Model Water-in-Oil Emulsions for Gas Hydrate Studies in Oil Continuous Systems

5 AUTHORS, INCLUDING:

José Delgado-Linares
University of the Andes (Venezuela)

12 PUBLICATIONS   **50** CITATIONS

SEE PROFILE

Ahmad Afif Abdul Majid
Colorado School of Mines

7 PUBLICATIONS   **10** CITATIONS

SEE PROFILE

Carolyn Ann Koh
Colorado School of Mines

199 PUBLICATIONS   **5,181** CITATIONS

SEE PROFILE

Model Water-in-Oil Emulsions for Gas Hydrate Studies in Oil Continuous Systems

José G. Delgado-Linares,[†,‡] Ahmad A. A. Majid,[†] E. Dendy Sloan,[†] Carolyn A. Koh,[†] and Amadeu K. Sum*,[†]

[†]Center for Hydrate Research, Chemical & Biological Engineering Department, Colorado School of Mines, 1600 Illinois Street, Golden, Colorado 80401, United States

[‡]Laboratorio FIRP, Escuela de Ingeniería Química, Universidad de Los Andes, Mérida 5101, Venezuela

Ⓢ Supporting Information

ABSTRACT: Stable water-in-oil emulsions with water volume fraction ranging from 10 to 70 vol % have been developed with mineral oil 70T, Span 80, sodium di-2-ethylhexylsulfosuccinate (AOT), and water. The mean size of the water droplets ranges from 2 to 3 μm. Tests conducted show that all emulsions are stable against coalescence for at least 1 week at 2 °C and room temperature. Furthermore, it was observed that the viscosity of the emulsion increases with increasing water volume fraction, with shear thinning behavior observed above certain water volume fraction emulsions (30 vol % at room temperature and 20 vol % at 1 °C). Viscosity tests performed at different times after emulsion preparation confirm that the emulsions are stable for 1 week. Differential scanning calorimetry performed on the emulsions shows that, for low water volume fraction emulsions (<50 vol %), the emulsions are stable upon ice and hydrate formation. Micromechanical force (MMF) measurements show that the presence of the surfactant mixture has little to no effect on the cohesion force between cyclopentane hydrate particles, although a change in the morphology of the particle was observed when the surfactant mixture was added into the system. High-pressure autoclave experiments conducted on the model emulsion resulted in a loose hydrate slurry when the surfactant mixture was present in the system. Tests performed in this study show that the proposed model emulsion is stable, having similar characteristics to those observed in crude oil emulsions, and may be suitable for other hydrate studies.

1. INTRODUCTION

Gas hydrates are crystalline compounds in which small gas molecules are enclathrated by hydrogen-bonded water molecules,[1] typically forming at high pressure and low temperature. The condition of high pressure and low temperature in crude oil production pipelines provides favorable conditions for gas hydrate formation. The accumulation and aggregation of hydrates in pipelines can result in pipeline blockage.[1,2]

Significant advances in the area of thermodynamics, such as phase equilibria of different gas hydrate systems, has been achieved.[3] In fact, much of the current knowledge in thermodynamics is being used as a predictive tool in phase equilibrium programs.[4] In contrast, the kinetics of hydrate formation (from nucleation to growth) is less well understood and constitutes the subject of numerous current investigations.[4,5] Over the past decade, a conceptual model that depicts hydrate plug formation in water, oil, and gas systems has been developed and gained acceptance within the flow assurance community[6] (Figure 1).

Due to the turbulence in flow in pipelines, water typically is dispersed into the oil phase, creating a water-in-oil (W/O) emulsion. At the interface of water droplets, hydrate shells will grow. Interactions among hydrate-encapsulated water droplets cause agglomeration of hydrate particles that can become large aggregates and eventually plug pipelines. For hydrate growth at water/oil interfaces, Taylor et al.[7] proposed a mechanism that comprises three stages: (1) formation of a thin and porous hydrate film that propagates across the interface, (2) film
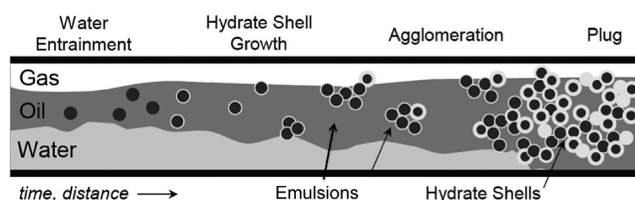

Figure 1. Conceptual model of hydrate formation, agglomeration and plugging in a water-in-oil emulsified system under flowing conditions (from Turner[6] in collaboration with J. Abrahamson).

thickening over time and filling of the pores, and (3) bulk conversion of the hydrate film with filling of the pores. In emulsified systems, irrespective of the amount of water, formation of hydrates can lead to droplet agglomeration, which will then lead to plugging of pipelines, whereas their dissociation promotes the destabilization and/or inversion of the emulsion.[8]

Several studies have demonstrated that emulsion stability is an important criterion in preventing hydrate plug formation;[9,10] the higher the emulsion stability, the lower the risk of hydrate agglomeration. In addition, it has been identified that natural surfactants (such as asphaltenes and organic acids) present in

petroleum crude play a major role in emulsion stability and, as a consequence, in hydrate agglomeration and plugging.[9−11]

Salager and Forgiarini[12] have suggested applying the concepts of the physicochemical formulation of surfactant−oil−water systems to control the transportability of hydrates in emulsified systems. Stabilizing the emulsions by use of appropriate surfactants will create a stable dispersed system and resistance against agglomeration even in the presence of hydrates. Once the fluid arrives at separation facilities, the formulation may be shifted by various methods, such as by changing the temperature. Emulsion breakage is then attained after hydrate dissociation.

Hydrate studies, specifically in water-in-oil emulsions, require the use of a stable and well-defined system in order to obtain reproducible results and to separate the impact of hydrates from those of crude oil chemistry. Many studies using water-in-crude oil emulsions have contributed to important under-standing of hydrate behavior. However, the complexity of crude oils presents a number of issues, which involves not only differences from one type of crude oil to another but also differences from batch to batch of the same crude oil.[10,13]

In this context, the work presented in this paper focuses on the development and characterization of a model water-in-oil emulsion suitable for hydrate studies. As the model system will be used to for hydrate studies in oil continuous systems, stability is the main requirement set for the model system. The emulsion should remain stable throughout the experimental studies, which for our interest is about 1 week. Another requirement for the model emulsion is to have a system with well-defined surface-active component(s) in order to separate the contributions to hydrate formation and behavior in the emulsified system. The use of asphaltenes to stabilize the emulsion is not suitable in the present work since the specific structure and interfacial behavior of asphaltenes are unknown. The model system developed here is a water-in-mineral oil emulsion stabilized by a surfactant mixture (Span 80 and AOT). Results are presented on the development and characterization of the model emulsion, including several tests of the model emulsion with hydrates, under static and dynamic conditions.

2. EXPERIMENTAL METHODS

2.1. Emulsion Preparation. Water-in-oil emulsions with water volume fraction (or water cut, as commonly denoted in the oil industry) ranging from 10 to 70 vol % are prepared by use of Crystal Plus mineral oil 70T (STE Oil Company, Inc.) with reported viscosity of 10.2 cP at 40 °C and density of 0.857 g/cm^3 at 20 °C. A compositional analysis of mineral oil 70T is shown in Table 1. In all

Table 1. Mineral Oil 70T Composition[a]

component	mass %	component	mass %
C_{16}	0.09	C_{24}	4.23
C_{17}	1.23	C_{25}	3.76
C_{18}	5.22	C_{26}	3.29
C_{19}	11.75	C_{27}	2.66
C_{20}	16.04	C_{28}	2.27
C_{21}	17.04	C_{29}	1.56
C_{22}	12.20	C_{30}^{+}	12.34
C_{23}	6.34		
avg MW	311	density (g/cm^3)	0.856

[a]Data provided by Chevron ETC.

cases, the emulsifier agents are composed of an nonionic−anionic surfactant mixture. Two surfactant concentrations are studied and reported here: 1 and 5 wt % surfactant mixture with respect to the total emulsion system. Deionized water is used as the aqueous phase in all emulsions.

