

# Comparing Effectiveness of Rhamnolipid Biosurfactant with a Quaternary Ammonium Salt Surfactant for Hydrate Anti-Agglomeration

J. Dalton York and Abbas Firoozabadi\*<sup>†</sup>

Department of Chemical Engineering, Mason Lab, Yale University, New Haven, Connecticut 06520

Received: September 10, 2007; In Final Form: October 25, 2007

Natural gas is projected to be the premium fuel of the 21st century because of availability, as well as economical and environmental considerations. Natural gas is coproduced with water from the subsurface forming gas hydrates. Hydrate formation may result in shutdown of onshore and offshore operations. Industry practice has been usage of alcohols—which have undesirable environmental impacts—to affect bulk-phase properties and inhibit hydrate formation. An alternative to alcohols is changing the surface properties through usage of polymers and surfactants, effective at 0.5–3 wt % of coproduced water. One group of low-dosage hydrate inhibitors (LDHI) are kinetic inhibitors, which affect nucleation rate and growth. A second group of LDHI are anti-agglomerants, which prevent agglomeration of small hydrate crystallites. Despite great potential, reported work on hydrate anti-agglomeration is very limited. In this paper, our focus is on the use of two vastly different surfactants as anti-agglomerants. We use a model oil, water, and tetrahydrofuran as a hydrate-forming species. We examine the effectiveness of a quaternary ammonium salt (i.e., quat). Visual observation measurements show that a small concentration of the quat (0.01%) can prevent agglomeration. However, a quat is not a green chemical and therefore may be undesirable. We show that a rhamnolipid biosurfactant can be effective to a concentration of 0.05 wt %. One difference between the two surfactants is the stability of the water-in-oil emulsions created. The biosurfactant forms a less stable emulsion, which makes it very desirable for hydrate application.

## I. Introduction

Natural gas may provide a larger share of energy consumption and surpass oil consumption due to clean burning features. There is less CO<sub>2</sub> produced from burning natural gas than other fossil fuels. Furthermore, produced CO<sub>2</sub> can be separated from the combustion products and sequestered more readily than oil combustion products for improved CO<sub>2</sub> recovery or permanent storage in saline aquifers. However, thermodynamic conditions prevailing in gas production lines are often favorable to the formation of crystalline inclusion compounds known as gas hydrates. Water, which is coproduced with natural gas, forms lattice structures through hydrogen bonding; the structures become stabilized by guest molecules such as methane and propane under high pressures and temperatures in the range of a few degrees to 25 °C.<sup>1</sup> The formation of gas hydrates is very rapid, unlike corrosion, scale, or wax buildup. The rapidity has undesirable safety and environmental consequences. Plug formation from hydrate formation often leads to production shutdown.

Traditional methods of hydrate prevention include physical means, such as insulation and electrical heating, and thermodynamic inhibition by methanol and ethylene glycol. Thermodynamic inhibitors shift equilibrium conditions to lower temperature and higher pressure.<sup>2</sup> These inhibitors are well-characterized, but large concentrations—as high as 60 wt % of coproduced water—are often needed, which increase costs and have serious environmental impacts.<sup>3</sup>

An alternative to thermodynamic inhibitors, which affect through change of bulk-phase properties, is the use of low-dosage hydrate inhibitors (LDHI). The LDHI influence mainly the surface properties and are effective at concentrations of 0.5–3 wt %; they do not affect thermodynamic equilibrium but rather the kinetics or agglomeration. Kinetic hydrate inhibitors (KHI) are typically polymeric compounds that delay nucleation and decrease growth rate.<sup>4,5</sup> KHI may result in complete inhibition of hydrates<sup>6</sup> but do not perform well at pipeline/well shut-in conditions or at high operating subcoolings—i.e.,  $\Delta T_{op}$ , the difference between equilibrium temperature and operating temperature at a given pressure. In some flow conditions,  $\Delta T_{op}$  can be as high as 20 °C; therefore, one would require effective LDHI for  $\Delta T_{op} \geq 20$  °C. Shut-in conditions may occur when well or pipeline maintenance is required.

A second group of LDHI is anti-agglomerants (AA), which prevent agglomeration—but not formation—of hydrate crystals and allow hydrates to be transported as slurries. Agglomeration occurs in the growth phase, but it has been proposed that it may also occur among unstable clusters in the nucleation phase.<sup>5</sup> AA are intended to be effective at high  $\Delta T_{op}$  or at shut-in conditions—i.e., when pipeline flow is paused for a period of time.<sup>7–9</sup> AA may also possess kinetic inhibition ability.<sup>10–12</sup> They are generally surfactants but may be low molecular weight oligomeric species.<sup>9,13</sup> AA have not been studied as extensively as KHI.

AA structure is key to their effectiveness and mechanism.<sup>14</sup> Effective AA contain the head group that can interact with a water lattice—such as amine or carbonyl groups—through hydrogen bonding or electrostatic attraction. AA compounds may also contain head groups that act as hydrate guest

\* To whom correspondence should be addressed. E-mail: abbas.firoozabadi@yale.edu.

<sup>†</sup> Also affiliated with the Reservoir Engineering Research Institute, Palo Alto, CA 94306.

molecules—this feature combined with hydrogen bonding may incorporate the AA into crystals. Molecules in this case may adsorb too strongly and become engulfed in the growing crystal, requiring higher concentrations. The hydrophobic tail renders hydrate more oil-wet—thus dispersible in the oil phase—and prevents separate crystals from agglomerating.<sup>15</sup> AA often produce water-in-oil emulsions—thus limiting hydrate growth to water droplets dispersed in oil.<sup>9,14,16–20</sup> However, problems may arise if the emulsion generated is too stable.<sup>21</sup> Once transportation of well fluids is complete, it is desired that phase separation be attainable so that product quality standards can be met. If these emulsions are too stable, then additional processing or additives may be required once hydrate formation is of no concern.

