cyclopentane hydrates form at the water/oil interface, whereas THF hydrates may form in the bulk water phase.<sup>10,18</sup> However, small amount of THF (e.g., 2 wt % to water) is used as hydrate formation helper due to the extremely slow cyclopentane hydrate formation rate. Both water and brine are used to serve as the aqueous phase for applications in gas and in oil systems as well as the conditions in deep sea from oil leakage. A multiple screening-tube rocking apparatus is used in this investigation; the agglomeration state is examined visually and by a bore-scope.

**2.1. Apparatus.** The experimental setup, a multiple screening-tube rocking apparatus as shown in Figure 1, is the same as we used in



**Figure 1.** Multiple screening-tube rocking apparatus.

previous investigations,<sup>9,10,15,17,19</sup> The rocking cell method is chosen because the milder agitation yields a more conservative criterion than a conventional autoclave method with stirring. In this apparatus, a motor driven agitator is connected to a rack holding up to 20 separate borosilicate glass scintillation vials. Each vial has dimensions of 17 mm (diameter) and 60 mm (height), holding 7 mL of test mixture and an 8-mm diameter stainless steel 316 ball to aid agitation. The vial is sealed by a Teflon-lined plastic screw cap and Teflon tapes and is submerged in a temperature bath. The rack rotates the vials 150° to either side of the vertical direction, completing a cycle every 5 s.

The temperature bath used in this investigation is a Huber CC515 with silicone oil (10 cSt at 24 °C, from Clearco Products, Bensalem, PA). Thermocouples (from ThermoWorks, Lindon, UT) are attached outside the vials to measure temperature of test mixture, with an accuracy of  $\pm 0.2$  °C and range from  $-20$  to  $70$  °C. An Agilent 34970A data acquisition unit records temperature every 20 s using water-ice bath as the fixed junction reference temperature. The agglomeration state is recorded by digital camera through a bore-scope (from Gradient Lens Corp., Rochester, NY).

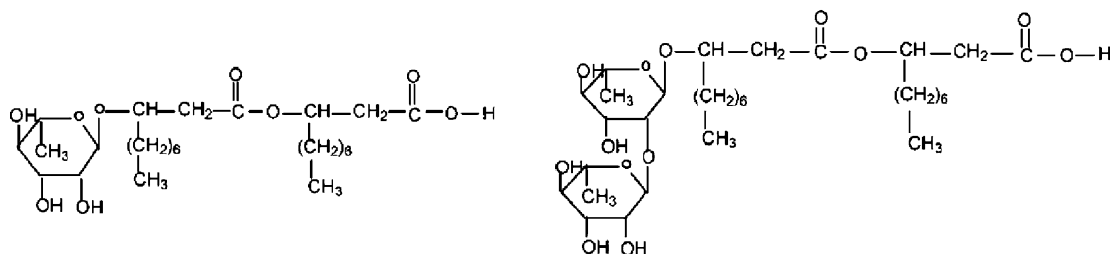
**2.2. Materials.** In all test mixtures, deionized water obtained from a Barnstead Nanopure Infinity system and 99%+ purity cyclopentane (CP, from Acros) are used as aqueous and oil phases, respectively. CP serves as the hydrate guest molecule with tetrahydrofuran (THF, 99.9% from Acros) as hydrate former helper, discussed in our previous work in detail.<sup>10</sup> Sodium chloride, potassium chloride, sodium bromide, and sodium sulfate (NaCl, KCl, NaBr, and Na<sub>2</sub>SO<sub>4</sub>, all from Fisher Scientific) brines are used in this study as model aqueous phase. The biosurfactant used in this investigation is the rhamnolipid (Rh, product JBR425, from Jeneil Biosurfactant Co., Madison, WI); it is a mixture of two compounds (as shown in Figure 2) at 25 wt % in water. The alcohols used as cosurfactants are methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA), 1-butanol (1-BtOH), 2-butanol (2-BtOH), tert-butanol (t-BtOH), 1-pentanol, 2-methyl-2-butanol (2-m-2-BtOH), 1-hexanol, 2-ethyl-1-butanol (2-e-1-BtOH), 3-ethyl-3-entanol, and benzyl alcohol; all are from Sigma-Aldrich (purity of 99% or higher).