The composition of the surfactant mixture is 90 wt % Sorbitan monooleate (Span 80, MW 428.61 g/mol, Sigma Aldrich) and 10 wt % sodium di-2-ethylhexylsulfosuccinate (AOT, MW 444.56 g/mol, Fisher Scientific). The chemical structures of the surfactant molecules are shown in Figure 2. This surfactant mixture is suitable to produce
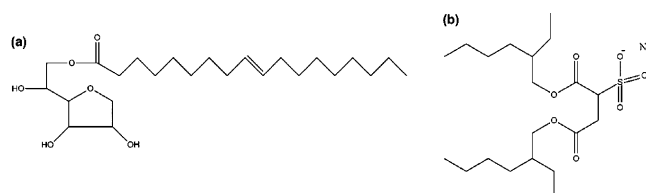

Figure 2. Molecular structure for surfactants: (a) sorbitan monooleate (Span 80); (b) sodium di-2-ethylhexylsulfosuccinate (AOT).

oil continuous emulsions, since both surfactants are oil-soluble (lipophilic) molecules. This is supported by Bancroft's rule, stating that in, any emulsion, the external (continuous) phase is the one that solubilizes the surfactant.[14,15] Furthermore, the major component of the surfactant mixture, Span 80, is a surfactant with a hydrophilic lipophilic balance (HLB) value of 4.3. The HLB is a measure of the surfactant hydrophilicity, which is defined as $^{1}/_{5}$ the weight percent of ethylene oxide in the molecule.[16,17] Generally, surfactants with HLB values below 10 will produce water-in-oil emulsifiers.[18]

The emulsions are prepared by dissolving the surfactant mixture in mineral oil by use of a magnetic stirrer and low heating (∼50 °C). For water cut ≤50%, the mixture is stirred with a high-speed homogenizer at 8000 rpm for 3 min, while water is slowly added during the first minute. For 60% and 70% water cut emulsions, the mixture is stirred at 8000 rpm for 6 min while water is added during the first 4 min (a longer stirring time was required to avoid phase inversion). After preparation, the emulsions are poured into 100-mL glass flask. In all cases, with the exception of the autoclave experiments, 30 mL emulsion samples are prepared. One liter emulsion samples are prepared for the autoclave experiments.

2.2. Interfacial Tension Measurements. Water−mineral oil interfacial tension (IFT) is measured at ambient temperature and pressure through a pendant drop tensiometer from KSV Instruments, Ltd. equipped with a CAM 200 apparatus. IFT tests are performed on systems with different surfactant concentrations in the oil phase. The data for each experiment are collected every 10 s for 290 s. This total time is sufficient to reach an equilibrium value of interfacial tension, which is calculated by the tensiometer software. The densities of both fluids (water and oil), required as input in the calculations of interfacial tension, are experimentally measured by an Anton Paar DMS60 densitometer connected to an Anton Paar DMA602HT measuring cell.

2.3. Emulsion Characterization. *2.3.1. Stability Test.* Phase separation is monitored daily by visual observations (classical bottle test) for a period of 1 week. This test is performed at room temperature (∼22 °C) and 2 °C.

2.3.2. Droplet Size Measurements. Droplet size measurements are performed with an optical microscope (Olympus IX71) coupled to a digital camera (Olympus XM10). Several images of the emulsions are recorded over the course of 1 week and analyzed by use of ImageJ. In measuring the droplet size, an average of about 250 water droplets is measured for each water cut. The reported mean droplet size is then the numerical average of the measured water droplets.

2.3.3. Viscosity Measurements. With the purpose of observing the relationship between viscosity and water cut, viscosity measurements are performed at ambient pressure on the emulsions by use of a TA Instruments hybrid rheometer DHR-3. In this study, cone and plate geometry is used with a gap size of 52 μm. The cone has a diameter of

40 mm and an angle of 1.995°. Viscosity measurements are conducted at room temperature (~22 °C) and 1 °C. To determine the stability of the emulsions over time, viscosity measurements are conducted at three different times: 24 h, 72 h, and 1 week after preparation.

A sample of ~580 μL of the emulsion is used in all measurements. The sample is allowed to rest at the experimental temperature for 2 min prior to the measurement. Measurements are performed at shear rates ranging from 0.1 to 1000 s⁻¹. In each test, 10 viscosity points per decade on a log scale were taken and each point at steady state, which we define as three consecutive points within 3% variation.

2.4. Emulsion Behavior under Hydrate Formation. *2.4.1. Differential Scanning Calorimetry.* To measure the thermal properties of the emulsions, differential scanning calorimetry (DSC) tests at ambient pressure and high pressure are conducted by use of a microdifferential scanning calorimeter (μ-DSC VIIa, Setaram Inc.). For ambient pressure DSC tests, ~15 mg of an emulsion sample is placed in a vessel. The sample is cooled from 30 to −45 °C at a rate of 0.3 °C/min. The sample is then heated back to 30 °C at the same rate. This cycle is repeated three times to observe the effect of ice formation on emulsion stability. In the high-pressure tests, a similar amount of emulsion sample is added into the vessel. Methane gas (99.99% ultra high purity, General Air) is then introduced into the vessel with the sample up to a pressure of 125 bar. The sample is left at 125 bar and 30 °C for 3 h to allow for saturation of the sample with methane. Next, the sample is cooled from 30 to −25 °C at a rate of 0.3 °C/min and then heated at a rate of 0.3 °C/min to 30 °C. Similarly, the cycle is repeated three times to observe the effect of hydrate formation on emulsion stability.

2.4.2. Micromechanical Force Measurements. A micromechanical force (MMF) apparatus is used to measure the cohesion forces between cyclopentane (CyC5, 99% by Acros Organic) hydrates particles in CyC5/mineral oil and CyC5/surfactant/mineral oil systems. A detailed description of MMF apparatus and experimental method are reported elsewhere.[19−22] Briefly, a hydrate particle is attached to a spring-constant-calibrated glass cantilever and another hydrate particle at the tip of a glass fiber is attached to a moving micromanipulator. The cantilevers and hydrate particles are immersed in a cooled CyC5 bath at 3.2 °C and atmospheric pressure. Forty "pull-off" measurements are conducted, where a pull-off corresponds to the contact of the particles, a 10 s waiting period, and the pull-off of the particles until they are no longer in contact. The cohesive force (F_A) between the particles is obtained from Hooke's law on the displacement of the cantilever and the cantilever spring constant. The reported cohesive force is the average of 40 pull-off trials.

With the aim of studying the effect of Span 80−AOT surfactant mixtures on the hydrate cohesion forces, two experiments are performed. The first system consisted of 97 wt % CyC5 and 3 wt % mineral oil 70T. The second system consists of 98 wt % CyC5 and 2 wt % mineral oil 70T with 5 wt % surfactant mixture.

