Effect of Brine on Hydrate Antiagglomeration

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Natural gas production poses a risk of flow-line hydrate blockage from coproduced water and hydrate-forming species. Our previous studies have focused on gaining further understanding of hydrate antiagglomerants through systematic experimentation as well as testing of a new biosurfactant. Despite great potential, work on hydrate antiagglomeration is still very limited. This work centers on the effect of NaCl and $MgCl_2$ in mixtures of two vastly different antiagglomerants. We use a model oil, water, and tetrahydrofuran as hydrate-forming species. Results show that both salts—added in sufficient quantities—may result in the agglomeration of hydrates. Our results reveal a nonmonotonic agglomeration behavior at low salt and/or large surfactant concentrations. Specifically, dissolved $MgCl_2$ results in agglomeration more than the dissolved NaCl. Our measurements also show that the quaternary ammonium salt—i.e., quat—is more sensitive to dissolved salt than the nonionic rhamnolipid biosurfactant. In this work we show that the rhamnolipid biosurfactant is effective to a low concentration of 0.05 wt %, yet quat has effectiveness down to 0.01 wt %. The biosurfactant—with less toxicity and higher biodegradability—is an attractive alternative to chemical surfactants in antiagglomeration. Results on the model systems show the promise for testing in real fluid systems and field testing of the ideas.

Introduction

Due to a potential supply from various subsurface formations and clean-burning characteristics, natural gas may provide a larger share of primary energy and surpass oil consumption in the 21st century. There is less CO_2 produced from burning natural gas than other fossil fuels. Furthermore, produced CO_2 can be separated from the combustion products and sequestered more readily than oil combustion products for improved oil recovery or storage in saline aquifers. However, thermodynamic conditions existing in gas production lines often favor formation of crystalline inclusion compounds known as gas hydrates. Water, coproduced with natural gas, forms lattice structures by hydrogen bonding; the structures are stabilized by guest molecules such as methane, propane, etc., under high pressures and temperatures in the range of a few degrees to 25 °C.[1] Formation of gas hydrates occurs rapidly—unlike corrosion, scaling, or wax buildup. This rapidity has undesirable safety and environmental consequences. Hydrate plug formation may lead to production shutdowns and even explosions due to large amounts of methane often contained within such plugs.

Traditional hydrate prevention methods include physical means, such as insulation and electrical heating. A change of bulk-phase properties through thermodynamic inhibition with methanol (MeOH) and monoethylene glycol (MEG) is widely used. Thermodynamic inhibitors shift equilibrium conditions to lower temperature and higher pressure.[2] Although well-characterized, these inhibitors often require large concentra-tions—as high as 60 wt % of coproduced water—which increase costs and have serious environmental impacts.[3] An additional problem is that large concentrations of such inhibitors induce precipitation of salts when present in coproduced water.[4] Such precipitation could lead to additional flow assurance problems.

An alternative to thermodynamic inhibitors is the use of low-dosage hydrate inhibitors (LDHIs). LDHIs mainly influence the hydrate interface properties and are effective at concentrations of 3−0.5 wt % (or much less as we have shown recently); rather than affecting the thermodynamic equilibrium, they act upon the kinetics or agglomeration. Kinetic hydrate inhibitors (KHIs) are generally polymeric compounds that delay nucleation and decrease the growth rate.[5,6] KHIs may result in complete inhibition of hydrates but do not perform well at pipeline/well shut-in conditions or at high operating subcoolings—i.e., ΔT_{op}, the difference between the equilibrium temperature and operating temperature at a given pressure.[7] In some flow conditions, ΔT_{op} may be as high as 20 °C; therefore, these severe conditions would require effective LDHIs as well.

A second class of LDHIs are antiagglomerants (AAs) which prevent agglomeration—but not formation—of hydrate crystals and enable hydrate transportation as slurries. AAs are generally effective at high ΔT_{op} or at shut-in conditions.[8−10] AAs may

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(1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; Taylor & Francis, CRC Press: New York, 2007.
(2) Dholabhai, P. D.; Parent, J. S.; Bishnoi, P. R. *Fluid Phase Equilib.* **1997**, *141*, 235–246.

(3) Anderson, F. E.; Prausnitz, J. M. *AIChE J.* **1986**, *32*, 1321–1333.
(4) Masoudi, R.; Tohidi, B.; Danesh, A.; Todd, A. C.; Yang, J. *SPE Prod. Oper.* **2006**, *21*, 182–187.
(5) Christiansen, R. L.; Sloan, E. D. *Ann. N. Y. Acad. Sci. (Natural Gas Hydrates)* **1994**, *715*, 283–305.
(6) Lederhos, J. P.; Long, J. P.; Sum, A.; Christiansen, R. L.; Sloan, E. D. *Chem. Eng. Sci.* **1996**, *51*, 1221–1229.
(7) Anklam, M. R.; Firoozabadi, A. *J. Chem. Phys.* **2005**, *123*, 144708.
(8) Kelland, M. A.; Svartaas, T. M.; Dybvik, L. A. Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, LA, 1994; SPE 28506.
(9) Urdahl, O.; Lund, A.; Mork, P.; Nilsen, T. N. *Chem. Eng. Sci.* **1995**, *50*, 863–870.
(10) Huo, Z.; Freer, E.; Lamar, M.; Sannigrahi, B.; Knauss, D. M.; Sloan, E. D. *Chem. Eng. Sci.* **2001**, *56*, 4979–4991.

also possess kinetic inhibition features.[11−13] They are generally surfactants but may be low molecular weight oligomeric species.[10,14] AAs have not been reported on as extensively as KHIs in the open literature.

AAs may produce water-in-oil (w/o) emulsions—thus limiting hydrate growth to water droplets dispersed in the oil phase; however, emulsification is not a requirement for an effective AA, and some good emulsifiers have even been proven to be poor AAs.[9,10,15−20] Emulsion stability is generally undesired in gas and oil production.[21,22] Once transportation of well fluids is complete, it is desired that phase separation be attainable so that product quality standards can be met. If the emulsions are too stable, then additional processing or additives may be required once hydrate formation is of no concern. AAs may become ineffective if water occupies one-third or more of the total liquid volume of the process stream—i.e., limited to 50% water cut. This requirement may be related to w/o emulsion formation, but other reasons such as high slurry viscosity with high hydrate volume fraction are also cited in the literature.[15,16,23] A recent study[24] showed that a new AA inhibitor is effective at water cuts as high as 80% in both wet-tree and dry-tree applications. This may be the only known exception to the 50% water cut limitation.

Biosurfactants possess favorable characteristics compared to chemical surfactants—more specifically, the quaternary ammonium compounds and related structures. The favorable characteristics include (1) higher biodegradability, (2) lower toxicity, and (3) safety.[25,26] These features—coupled with the fact that environmentally unfriendly quaternary ammonium salts are currently the most successful AA chemistry in industrial experiments and field applications[15]—have motivated us to include biosurfactants in our work.

In a recent study on hydrate antiagglomeration, we showed that rhamnolipid at concentrations as low as 0.05 wt % is effective as an AA in tetrahydrofuran (THF) mixtures with sufficient model oil—i.e., 4 parts by weight or higher.[27] We

subsequently showed that the limit at which rhamnolipid concentrations are effective in antiagglomeration may be adversely impacted by an increased water/oil ratio—i.e., in similar mixtures but with 2 parts by weight of the same model oil. We also showed that a very small amount of alcohol cosurfactant may help assuage the repercussions of such variations.[28] In the past we have used pure water in the model mixtures. The major theme of this work centers on the investigation of the effect of dissolved salts in the aqueous phase on antiagglomeration.