**2.3. Procedure.** We follow the same procedure as in our previous work.<sup>9,10,15,17</sup> Mixtures with 2/1/0.02/*x*/*y*/*z* parts by weight in water of CP/H<sub>2</sub>O/THF/AA/cosurfactant/salt are employed, where *x* is the concentration of Rh, *y* is the concentration of the alcohol, and *z* is the concentration of salt. In both kinetic/thermodynamic and agglomeration tests, each composition is prepared in duplicate and tested repeatedly.

**2.3.1. Mixture Preparation.** Chemicals are added into the precleaned test vial (with stainless steel ball) in the following sequence, salt then water, Rh, alcohol, THF, and CP. The mixture is hand-shaken for 2 min before the test.

**2.3.2. Hydrate Dissociation Data Acquisition.** Typical sets of temperature data, referred to as freeze–thaw cycles, are measured with time. The equilibrium crystallization temperature of the CP hydrate at ambient pressure is reported to be about 7 °C.<sup>18</sup> The mixtures are brought to 11 °C and allowed to reach equilibrium before a  $-5$  °C/hour cooling rate to  $-2$  °C. After being kept at  $-2$  °C for 2 h, the test samples are heated to 15 °C at ramping rate of 15 °C/hour. The exothermic peaks at  $\sim -2$  °C in freeze–thaw cycles indicate the formation of hydrate. Hydrate dissociation temperature ( $T_d$ ), that is, equilibrium crystallization temperature, is determined based on the start of the endothermic reaction. In all tests, no ice forms. Ice formation is easily detectable, as discussed in ref 10; the same reference also shows the exothermic and endothermic peaks from phase transformation.

**2.3.3. Agglomeration State.** A separate set of experiments are performed, similar to crystallization/dissociation tests, to observe the state of agglomeration and hydrate particles. The mixtures in the vials are cooled to  $-2$  °C at a rate of  $-5$  °C/h and held at  $-2$  °C for 24 h with agitation before the observations. We then inspect visually the



**Figure 2.** Two chemical compounds in rhamnolipid (Rh).

**Table 1. Dissociation Temperature, Interfacial Tension, and Antiagglomeration State of Mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol at the weight ratio of 2/1/0.02/0.001/*x***

alcohol name	dosage molar ratio to water ×1000	dissociation temperature, °C	interfacial tension, mN/m	antiagglomeration status
no alcohol, no Rh		6.65 ± 0.20	26.44 ± 0.05	plug
no alcohol		6.40 ± 0.20	7.87 ± 0.03	plug
methanol	2.81	5.57 ± 0.20	7.64 ± 0.03	plug
	4.21	4.80 ± 0.20	7.58 ± 0.02	plug
	5.62	3.86 ± 0.20	7.52 ± 0.02	plug
	11.24	−0.22 ± 0.20	7.29 ± 0.02	effective
ethanol	1.95	5.87 ± 0.20	7.51 ± 0.03	plug
isopropanol	1.50	5.98 ± 0.20	7.28 ± 0.02	effective
1-butanol	1.21	6.08 ± 0.20	7.31 ± 0.03	wall adhesion
2-butanol	1.21	6.05 ± 0.20	7.26 ± 0.03	effective
tert-butanol	1.21	6.06 ± 0.20	7.23 ± 0.02	effective
1-pentanol	1.02	6.15 ± 0.20	7.32 ± 0.02	wall adhesion
2-methyl-2-butanol	1.02	6.11 ± 0.20	7.28 ± 0.02	effective
1-hexanol	0.881	6.20 ± 0.20	7.42 ± 0.03	wall adhesion
2-ethyl-1-butanol	0.881	6.18 ± 0.20	7.29 ± 0.02	wall adhesion
benzyl alcohol	0.832		7.74 ± 0.03	plug
3-ethyl-3-pentanol	0.775	6.23 ± 0.20	7.41 ± 0.03	wall adhesion

vials to examine the states of agglomeration, which include hydrate plugging, wall adhesion, and effective (well-dispersed). Detailed descriptions are discussed later.