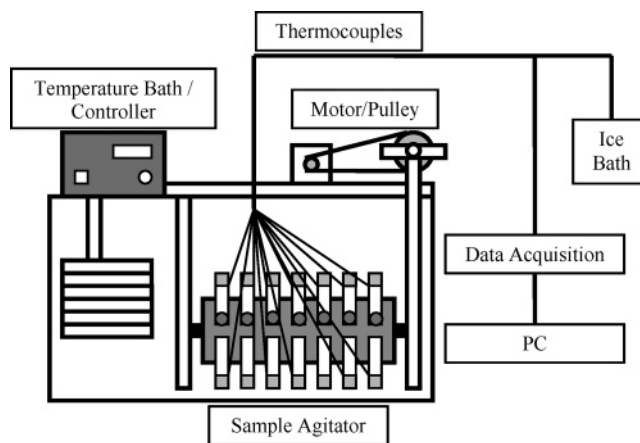
AA are believed ineffective if water occupies one-third or more of the process stream volume. This requirement may be related to w/o emulsion formation, but other reasons such as high slurry viscosity with high hydrate volume fractions is also cited in the literature.<sup>14,16</sup> In most gas production flow lines the amount of hydrocarbon liquid is more than the amount of coproduced water, and therefore, difficulty in generating water-in-oil emulsions may not be an issue. Other insights into AA ability and mechanism are found in surfactant and colloidal science.<sup>22–24</sup>

Very recently, there has been interest in biosurfactants as anti-agglomerants for ice<sup>25</sup> and hydrates.<sup>26</sup> Biosurfactants are often superior to chemical surfactants because of (1) higher biodegradability, (2) lower toxicity, and (3) safety.<sup>27,28</sup> To the best of our knowledge, there is only one report of the use of biosurfactants in the hydrate literature.<sup>26</sup> In ref 26, 500 ppm of a rhamnolipid surfactant exhibited AA ability, but only for one of the oils used in the study. Because of the presence of natural surfactants in the oil, results from ref 26 may not apply to hydrates in natural gas systems. Thus, the true potential of biosurfactants is largely unknown.

Chemically, the major rhamnolipids are glycosides of rhamnose (6-deoxymannose) and B-hydroxydecanoic acid. Rhamnolipids are known to have desirable effects on surface and interfacial tension<sup>29</sup> and have been used to create stable microemulsions.<sup>30</sup> Typical commercial products consist of both the monorhamnolipid and dirhamnolipid forms and are generally more expensive than the chemical counterparts. Prices range around \$35/lb for the more dilute—e.g., JBR 425 from Jeneil Biosurfactant Co., the chemical used in this study. In comparison, the chemical surfactant used in this work costs around \$5/lb.

We use a multiple screening-tube rocking apparatus to explore rhamnolipid as potential AA. A quaternary ammonium salt, shown effective in a previous study,<sup>18</sup> is also included in our paper. The influence of AA concentration,  $\Delta T_{op}$ , and residence time at  $\Delta T_{op}$  are the main variables of focus. Shut-in testing, in which the vial with hydrates is allowed to stand unagitated for a given period, and emulsion stability tests are also included. Through these variables, model water-in-oil emulsions are judged according to hydrate formation/dissociation temperatures and visual observations of agglomeration state after hydrate formation.

Tetrahydrofuran (THF) is used as the guest molecule since it forms structure II hydrates—the same type that forms in most pipelines—at atmospheric pressure.<sup>31</sup> There are several differences between THF and real systems, but THF is still considered to be an adequate model system. THF may partition significantly between the aqueous and organic phases.<sup>18</sup> Another major difference is that THF is much more soluble in water than any



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

species found in a typical natural gas mixture. THF and some gases—e.g.,  $\text{CO}_2$ —may initiate hydrate in the bulk water phase;<sup>32–34</sup> however, some authors present data and show methane, methane–ethane, and methane–propane hydrates form at the water/oil interface.<sup>34,35</sup> Since surfactants will reside at or near the interface in any system, AA shown effective for THF systems may also be effective for systems where hydrate formation and growth occur at the interface.<sup>18</sup>

## II. Experimental Methods

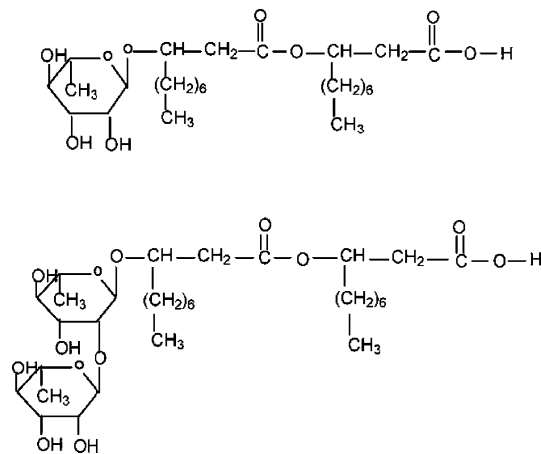
**A. Apparatus.** The experimental setup, a multiple screening-tube rocking apparatus, is shown in Figure 1—similar to that used in the work of Zanota et al.<sup>18</sup> It consists of a motor-driven agitator—with rack holding up to 20 separate borosilicate glass scintillation vials with dimensions of 17 (diameter)  $\times$  60 (height) mm—submerged in a temperature bath. Each vial holds roughly 7.4 mL of a test mixture and a  $\sim$ 8 mm diameter stainless steel 316 ball to aid agitation as well as visual observations; a Teflon-lined plastic screw cap is used along with Teflon tape—around threads—to seal vials. The rack rotates the vials  $150^\circ$  to either side of the vertical direction, completing a cycle every 5 s. The temperature bath used is a Huber CC2-515 vpc filled with 10 cSt—at  $24^\circ\text{C}$ —silicon oil from Clearco Products Co., Inc., Bensalem, PA. Thermocouples—with accuracy of  $\pm 0.2^\circ\text{C}$  from  $70^\circ\text{C}$  down to  $-20^\circ\text{C}$ —are attached to the outside of the vials when crystallization and melting data are desired. An Agilent 34970A data acquisition unit—recording temperature every 20 s—and ice bath as a fixed junction reference temperature are used with all thermocouples.

