# INFLEUENCE OF SURFACTANT-NANOPARTICLE INTERACTIONS ON EMULSION BEHAVIOR WITH APPLICATIONS TO FLOW ASSURANCE

By

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То

The Holy Feet of Paramacharya Shri Shri Shri Chandrashekarendra Saraswathi Swamigal (Fondly called as "Mahaperiyava" – my Ummachi Thatha)

## कर्मण्येवाधिकारस्ते मा फलेषु कदाचन ।

# मा कर्मफलहेतुर्भुर्मा ते संगोऽस्त्वकर्मणि ॥

Karmanye Vadhikaraste, Ma phaleshou kada chana,

Ma Karma Phala Hetur Bhurmatey Sangostva Akarmani

You have a right to perform your prescribed duty, but you are not entitled to the fruits of action. Never consider yourself the cause of the results of your activities, and never be attached to not doing your duty – Bhagwat Gita

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#### PREFACE

This thesis is written in manuscript format. The first chapter entitled "Demulsification of Surfactant Stabilized Water-in-Oil (Cyclohexane) Emulsions using Silica Nanoparticles" was published in Energy and Fuels (*Energy and Fuels, 2018, 32 (8), 8121-8130*). The second chapter entitled "Influence of Non-Ionic Surfactant Addition on the Stability and Rheology of Particle-stabilized Emulsions" is under review in Journal of Colloid and Interfacial Science. The third chapter entitled "Influence of Surfactants and Nanoparticles on the Formation and Rheology of Oil-in-Oil Emulsions" is under review in Langmuir. The fourth chapter entitled "A Comparison of the Rheological Behavior of Hydrate Forming Emulsions Stabilized using either Solid Particles or a Surfactant" was published in Fuel (*Fuel, 2016, 179,141-149*). The fifth chapter entitled "Emulsion Stability of Surfactant and Solid Stabilized Water-in-Oil Emulsions After Hydrate Formation and Dissociation" was published in Colloids and Surfaces A: Physicochemical and Engineering Aspects (*Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016, 506, 607-621*). The sixth chapter entitled "The Effect of Particle Hydrophobicity on Hydrate Formation in Water-in-Oil Emulsions in the Presence of Wax" was published in Energy and Fuels (*Energy and Fuels, 2017, 31(5), 4817-4825*).

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### Title of Study: INFLUENCE OF SURFACTANT-NANOPARTICLE INTERACTIONS ON EMULSION BEHAVIOR WITH APPLICATIONS TO FLOW ASSURANCE

### Major Field: CHEMICAL ENGINEERING

Abstract: Emulsions have wide industrial applications such as those in paints, cosmetics, food, energy, and pharmaceuticals. The surfactant-nanoparticle interactions play a critical role in determining the stability of the interfacial film. My research aims at probing the fundamental mechanisms governing the surfactant-nanoparticle interactions at the fluid-fluid interface and the consequence of surfactant-nanoparticle interactions on the stability and rheology of emulsions. My research consisted of four parts: a) probing the influence of nanoparticle addition to surfactant-stabilized emulsions b) elucidating the effect of surfactant addition to nanoparticle-stabilized emulsions c) investigating the influence of surfactant-nanoparticle interactions d) examining the influence of surfactant-nanoparticle interactions and nanoparticle wettability on hydrate formation.

Literature shows that the presence of both surfactants and nanoparticles enhance emulsion stability. On the contrary, our data showed that the addition of silica nanoparticles to surfactant-stabilized emulsions could lead to destabilization of water-in-oil emulsions. Partially hydrophobic silica nanoparticles had higher destabilization efficiency as compared to hydrophilic and hydrophobic silica nanoparticles.

Our results showed that the addition of surfactants significantly influenced the droplet size of Pickering emulsions depending on the wettability of nanoparticles at the liquid-liquid interface. For water-in-oil emulsions stabilized using hydrophobic nanoparticles, there was a significant decrease in the droplet size upon the addition of a surfactant. On the contrary, for water-in-oil emulsions stabilized using partially hydrophobic nanoparticles, no significant change in the droplet size was observed upon the addition of a surfactant. Based on our data, we postulate that the addition of a non-ionic surfactant aided in partial displacement of hydrophobic nanoparticles from the oil-water interface unlike partially hydrophobic nanoparticles, which in turn affected the droplet size of emulsions.

Furthermore, our results showed that simultaneous emulsification using hydrophobic nanoparticles and a surfactant (either Span 80 or Triton X-100) resulted in a single-step formation of multiple oil-in-oil-in-oil (O/O/O) emulsions. Multiple O/O/O emulsions had lower viscosity when compared to simple oil-in-oil (O/O) emulsions. Simple O/O emulsions had a lower degree of shear thinning behavior when compared to multiple O/O/O emulsions.

In addition, our results showed that nanoparticle wettability influenced the formation and rheology of hydrates in water-in-oil emulsions.

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### CHAPTER I

### DEMULSIFICATION OF SURFACTANT STABILIZED WATER-IN-OIL (CYCLOHEXANE) EMULSIONS USING SILICA NANOPARTICLES

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#### 1.1 Abstract

Efficient phase separation of oil and water in emulsions is critical for water treatment processes and hydrocarbon processing. Our research aims at elucidating the separation of water-in-oil emulsions using silica nanoparticles (SNP's). By probing the surfactant-nanoparticle interactions, we showed that surfactant stabilized emulsions can be destabilized depending on the nanoparticle wettability and the mode of nanoparticle addition. The efficiency of nanoparticles to demulsify surfactant stabilized emulsions depended on both the nanoparticle and surfactant concentration. Water-in-oil emulsions were destabilized when partially hydrophobic nanoparticles were added to the surfactant-stabilized emulsion after emulsion formation (post-mixing). Hydrophilic and partially hydrophobic nanoparticles adsorb the surfactants via hydrogen bonding that in turn leads to depletion of surfactants at the oil-water interface. Upon the addition of hydrophilic nanoparticles, the preferential distribution of nanoparticles in the water phase led to lower adsorption of surfactants from the oil phase resulting in inefficient destabilization as compared to partially hydrophobic nanoparticles. Water-in-oil emulsions were not destabilized upon postmixing hydrophobic nanoparticles due to weak hydrophobic interactions between surfactants and hydrophobic nanoparticles.