Dissolved salts exist in formation water. Data from North American fields[29] reveal concentrations of individual ions—e.g., Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}—vary from small amounts to concentrations close to the solubility limit.[4] The principle electrolytes found in oil formation waters are NaCl, $CaCl_2$, and KCl, but other salts are also present.[4]

There is very limited work on salinity effects upon AA performance. Fundamental antiagglomeration studies either employ pure water[9,10,17,30] or use a constant value of less than 5 wt % brine concentration in the test mixtures.[31−33] Some other industrial studies[34] employ higher salinities—e.g., 10 wt %—on the basis of field data relevant to the actual mixtures for which hydrate inhibition is desired. There is some discussion in the literature related to how different salt concentrations affect AA performance. The results are not, however, clear. In a more recent work, one nonionic alkylamide AA out of many that were synthesized and tested was subjected to variable salinity: it was found that the AA was effective at 3.5% synthetic seawater, but not effective—i.e., hydrate deposits in the test vessel ensued—when the synthetic seawater amount was lowered to 0.5 wt %.[13] In other work,[35] it is mentioned that initial AA formulations were effective in high-salinity brines but did not work in low salinity-brines and that the problem has since been addressed by development of inhibitors effective in a wider salinity range. It should be pointed out that, in ref 35, the actual values that are considered as high and low salinities are not given, but in general, a normal salinity is around 3%, which makes a "low" value much lower than this—i.e., 1.0%—and a "high" salinity a value much higher—i.e., 10 wt % and higher. In another study[34] the authors state that the particular AA employed required a minimum salinity of 1.5 wt % to be effective—per vendor specifications. Although these comments provide insight into salinity effects upon AA performance, they are not clear, and overall, no systematic data are reported. There is need for fundamentally and systematically broad investigations on the effect of salts on antiagglomeration.

In this work, we investigate the effect of salt valency and concentration in the aqueous phase on hydrate antiagglomeration. The influence of AA concentration, ΔT_{op}, and residence time at ΔT_{op} are other variables of focus. Rhamnolipid biosurfactant and a quaternary ammonium salt (quat) are the AAs—the same surfactants used in our previous work.[27,28] Crystal-

(11) Karaaslan, U.; Parlaktuna, M. *Energy Fuels* **2000**, *14*, 1103–1107.

(12) Arjmandi, M.; Ren, S. R.; Yang, J.; Tohidi, B. *Proceedings of the Fourth International Conference on Gas Hydrates*, Yokohama, Japan, 2002; pp 516−519.

(13) Kelland, M. A.; Svartaas, T. M.; Ovsthus, J.; Tomita, T.; Mizuta, K. *Chem. Eng. Sci.* **2006**, *61*, 4290–4298.

(14) Pakulski, M.; Hurd, D. *Proceedings of the Fifth International Conference on Gas Hydrates*, Trondheim, Norway, 2005; pp 1444−1451.

(15) Kelland, M. A. *Energy Fuels* **2006**, *20*, 825–847.

(16) Sloan, E. D. *Fluid Phase Equilib.* **2005**, *228−229*, 67–74.

(17) Zanota, M. L.; Dicharry, C.; Graciaa, A. *Energy Fuels* **2005**, *19*, 584–590.

(18) Behar, P.; Kessel, D.; Sugier, A.; Thomas, A. *Proceedings of the 70th Gas Processors Association Conference*, San Antonio, TX, 1991.

(19) Phillips, N. J.; Kelland, M. A. In *Industrial Applications of Surfactants IV*; Karsa, D. R., Ed.; Royal Society of Chemistry: London, 1999; pp 244−259.

(20) Jakobsen, T.; Sjoblom, J.; Ruoff, P. *Colloids Surf., A* **1996**, *112*, 73–84.

(21) Sjoblom, J.; Hemmingsen, P. V.; Kallevik, H. In *Asphaltenes, Heavy Oils, and Petroleomics*; Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G., Eds.; Springer-Verlag: New York, 2007; pp 549−587.

(22) Fordedal, H.; Schildberg, Y.; Sjoblom, J.; Volle, J.-L. *Colloids Surf., A* **1996**, *106*, 33–47.

(23) Andersson, V.; Gudmundsson, J. S. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 322–329.

(24) Alapati, R.; Lee, J.; Beard, D. Presented at the Offshore Technology Conference, Houston, TX, 2008; OTC 19505.

(25) Kitamoto, D.; Isoda, H.; Nakahara, T. *J. Biosci. Bioeng.* **2002**, *94*, 187–201.

(26) Fu, B.; Houston, C.; Spratt, T. *Proceedings of the Fifth International Conference on Gas Hydrates*, Trondheim, Norway, 2005; pp 1385−1394.

(27) York, J. D.; Firoozabadi, A. *J. Phys. Chem. B* **2008**, *112*, 845–851.

(28) York, J. D.; Firoozabadi, A. *J. Phys. Chem. B* **2008**, *112*, 10455–10465.

(29) *Petroleum Engineering Handbook*; Bradley, H. B., Ed.; Society of Petroleum Engineers: Richardson, TX, 1987.

(30) Lund, A.; Urdahl, O.; Kirkhorn, S. S. *Chem. Eng. Sci.* **1996**, *51*, 3449–3458.

(31) Fadnes, F. H. *Fluid Phase Equilib.* **1996**, *117*, 186–192.

(32) Camargo, R.; Palermo, T. *Proceedings of the Fourth International Conference on Gas Hydrates*, Yokohama, Japan, 2002; pp 880−885.

(33) Hemmingsen, P. V.; Li, X.; Peytavy, J.-L.; Sjoblom, J. *J. Dispersion Sci. Technol.* **2007**, *28*, 371–382.

(34) Mehta, A. P.; Hebert, P. B.; Cadena, E. R.; Weatherman, J. P. Presented at the Offshore Technology Conference, 2002; OTC 14057.

(35) Cowie, L.; Bollavaram, P.; Erdogmus, M.; Johnson, T.; Shero, W. Presented at the Offshore Technology Conference, 2005; OTC 17328.
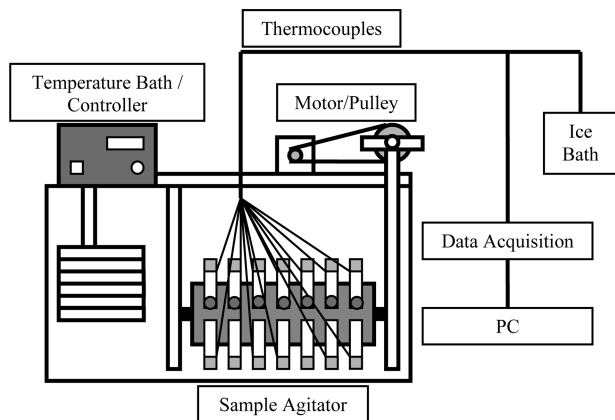
Figure 1. Multiple-screening-tube rocking apparatus.

lization and dissociation characteristics are obtained via thermocouples. Shut-in testing in which vials with hydrates are allowed to stand unagitated for a given period and emulsion stability tests are also included. Through these variables and primarily visual observations of the agglomeration state after hydrate formation, two potential antiagglomerants are judged in model w/o emulsions. THF is used as the guest molecule, since it forms structure II hydrates at atmospheric pressure—the same type that forms in most pipelines.[36,37]

Experimental Section

Apparatus. The experimental setup consisting of a multiple-screening-tube rocking apparatus—as shown in Figure 1—a temperature bath with silicon oil, thermocouples, a data acquisition unit, and a borescope is the same as used in our previous work.[27,28]

Chemicals. In all test mixtures, deionized water—obtained from a Barnstead Nanopure Infinity system with a quality of roughly 5.5×10^{-2} μS/cm—and 99.5%+ purity THF (from Acros) were used. The oil phase consists of 99% purity 2,2,4-trimethylpentane (i.e., isooctane, from Acros). Brine was introduced through addition of NaCl or $MgCl_2 \cdot 6H_2O$ (both obtained from Fisher); during sample mixing, both salts were added to the water and surfactant prior to addition of THF and model oil.

The following surfactants were 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—dicetyldimethylammonium chloride—was obtained from Akzo-Nobel and is shown in Figure 3. It consists of 75 wt % surfactant in solvent consisting of water (at 5−10 wt %) and 2-propanol (at 15−20 wt %). Both were used as supplied. Both of the above chemicals used are the same as discussed in our previous work.

Procedure. The experimental procedures are the same as in our previous work, unless noted below.[27,28] These procedures are also similar to those employed by Zanota and co-workers.[17] In these mixtures, "water" refers to pure water not containing any dissolved salts. THF remains as the model hydrate former, although cyclopentane is another option that has received increased attention more recently.[38−40] However, THF is the best choice for such studies where large subcoolings are employed to study antiagglomeration; this assessment is based on the vast difference in aqueous-phase
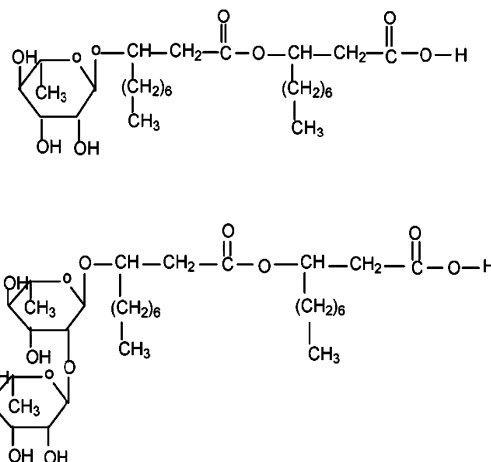
(36) Hanley, H. J., M.; Meyers, G. J.; White, J. W.; Sloan, E. D. *Int. J. Thermophys.* **1989**, *10*, 903–909.