**2.3.4. Emulsion Size Measurement.** Dynamic light scattering (ZetaPALS, from Brookhaven Instrument Corp.) is used to measure emulsion size of the fluid mixtures at room temperatures. Measurements are performed quickly after 2 min of hand-shaking. Each measurement is completed in 30 s where the mixture remains in the emulsion state. We repeat all the size measurements 10 times to obtain the derivations.

**2.3.5. Interfacial Tension Measurement.** A tensiometer (K12, from Kruss) is used to measure the interfacial tension between the oil and aqueous phases at 20 °C. We perform five measurements to compute the derivation.

### 3. RESULTS AND DISCUSSION

#### 3.1. Alcohols as a Cosurfactant and Biosurfactant Rh.

In this investigation, we first use the biosurfactant Rh at a very low concentration (i.e., 0.1 wt % in water), and the mixture chemical compositions of CP/H<sub>2</sub>O/THF/Rh/Methanol are set to weight ratios (to water) of 2/1/0.02/0.001/*y*, where *y* = 0.005, 0.0075, 0.010, 0.020, and 0.050.

The effectiveness is examined by the state of agglomeration at −2 °C after 24 h. There is no agglomeration in the mixture containing 2 wt % (in water) methanol, and no hydrate is formed at −2 °C when the methanol concentration is 5 wt %. As a comparison, mixtures without methanol are also investigated with the chemical compositions of CP/H<sub>2</sub>O/THF/Rh at the weight ratio of 2/1/0.02/*x*, where *x* represents the concentration of Rh. The minimum effective amount of Rh is found to be 0.5 wt % without alcohol cosurfactant. Addition of 2 wt % methanol lowers the effective AA concentration from 0.5% to 0.1%. The experiment with the mixture containing 2 wt % methanol without Rh shows agglomeration at −2 °C, as expected. The synergetic effect of biosurfactant and methanol results in the antiagglomeration. In some other alcohols, as we will see later, the effectiveness of the process can be improved significantly.

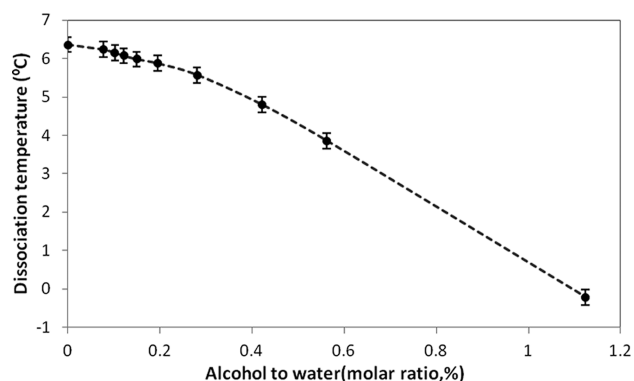
Methanol behaves as a cosurfactant through reduction of water/oil interfacial tension, by accumulation at the interface. Adding 0.5 wt % methanol reduces the interfacial tension from 7.87 ± 0.03 mN/m to 7.64 ± 0.03 mN/m. Methanol also

dissolves substantially in the aqueous phase. Bulk phase dissolution relates to thermodynamic inhibition because methanol molecules form hydrogen bonds with water molecules and change the bulk phase properties. Therefore, high concentrations are required in order to be effective at high subcoolings.<sup>4</sup>

A large part of methanol molecules stay in the aqueous phase rather than transferring to the water/oil interface. In this respect, methanol may not be an effective cosurfactant. The solubility of alcohols in water depends on the formation of a hydrogen bond between the −OH group of the alcohol and the water molecules. When the chain length increases, the ratio of the hydrophilic −OH group to the alkyl part decreases, which results in a decrease in the solubility in water. The long chain alcohols have a low solubility in water; *n*-octanol has a solubility of 0.584 g/L in water at 25 °C.<sup>20</sup> Alcohol molecules of medium chain length are effective cosurfactants; they are more likely to appear at the water/oil interface. The tail of high molecular weight alcohols have a high affinity for the oil and result in the less adsorption in the water/oil interface. The focus of this work is on short and medium chain alcohols including methanol, ethanol, isopropyl alcohol, 1-butanol, 2-butanol, tert-butanol, 1-pentanol, 2-methyl-2-butanol, 1-hexanol, 2-ethyl-1-butanol, 3-ethyl-3-pentanol, and benzyl alcohol.