Agglomeration state images are obtained with a  $\sim$ 169 mm rigid borescope—Hawkeye Pro Hardy from Gradient Lens Corp., Rochester, NY—and Nikon Coolpix 5400 digital camera with samples still in bath fluid.

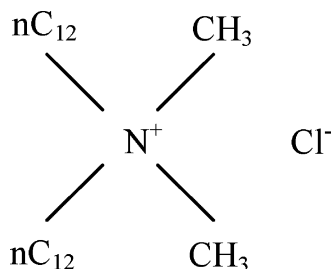
**B. Chemicals.** In all test mixtures, deionized water—obtained from a Barnstead Nanopure Infinity system with quality of roughly  $5.5 \times 10^{-2} \mu\text{S}/\text{cm}$ —and 99.5+% purity THF (from Acros) are used. The oil phase consists of 99% purity 2,2,4-trimethylpentane (i.e., isooctane, from Acros).

The following surfactants are used: rhamnolipid (product JBR 425) was obtained from Jeneil Biosurfactant Co., Madison, WI. It is a mixture of two forms, shown in Figure 2, at 25 wt % in water. Arquad 2C-75 was obtained from Akzo-Nobel and is shown in Figure 3. It consists of 75 wt % surfactant in solvent consisting of water and isopropanol. Both were used as supplied.

**C. Procedure.** We use a composition of 1/1/4/x parts—x is for varying surfactant concentration in different tests—by weight of water/THF/isooctane/surfactant similar to the work of Zanota



**Figure 2.** Two forms of rhamnolipid—monorhamnolipid and dirhamnolipid—present in the sample used in the current work.



**Figure 3.** Structure for dicetyl dimethyl ammonium chloride.

et al.<sup>18</sup> Stoichiometric ratio of 0.235/1 of THF/water may lead to ice formation from heterogeneous nucleation.<sup>36</sup> Higher concentration of THF avoids ice formation.<sup>37</sup> Sample volumes are roughly 7.4 mL.

Temperature data were acquired separate from visual observations since half of the sample vial surface area is covered when thermocouples are attached. However, temperature control of the bath and agitation are the same for both types of experiments.

**Kinetic/Thermodynamic Data Acquisition.** A typical trend of measured temperature data—referred to as a freeze–thaw cycle—is shown in Figure 4. Mixtures are brought to 7 °C and allowed to reach equilibrium, and then a 10 °C/h cooling ramp is employed to –8 °C. The temperature is then heated back to 7 °C at 14 °C/h. 7 °C is chosen because it was used in a previous study.<sup>18</sup> The equilibrium temperature for these mixtures—i.e., water/THF of 1/1 by weight—is expected to be around 3.5 °C after some THF partitions into the oil phase. The equilibrium temperature for the 50% THF water hydrate is around 2.5 °C.<sup>18,31</sup> As a mixture is cooled below the equilibrium, it reaches an onset of crystallization and an exothermic heat release begins. The temperature of this transition is the crystallization temperature, or  $T_c$ . Once crystallization has occurred, the sample temperature rejoins that of the bath fluid. The time,  $t_c$ , that the mixture spends crystallizing relates directly to the growth rate. Dissociation of the mixture during heating shows as an endotherm, the beginning of which is labeled the dissociation temperature,  $T_d$ . This is the same as the equilibrium temperature. The accuracies of individual  $T_c$  and  $T_d$  values are determined at  $\pm 0.2$  and  $\pm 0.5$  °C, respectively. The accuracy of  $t_c$  values is  $\pm 1.0$  min.

Each composition was prepared in triplicate and experiments were repeated five times per sample. That is, each sample was

reused for five consecutive experiments. Some runs were separated by periods of heating at 7 °C for at least 20 min. In some other tests, unagitated samples were kept in the bath overnight as it warmed gradually to room temperature before proceeding to the next test. There was no difference between the results from the use of samples exposed to room temperature and to those limited to heating at 7 °C. The data presented below is the average of 15 separate experiments per composition.

**Agglomeration States.** Experiments for gathering visual observations are conducted similarly to crystallization/dissociation testing. Agitated mixtures are allowed to equilibrate at 7 °C and then 10 °C/h cooling is applied to bring the mixtures to a minimum temperature of –8, –12, –16, or –20 °C. The procedure deviates here whereby the minimum temperature is held constant. Observations were made at 10 min, 1 h, and 24 h into this period. This was repeated twice for each of the triplicate mixtures of a given composition, separated by periods of heating at a minimum of 10 °C for 30 min. Observations were made mainly with the naked eye but also with the borescope. These observations show whether a dispersion of hydrate crystals is facilitated by the surfactant or agglomeration occurs. Images are captured with vials at various angles—details given below—and borescope/camera held above the agitator/bath with the borescope submerged in bath fluid at roughly a 30–45° angle with vertical.