(37) Pickering, P. F.; Edmonds, B.; Moorwood, R. A. S.; Szczepanski, R.; Watson, M. J. Presented at the IIR Conference, Aberdeen, Scotland, 2001.

(38) Fan, S. S.; Liang, D. Q.; Guo, K. H. *J. Chem. Eng. Data* **2001**, *46*, 930–932.

(39) Taylor, C. J.; Miller, K. T.; Koh, C. A.; Sloan, E. D. *Chem. Eng. Sci.* **2007**, *62*, 6524–6533.

(40) Nakajima, M.; Ohmura, R.; Mori, Y. H. *Ind. Eng. Chem. Res.* **2008**, *47*, 8933–8939.

Figure 2. Two forms—monorhamnolipid and dirhamnolipid—used in the rhamnolipid mixture.
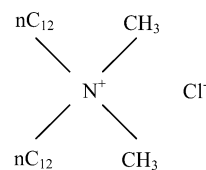

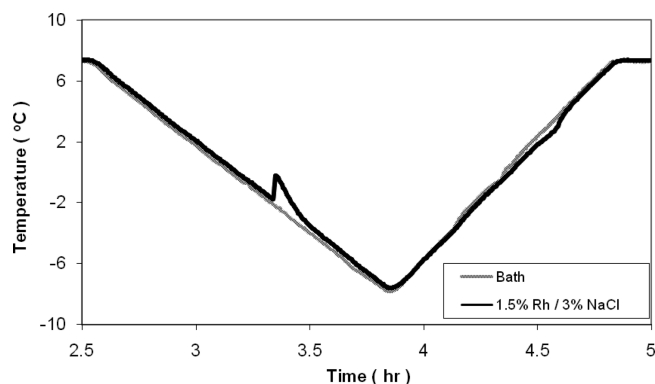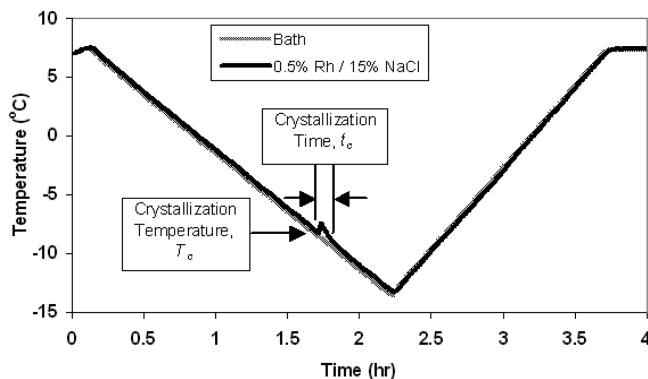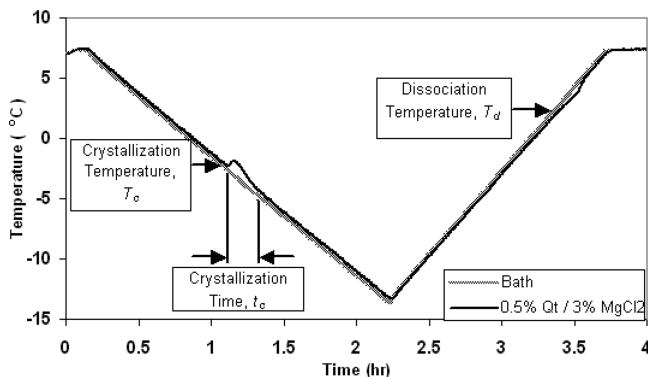**Figure 3.** Structure for dicetyldimethylammonium chloride.

Figure 4. Typical freeze−thaw cycle data for a mixture containing 3 wt % NaCl. The mixture also contains 1.5% rhamnolipid.

solubilities between THF and cyclopentane. In both kinetic/thermodynamic and agglomeration-state tests, each composition was prepared in triplicate and each sample tested five times. The data are averaged for the kinetic/thermodynamic data presentation.

Kinetic/Thermodynamic Data Acquisition. Select mixtures with $1/1/4/x$ parts by weight of water/THF/isooctane/surfactant—x is for varying surfactant concentration in different tests—with 3 and 15 wt % NaCl and $MgCl_2$ (with respect to water) were tested. Three different surfactant concentrations employed were 1.5 and 0.5 wt % and either 0.01 wt % quat or 0.05 wt % rhamnolipid. The lower limit for both surfactants is based on our previously reported results—in mixtures of the same composition and surfactants, but with pure water.[27] A typical trend of measured temperature data—referred to as a freeze−thaw cycle—is shown in Figure 4 for a mixture of 1.5% rhamnolipid and 3% NaCl. The 10 °C/h cooling ramp is employed to temperatures below −8 °C in cases where $MgCl_2$ or higher salt concentration significantly depresses the crystallization temperature. Such an effect is shown in Figure 5, presenting data for a mixture of 0.5% rhamnolipid and 15% NaCl.

The hydrate equilibrium temperature for the mixtures without the salt is around 3−4 °C due to THF partitioning into the oil phase.[17,36] We confirmed proper measurement of the same parameter using our method in an earlier paper;[27] many of the same data are shown in Figure 15 of this work. The hydrate equilibrium temperature is lower when the thermodynamically inhibiting salts

Figure 5. Typical freeze−thaw cycle data for a mixture containing 15 wt % NaCl. The mixture also contains 0.5% rhamnolipid.

Figure 6. Typical freeze−thaw cycle data for a mixture containing 3 wt % MgCl₂. The mixture also contains 0.5 wt % quat.
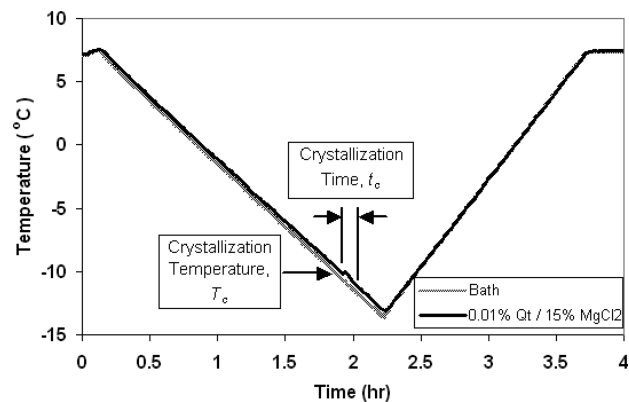

Figure 7. Typical freeze−thaw cycle data for a mixture containing 15 wt % MgCl₂. The mixture also contains 0.01 wt % quat.

are included. The effect of salt upon THF partitioning under hydrate formation conditions—and especially at the high subcoolings examined—would be difficult to determine accurately, and thus, this information has not been sought in the present study.

The crystallization temperature, T_c, crystallization time, t_c, and dissociation temperature, T_d, are all defined and determined as in our previous work. The accuracies of individual T_c and T_d values—where applicable—are determined at ±0.2 and ±0.5 °C, respectively. The accuracy of the t_c data is ±1.0 min.

Higher salt concentrations—i.e., 15% (see Figure 5)—rendered T_d values undetectable by our first-order measurement. Comparison of Figures 4 and 5 reveals that the crystallization peak appears to be reduced with the additional NaCl; perhaps this lack of T_d detection is due to a slowing of the dissociation process comparable to what may be occurring upon crystallization. There may be inhibition of hydrate formation through buildup of excess salt as hydrate is formed. That is, salt is likely accumulating in the aqueous phase and thermodynamically inhibiting full water conversion as the salt-rejecting hydrate phase forms. However, T_c values are always observed as opposed to clear T_d points. The same distinction is observed in MgCl₂ samples as well (see Figures 6 and 7).