CP hydrate forms in all mixtures at a temperature around −2 °C and no ice forms, as mentioned above. The dissociation temperature  $T_d$  in mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol at weight ratio of 2/1/0.02/0.001/*x* is presented in Table 1. When there is no alcohol cosurfactant in the mixture, the  $T_d$  is 6.4 °C. Adding 0.5 wt % methanol lowers  $T_d$  by 0.8 °C, while 2.0 wt % methanol lowers  $T_d$  by 6.6 °C. The dosage of other alcohols (alkyl chain length from 2 to 7) is 0.5 wt %. The same mass amount of smaller alcohols gives a higher  $T_d$  depression, due to lower molecular weight. In other words, different alcohols of the same molecular weight give the same dissociation temperature because of having the same mole fractions. For instance, the mixtures containing 1-butanol, or 2-butanol, or tert-butanol at 0.5 wt % (0.12 mol %) all have  $T_d$  of 6.1 °C. Figure 3 shows that all the alcohol species follow the same trend based on colligative properties from the data in Table 1. The dashed line is the fit to the data.





**Figure 3.** Dependence of dissociation temperature on the molar ratio of alcohol to water in mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol = 2/1/0.02/0.001/*x* by weight. The error bar represents the standard deviation based on five measurements.

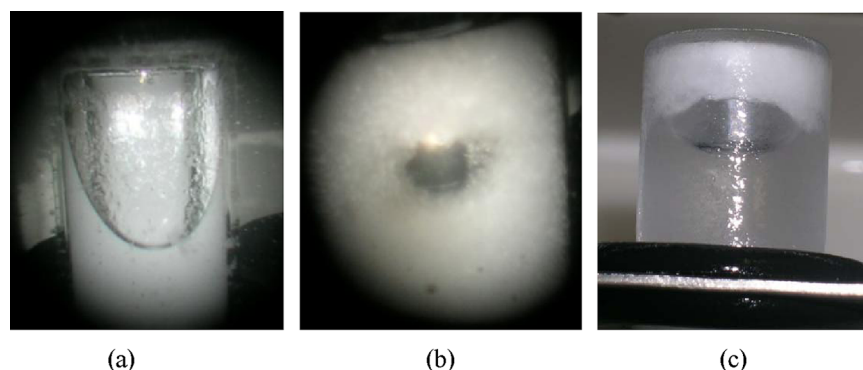
Despite nearly the same thermodynamic inhibition property, the effectiveness of different alcohols in antiagglomeration is expected to be very different. Table 1 summarizes the effectiveness of various alcohols in antiagglomeration. Hydrate plugging is observed in test mixtures with 0.5–1.0 wt % methanol and 0.5 wt % ethanol and benzyl alcohol. Methanol and, to a lesser extent, ethanol dissolve significantly in the bulk aqueous phase rather than being adsorbed with the surfactant onto the hydrate surface. When the biosurfactant Rh dosage is very low (e.g., 0.1 wt %), a small concentration of methanol or ethanol is not effective in antiagglomeration. Benzyl alcohol is also not an effective cosurfactant because of its rigid molecular structure. On the other hand, the same concentration of isopropanol, 2-butanol, tert-butanol, or 2-methyl-2-butanol is effective to form a well-dispersed hydrate slurry. There is hydrate adhesion on the vial wall in mixtures containing 1-butanol, 1-pentanol, 1-hexanol, and 3-ethyl-3-pentanol. The stainless steel ball and the air-bubble can be moved along the test vial, but hydrate adhesion is a sign of ineffectiveness. Images of the three cases are shown in Figure 4. “Effectiveness” is defined at the condition that the entire mixture can flow inside the vial during rocking. “Plug” is defined when the entire or part of the mixture freezes inside the vial with the steel ball (and air bubble in some cases) trapped in the hydrate crystal. “Wall adhesion” is defined when most of the mixture can flow inside the vial, but there are visible crystals on the vial wall. Both plug and wall adhesion conditions are considered ineffective.