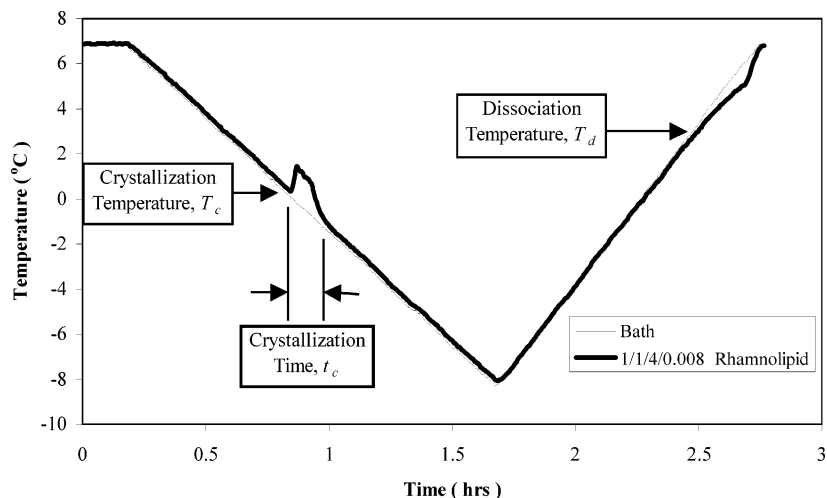
Shut-in testing was also conducted. All mixtures were left unagitated at the various  $\Delta T_{op}$  for up to 60 min—this test was conducted at the termination of the cooling ramp when the desired temperature was reached. Agitation was then resumed to assess whether hydrates are re-dispersed or irreversible agglomeration occurred.

**Emulsion Stability.** The procedure for emulsion stability testing is similar to that employed by Zanota et al.<sup>18</sup> Mixtures of 1/1/4/x of water/THF/isooctane/surfactant by weight are prepared without the stainless steel ball and homogenized by shaking by hand. The fluid is transferred at room temperature to a graduated cylinder—with glass stopper—and the time it takes for 60 vol % of the initial aqueous phase to separate is measured and used as an indicator of emulsion stability. This procedure is referred to as formal emulsion stability testing. Tests at each composition are repeated three times.

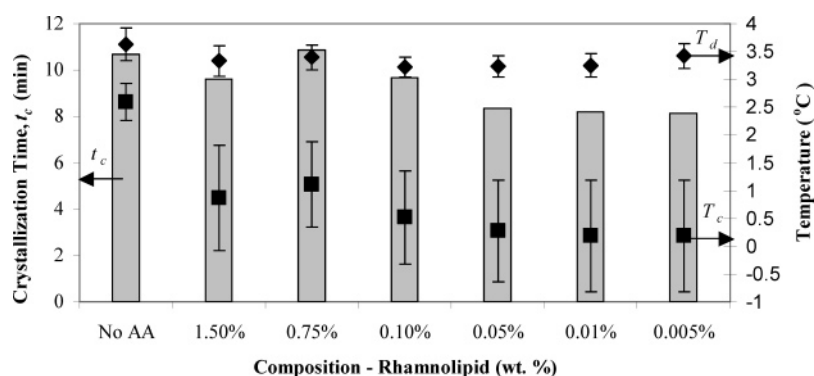
Alternative assessment of emulsion stability is performed in the following manner. After a visual observation test is finished, mixtures are allowed to equilibrate at room temperature—i.e., agitated for about 20 min in a bath. Samples are removed from the bath and agitation is stopped in such a way that the mixtures can be viewed while in the rack—vials are left vertical in the rack so that water separation is visible at the bottom. The mixtures are then monitored for phase separation, with an approximate indicator of the 60 vol % separation being marks made on the vial during mixing that also corresponds to roughly half the height of the steel ball. Tests at each composition are repeated three times. Note that one difference between the two types of tests is the presence of the steel ball in the latter.

### III. Results

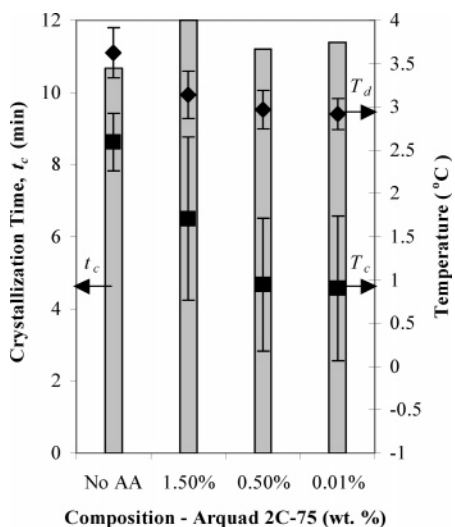
**A. Kinetic/Thermodynamic Characteristics.** Figure 5 shows freeze–thaw cycle results for mixtures without surfactant and select mixtures with rhamnolipid. The concentration of rhamnolipid in these mixtures varies from 1.5 wt % (i.e., 0.015 parts by weight) to 0.005 wt % with respect to the water phase. Figure 6 shows the same data for select Arquad 2C-75 mixtures of 1.5, 0.5, and 0.01 wt %. The difference between the dissociation temperature  $T_d$  and the crystallization temperature  $T_c$  is the onset



**Figure 4.** Typical freeze–thaw cycle data; example for mixture with 0.75 wt % rhamnolipid.



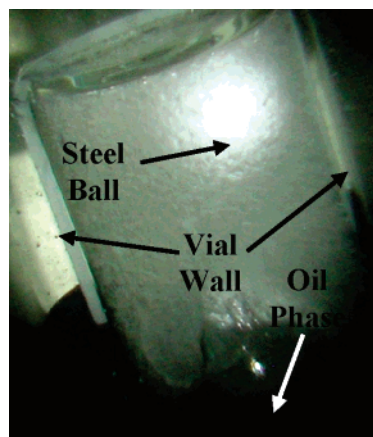
**Figure 5.** Average of freeze–thaw cycle data for mixtures with rhamnolipid and no surfactant. Given are  $T_c$  (shown as ■),  $t_c$  (shown as columns), and  $T_d$  (shown as ♦).



**Figure 6.** Average of freeze–thaw cycle data for mixtures with Arquad 2C-75 and no surfactant. Given are  $T_c$  (shown as ■),  $t_c$  (shown as columns), and  $T_d$  (shown as ♦).