Differential scanning calorimetry (DSC) could be a technique utilized to investigate the dissociation temperature, yet this would require different types of experiments and potential errors not encountered here. In DSC, the sample size would be much smaller—on the order of 0.5 mL. Consequently, error in the sample composition would be more difficult to prevent; also, DSC samples are not agitated, so such a measurement with these same surfactants would not be conducted upon an emulsified sample. That is, the surfactants employed here do not facilitate stable emulsions,[27] so other surfactants—which would significantly alter the purpose of such work—would need to be considered for DSC tests. Other recent studies successfully employed DSC but only through use of emulsions stable for 3 h or more by choosing appropriate surfactants

or using crude oil.[41,42] The best practice here is to conduct these measurements for crystallization and dissociation characteristics on the very samples and under the conditions used for agglomeration-state assessment—the primary focus of our studies.

We point out there is no evidence of ice formation in any of our tests. This evidence is in line with the high solubility of THF in water even when hydrate is formed.

Agglomeration State. Salt concentration variation for the agglomeration study is extensive in our work. Up to 25 wt % NaCl was used in mixtures of both AAs. Up to 20 wt % MgCl₂ was used in mixtures containing quat. These limits to salt addition were chosen on the bsais of the solubility limit of each salt at −20 °C but also due to crystallization temperature depression due to salt. We ensured that both salts would be dissolved at all temperatures tested for NaCl[43−45] and for MgCl₂.[45] The data from the literature reveal that, at −20 °C, the maximum solubility is roughly 29 and 26 wt % NaCl and MgCl₂, respectively. However, these maximum salt concentrations may depress the hydrate crystallization temperature below −20 °C. Only a maximum of 15 wt % MgCl₂ was used in rhamnolipid mixtures; this is due to the fact that much lower MgCl₂ concentrations rendered the rhamnolipid ineffective as an AA. In addition, surfactant-free samples with 3 and 15 wt % salt—for both salts, separately—have also been tested. Similarly to THF partitioning, the effect of salt on the surfactant concentration at the oil/water interface or within the aqueous phase would be difficult to determine under the various hydrate formation conditions and subcoolings examined here; thus, these data are not provided here.

Experiments for visual observations were performed similarly to crystallization/dissociation testing. Agitated mixtures are equilibrated 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. Some of these minimum temperatures were not used for mixtures containing higher salt concentrations, since the hydrate crystallization temperature is depressed below them.

Shut-in testing was also conducted. All mixtures were left unagitated at the various ΔT_{op} values for 60 min; the testing was conducted at the termination of the cooling ramp when the desired temperature was reached. Agitation was then resumed to assess whether hydrates are redispersed or irreversible agglomeration occurred.

Emulsion Stability. The procedure for emulsion stability testing is the same as we used in our previous work and similar to that employed by Zanota et al.[17] A similar approach was used in other
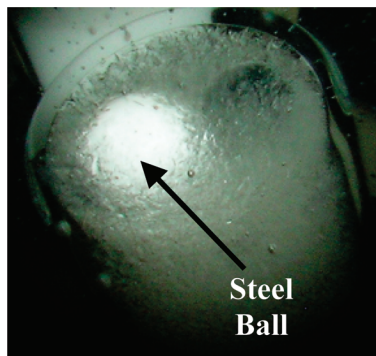
(41) Zhang, Y.; Debenedetti, P. G.; Prud'homme, R. K.; Pethica, B. A. *J. Phys. Chem. B* **2004**, *108*, 16717–16722.

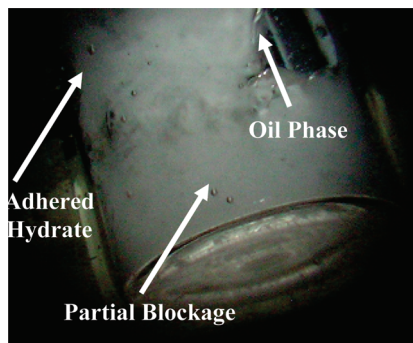(42) Lachance, J. W.; Sloan, E. D.; Koh, C. A. *Chem. Eng. Sci.* **2008**, *63*, 3942–3947.

(43) Akinfiev, N. N.; Mironenko, M. V.; Grant, S. A. *J. Solution Chem.* **2001**, *30*, 1065–1080.

(44) Konigsberger, E. *Monatsh. Chem.* **2001**, *132*, 1363–1386.

(45) Spencer, R. J.; Moller, N.; Weare, J. H. *Geochim. Cosmochim. Acta* **1990**, *54*, 575–590.

Figure 8. Sample image of the hydrate plug. The mixture shown here is for 1.5 wt % quat and 3 wt % NaCl.


Figure 9. Image showing the extent of significant hydrate adhesion upon the vial walls observed in certain rhamnolipid mixtures. Also shown here is a partial plug resulting from partial blockage of the sample vial. This particular sample has a composition of 0.5 wt % rhamnolipid and 9 wt % MgCl$_2$.

hydrate antiagglomeration studies.[31] Select mixtures with 1/1/4/*x* parts by weight of water/THF/isooctane/surfactant—with 3 or 15 wt % NaCl or MgCl$_2$—were prepared. Three different surfactant concentrations employed were 1.5 and 0.5 wt % and either 0.01 wt % for quat or 0.05 wt % for rhamnolipid. After 1 min of hand agitation resulting in emulsification, the mixtures are allowed to stand unagitated and the time required for separation of 60 vol % of the initial water phase is recorded.

As in our previous work, this testing has been performed on both "fresh" and "used"—i.e., unused samples without stainless steel balls and those samples used in agglomeration-state and kinetic/thermodynamic tests, respectively. Each composition was tested in triplicate in both variations. Both types of tests were performed at room temperature for the following reasons. These results are primarily relevant to potential emulsion stability of downstream fluids. The claim has also been made that surfactants used to generate more stable emulsions in these model mixtures at room temperature are more effective as antiagglomerants.[17]

Results

Agglomeration State. The following physical images of various agglomeration states were obtained. Figure 8 shows the plug appearance observed in this work—where the steel ball is clearly stuck in place within the plug. These full plugs are mostly observed in quat mixtures. Figure 9 shows another form of agglomeration—i.e., significant adhesion of hydrate upon vial walls that are observed in certain rhamnolipid mixtures. In these cases, hydrate would accumulate along the vial walls and often the accumulation at the bottom of the vial would be significant enough to create a partial hydrate plug—keeping the steel ball from traveling the vial's entire length. Effective antiagglomeration is exhibited through stable hydrate slurries, as shown in Figure 10. Stable slurries are those that remain dispersed and
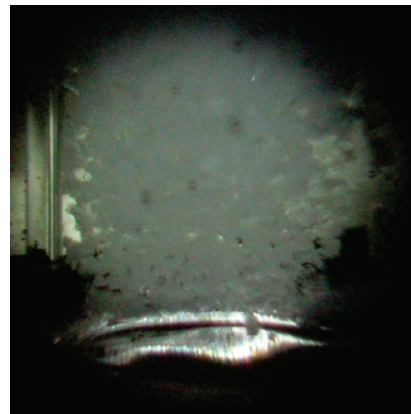
Figure 10. Image showing a hydrate dispersion—or slurry—evident when effective antiagglomeration is observed. Shown here is a slurry prior to settling; i.e., the sample vial is tilted in a manner showing individual hydrate crystallites prior to complete settling due to gravity. Upon complete settling, it is difficult to distinguish between individual crystallites. This particular sample has a composition of 1.5 wt % rhamnolipid and 3 wt % NaCl.
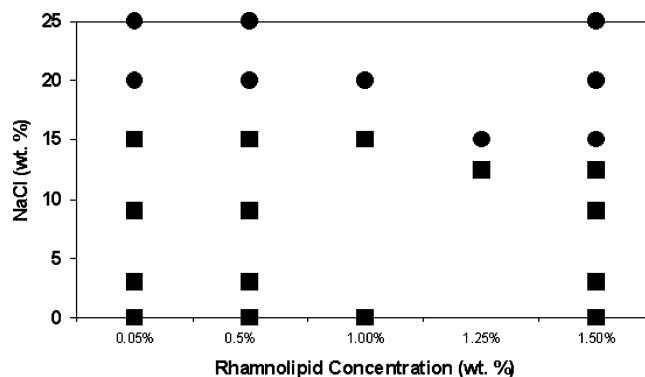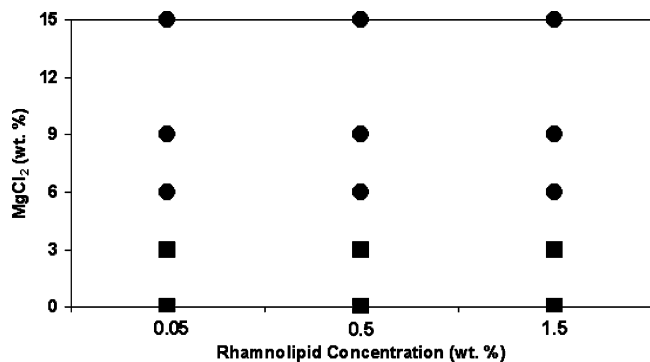