All the four effective alcohols (isopropanol, 2-butanol, tert-butanol, and 2-methyl-2-butanol) are of medium chain length and have a secondary/tertiary alcohol structure with a small methyl group in their polar moiety. Methyl groups may form van der Waals interaction with hydrate crystal lattice, thus stabilizing alcohol molecules on hydrate particle surface. However, ethyl groups do not have such an effect, indicated by the ineffectiveness of 2-ethyl-1-butanol and 3-ethyl-3-pentanol. The effectiveness of medium chain alcohols with methyl groups is similar to the hydrate antiagglomeration process described by Zanota et al.,<sup>19</sup> in which it is reasoned that the most effective quaternary amines as AA contain methyl groups. Similar phenomena have also been observed in ice antiagglomeration. Chao et al. report that the replacement of the middle two threonines of a winter flounder antifreeze protein (AFP) by serines causes the loss of ice AA activity.<sup>21</sup> By contrast, replacement by valines causes little loss of activity, indicating that the methyl group of threonine might be important for ice surface binding. In the model by Fraether et al.,<sup>22</sup> it is shown that the methyl group in threonine may have strong van der Waals attraction on ice surface besides hydroxyl group forming hydrogen bond. Such structure enhances the antifreeze effectiveness dramatically. Here, we report the same mechanism in hydrate antiagglomeration for the first time, since hydrate surface is expected to be similar to ice. The four alcohols are effective surface-active compounds; small amounts of these alcohols reduce the surface tension of water.<sup>23</sup> In Table 1, we show that medium size alcohols reduce the interfacial tension between the oil and the aqueous phase.

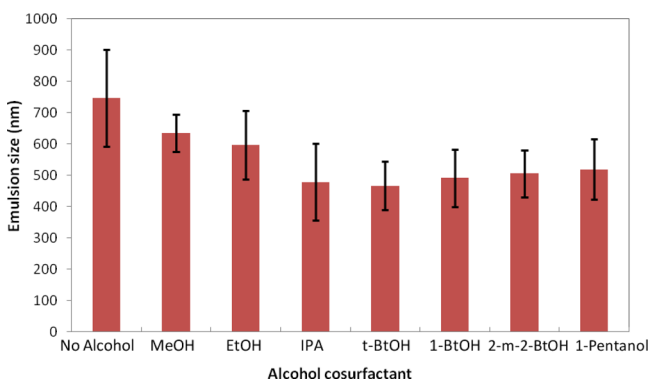
The emulsion size measurements can provide further insight into the effectiveness of medium size alcohols. Size measurements in mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol at the weight ratio of 2/1/0.02/0.0025/0.005 are presented in Figure 5. Without cosurfactant, the emulsions formed in the mixtures are large, for example  $747.2 \pm 154.2$  nm. Adding 0.5 wt % alcohol cosurfactant reduces the emulsion size. The size reduction and increased adsorption density evidenced by reduction of interfacial tension from the alcohol cosurfactant provides antiagglomeration. Isopropanol and tert-butanol make the emulsions smaller with average size of around 470 nm; 63% of the original size without alcohol cosurfactant. Interestingly, tert-butanol is a more effective surface active agent than 1-butanol perhaps due to a higher adsorption at the interface. A similar behavior is also seen for 2-methyl-2-butanol compared to 1-pentanol.