2.4.3. Autoclave Experiments. To obtain information about hydrate formation under dynamic conditions of the model emulsion, high-pressure autoclave cell tests are performed. A complete description of autoclave components and operation may be found in the literature.[7,8,10,23] The autoclave is a 2-L stainless steel vessel with 9 in. height and 4 in. inner diameter. Mixing in the cell is done with a four-blade vane impeller, each blade at 90°, with 5.5 in. height and 0.9 in. width. One liter of emulsion with a 30 vol % water cut is charged into the autoclave cell. Once sealed, the system is placed in a cooling bath that is initially set at 20 °C. Next, the system is stirred at constant 300 rpm. The cell is then pressurized with methane gas (99.99% ultra high purity, General Air) to 65.5 barg (950 psig). The system is kept at these conditions for 12 h to ensure the emulsion is fully saturated with methane. Following this step, the cell is cooled down to 1 °C. Throughout the test, the pressure in the cell is maintained at 65.5 barg by feeding the cell with methane gas from a secondary gas reservoir tank. The time when the pressure in the secondary reservoir started to decrease is taken as onset of hydrate formation. The current required by the impeller motor to maintain the stirring at 300 rpm is a qualitative measurement of the relative viscosity of the fluids/slurry in the autoclave cell. The duration of each test is at least 24 h after

hydrate formation. The amount of hydrate formed is estimated from the consumption of gas in the reservoir.

3. RESULTS AND DISCUSSION

3.1. Emulsion Stability and Droplet Size. Visual observation confirmed that all emulsions (1 and 5 wt % surfactant) were stable without evidence for droplet coalescence (see Figure 3); that is, no free water was observed after 1
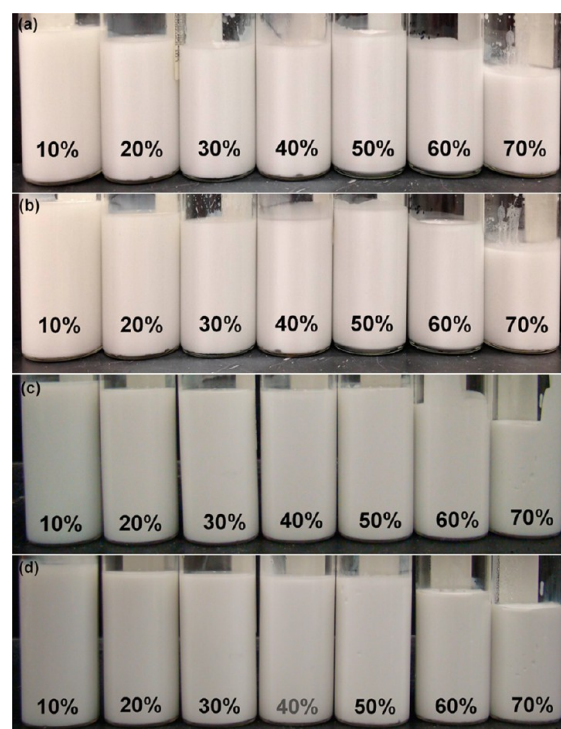

Figure 3. Images of water-in-oil emulsions for a range of water cut prepared with mineral oil 70T (continuous phase) and a surfactant mixture of Span 80 + AOT: (a, b) 1 wt % surfactant after (a) 24 h and (b) 1 week; (c, d) 5 wt % surfactant after (c) 24 h and (d) 1 week.

week. However, at low temperature (2 °C), emulsions prepared with 10 and 20 vol % water cut showed settling of water droplets (sedimentation) identified by the presence of a thin oil layer at the top of the samples. This settling of the droplets was observed 24 h after the samples were placed in a chiller at 2 °C. The samples became redispersed by daily gentle hand-stirring, thus helping the emulsion to remain homogeneous. For our purposes, the settling is not a major concern since these emulsions will be later used in experiments where mixing is typically constantly applied (e.g., rheometer, autoclave). It should be noted that mixtures prepared with less than 1 wt % surfactant did not result in stable emulsions, resulting in phase separation within 24 h after preparation. Measurements of water droplets at different times in the studies shows that coalescence was negligible even for samples that showed sedimentation of water droplets (see Supporting Information for droplet sizes measured over days). For these emulsions, increasing the water cut reduces the tendency for sedimentation, while the stability of the emulsion is maintained by the presence of the two surfactants.

The high stability of the emulsions can be attributed to the strong lipophilic character of the surfactant mixture. Additionally, one may suggest that there are two mechanisms of dispersion stabilization:[24,25] steric repulsions, produced by the
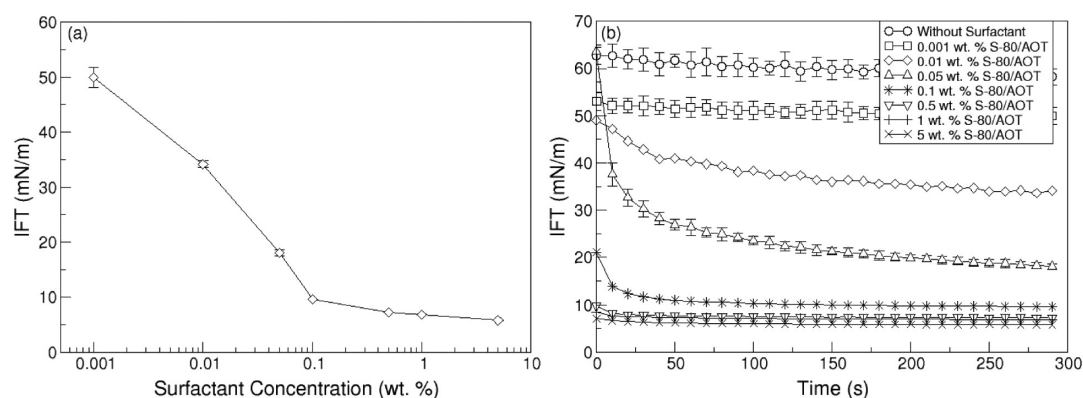
Figure 4. (a) Interfacial tension as a function of surfactant concentration; (b) interfacial tension dependence on concentration and time.

interaction between hydrocarbon tails present in both surfactant molecules, and electrical repulsions, due to the negative charge present in the anionic group (SO_3^-) in AOT molecules. The application of surfactant mixtures to stabilize emulsions has been demonstrated to be in most cases more efficient than a single surfactant, owing to synergetic mechanisms that reduce coalescence of droplets.[26,27] Furthermore, due to the small size of water droplets, sedimentation of water droplets is reduced.

The concentration of surfactant (1 and 5 wt %) used in all the emulsions prepared for this study was higher than the critical concentration of aggregation (CCA), that is, the concentration at which inverse micelles may form. Figure 4a shows the interfacial tension values for the mineral oil−water system at different surfactant concentrations. A change in the slope of the IFT curve represents the surfactant aggregation threshold. According to Figure 4a, the CCA of the surfactant mixture in mineral oil is approximately 0.1 wt %. All emulsions were prepared with either 1 or 5 wt % surfactant (Span 80−AOT) with respect to the total mass of the emulsion. The concentration of the surfactants above the CCA in the oil phase guarantees that once the emulsion is created, the new interface is quickly covered by adsorbed surfactant molecules; the barrier against coalescence is instantly present and the coalescence rate decreases.[28,29]

The IFT as a function of time is shown in Figure 4b. It can be appreciated that IFT equilibrium values were reached in short times (lesser than 290 s), which is a clear indication of the rapid adsorption of surfactant at the interface. It is remarkable that, for surfactant concentrations beyond the CCA, equilibrium was attained at even shorter times (<50 s). This higher adsorption rate can lead to quick droplet coverage by the surfactant mixture, and as a consequence, a barrier against coalescence is consolidated during emulsification time (3 min).[29,30]