Figure 11. Agglomeration-state results for mixtures of rhamnolipid and NaCl: (■) stable dispersion—i.e., effective antiagglomeration, (●) agglomeration tendency. Agglomeration tendency means that either significant adhesion upon the vial walls is observed or partial (i.e., the steel ball is unable to move through the entire length of the vial) plugs occur. The data represent the behavior of a given composition across all minimum temperatures tested. The results for 0% salt are from previous work;[27] however, the data for salt-free mixtures of 0.5 and 1.0 wt % Rh are previously unpublished.

allow the steel ball to travel across the vial's entire length for the full 24 h observation period.
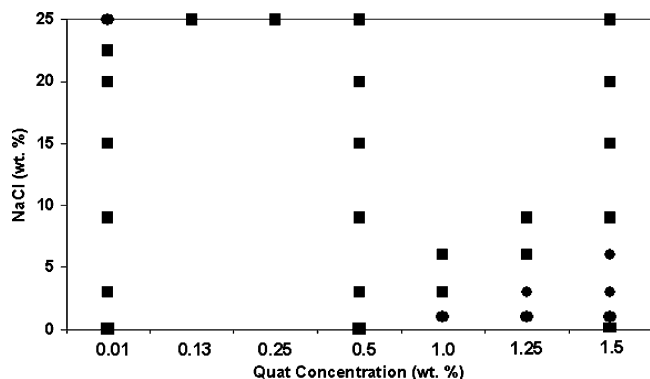
Figures 11−14 show agglomeration-state results in mixtures with the two different AAs and salts. Data from mixtures without dissolved salts—most of which have been reported previously[27]—are also included in each of the figures.

All mixtures exhibiting stable hydrate slurries passed shut-in testing. These results are for all minimum temperatures. That is, mixtures that initially contain hydrate slurries at any minimum temperature are able to have the hydrate redispersed after agitation is paused for 60 min and then resumed.

Kinetic/Thermodynamic Characteristics. Figures 15−19 show the results of freeze−thaw cycles for select mixtures of both rhamnolipid and quat with and without NaCl and MgCl$_2$. Figure 15 presents the data for salt-free mixtures with and without AAs; note from Figure 15 that the two surfactants exhibit a modest kinetic effect. The difference between the dissociation temperature T_d and the crystallization temperature T_c is the onset of subcooling denoted by ΔT_{on}. ΔT_{on} is an indicator of the driving force for hydrate formation; however, this parameter only factors into the kinetic and thermodynamic

Figure 12. −Agglomeration-state results for mixtures of rhamnolipid and MgCl₂: (■) stable dispersion—i.e., effective antiagglomeration, (●) agglomeration tendency. Agglomeration tendency means that either significant adhesion upon the vial walls is observed or partial (i.e., the steel ball is unable to move through the entire length of the vial) plugs occur. The data represent the behavior of a given composition across all minimum temperatures tested. The results for 0% salt are from previous work;[27] however, the data for salt-free mixtures of 0.5 wt % Rh are previously unpublished.


Figure 13. Agglomeration-state results for mixtures of quat and NaCl: (■) stable dispersion—i.e., effective antiagglomeration, (●) plugging tendency. Plugging tendency means that either total (i.e., the steel ball is unable to move) or partial (i.e., the steel ball is unable to move through the entire length of the vial) plugs occur. The data represent the behavior of a given composition across all minimum temperatures tested. The results for 0% salt are from previous work.[27]
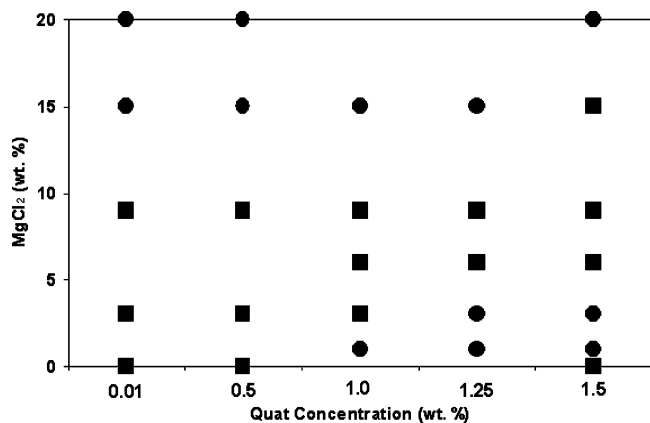
Figure 14. Agglomeration-state results for mixtures of quat and MgCl₂: (■) stable dispersion—i.e., effective antiagglomeration, (●) plugging tendency. Plugging tendency means that either total (i.e., the steel ball is unable to move) or partial (i.e., the steel ball is unable to move through the entire length of the vial) plugs occur. The data represent the behavior of a given composition across all minimum temperatures tested. The results for 0% salt are from previous work.[27]

effects since $\Delta T_{op} > \Delta T_{on}$ for all agglomeration-state tests. Figures 16−19 show the results for AA/brine mixtures.
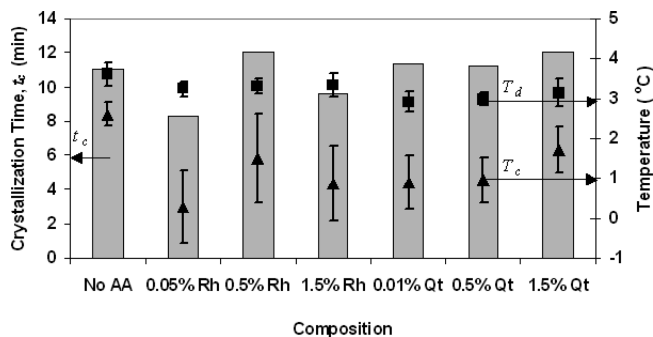
Figure 15. Average of freeze−thaw cycle data for salt-free mixtures with and without AAs. Given are T_c (shown as ▲), t_c (shown as columns), and T_d (shown as ■). Error bars are present for all points; some may not be clear due to magnitude. "Rh" and "Qt" refer to mixtures with rhamnolipid and quat, respectively. All data—except for "0.5% Rh" values—have been reported previously.[27]
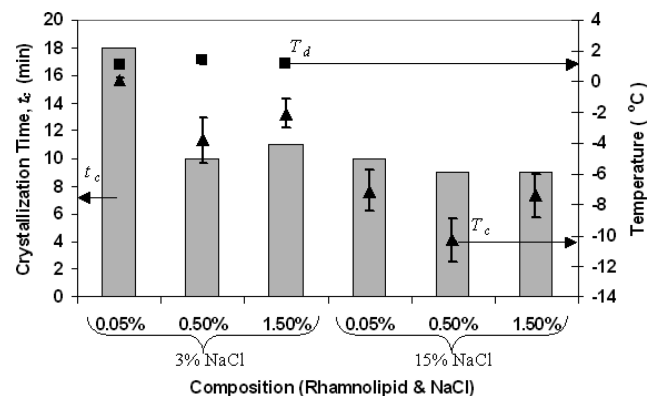
Figure 16. Average of freeze−thaw cycle data for rhamnolipid and NaCl mixtures. Given are T_c (shown as▲), t_c (shown as columns), and T_d (shown as ■). Error bars are present for all points; some may not be clear due to magnitude.

Emulsion Stability. Tables 1 and 2 and Tables 3 and 4 provide emulsion stability results for rhamnolipid and quat, respectively. Average and standard deviations are given to the nearest 0.1 min, due to the relative instability of most compositions tested. Data reported previously for salt-free mixtures[27] are also included in these tables. One item to note is that the lowest concentration of rhamnolipid in these salt-free mixtures tested was 0.01 wt %, and not 0.05 wt %, as is the case for all other rhamnolipid mixtures with dissolved salt included.

Discussion

Agglomeration State. As expected, the surfactant-free mixtures resulted in agglomeration at all minimum temperatures tested. These mixtures were 3 and 15 wt % NaCl or MgCl₂—so four different compositions in all.