### 3.2. Effect of Alcohol in Brines of Different Salinity.

The objective of this work is the use of antiagglomeration in oil

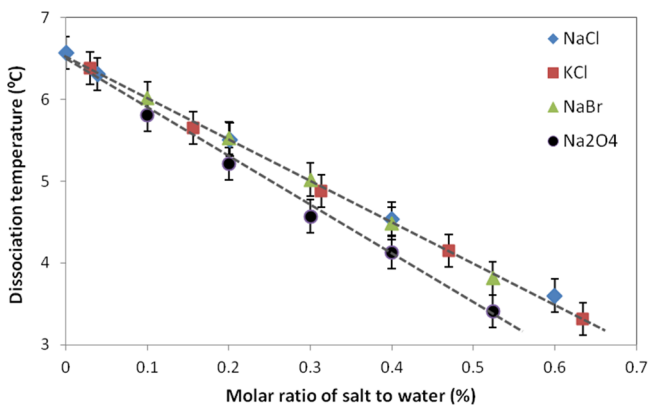


**Figure 4.** Images of three antiagglomeration states: (a) effective, (b) plug, and (c) wall adhesion.



**Figure 5.** Emulsion size in different alcohol cosurfactants in mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol at the weight ratio of 2/1/0.02/0.0025/0.005. The error bar represents the standard deviation based on 10 measurements.

capture and in oil and gas flowlines. In deepwater, the salinity is around 3.5 wt %.<sup>24</sup> In natural gas production, the salinity may be very low due to the source of water being mainly from condensation of the gas phase. In coproduction of water and oil, the salinity can be very high. The aqueous phase in most conditions often contains some salts.<sup>25</sup> Similar to an alcohol, salt is a thermodynamic inhibitor that lowers the dissociation temperature ( $T_d$ ). The dependence of  $T_d$  of our test mixtures on salt concentration (in terms of moles) in water is presented in Figure 6. The three different salts (i.e., NaCl, KCl, and

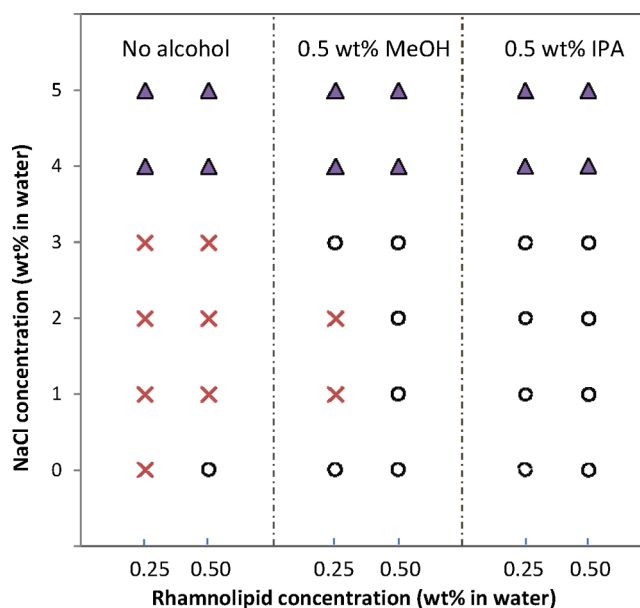


**Figure 6.** Dissociation temperature ( $T_d$ ) vs salt concentration in the mixtures of CP/H<sub>2</sub>O/THF/Rh/Salt at the weight ratio of 2/1/0.02/0.0025/ $z$ . Salts are NaCl, KCl, NaBr, and Na<sub>2</sub>SO<sub>4</sub>. The error bar represents the standard deviation based on five measurements.

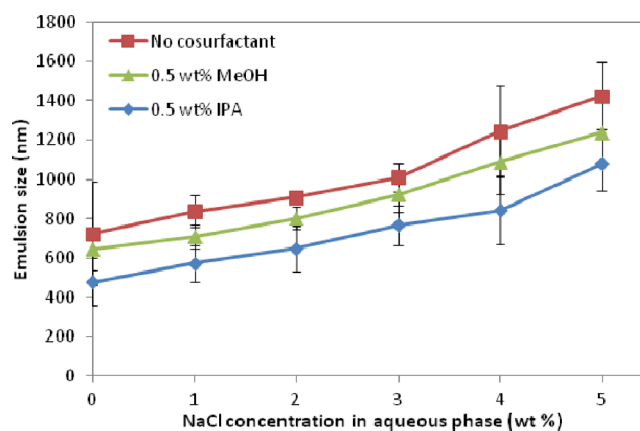
NaBr) show the same effect, as expected, independent of the cation and anion species. However, Na<sub>2</sub>SO<sub>4</sub> shows a stronger effect on  $T_d$  because SO<sub>4</sub><sup>2-</sup> is a divalent anion and there are two Na<sup>+</sup> cations in each molecule.