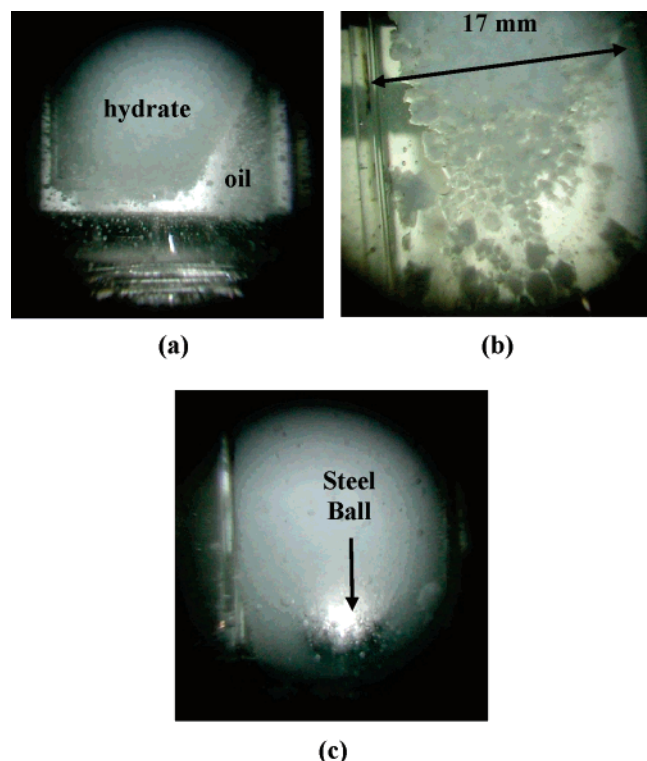
subcooling denoted by  $\Delta T_{on}$ . Note that the two surfactants show a modest kinetic effect.

**B. Agglomeration State.** Physical images taken in the visual observations are as follows—all images shown were obtained at  $-8\text{ }^{\circ}\text{C}$ . A hydrate plug—when the mixture is frozen solid and steel ball motion is prevented—is shown in Figure 7. Effective anti-agglomeration is achieved when stable dispersions—

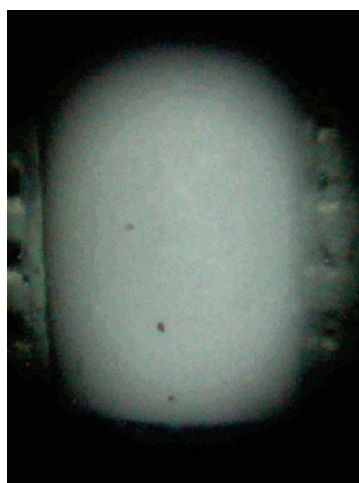


**Figure 7.** Hydrate plug with stainless steel ball frozen in place. In this image, vial is upside down—i.e., completely vertical—with roughly 50–60 vol % of vial blocked and remaining volume occupied by clear oil phase. Calculations using measured THF hydrate density<sup>42</sup> show the volume fraction of hydrate in these mixtures is 0.16.

or slurries—of hydrate crystallites exist. Rhamnolipid mixtures exhibited dispersions as seen in Figure 8, marked by relatively large crystallites distinct from the oil phase especially upon settling. The steel balls can travel freely and without delay in the vials, though these dispersions are relatively viscous. Most Arquad 2C-75 mixtures exhibited stable dispersions of the same character as the rhamnolipid ones—see Figure 9. The exception is the lowest concentration of 0.01 wt %, which exhibited



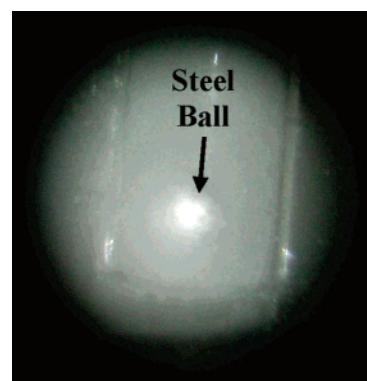
**Figure 8.** Examples of 0.75 wt % rhamnolipid slurries. Image (a) depicts crystallite dispersion with vial tilted roughly 20° from horizontal to depict crystallites just before settling. Notice there is clear distinction between opaque crystallites and the clear oil phase. Image (b) shows a closer view of the slurry before settling, where care has been taken to show distinct crystallites. With knowledge of the vial diameter—shown in the image—a rough crystallite size range is calculated to be from 0.2 to 4 mm. Image (c) shows the appearance of slurry after crystallites have settled to the bottom of the vial. The appearance here is very similar to a plug, except that crystallites are dispersed when the vial is agitated.



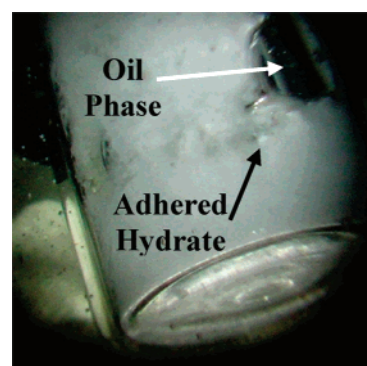
**Figure 9.** Image depicting 0.5 wt % Arquad 2C-75 slurry, after crystallite settling. The appearance is noticeably opaque.

relatively small hydrate crystallites—seen in Figure 10. For both surfactants, a stable hydrate dispersion means stability for 24 h.

Rhamnolipid mixtures of 0.01 wt % began the constant minimum temperature period as slurries but did not last as such for a 24 h period; these cases are depicted as metastable and are marked by significant crystallite adhesion onto the vial walls. Very low concentration rhamnolipid mixtures—i.e., 0.005 wt %—exhibited significant crystallite adhesion upon vial walls



**Figure 10.** Image depicting 0.01 wt % Arquad 2C-75 slurry, after settling of crystallites—i.e., vial is at roughly 60° angle with horizontal here. At this concentration, the appearance is noticeably less opaque, indicative of smaller crystallites. Here, the steel ball resides toward the rear of the vial and is visible through the fluid, whereas with other mixtures the steel ball is not visible unless it is manipulated to be in the front of the vial—such is the case with Figure 8c.