Figures 11 and 12 reveal that rhamnolipid is more effective in NaCl brine than in MgCl₂. In Figure 11 we observe agglomeration only at high NaCl concentrations. Interestingly, there is no agglomeration with 15 wt % NaCl for mixtures of 1.0 wt % rhamnolipid and less. It is known that the nonionic surfactant solubility in water—i.e., cloud point—is reduced by salinity. This effect is explained by the strong ion−water interactions dehydrating oxide groups of such surfactants—such as ethylene oxide or carboxylic acid groups—thus resulting in decreased hydrogen bonding between the surfactant and water. The ultimate effect from this would be an increased repulsion— and so larger distances—between surfactant and water species
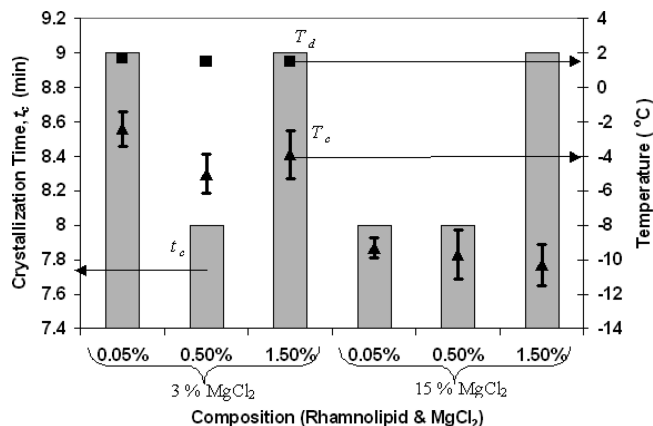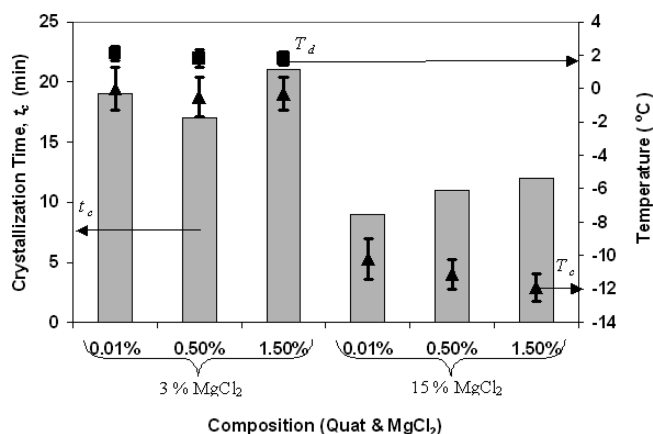
Figure 17. Average of freeze−thaw cycle data for rhamnolipid and MgCl$_2$ mixtures. Given are T_c (shown as ▲), t_c (shown as columns), and T_d (shown as ■). Error bars are present for all points; some may not be clear due to magnitude.
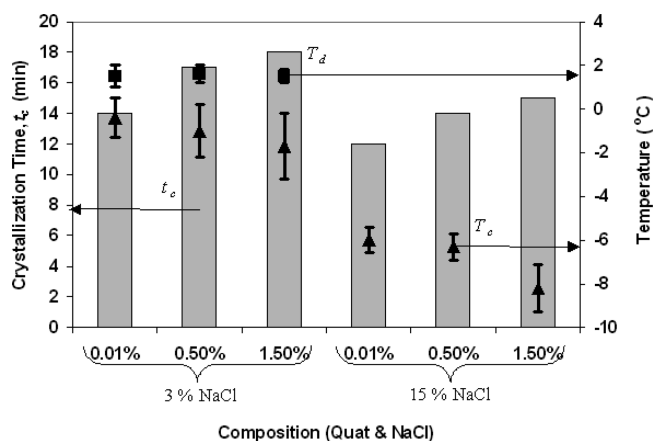
Figure 18. Average of freeze−thaw cycle data for quat and NaCl mixtures. Given are T_c (shown as ▲), t_c (shown as columns), and T_d (shown as ■). Error bars are present for all points; some may not be clear due to magnitude.

Figure 19. Average of freeze−thaw cycle data for quat and MgCl$_2$ mixtures. Given are T_c (shown as ▲), t_c (shown as columns), and T_d (shown as ■). Error bars are present for all points; some may not be clear due to magnitude.

at higher salinity. A recent paper[46] reports on the effect of salinity on a nonionic surfactant—Triton X-100—at a methylbenzene model oil/water interface: both experimental and modeling results reveal that the effects of high salinity detailed above increase the oil/water interfacial tension due to a decrease

in surfactant density at the interface. Results from Figure 12 show that the effect of MgCl$_2$ is more pronounced on agglomeration of rhamnolipid mixtures than that of NaCl. These results reveal that MgCl$_2$ concentrations as low as 6 wt % result in agglomeration within these mixtures.

Figures 13 and 14 show unusual results, on the basis of the ionic nature of the surfactant. For both NaCl and MgCl$_2$ brine, quat becomes ineffective at forming hydrate slurries at low salt and relatively high surfactant concentrations; such observations are noted elsewhere and were described in the Introduction.[34,35] These concentration ranges are 1−3 wt % salt—up to 6 wt % NaCl—and 1.0−1.5 wt % quat. The nonmonotonic behavior seen in Figures 13 and 14 is very pronounced for the MgCl$_2$ brine. Perhaps there is some difficulty that the relatively high concentration of quaternary ammonium salt faces at low salinity—such as in dissociating from the Cl$^-$ counterion. This could be considered as a "salting-in" effect that occurs at low salinity; however, this effect typically applies to nonionic organic molecules—with polar components—that exhibit increased solubility in water at low salinity.[47,48] As with rhamnolipid, a decrease in the antiagglomeration effectiveness of the quat mixtures at higher salinities—observed in both Figures 13 and 14—can be explained by the dissociated ions affecting surfactant−water interactions: in this case, charge screening at higher salinities would reduce the quat head−head electrostatic repulsions and thus increase the tendency for the quat compounds to self-associate and be less effective at the oil/water interface and oil/hydrate interface. Since a hydrate surface also possesses a slight negative charge, this would also affect the adsorption of quat compounds to a hydrate surface.

Preliminary calculations in such systems—using both low, 1 wt %, and high, 25 wt %, amounts of either salt with isooctane's dielectric constant[49] found to be 1.943—show Debye lengths on the order of 0.2−1 Å. It is still unclear whether quat compounds would have difficulty interacting with the hydrate surface under these conditions. Negative ζ potentials of hydrate/water interfaces favorable for quat adsorption have recently been measured,[50,51] but there are no such data for hydrate in brine or a nonpolar solvent. Thus, with a compact double layer as the above calculation indicates, quat compounds may not adsorb.

This calculation does reveal that the electrostatic interactions between such crystallites should not be significant. There is a report of significant electrostatic interactions for colloids in nonpolar solvents with the aid of reverse micelles, with Debye lengths of 0.2−1.4 μm[52] or even as large as 9 μm.[53] This is compared to highly charged aqueous colloidal systems, where Debye lengths have been measured at 10−100 nm.[54]

The effect of salt valency at higher concentrations is evident through all agglomeration-state data. Upon dissociation in water, MgCl$_2$ contributes more ions than NaCl, and thus, the effect of MgCl$_2$ is markedly stronger for both rhamnolipid and quat mixtures—as shown in Figures 12 and 14, respectively. That

(46) Li, Y.; He, X.; Cao, X.; Zhao, G.; Tian, X.; Cui, X. *J. Colloid Interface Sci.* **2007**, *307*, 215−220.

(47) Bockris, J. O. M.; Bowler-Reed, J.; Kitchener, J. A. *Trans. Faraday Soc.* **1951**, *47*, 184−192.

(48) Austad, T. *Force Seminar on Low Salinity Water Flooding*; Norwegian Petroleum Directorate: Stavanger, Norway, 2008.

(49) Wohlfarth, C. In *CRC Handbook of Chemistry and Physics*, 88th ed.; Lide, D. R., Ed.; CRC Press: New York, 2007.

(50) Lo, C.; Zhang, J. S.; Somasundaran, P.; Lu, S.; Couzis, A.; Lee, J. W. *Langmuir* **2008**, *24*, 12723−12726.

(51) Zhang, J. S.; Lo, C.; Somasundaran, P.; Lu, S.; Couzis, A.; Lee, J. W. *J. Phys. Chem. C* **2008**, *112*, 12381−12385.