The mean droplet size for the emulsions with both 1 and 5 wt % surfactant is in the range 2−3 μm diameter, at room temperature and 2 °C, for all water cuts studied in this work. These observations are in good agreement with other reported data[31] for water-in-crude oil emulsions. In all cases, the droplet size is relatively similar for all water cuts (see Figure S1 in Supporting Information). We also observe that the variation in droplet size for emulsions with 5 wt % surfactant is smaller than that with 1 wt % surfactant, reinforcing the high stability of the emulsion with higher surfactant concentration (see Supporting Information for additional results on measures of droplet sizes over the 1-week testing period). Figure 5 shows examples of

microscopy images of the appearance of the emulsions at 10% and 50% water cuts immediately after their preparation for emulsions with 1 and 5 wt % surfactant.
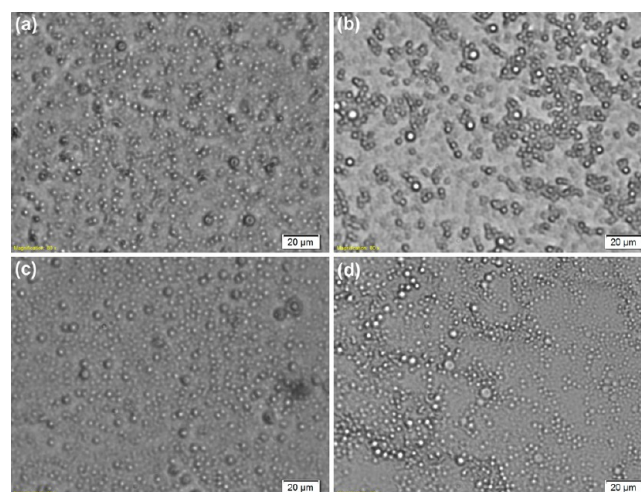

Figure 5. Sample microscope images of water-in-oil emulsions: (a, b) 1 wt % surfactant with (a) 10 water vol % and (b) 50 water vol %; (c, d) 5 wt % surfactant with (c) 10 water vol % and (d) 50 water vol %.

3.2. Viscosity Results. Viscosity profiles for emulsions prepared with 1 and 5 wt % surfactant measured at ambient pressure for two temperatures (room temperature and 1 °C) are presented in Figure 6. As can be seen, the apparent viscosity of the emulsions increases significantly with the water cut. This increase in apparent viscosity is due to the increase in packing of the water droplets.[27] Since the viscosity of the emulsion is proportional to the viscosity of the external phase, the viscosity of the emulsion will deviate further from the viscosity of mineral oil 70T as the water cut increases. This observation holds true at both temperatures tested.

Furthermore, shear-thinning behavior was observed above certain water cuts: above 30 vol % at room temperature and 20 vol % at 1 °C for both surfactant concentrations. This behavior is typical for complex dispersed systems such as human blood, food emulsions, and even water-in-crude oil emulsions[32,33] and can be attributed to, in emulsion cases, the rupture of clusters or droplet aggregates, followed by droplet alignment under shear.[33] Thus the shear-thinning effect is more significant at high water cuts and low temperatures because the system
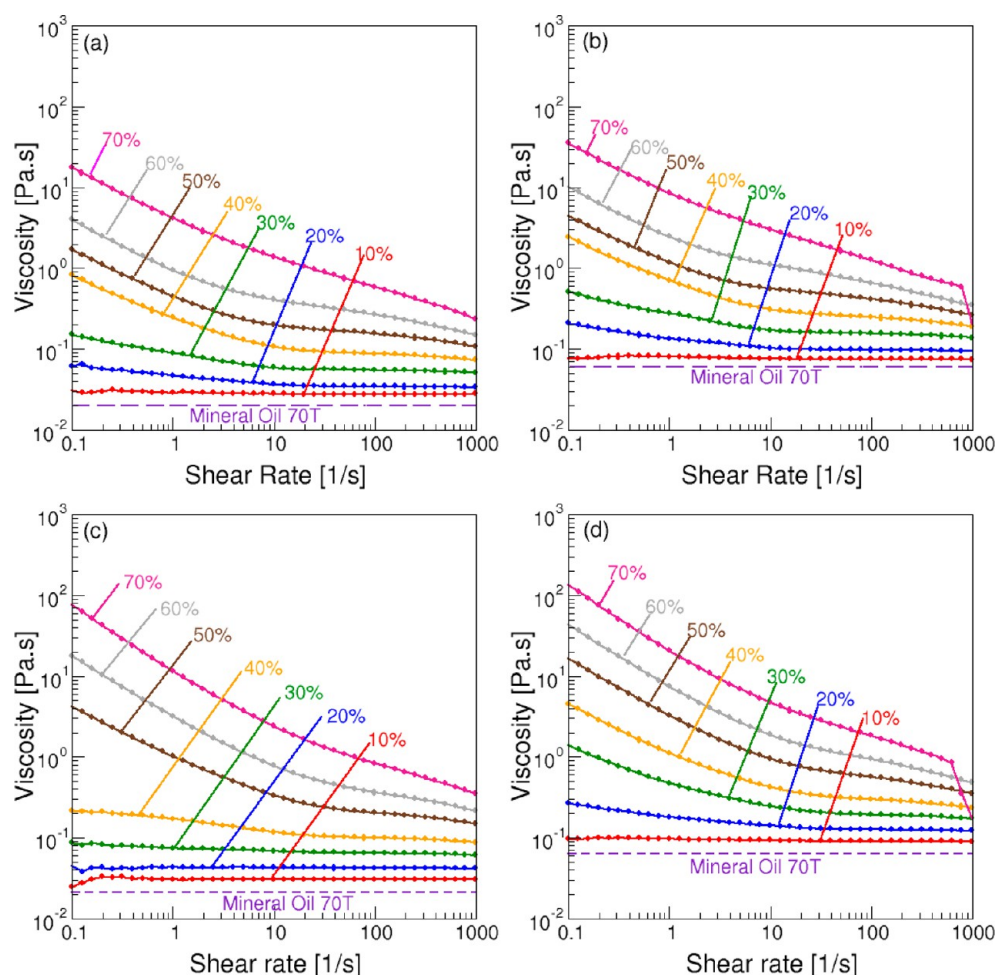
Figure 6. Viscosity profiles at various water cuts: (a, b) emulsion prepared with 1 wt % surfactant at (a) 22 °C and (b) 1 °C; (c, d) emulsion prepared with 5 wt % surfactant at (c) 22 °C and (d) 1 °C.

becomes highly packed and the droplet–droplet interactions increase.

Furthermore, the viscosity profiles at room temperature (∼22 °C) show that, for 10 and 20 vol % water cuts, the viscosity of the emulsion is relatively similar for both surfactant concentrations. However, at 30 and 40 vol % water cuts, the viscosity of the emulsion is greater for the system with 1 wt % surfactant; and at water cuts >50 vol %, the viscosity of the emulsion with 1 wt % surfactant is lower than that with 5 wt % surfactant at the same water cut. The viscosity is related to the size and packing (concentration) of water droplet in the emulsion, and it is known that the increase in droplet–droplet interactions increases the viscosity of the emulsion.[24] We also see that the viscosity of the emulsions with 1 wt % surfactant (Figure 6b) is slightly lower than the emulsions with 5 wt % surfactant (Figure 6d) for all water cuts studied at 1 °C.

Moreover, in Figure 6b,d, it can be noted that for the sample with 70 vol % water cut, the viscosity of the emulsions drops significantly at high shear rate. This suggests a possible phase inversion of the emulsion. To confirm this phenomenon, a small sample of the emulsion was stirred at a high shear rate of 1000 s^{-1} for 2 min. Next, a small drop of the sample was placed into water. As the emulsion completely dispersed in water, it was confirmed that water was the continuous phase.[34] Emulsion inversion induced by stirring has been well studied.[35] In systems with high internal phase content, physicochemical

formulation leads to important changes in emulsion morphology.[35] This experimental evidence suggests that hydrate studies using the model emulsion proposed here will have to consider possible phase inversion for samples with high water cut and experiments with high shear rate.