**Figure 11.** Image of crystallite adhesion to vial walls in mixture of 0.01 wt % rhamnolipid. This is not a solid plug, but rather with sections of vial wall covered with hydrate and the rest still occupied by the clear oil phase. The steel ball in such cases can travel the length of the vial.

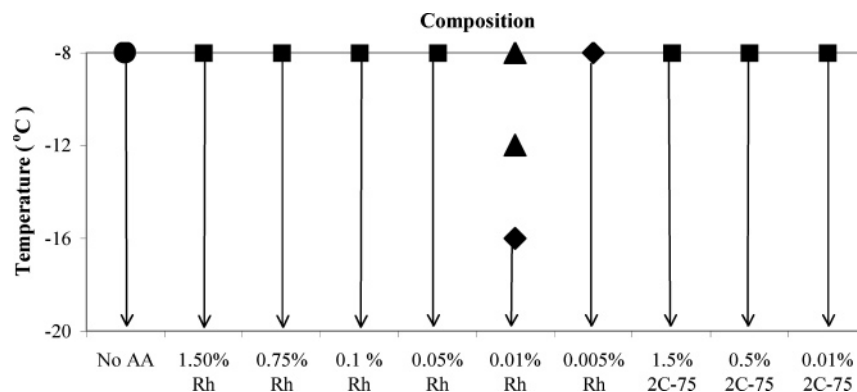
immediately at certain minimum temperatures. An example of such adhesion is shown in Figure 11.

Figure 12 shows dispersion and agglomeration state results for all tests with the two surfactants.

**C. Emulsion Stability.** Table 1 gives average emulsion stability results for both test types, along with standard deviations. Average and standard deviation values are given to the nearest minute. The only concentrations tested were 1.50, 0.50, and 0.01 wt % of both surfactants.

#### IV. Discussion

**A. Kinetic/Thermodynamic Characteristics.** As in a previous study,<sup>18</sup> both surfactants tested exhibit some kinetic inhibition ability. Both surfactants increase  $\Delta T_{on}$  by about 2–3 °C compared to roughly 0.5 °C for surfactant-free mixtures. For both surfactants, this increase is greater for lower concentrations. The increase in  $\Delta T_{on}$  at lower concentrations is small but just beyond the uncertainty in these measurements. Thus, this behavior may be significant but no explanation can be given at the present time. It is expected for mixtures with lower  $T_c$  values to have smaller  $t_c$  due to increased driving force for phase change—i.e., supersaturation.<sup>38</sup> Rhamnolipid mixtures exhibit this feature; however, the opposite is seen for Arquad mixtures. That is,  $T_c$  values in Arquad mixtures are slightly lower but  $t_c$  values are larger than those in mixtures without AA. The differences are insignificant, due in part to the fairly large uncertainty involved in  $t_c$ .



**Figure 12.** State of agglomeration for all conditions in visual observation experiments: (●) plugging, (◆) immediate agglomeration upon vial walls, (▲) metastable dispersion, and (■) stable dispersion—i.e., successful anti-agglomeration—at all subcoolings. Arrows indicate the range of  $\Delta T_{op}$  for which the same behavior is exhibited. “Rh” stands for rhamnolipid and “2C-75” represents quat mixtures.

**TABLE 1: Emulsion Stability Results**

composition (wt %)	formal method <sup>a</sup> (min)	alternative method <sup>b</sup> (min)
1.5% rhamnolipid	2 ± 1	117 ± 15
0.5% rhamnolipid	2 ± 1	87 ± 10
0.01% rhamnolipid	1 ± 0	12 ± 3
1.5% Arquad 2C-75	121 ± 9	421 ± 16
0.5% Arquad 2C-75	21 ± 2	333 ± 8
0.01% Arquad 2C-75	6 ± 1	10 ± 3

<sup>a</sup> Procedure used by Zanota et al.<sup>18</sup> A hand-shaken sample—without stainless steel ball—is transferred at room temperature to a graduated cylinder and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability. <sup>b</sup> Test samples used for visual observation and other experiments—with stainless steel included—are agitated at room temperature and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability.

**B. Agglomeration State.** Stable dispersions are seen for rhamnolipid concentrations of 1.5–0.05 wt % to  $-20$  °C and to 24 h. However, performance declines for lower concentrations. At  $-8$  and  $-12$  °C, 0.01 wt % rhamnolipid mixtures exhibit stable dispersions for up to 1 h, but significant agglomeration upon the vial occurs before 24 h. These mixtures were also observed during the cooling ramp and slurries were observed during the cooling period. At the same rhamnolipid concentration, crystallite adhesion occurs immediately at  $-16$  and  $-20$  °C. When rhamnolipid concentration is lowered further to 0.005 wt %, the same crystallite adhesion occurs at all minimum temperatures. The minimum temperatures of  $-8$ ,  $-12$ ,  $-16$ , or  $-20$  °C correspond to subcoolings of roughly 11, 15, 19, and 23 °C.

Crystallite adhesion upon vials became a concern regarding experiment integrity. However, multiple samples made with glassware and other components cleaned by different methods all exhibited this behavior, so it is not thought that apparatus contamination was the result of such observations. In addition, other studies report such behavior.<sup>17,39</sup> Urdahl et al.<sup>17</sup> report that nonionic surfactants tested tended to deposit hydrates upon apparatus walls. Another study<sup>40</sup> reports extensive hydrate growth on a reaction vessel wall for an anionic surfactant mixture—i.e., sodium dodecyl sulfate, generally not considered among effective AA compounds. This may help to explain the reason why rhamnolipid mixtures exhibited this behavior while Arquad mixtures did not. Rhamnolipid is known to ionize to anionic form by dissociation of the carboxylic acid group when pH is above 4.0<sup>29</sup>—which is presently the case with Millipore water giving a pH of 5.0—although indications are given

elsewhere<sup>30,41</sup> that more alkaline pH may be required for ionization. In real systems, the pH may vary due to the presence of dissolved salts, or brine, in the water phase. Adhesion is prevented by using sufficient amounts of rhamnolipid, indicating the phenomena may be simply due to not only the chemical itself but also the concentration. In this respect, sufficient amounts—i.e., 0.05 wt % or higher—of rhamnolipid prevent adhesion on vessel walls as well as agglomeration of hydrate crystallites.