The strong ionic strength in the aqueous phase weakens the hydrogen bonding between surfactant and water at the interface due to the strong ion–water interactions, which dehydrate the oxide groups (e.g., hydroxyl or carboxylic acid groups), as discussed by York and Firoozabadi (in THF hydrates).<sup>17</sup> We observe the same behavior in CP hydrates, as presented in Figure 7. Rh at 0.5 wt % becomes ineffective when the concentration of NaCl is above 1 wt %.

The measurements in Figure 8 show that emulsion size increases with salinity increase due to lower interface adsorption. Note that there is no hydrate formation in mixtures



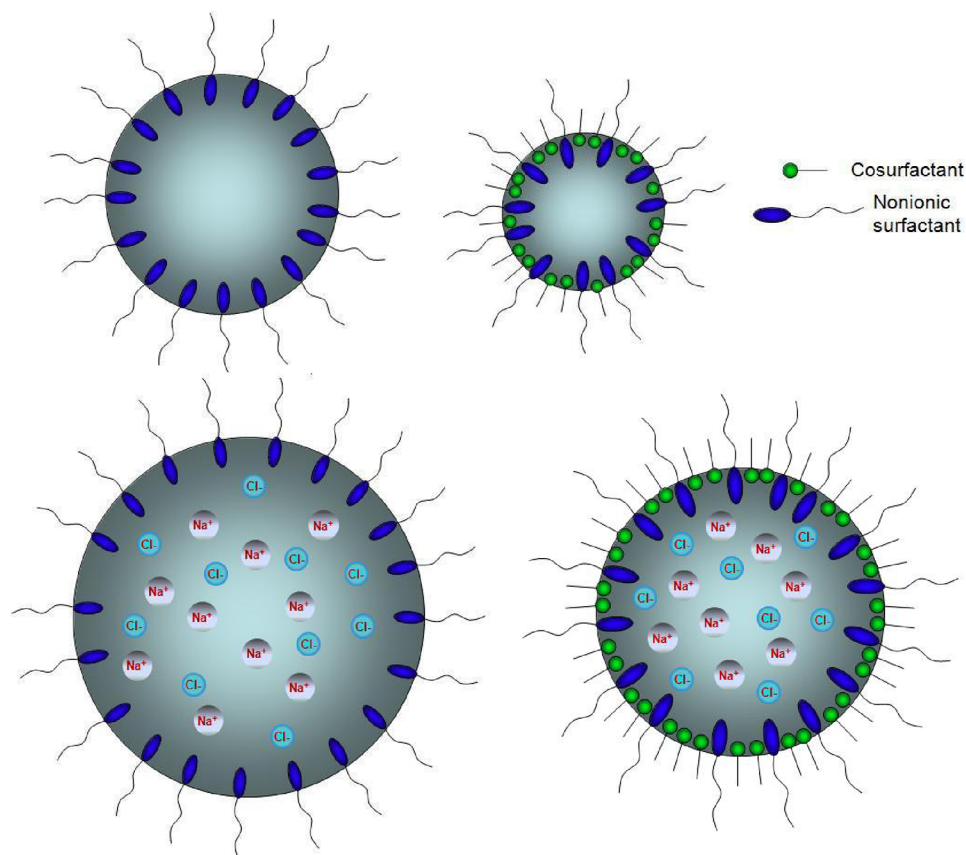
**Figure 7.** Agglomeration states of mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol/NaCl at the weight ratio of 2/1/0.02/ $x$ /0.005/ $z$  at  $-2.5$  °C, where  $x$  is Rh dosage and  $z$  is NaCl concentration: (O) stable dispersion; (X) plugging or adhesion; (▲) no hydrate is formed at this temperature.