The viscosity of the emulsions was measured at different times to determine their stability. Since the viscosity of the emulsion is proportional to the water cut, any instability in the emulsion (phase separation or sedimentation) will be captured by a large deviation in the viscosity measurements. Figure S4a in Supporting Information shows the apparent viscosity of 30 vol % water cut emulsion with 1 wt % surfactant. As can be seen, there is a noticeable change in the viscosity of the emulsion over the testing time. This is an indication that sedimentation and phase inversion might occur in the sample but were not detected by visual observation. In contrast, the viscosity of a 30 vol % water cut emulsion prepared with 5 wt % surfactant shows relatively small changes in the viscosity over the testing time (Figure S4b in Supporting Information). A small change in the viscosity of the emulsion indicates that the emulsions prepared with 5 wt % surfactant remain stable for at least 1 week, thus making them particularly suitable for our intended hydrate studies. It can also be concluded that the emulsion prepared with 1 wt % surfactant is less stable as compared to that prepared with 5 wt % surfactant.
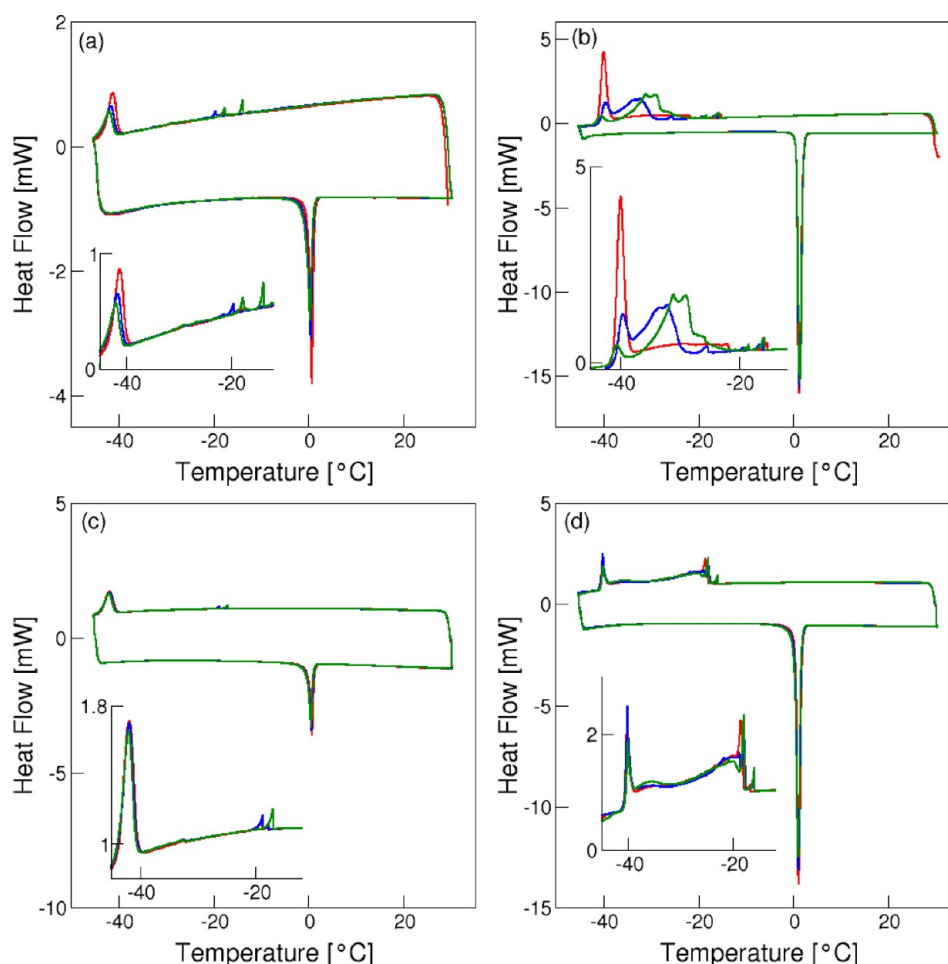
Figure 7. Ambient pressure thermograms of emulsions: (a, b) prepared with 1 wt % surfactant for (a) 10 vol % and (b) 50 vol % water cut; (c, d) prepared with 5 wt % surfactant for (c) 10 vol % and (d) 50 vol % water cut. For each plot: (red) cycle 1, (blue) cycle 2, (green) cycle 3.

3.3. Differential Scanning Calorimetry Results. DSC tests of the emulsions at ambient pressure and high pressure were conducted to determine their stability upon ice and hydrate formations. Figure 7a shows the thermogram for a 10 vol % water cut emulsion with 1 wt % surfactant. In cycle 1, there is a small peak at ~−18 °C and another at ~−42 °C upon cooling. In cycle 2, two exothermic peaks are seen upon cooling, one at ~−19 °C and another at ~−42 °C. In cycle 3, three exothermic peaks are evident upon cooling: one at ~−13 °C, another at ~−18 °C, and the third at ~−42 °C . The peaks at ~−42 °C in all cycles confirm that the samples are a water-in-oil emulsion.[9,36−38] Since there are at least two exothermic peaks upon cooling, it is likely that the emulsion with 1 wt % surfactant has at least two water droplet sizes. It can also be noticed that the intensity of the peaks at ~−42 °C decreases with each cycle, indicating that the amount of small water droplets decreases with each cycle. This suggests that agglomeration of water droplets may be occurring upon ice formation and melting. In the heating portion of the thermogram, only one endothermic peak near 0 °C is observed, corresponding to ice melting.

Figure 7b shows the thermogram for 50 vol % water cut emulsion with 1 wt % surfactant at ambient pressure. It can be immediately noticed that there is only one sharp peak at ~−40 °C upon cooling during cycle 1, confirming the sample is a water-in-oil emulsion.[9,36−38] However, for cycles 2 and 3, several exothermic peaks are seen upon cooling. These peaks

are low and broad, suggesting that the water droplets are not well dispersed. Also, because the intensity of the peak at ~−40 °C significantly decreases with each cycle, water droplet agglomeration/coalescence is likely occurring upon ice formation/melting. In the heating portion of the thermogram, there is only one endothermic peak correspond to ice melting. These results suggest that ice formation and melting destabilize this emulsion.

Figure 7c shows the thermograms for the emulsion with 5 wt % surfactant and 10 vol % water cut at ambient pressure. There are two exothermic peaks upon cooling: one at ~−18 °C in cycles 1 and 2 and ~−19 °C in cycle 3, and another at ~−42 °C. The latter peak again confirms the sample is a water-in-oil emulsion with small droplets.[9,36−38] The near-symmetrical shape of the peak at ~−42 °C indicates the water droplets are well dispersed. The other small peaks at high temperature may be from ice formation from bulk water or from freezing of aggregates of small water droplets.[37] However, from the low intensity of the peak, only a small amount of free water or large water aggregates is present in the sample. In the heating portion of the thermogram, there is only one endothermic peak near 0 °C, corresponding to ice melting. The peaks observed in the cooling and heating stages for all three cycles remain relatively unchanged, indicating the emulsion remains stable upon ice formation and melting.