The Arquad 2C-75 mixtures exhibited stable dispersions for the entire concentration range of 1.5–0.01 wt % and for all minimum temperatures and residence times. Lower Arquad 2C-75 concentrations were not tested due to limitations in the sample preparation method. A similar quat surfactant—i.e., M2SH1 produced by CECA, also known as distearyl dimethyl ammonium chloride—is shown in a previous study<sup>18</sup> to lose its effectiveness in the same mixtures around 0.25 wt %. It is thought that Arquad 2C-75 is much more effective at lower concentrations because it is more water-soluble than a M2SH1 structure.

An interesting observation is the apparent difference in crystallite size for mixtures with 0.01 wt % Arquad 2C-75, whereas the higher concentrations appear similar to all rhamnolipid mixtures. Figure 9 resembles Figure 8c in appearance because most slurries observed are very opaque after settling. In fact, the settled slurries resemble plugs, except that crystallites flow when the vials are rocked. Thus, it is surprising to see the less opaque slurry created with 0.01 wt % Arquad 2C-75, as depicted in Figure 10. According to ref 18, this change in appearance indicates that the crystallites are smaller.

All of these mixtures were tested for shut-in conditions when the vial was allowed to sit unagitated. All Arquad 2C-75 mixtures were redispersed at all  $\Delta T_{op}$  once the agitation was resumed. The same occurred for mixtures with 1.5–0.05 wt % rhamnolipid; however, mixtures with 0.01 wt % rhamnolipid at all  $\Delta T_{op}$  exhibited significant crystallite adhesion to vial walls after resuming agitation.

The surfactants chosen for this study are either soluble—i.e., rhamnolipid—or dispersible—i.e., Arquad 2C-75—in water. Both are thought to be suitable AA candidates for real systems because they are effective in a THF system where the environment for hydrate formation is very friendly.<sup>18</sup> In a real system, hydrate formation and growth may occur at the interface and even in a thick layer; in this case, exact placement of surfactant at the interface is crucial for ensuring surfactant is available where needed to prevent hydrate agglomeration. Thus, tests on real systems should still be conducted to determine the effectiveness of these two AA.

**C. Emulsion Stability.** Emulsions are formed during agitation for all mixtures, and only a few seconds of shaking is needed to emulsify. Emulsions formed by rhamnolipid are generally less stable than those formed by Arquad 2C-75, and the difference is more significant at higher surfactant concentrations (see Table 1).

The emulsion results coupled with agglomeration observations reveal that highly stable emulsions are not necessary for effective anti-agglomeration, unlike the results found in the work reported by Zanota et al.<sup>18</sup> Once crystallization occurs in such mixtures with rhamnolipid, the relative instability of water-in-oil emulsions is inconsequential. The relative instability of emulsions created by rhamnolipid also may be beneficial for processing after well extraction and transportation through pipelines.

Stability values for the alternative method are consistently larger than those measurements obtained with graduated cylinders. Even though the alternative method involves larger uncertainty, it is believed that this method may be advantageous since transferring of mixtures in the formal method involves some error from vapor loss and material loss due to wetting of fluids on the scintillation vial walls and Teflon-lined caps. Also, the alternative method may be showing an effect of hydrate formation and dissociation, present as noticeably greater emulsion stabilities.

## V. Conclusions

In this work we have shown that rhamnolipids may be an effective AA comparable to that of chemical surfactants. The effectiveness of the rhamnolipids has been demonstrated through visual observations with a multiple screening-tube rocking apparatus using high operating subcooling and residence time as indicators of performance. Shut-in and emulsion stability tests also lend supporting evidence.

Several important conclusions can be drawn from this study. One important result is that both surfactants tested are effective at an order of magnitude less than what conventional limits—i.e., 0.5 wt %—are thought to be. Another result is that highly stable water-in-oil emulsions are not required for an effective AA. Another observation is that relatively large hydrate crystallites may not be detrimental to flow assurance in pipelines.

Rhamnolipid will be studied further in the future. One area of focus will be the effect of different types as well as varying amounts of oil. Although rhamnolipids are currently more expensive to produce than chemical surfactants, biosurfactants are friendly to the environment. Typical quat AA compounds are toxic to the environment and living organisms. Not only is rhamnolipid more benign but also manufacture is possible with waste such as vegetable oils or laboratory-grade organic chemicals. In this respect, the use of biosurfactants has huge potential for green practices in industry. It is only a matter of time until rhamnolipid costs become comparable to chemical surfactants.

**Acknowledgment.** We are grateful to Jeneil Biosurfactant Co. for providing the rhamnolipid sample, as well as to Akzo Nobel for providing the quaternary ammonium salt sample. This work was supported by the member companies of the Reservoir Engineering Research Institute (RERI) in Palo Alto, CA.