(52) Hsu, M. F.; Dufresne, E. R.; Weitz, D. A. *Langmuir* **2005**, *21*, 4881−4887.

(53) Sainis, S. K.; Germain, V.; Mejan, C. O.; Dufresne, E. R. *Langmuir* **2008**, *24*, 1160−1164.

(54) Crocker, J. C.; Grier, D. G. *Phys. Rev. Lett.* **1996**, *77*, 1897−1900.

Table 1. Rhamnolipid- and NaCl-Induced Emulsion Stability (min)

NaCl concn (wt %)	rhamnolipid concn 1.5 wt %		rhamnolipid concn 0.5 wt %		rhamnolipid concn 0.05 wt %	
	fresh[a]	used[b]	fresh	used	fresh	used
0[c]	2.0 ± 1.0	117 ± 15	2.0 ± 1.0	87 ± 10	1.0 ± 0.0[d]	12 ± 3[d]
3	0.5 ± 0.0	0.9 ± 0.1	0.6 ± 0.0	0.5 ± 0.0	0.6 ± 0.1	0.1 ± 0.1
15	0.4 ± 0.1	2.1 ± 0.9	0.5 ± 0.1	1.3 ± 0.2	0.5 ± 0.1	0.2 ± 0.0

[a] Procedure used by Zanota et al.[17] A fresh sample—without a stainless steel ball—is hand-agitated for 1 min and 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. [b] Samples used for visual observation and freeze−thaw cycles with stainless steel included are hand-agitated at room temperature for 1 min, and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability. Used samples without salt—i.e., data from previous work[27]—were agitated for 20 min in a screening apparatus. [c] Data for mixtures without dissolved salt taken from previous work.[27] [d] Results reported previously[27] are for mixtures containing 0.01 wt % rhamnolipid and not 0.05 wt %.

Table 2. Rhamnolipid- and MgCl₂-Induced Emulsion Stability (min)

MgCl$_2$ concn (wt %)	rhamnolipid concn 1.5 wt %		rhamnolipid concn 0.5 wt %		rhamnolipid concn 0.05 wt %	
	fresh[a]	used[b]	fresh	used	fresh	used
0[c]	2.0 ± 1.0	117 ± 15	2.0 ± 1.0	87 ± 10	1.0 ± 0.0[d]	12 ± 3[d]
3	0.2 ± 0.1	0.1 ± 0.0	0.4 ± 0.1	0.1 ± 0.0	0.2 ± 0.2	0.1 ± 0.0
15	0.3 ± 0.0	0.4 ± 0.1	0.4 ± 0.1	0.3 ± 0.2	0.5 ± 0.1	0.0 ± 0.0

[a] Procedure used by Zanota et al.[17] A fresh sample—without a stainless steel ball—is hand-agitated for 1 min and 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. [b] Samples used for visual observation and freeze−thaw cycles with stainless steel included are hand-agitated at room temperature for 1 min, and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability. Used samples without salt—i.e., data from previous work[27]—were agitated for 20 min in a screening apparatus. [c] Data for mixtures without dissolved salt taken from previous work.[27] [d] Results reported previously[27] are for mixtures containing 0.01 wt % rhamnolipid and not 0.05 wt %.

Table 3. Quat- and NaCl-Induced Emulsion Stability (min)

NaCl concn (wt %)	quat concn 1.5 wt %		quat concn 0.5 wt %		quat concn 0.01 wt %	
	fresh[a]	used[b]	fresh	used	fresh	used
0[c]	121 ± 9	421 ± 16	21 ± 2	333 ± 8	6 ± 1	10 ± 3
3	1.6 ± 0.3	3.1 ± 0.8	1.1 ± 0.2	1.2 ± 0.2	0.6 ± 0.0	0.4 ± 0.0
15	2.1 ± 0.4	0.3 ± 0.1	1.9 ± 0.5	0.2 ± 0.1	0.6 ± 0.2	0.2 ± 0.2

[a] Procedure used by Zanota et al.[17] A fresh sample—without a stainless steel ball—is hand-agitated for 1 min and 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. [b] Samples used for visual observation and freeze−thaw cycles with stainless steel included are hand-agitated at room temperature for 1 min, and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability. Used samples without salt—i.e., data from previous work[27]—were agitated for 20 min in a screening apparatus. [c] Data for mixtures without dissolved salt taken from previous work.[27]

Table 4. Quat- and MgCl₂-Induced Emulsion Stability (min)

MgCl$_2$ concn (wt %)	quat concn 1.5 wt %		quat concn 0.5 wt %		quat concn 0.01 wt %	
	fresh[a]	used[b]	fresh	used	fresh	used
0[c]	121 ± 9	421 ± 16	21 ± 2	333 ± 8	6 ± 1	10 ± 3
3	1.3 ± 0.3	2.4 ± 0.6	0.8 ± 0.1	1.1 ± 0.1	0.6 ± 0.1	0.8 ± 0.2
15	1.5 ± 0.3	0.8 ± 0.3	0.9 ± 0.1	0.4 ± 0.1	0.5 ± 0.1	0.3 ± 0.1

[a] Procedure used by Zanota et al.[17] A fresh sample—without a stainless steel ball—is hand-agitated for 1 min and 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. [b] Samples used for visual observation and freeze−thaw cycles with stainless steel included are hand-agitated at room temperature for 1 min, and the time for separation of 60 vol % of the initial aqueous phase is measured and used as an indicator of emulsion stability. Used samples without salt—i.e., data from previous work[27]—were agitated for 20 min in a screening apparatus. [c] Data for mixtures without dissolved salt taken from previous work.[27]

is, lower MgCl$_2$ concentrations—9 and 15 wt % as opposed to 15 and 25 wt % for rhamnolipid and quat, respectively—disrupt the antiagglomerant ability of both surfactants as opposed to NaCl. That these values are presented in weight percent and not mole percent is irrelevant to the presentation of the results: converting weight percent values for both salts into mole percent reveals that a certain weight percent of both salts corresponds to roughly the same mole percent as well. Presenting these data in weight percent, rather than mole percent, does not lead to data misrepresentation.

The surfactants chosen for this study are either soluble—i.e., rhamnolipid—or dispersible—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.[17] In a real system, hydrate formation and growth may occur at the interface and even in a thick layer of a few tens of micrometers; in this case, exact placement of surfactant at the interface is crucial to ensure surfactant is available where needed to prevent hydrate agglomeration. The emulsion droplet size would also be important in extrapolating the results from THF systems to a real system. Zanota et al.[17] present optical microscopy images showing droplet sizes in the same systems—with the exception that they used a distearyldimethyl quat to produce extremely stable emulsions, allowing them to obtain such images. Their data show droplet diameters of roughly 38−75 μm. Measured droplet sizes in water-in-crude oil systems range widely from 0.5−3 μm[32] to upward of 10−140 μm.[55] If the droplet size range of a real system is similar to those reported by Zanota et al., then the results from this work may be applied to real systems, but the comparison is still unclear. Thus, tests on real systems should still be conducted to determine the effectiveness of these two AAs.

(55) Aichele, C. P.; Flaum, M.; Jiang, T.; Hirasaki, G. J.; Chapman, W. G. *J. Colloid Interface Sci.* **2007**, *315*, 607–619.

Before proceeding to discussion of other data obtained in this study, comparisons of rhamnolipid and quat biodegradability and toxicity will be discussed. To the present, specific data for surfactants can vary depending on the methods—testing methods dependent on simple parameters such as concentration as well as analytical techniques used to determine the results—and specific structure, even within a single class of compounds such as quat species. Nonetheless, it appears that rhamnolipid is generally less toxic and equally biodegradable compared to quat compounds. It is likely that rhamnolipids are even more biodegradable than quat compounds.

Specific data are as follows. Acute oral toxicity in rats is shown to be >5000 mg/L for rhamnolipids[56] as opposed to 100−5000 mg/L for most quat compounds.[57] Rhamnolipids show toxicity to *Daphnia magna*—i.e., water fleas—at levels of roughly 36 mg/L, an extremely low toxicity value for commercial surfactants;[58] however, acute toxicities to invertebrates, snails, and fish from some quat compounds are as low as 1 mg/L.[59] Data for growth inhibition on aquatic plants or microorganisms show quat compounds provide acute toxicities at 3−5 mg/L[60] while rhamnolipids show no adverse affects on similar species at concentrations above 1000 mg/L[58]—the best result possible for such a test.