Figure 7d shows the thermogram for the emulsion with 5 wt % surfactant and 50 vol % water cut at ambient pressure.
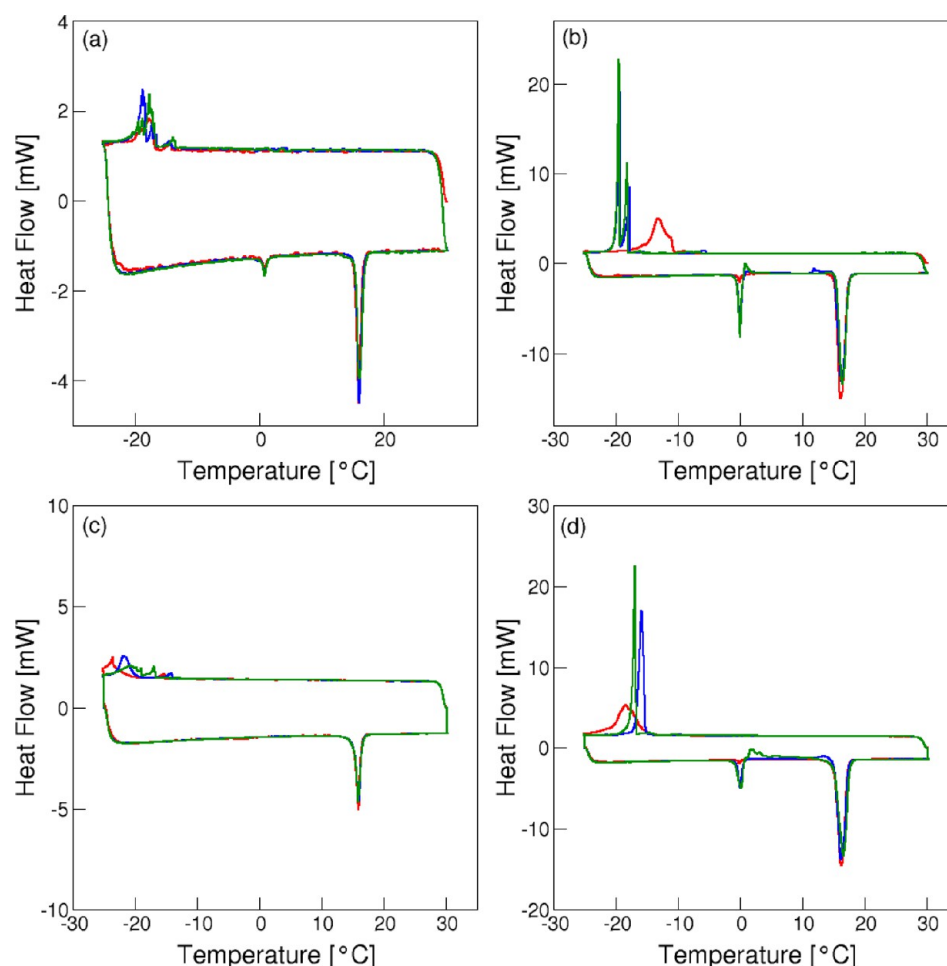
Figure 8. High-pressure thermogram of emulsions: (a, b) prepared with 1 wt % surfactant for (a) 10 vol % and (b) 50 vol % water cut; (c, d) prepared with 5 wt % surfactant for (c) 10 vol % and (d) 50 vol % water cut. For each plot: (red) cycle 1, (blue) cycle 2, (green) cycle 3.

Several exothermic peaks are observed upon cooling, ones clustered near ∼−20 °C and another at ∼−40 °C. Similarly, the peak at ∼−40 °C confirms a water-in-oil emulsion with small droplets. Since the location of the peak is at a slightly higher temperature, it may indicate that the water droplets are slightly larger in this 50 vol % water cut sample compared to the one with 10 vol % (Figure 7c). The other peaks at ∼−20 °C suggest the presence of bulk water or isolated large water droplets. For this water cut, it can also be observed that the intensity of the peaks also is relatively unchanged from cycle to cycle, confirming that the emulsion remains stable upon ice formation and melting.

Measurements in the DSC were also made to determine the stability of the emulsions upon hydrate formation at 125 bar with methane gas. Figure 8a is the high-pressure thermogram for 10 vol % water cut emulsion with 1 wt % surfactant. In all cycles, there are several exothermic peaks upon cooling, corresponding to both hydrate and ice formation. The heating portion of the thermogram shows ice melting (∼0 °C) and hydrate dissociation (∼15 °C). The reported dissociation temperature for methane hydrate at 125 bar is 14.82 °C.[1] It is seen that the intensity of the ice melting peak slightly increases while the intensity of the hydrate dissociation peak slightly decreases progressively with each cycle; that is, the amount of ice formed increases while the amount of hydrate formed decreases with each cycle. These results indicate that there is likely some agglomeration of the water droplet upon hydrate

formation/dissociation, resulting in either larger water droplets or droplet coalescence.

Figure 8b shows the thermogram at high pressure for a 50 vol % water cut emulsion with 1 wt % surfactant. The general features of the thermogram are very similar to those in Figure 8a (10 vol % water cut emulsion with 1 wt % surfactant); however, the ice melting peaks are much more intense, indicating there is a much larger amount of ice being formed after the first cycle at higher water cut. For this water cut, agglomeration of water droplets is much more significant upon hydrate formation/dissociation.

Figure 8c shows high-pressure thermogram results for a 10 vol % water cut emulsion prepared with 5 wt % surfactant. For this emulsion, it is observed that only hydrates are formed/ dissociated, as evidenced by the endothermic peak at ∼15 °C. The absence of the ice melting peak and nearly constant intensity of the hydrate dissociation peak show this emulsion is highly stable. It should be noted that hydrate formation is stochastic, so the formation peaks upon cooling should not be expected to be reproducible from cycle to cycle.

Much different behavior is observed in Figure 8d for a 50 vol % water cut emulsion with 5 wt % surfactant. Only one exothermic peak is measured upon cooling in each cycle. Upon heating in the first cycle, only one endothermic peak at ∼15 °C is seen, corresponding to hydrate dissociation. In cycles 2 and 3, an ice melting peak is observed, accompanied by a less intense hydrate dissociation peak. These results suggest that, after the

first cycle, agglomeration/coalescence of water droplets occurs upon hydrate formation/dissociation.[9] By comparison of Figure 8d to Figure 7d, it can be concluded that this emulsion is highly stable to ice formation/dissociation but less so to hydrate formation/dissociation.

The DSC results are insightful in providing an understanding of the stability of the emulsions, especially with respect to ice and hydrate formation/dissociation. As the water cut increases, the emulsion becomes more packed with water droplets. The increase in droplet interactions can cause droplet coalescence and thus lower the emulsion stability. We see from these results that the emulsions at low water cut and with 5 wt % surfactant are the most stable and may be the best ones for our later studies with hydrates. Additional results from high-pressure DSC measurements of the emulsions at 20, 30, and 40 vol % water cuts can be found in the Supporting Information.

3.4. Micromechanical Force Results. All of the emulsion systems were prepared with surfactant concentration greater than the CCA. It is thus necessary to measure how the surfactants impact the interaction of hydrate particles. For a system with 3 wt % mineral oil 70T in cyclopentane, the average interparticle cohesion force was measured to be 4.1 ± 1.9 mN/m. This result is consistent with the value measured by Aman et al.[39] of 6.1 ± 1.3 mN/m based on mineral oil 200T. The presence of 5 wt % surfactant mixture in mineral oil 70T results in an interparticle cohesion force of 2.1 ± 0.8 mN/m. When the two systems with mineral oil 70T are compared, the difference in the cohesion force is not statistically significant, even though there is a change in the morphology of the hydrate particles. As can be seen in Figure 2, both Span 80 and AOT have hydrophilic and hydrophobic groups. The hydrophilic part of the surfactant likely attaches to the surface of the hydrate particles, causing the hydrophobic part to extend toward the oil phase.[39]

The morphological changes observed are likely induced by Span 80.[40] Several previous studies have reported similar morphological changes when Span-type surfactants are used.[40,41] Figure 9 shows the observed changes on the hydrate
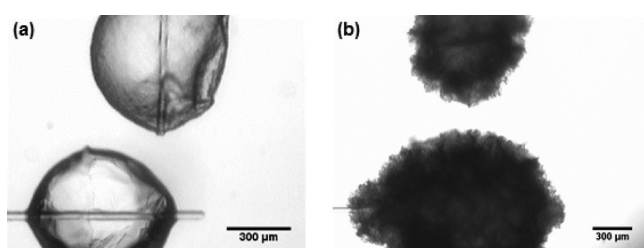

Figure 9. Morphological changes observed when the surfactant mixture was added into the MMF for cohesive force measurements: (a) system without surfactant; (b) system with addition of 5 wt % surfactant mixture.

particles with the introduction of surfactants used in preparing the emulsion. The increase in surface roughness on the particle can lead to a decrease in capillary water bridges between hydrate particles and a slight decrease in the cohesion force. The presence of the surfactant mixture (Span 80 and AOT) does not have a significant impact on the cohesion force between cyclopentane hydrate particles. It has been reported that other surface-active chemicals such as naphthenic acid can reduce the cohesion force by as much as 80%.[21] Therefore, the

surfactant mixture used in the emulsions is suitable for hydrate studies.