## References and Notes

(1) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

- (2) Dholabhai, P. D.; Parent, J. S.; Bishnoi, P. R. *Fluid Phase Equilib.* **1997**, *141*, 235.
- (3) Anderson, F. E.; Prausnitz, J. M. *AIChE J.* **1986**, *32*, 1321.
- (4) Christiansen, R. L.; Sloan, E. D. *Anal. N. Y. Acad. Sci.* **1994**, 283.
- (5) Lederhos, J. P.; Long, J. P.; Sum, A.; Christiansen, R. L.; Sloan, E. D. *Chem. Eng. Sci.* **1996**, *51*, 1221.
- (6) Anklam, M. R.; Firoozabadi, A. *J. Chem. Phys.* **2005**, *123*, 144708.
- (7) Kelland, M. A.; Svartaas, T. M.; Dybvik, L. A. Proceedings of the SPE 69th Annual Technical Conference and Exhibition 1994, New Orleans, LA.
- (8) Urdahl, O.; Lund, A.; Mork, P.; Nilsen, T. N. *Chem. Eng. Sci.* **1995**, *50*, 863.
- (9) Huo, Z.; Freer, E.; Lamar, M.; Sannigrahi, B.; Knauss, D. M.; Sloan, E. D. *Chem. Eng. Sci.* **2001**, *56*, 4979.
- (10) Karaaslan, U.; Parlaktuna, M. *Energy Fuels* **2000**, *14*, 1103.
- (11) Arjmandi, M.; Ren, S. R.; Yang, J.; Tohidi, B. Proceedings of the Fourth International Conference on Gas Hydrates, 2002, Yokohama, Japan.
- (12) Kelland, M. A.; Svartaas, T. M.; Ovsthus, J.; Tomita, T.; Mizuta, K. *Chem. Eng. Sci.* **2006**, *61*, 4290.
- (13) Pakulski, M.; Hurd, D. Proceedings of the Fifth International Conference on Gas Hydrates 2005, Trondheim, Norway.
- (14) Kelland, M. A. *Energy Fuels* **2006**, *20*, 825.
- (15) Klomp, U. C.; Kruka, V. C.; Reijndhart, R. World Patent Application WO 9517579, 1995.
- (16) Sloan, E. D. *Fluid Phase Equilib.* **2005**, 228–229, 67.
- (17) Urdahl, O.; Lund, A.; Mork, P.; Nilsen, T. N. *Chem. Eng. Sci.* **1995**, *50*, 863.
- (18) Zanota, M. L.; Dicharry, C.; Graciaa, A. *Energy Fuels* **2005**, *19*, 584.
- (19) Behar, P.; Kessel, D.; Sugier, A.; Thomas, A. Proceedings of the 70th Gas Processors Association Conference 1991, San Antonio, TX.
- (20) Phillips, N. J.; Kelland, M. A. In *Industrial Applications of Surfactants IV*; Karsa, D. R., Ed.; Royal Society of Chemistry: London, 1999; p 244.
- (21) Sjoblom, J.; Aske, N.; Auflem, I. H.; Brandal, O.; Havre, T. E.; Saether, O.; Westvik, A.; Johnsen, E. E.; Kallevik, H. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 399.
- (22) Luckham, P. F. *Adv. Colloid Interface Sci.* **1991**, *34*, 191.
- (23) Israelachvili, J. N.; Wennerstrom, H. *J. Phys. Chem.* **1992**, *96*, 520.
- (24) Taylor, C. J.; Dieker, L. E.; Miller, K. T.; Koh, C. A.; Sloan, E. D. *J. Colloid Interface Sci.* **2007**, *306*, 225.
- (25) Kitamoto, D.; Yanagishita, H.; Endo, A.; Nakaiwa, M.; Nakane, T.; Akiya, T. *Biotechnol. Prog.* **2001**, *17*, 362.
- (26) Hoiland, S.; Borgund, A. E.; Barth, T.; Fotland, P.; Askvik, K. M. Proceedings of the Fifth International Conference on Gas Hydrates, 2005, Trondheim, Norway.
- (27) Kitamoto, D.; Isoda, H.; Nakahara, T. *J. Biosci. Bioeng.* **2002**, *94*, 187.
- (28) Fu, B.; Houston, C.; Spratt, T. Proceedings of the Fifth International Conference on Gas Hydrates, 2005, Trondheim, Norway.
- (29) Nitschke, M.; Costa, S. G. V. A. O.; Contiero, J. *Biotechnol. Prog.* **2005**, *21*, 1593.
- (30) Xie, Y.; Ye, R.; Liu, H. *Colloids Surf. A* **2007**, *292*, 189.
- (31) Hanley, H. J., M.; Meyers, G. J.; White, J. W.; Sloan, E. D. *Int. J. Thermophys.* **1989**, *10*, 903.
- (32) Makogon, T. Y.; Larsen, R.; Knight, C. A.; Sloan, E. D. *J. Cryst. Growth* **1997**, *179*, 258.
- (33) Devarakonda, S.; Groysman, A.; Myerson, A. S. *J. Cryst. Growth* **1999**, *204*, 525.
- (34) Tohidi, B.; Anderson, R.; Clennell, M. B.; Burgass, R. W.; Biderkab, A. B. *Geology* **2001**, *29*, 867.
- (35) Lee, J. D.; Susilo, R.; Englezos, P. *Chem. Eng. Sci.* **2005**, *60*, 4203.
- (36) Zhang, Y.; Debenedetti, P. G.; Prud'homme, R. K.; Pethica, B. A. *J. Phys. Chem. B* **2004**, *108*, 16717.
- (37) Tombari, E.; Presto, S.; Salvetti, G.; Johari, G. P. *J. Chem. Phys.* **2006**, *124*, 154507.
- (38) Kashchiev, D.; Firoozabadi, A. *J. Cryst. Growth* **2002**, *241*, 220.
- (39) Lund, A.; Urdahl, O.; Kirkhorn, S. S. *Chem. Eng. Sci.* **1996**, *51*, 3449.
- (40) Kalogerakis, N.; Jamaluddin, A. K. M.; Dholabhai, P. D.; Bishnoi, P. R. Effect of Surfactants on Hydrate Formation Kinetics. In *The SPE International Symposium on Oilfield Chemistry*, New Orleans, LA, 1993.
- (41) Xie, Y.; Ye, R.; Liu, H.; Ye, R. *J. Dispersion Sci. Technol.* **2005**, *26*, 455.
- (42) Otake, K.; Tsuji, T.; Sato, I.; Akiya, T.; Sako, T.; Hongo, M. *Fluid Phase Equilib.* **2000**, *171*, 175.