Limited data for biodegradibility show that a 15 wt % mixture of the mono- and dirhamnolipid (these two structures are shown in Figure 2) in water biodegrades at a rate of roughly 68% within 10 days.[58] The procedure used for this test is the OECD 301D protocol, or the "closed bottle test", which dictates that a compound is readily biodegradable if it degrades more than 60% over 28 days.[61] Quat data often show higher rates, but for lower concentrations. Specifically, a 5 mg/L—or 0.05 wt %—concentration of a single-tailed quat shows up to 98% biodegradation in a 48 h period, yet the rate decreases to roughly 80% for slightly higher amounts—7.5 mg/L—of a dual-tailed species.[57] It is unclear which methods were used to obtain these quat data—since "technical data" from Akzo-Nobel, the employer of this particular author, are cited. However, other studies report on methods—such as potentiometric titration and the bichromate method—that render the primary constituents from biodegraded quat compounds undetectable.[62,63] It has been mentioned elsewhere the Norwegian environmental authorities' (SFT) objection to the low biodegradability rates of diester quat breakdown products,[15] and it is reasonable to conclude that other quat breakdown products may pose the same problems—since these primary products will still be amines or amine oxides.

Kinetic/Thermodynamic Characteristics. From Figure 15, the weak kinetic inhibition of either AA is clearly seen. The decrease in T_c with added AA is a kinetic effect since the T_d values in the same mixtures—i.e., for all rhamnolipid and quat mixtures—are all roughly the same. Another aspect to point out is how the T_c values generally decrease for lower AA concentration. This trend is accompanied by a slight downward trend

in T_d values as well. All ΔT_{on} values are in the range of 2−3 °C, except for the AA-free mixture, whose value is 1 °C. All t_c values are roughly the same for these mixtures.

The results for mixtures with salts are markedly different. Figures 16 and 17 show the data for rhamnolipid mixtures with NaCl and MgCl$_2$, respectively. As expected, T_c values in mixtures of both salts are lower than those in mixtures without salt—with MgCl$_2$ providing lower values than NaCl in general. A decrease in T_d values is observed, due to the thermodynamic inhibition posed by the salts. The amount of decrease for 3 wt % salt seen in both Figures 16 and 17 is consistent with basic melting temperature depression values calculated from simple colligative properties theory. Considering the same amount of either salt in pure water solvent, this depression is roughly 2 °C. Values for a 15 wt % concentration of either salt were not detected in our method, but the same melting temperature depression calculation could be used to estimate the depression. We estimate the melting point depression of roughly 9 °C, which means the hydrate dissociation temperature could be around −5 to −6 °C. This range would be consistent with measured T_c values, seen in both plots.

In both types of 3% salt and rhamnolipid mixtures, ΔT_{on} values are generally larger than observed in mixtures without salt. These values range from 4 to 7 °C, yet a single composition of 0.05% rhamnolipid/3% NaCl has a very low value of 1 °C. This is due to the relatively high T_c value of 0 °C in these mixtures. As a result, the t_c value for these mixtures is also higher—at 18 min—than the 8−11 min found for all other rhamnolipid/salt mixtures.

There are some slight differences in the data for quat/salt mixtures, shown in Figures 18 and 19. In these mixtures, T_c values are higher in mixtures of 3% salt, yet these same values in 15% salt solutions are comparable to those in the rhamnolipid mixtures. The most noticeable difference is the relatively high T_c values for mixtures of quat and MgCl$_2$, with values around −1 to 0 °C. Measured T_d values are in the same range as described above, and the same calculation based on colligative theory may provide estimates to undetectable values in mixtures of 15% salt. As a result of these differences, ΔT_{on} values are comparable to those in rhamnolipid mixtures, except for rather low ΔT_{on} values in the quat/3% MgCl$_2$ mixtures.

It is also noticed that the ΔT_{on} values for the quat/15% NaCl mixtures—in light of the estimated T_d values mentioned above—could be very small at 1 °C or less. Similarly, small ΔT_{on} values may be occurring in the rhamnolipid/15% NaCl mixtures. It is clear that the higher MgCl$_2$ amounts are producing lower T_c values for both surfactant mixtures. Thus, when only an estimate of T_d values can be used, it appears as if the ΔT_{on} values in most 15% NaCl mixtures are very low. Other relatively low values are also observed, such as in the 0.05% rhamnolipid/3% NaCl and quat/3% MgCl$_2$ mixtures—mentioned above. Since there is no consistent trend in the low ΔT_{on} values, no explanation can be offered at this time.

Values for t_c are also comparable or higher in quat mixtures. Owing to the higher T_c, the values in quat/3% salt mixtures are larger—ranging from 14 to 21 min—compared to those in most rhamnolipid mixtures. Mixtures of quat and 15% NaCl also exhibit larger t_c values; however, quat mixtures with 15% MgCl$_2$ exhibit t_c values comparable to those of the rhamnolipid mixtures.

Emulsion Stability. Emulsion stability data presented in Tables 1−4 show the emulsions in both used and fresh samples are relatively unstable, compared to emulsion stabilities in the same mixtures without dissolved salts. For quat mixtures, the

(56) Hollis, L. *Biopesticides Registration Action Document: Rhamnolipid Biosurfactant*; U.S. EPA: Washington, DC, 2004.

(57) Dery, M. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1997.

(58) *JBR215 Product Data Sheet*; Jeneil Biosurfactant Co.: Madison, WI, 2001.

(59) Vallejo-Freire, A.; Ribeiro, O. F.; Ribeiro, I. F. *Science* **1954**, *119*, 470–472.

(60) Walker, J. R. L.; Evans, S. *Mar. Pollut. Bull.* **1978**, *9*, 136–137.

(61) Garcia, M. T.; Gathergood, N.; Scammells, P. J. *Green Chem.* **2005**, *7*, 9–14.

(62) Cupkova, V.; Devinsky, F.; Sirotkova, L.; Lacko, I. *Pharmazie* **1989**, *44*, 577–578.

(63) Cupkova, V.; Sirotkova, L.; Mlynarcik, D.; Devinsky, F.; Lacko, I.; Kovackova, Z. *Folia Microbiol. (Prague)* **1993**, *38*, 43–48.

emulsions in mixtures with salt are very unstable compared to those in mixtures without salt. As in our previous work,[27,28] the emulsions facilitated by quat are more stable than those facilitated by rhamnolipid. Our earlier results also show significant differences between fresh and used samples, while this is not the case for mixtures with salts. For mixtures of rhamnolipid and NaCl, used samples are slightly more stable than the fresh ones—only for mixtures with 1.5 and 0.5% surfactant. There is little or no difference between fresh and used samples in 0.05% rhamnolipid and NaCl mixtures. Rhamnolipid and $MgCl_2$ mixtures offer little or no difference between the fresh and used samples.

Quat emulsions exhibit some different characteristics. Interestingly, the used samples with 15% $MgCl_2$ are less stable than the fresh samples. In the quat mixtures with 3% salt, the used samples are more stable than the fresh ones, although the difference is truly significant only in mixtures of 1.5% quat. For mixtures of 0.01% quat and both salts, the difference between fresh and used samples is small.

Conclusions

In this work, we have shown the effect of two different salts—NaCl and $MgCl_2$—dissolved in the aqueous phase of model mixtures used to study the antiagglomerant effectiveness of two vastly different surfactants. We have shown that both rhamnolipid and quat are effective down to very low concentrations in the presence of both salts; however, quat may lose its effectiveness at low salt/high surfactant concentrations. Rhamnolipid appears to be more effective in the presence of the same low salt amounts, yet both salts in large amounts negatively affect the rhamnolipid—thus rendering it an ineffective antiagglomerant—compared to quat. As expected, the divalent salt affects both surfactants more than the monovalent one.

As noted in our previous work, rhamnolipid is a viable antiagglomerant for testing with subsurface fluids and for field testing. This is confirmed further in this work by the antiagglomerant ability of rhamnolipid being retained in brine. We have also reconfirmed that stable emulsions are not a requirement for effective antiagglomeration. We have also shown that AA may be effective at concentrations an order of magnitude less than the literature limit of 0.5 wt %. In these model mixtures of 4 parts by weight of isooctane, this finding holds up even in the presence of substantial amounts of dissolved salts.

Experiments utilizing these ideas in this work are being planned in real fluids at high pressures.