3.5. Autoclave Test Results. Contrasting results are observed for the tests performed in the autoclave cell experiments with hydrate formation for model emulsion and West African Crude (WAC) emulsion compared with the system without surfactant. For the sample without surfactants (mineral oil + water), large hydrate chunks were seen at the end of the experiment upon opening the autoclave cell (Figure 10a). For the model emulsion and WAC system, small particles of loose hydrate slurry were obtained (Figure 10b,c). In the case of mineral oil + water (no surfactant), the hydrates formed quickly agglomerate, forming a solid mass of hydrates. In the model emulsion, the water droplets in the emulsion are quickly converted to hydrate, and because of the emulsion stability, the hydrate particles remain dispersed and create a slurry. Similar results are seen for WAC emulsion, which contains a natural surface-active component, creating a loose hydrate slurry.

Another useful quantity from the autoclave cell test is the motor current required to maintain the stirrer at 300 rpm (a measure of relative viscosity). Figure 11a shows the motor current over the course of the test after hydrate formation for all three systems tested. As clearly seen in Figure 11a, the model emulsion shows lower motor current requirement than the mineral oil + water and WAC emulsion systems, suggesting a lower relative viscosity. This result is again related to dispersion of the hydrate particles formed in the systems with surfactant, whereas large hydrate chunks in the mineral oil + water system resulted in relative high viscosity conditions. In comparing the model emulsion with WAC emulsion, it can be observed that the motor current for WAC system is slightly higher than that of model emulsion. This is as expected, as the viscosity of WAC at 25 °C is 60 cP[42] while the viscosity of mineral oil 70T at the same temperature is 20 cP. However, the motor current throughout the time of the experiment for model emulsion has the same general trend as that of WAC emulsion, suggesting the model emulsion has similar behavior to the WAC emulsion.

It is also interesting to compare the amount of hydrate formed for the systems tested in the autoclave cell. As shown in Figure 11b, a similar amount of hydrates formed in all systems by the end of the experiment. However, based on the slope of the curves, hydrates formed at a faster rate in the model emulsion, followed by WAC emulsion, and finally the mineral oil + water mixture. This result can be interpreted on the basis of size of the water droplets in the emulsion. The model emulsion is highly stable with water droplets ranging from 2 to 3 μm, while WAC emulsion has water droplets ranging from 3 to 5 μm. As for the mineral oil + water mixture, it does not form a stable emulsion, and any entrainments of the phases are quickly separated. The small water droplet size in the emulsions creates a high interfacial surface area to form hydrates, which is not the case in the mineral oil + water mixture, where the interfacial area is generated only from the mixing imposed by the stirrer. Since water droplets are smaller (larger surface area) in the model emulsion, hydrate formation is the fastest among the three systems.

4. CONCLUSIONS

Stable water-in-oil emulsions with water cut ranges from 10 to 70 vol % have been prepared from mineral oil 70T, Span 80, sodium di-2-ethylhexylsulfosuccinate (AOT), and water. Classical bottle tests conducted show that all emulsions
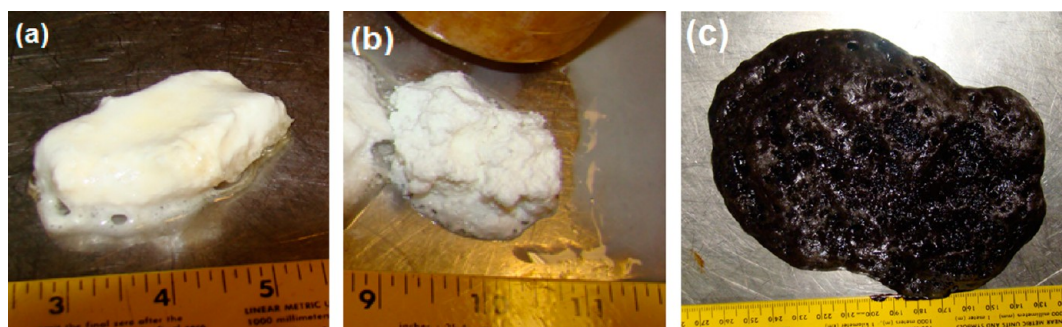
Figure 10. Type of hydrate particles observed for (a) mineral oil + water system, (b) model emulsion system, and (c) WAC emulsion at the end of high-pressure autoclave experiments.
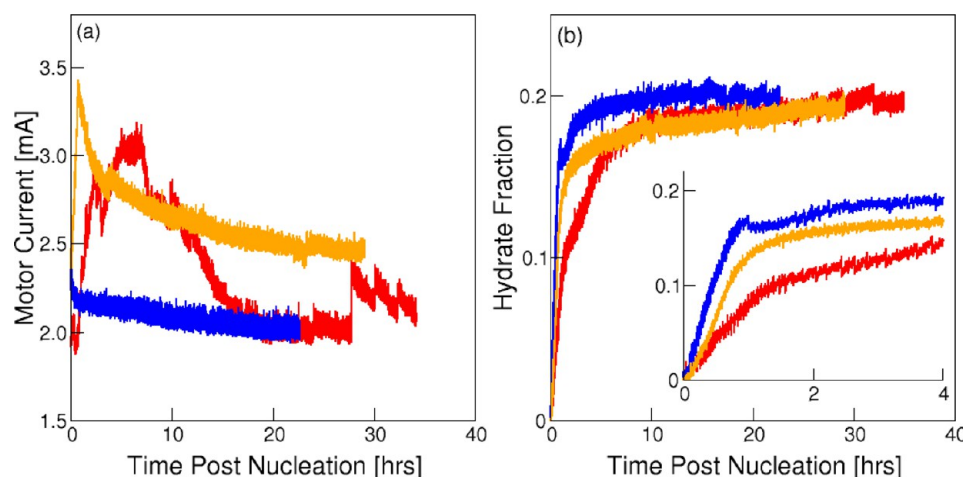

Figure 11. (a) Relative power input for the stirrer and (b) hydrate fraction in the autoclave as a function of time. Curves are for (red) mineral oil + water, (blue) model emulsion, and (orange) WAC emulsion.

(prepared with both 1 and 5 wt % surfactant mixture) are stable against coalescence for at least 1 week (the period of study). This high stability is attributed to the strong lipophilic interaction among the surfactant molecules. From the microscopy images of the emulsions, the average water droplet size ranges from 2 to 3 μm. Rheological measurements performed on these emulsions show a strong dependency of viscosity on the water cut: the viscosity of the emulsion increases with increasing water cut. It was also observed that these emulsions show shear thinning behavior above certain water cuts (30 vol % at 25 °C and 20 vol % at 1 °C). This behavior is similar to water-in-oil emulsions prepared with a crude oil.[9] The DSC measurements show that the emulsions prepared with 5 wt % surfactant with less than 50 vol % water are the most stable upon ice and hydrate formation/dissociation. For samples with high water cut (>50 vol %), the emulsions are slightly less stable after ice and hydrate formation/dissociation due to the increased packing density of water droplets and their interaction. MMF measurements show that the presence of the surfactant mixture has little impact in the cohesion force of hydrate particles, although a change in hydrate surface morphology was observed with the surfactant added. Autoclave cell experiments showed two different types of hydrate formation: large hydrate chunks for the system without surfactant and a loose hydrate slurry for the system with surfactant. It is also observed that the relative viscosity of the hydrate slurry is lower and the formation rate is higher for the emulsion compared to the mineral oil + water system. Autoclave cell experiments also show that the model emulsion

system behaves similarly to a crude oil emulsion. The tests performed in this study demonstrate that the proposed model emulsion is stable, having similar characteristics to those observed in crude oil emulsions, and may be suitable for other hydrate studies requiring long-term (~1 week) stability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Five figures showing average water droplet size for emulsions over the range of water cuts; average droplet size for emulsions over the 1-week testing period; viscosity of emulsions over time; and high-pressure DSC thermograms for emulsions with 20, 30, and 40 vol % water cuts. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone +1-303-273-3873; fax +1-303-273-3730; e-mail asum@mines.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press: Boca Raton, FL, 2008.