**Figure 8.** Emulsion size vs salinity in the mixtures of CP/H<sub>2</sub>O/THF/Rh/Alcohol/NaCl at the weight ratio of 2/1/0.02/0.0025/0.005/ $z$ , where  $z$  presents NaCl concentration in water. The error bar represents the standard deviation based on 10 measurements.

containing high concentrations of salt (above 4 wt % NaCl) at tested temperature ( $-2.5$  °C). This is because of the changes of bulk phase properties.

As we mention, alcohols are surface-active compounds that can lower water surface tension. Therefore, emulsion size is reduced by adding alcohol cosurfactants, as the illustration shows in Figure 9. Because the size of alcohol cosurfactant –OH headgroup is smaller than the surfactant headgroup, they can fit into the gap between the surfactant molecules and provide a bonus steric repulsion. The salt in the mixture removes some of the surfactants from the water/oil interface due to the dehydration effect. The hydrogen bonds between surfactant molecules and water droplets (or hydrate particles) become weaker as ionic strength increases. Additionally, the  $pK_a$  of Rh is 5.6 from the dissociation of its carbonyl headgroup, and the solution is acidic with pH of 5.9. Chloride



**Figure 9.** Illustration of the effect of alcohol cosurfactant and salt on water-in-oil emulsion.

ions ( $\text{Cl}^-$ ) have electrostatic repulsion with  $\text{RCOO}^-$  of the surfactant headgroup. As a result, there is less adsorption of surfactant onto the emulsion surface, and then, emulsion size become larger. Adding alcohols may weaken such ionic dehydration effects of salts. They provide nonionic bonding force with surfactant molecules to increase the surfactant adsorption at the water/oil interface. As shown in Figure 7 there is no hydrate agglomeration at a methanol concentration of 0.5 wt % in mixtures containing 1 to 3 wt % NaCl in the aqueous phase and 0.5 wt % Rh. The same is true in the mixture containing 3 wt % NaCl in the aqueous phase and 0.25 wt % Rh, but salt concentrations of 1 and 2 wt % result in agglomeration. At a concentration of 0.5 wt % IPA, there is no hydrate agglomeration in any of the mixtures. These results give a clear indication that IPA is a more effective cosurfactant than methanol. The emulsion size measurements are consistent with the results from agglomeration.

We have performed experiments similar to those presented in Figure 7 using KCl brine. The results are similar. Those measurements are not presented for the sake of brevity.

#### 4. CONCLUSIONS

In this work, a wide variety of alcohol cosurfactants are used in the study of hydrate antiagglomeration. All the alcohols have the same thermodynamic inhibition effect. However, due to different interfacial effects, the alcohols have a very different effectiveness. Unlike thermodynamic hydrate inhibition when large alcohol quantities are required, antiagglomeration effectiveness is based on small quantities. Fortunately the most effective alcohols for antiagglomeration are also the most environmentally friendly. Ultralow dosage antiagglomerants

(e.g., 0.1 wt %) can be achieved with the use of small amounts of alcohols of medium chain length. These effective alcohols are more active at the water/oil interface than either long or small chain alcohols. A methyl group next to hydroxyl group in an alcohol molecule (e.g., IPA, 2-BtOH, t-BtOH or 2-m-2-BtOH) is particularly effective probably due to the strong binding to the emulsion/hydrate surface.

Our results show that a small amount of a medium size alcohol such as IPA can overcome the negative ionic effect of salts on hydrate antiagglomeration, possibly because of providing a pronounced nonionic bonding between the surfactant and alcohol molecules.

As an essential component widely used in oil drilling, and flow assurance, the use of methanol has raised safety concerns.<sup>26</sup> IPA is more environmentally friendly because of its low toxicity. Therefore, considering the effectiveness and eco-friendliness, we propose the use of IPA as a promising cosurfactant in hydrate AA applications.

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##### Notes

The authors declare no competing financial interest.

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