(2) *Natural Gas Hydrates in Flow Assurance*; Sloan, D., Koh, C., Sum, A. K., Eds.; Elsevier: Amsterdam, 2010.

(3) Ballard, A. L.; Sloan, E. D. *Fluid Phase Equilib.* **2004**, *218*, 15−31.

(4) Sum, A. K.; Koh, C.; Sloan, E. D. *Ind. Eng. Chem. Res.* **2009**, *48*, 7457−7465.

(5) Sum, A. K.; Koh, C.; Sloan, E. D. *Energy Fuels* **2012**, *26*, 4046−4052.

(6) Turner, D. Clathrate Hydrate Formation in Water-in-Oil Dispersions. Ph.D. Dissertation, Colorado School of Mines, Golden, CO, 2005.

(7) Taylor, C.; Miller, K; Koh, C.; Sloan, D. *Chem. Eng. Sci.* **2007**, *62*, 6524−6533.

(8) Greaves, D.; Boxall, J.; Mulligan, J.; Sloan, D.; Koh, C. *Chem. Eng. Sci.* **2008**, *63*, 4570−4579.

(9) Lachance, J.; Sloan, E. D.; Koh, C. *Chem. Eng. Sci.* **2008**, *63*, 3942−3947.

(10) Sjöblom, J.; Øvrevoll, B.; Jentoft, G.; Lesaint, C.; Palermo, T.; Sinquin, A.; Gateau, P.; Barré, L.; Subramanian, S.; Boxall, J.; Davies, S.; Dieker, L.; Greaves, D.; Lachance, J.; Rensing, P.; Miller, K.; Sloan, D.; Koh, C. *J. Dispersion Sci. Technol.* **2010**, *31*, 1110−1119.

(11) Fadnes, F. H. *Fluid Phase Equilib.* **1996**, *117*, 186−192.

(12) Salager, J.; Forgiarini, A. *Energy Fuels* **2012**, *26*, 4027−4033.

(13) Webb, E.; Rensing, P.; Koh, C.; Sloan, E. D.; Sum, A. K.; Liberatore, M. *Energy Fuels* **2012**, *26*, 3504−3509.

(14) Bancroft, W. D. *J. Phys. Chem.* **1913**, *17*, 501−519.

(15) Bancroft, W. D. *J. Phys. Chem.* **1915**, *19*, 275−309.

(16) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1949**, *1*, 311−326.

(17) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249−256.

(18) *The HLB System a Time-Saving Guide to Emulsifier Selection*; ICI Americas Inc., Edited by CHEMMUNIQUE.

(19) Aman Z. M. Interfacial Phenomena of Cyclopentane Hydrate. Ph.D. Dissertation, Colorado School of Mines, Golden, CO, 2012.

(20) Aman, Z. M.; Brown, E. P.; Sloan, E. D.; Sum, A. K.; Koh, C. A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19796−19806.

(21) Aman, Z. M.; Sloan, E. D.; Sum, A. K.; Koh, C. A. *Energy Fuels* **2012**, *26*, 5102−5108.

(22) Dieker, L. E. Cyclopentane Hydrate Interparticle Adhesion Force Measurements. M.S. Thesis, Colorado School of Mines, Golden, CO, 2009.

(23) Turner, D.; Miller, K.; Sloan, E. D. *Chem. Eng. Sci.* **2009**, *64*, 3996−4004.

(24) Salager, J.-L. Pharmaceutical Emulsions and Suspensions. In *Emulsion Properties and Related Know-How to Attain Them*; Nielloud, F., Marti-Mestres, G., Eds.; Marcel Dekker: New York, 2000; pp 73−125.

(25) Walstra, P. Emulsion Stability. In *Encyclopedia of Emulsion Technology, Volume 4*; V Becher, P., Ed.; Marcel Dekker: New York, 1996; Chapt. 1, pp 1−62.

(26) Boyd, J.; Parkinson, C.; Sherman, P. *J. Colloid Interface Sci.* **1972**, *41*, 359−370.

(27) Tadros, T. *Applied Surfactants. Principles and Applications*; Wiley−VCH: Weinheim, Germany, 2005.

(28) Salager, J.-L.; Perez-Sanchez, M.; Ramirez-Gouveia, M.; Anderez, J.; Briceno-Rivas, M. I. Stirring-Formulation Coupling in Emulsification. IXth European Congress on Mixing, Paris, 1997; pp 122−130.

(29) Walstra, P. Formation of Emulsions. In *Encyclopedia of Emulsion Technology, Volume 1: Basic Theory*; Becher, P., Ed.; Marcel Dekker: New York, 1983; Chapt. 2, pp 57−127.

(30) Ford, R. E.; Furmidge, C. G. L. *J. Colloid Interface Sci.* **1966**, *22*, 331−341.

(31) Nöik, C.; Trapy, J.; Mouret, A. Design of a Crude Oil Dehydration Unit. SPE 77492, SPE Annual Technical Conference and Exhibition, San Antonio, TX, 2002.

(32) Briceño, M. I. *Rheology of Suspensions and Emulsions in Pharmaceutical Emulsions and Suspensions*; Nielloud, F., Marti-Mestres, G., Eds;, Marcel Dekker: New York, 2000; pp 557−607.

(33) Quintero C. Comportement Rhéologique et Propriétés Interfaciales des Systèmes Émulsionnés d'Intérêt Industriel. Ph.D. Dissertation, Université Paris-Sud 11, Paris, 2008.

(34) Ese, M. H.; Kilpatrick, P. K. *J. Dispersion Sci. Technol.* **2004**, *25*, 253−261.

(35) Rondón-González, M.; Madariaga, L. F.; Sadtler, V.; Choplin, L.; Salager, J.-L. *Ind. Eng. Chem. Res.* **2009**, *48*, 2913−2919.

(36) Dalmazzone, C.; Noïk, C.; Clausse, D. *Oil Gas Sci. Technol.* **2009**, *64*, 543−555.

(37) Santini, E.; Liggieri, L.; Sacca, L.; Clausse, D.; Ravera, F. *Colloids Surf., A.* **2007**, *309*, 270−279.

(38) Lachance J. W. Investigation of Gas Hydrates Using Differential Scanning Calorimetry with Water-In-Oil Emulsion. M.S. Thesis, Colorado School of Mines, Golden, CO, 2008.

(39) Aman, Z. M.; Dieker, L. E.; Aspenes, G.; Sum, A. K.; Sloan, E. D.; Koh, C. A. *Energy Fuels* **2010**, *24*, 5441−5445.

(40) Karanjkar, P.; Lee, J.; Morris, J. *Cryst. Growth Des.* **2012**, *12*, 3817−3824.

(41) Taylor, C. J.; Dieker, L. E.; Miller, K. T.; Koh, C. A.; Sloan, E. D. *J. Colloid Interface Sci.* **2007**, *306*, 255−261.

(42) Rensing P. J. Studies on the Rheology of Ice and Clathrate Hydrate Slurries Formed In Situ from Water-in-Oil Emulsions. Ph.D. Thesis, Colorado School of Mines, Golden, CO, 2010.