#### **1.2 Introduction**

Emulsions are a type of colloid that consist of one liquid being dispersed in another immiscible liquid.<sup>1, 2</sup> Emulsions have wide industrial applications such as those in paints, cosmetics, food, energy, and pharmaceuticals.<sup>2</sup> Water-in-oil emulsions are a commonly encountered multi-phase flow problem during the production and transportation stages of crude oil.<sup>3</sup> The presence of surface-active agents leads to the formation of strong, viscoelastic, rigid films, <sup>3-10</sup> that increase the stability of water droplets to coalescence in water-in-oil emulsions. In addition to surfactants, particles such as inorganic scales, clays, silica particles can potentially stabilize emulsions.<sup>3, 11-18</sup> Stabilization of emulsions by fine particles has been well established.<sup>12, 19, 20</sup> Upon sufficient surface coverage, the presence of a tightly packed colloidal network structure at the fluid-fluid interface provides enhanced mechanical rigidity and viscosity to the interfacial film.<sup>12, 21-26</sup>

The control of problematic emulsion formation is a critical challenge in a number of industrial sectors involving fluid processing. There is an urgent and growing need for more efficient and environmentally benign approaches to demulsification (oil-water separation) strategies, nowhere more critically than in energy production. The demulsifier market, mainly driven by the demands from the petroleum industry, is expected to reach \$2.5 billion by 2020.<sup>27</sup> Demulsification can be carried out using chemical, thermal, electrical, membrane and other physical treatment methods such as gravity settling and centrifugation.<sup>28</sup>

Existing technologies for chemical demulsification in the energy industry largely focus on molecular surfactants, which primarily work by reducing the dynamic interfacial tension gradient, thereby leading to film drainage and droplet coalescence. Molecular surfactants, however, are a non-ideal choice in many cases due to poor separation efficiency and potential environmental concerns. Therefore, there is a critical need to develop alternative strategies to improve separation efficiencies and to reduce the overall environmental impact of oil/water separations.

The objective of this work is to elucidate the demulsification potential of silica nanoparticles for water-in-oil emulsions. For demulsification using silica nanoparticles, it is critical to understand the influence of nanoparticle-surfactant interactions on emulsion stability. Investigations on the interaction of silica nanoparticles and surfactants in water-in-oil emulsions<sup>10, 26, 29-32</sup> are limited as compared to oil-in-water emulsions.<sup>22, 23, 33-41</sup> Sullivan et al. <sup>10</sup>, Menon et al. <sup>26</sup>, Nestenrenko et al. <sup>29</sup> found that the presence of particles increased the stability of water-in-oil emulsions. In prior studies available in the literature, the nanoparticles and the surfactant were pre-mixed in either the oil or aqueous phase before emulsion preparation. The presence of both surfactants and nanoparticles led to enhanced emulsion stability.

In contrast to the above studies, we investigated the potential of silica nanoparticles as demulsifiers for water-in-oil emulsions. Katepalli et al. investigated the effect of particles on destabilization of oilin-water emulsions.<sup>42</sup> Silica is chosen, as it is known to be environmentally benign, especially in its suspension form. Silica nanoparticle suspensions have been used as additives in various agriculture and food products, and studies have shown that silica nanoparticles are indeed safe for human consumption.<sup>43</sup> We probed the influence of surfactant-nanoparticle interactions on the instability, viscoelastic and rheological properties of water-in-oil emulsions. Dynamic oscillatory measurements were performed to determine the network strength of emulsions in the presence of nanoparticles and surfactants. Interfacial tension, emulsion droplet size distribution, and macroscopic emulsion stability were determined to elucidate demulsification potential of silica nanoparticles. Confocal microscopy was performed to further examine the interaction between nanoparticles and surfactants.

#### **1.3 Materials and Methods**

For preparation of water-in-oil emulsions, cyclohexane (+99 % purity, Alfa Aesar) was used as the continuous oil phase and de-ionized water (resistivity of 18 m $\Omega$  cm<sup>-1</sup>) was used as the dispersed phase. Sorbitan monooleate (Span 80), an oil soluble, non-ionic surfactant with an HLB <sup>2</sup> value of
4.3±1.0 (as stated by the vendor) was used as the surfactant. Fumed silica nanoparticles of different hydrophobicities were purchased from Evonik Inc. Three different silica nanoparticles were used – hydrophilic silica nanoparticle (A200), partially hydrophobic silica nanoparticle (R816), and hydrophobic silica nanoparticle (R812S). The fumed silica nanoparticles consists of a three-dimensional network (Figure 1.1), which is a combination of primary particles, aggregates of fused primary particles and agglomeration of fused primary particles aggregates.<sup>44-46</sup> Carbon content, silanol content, and methanol wettability were used to determine the hydrophobicities of silica nanoparticles.<sup>47, 48</sup> The residual silanol content (SiOH) on the surface of nanoparticles was determined by titration with aqueous NaOH.<sup>47, 49</sup> Hydrophilic silica nanoparticles have higher silanol content, <sup>47</sup>



Figure 1.1: TEM images of fumed silica nanoparticles a) hydrophilic silica nanoparticle b) partially hydrophobic silica nanoparticle c) hydrophobic silica nanoparticle

The silanol content, carbon content, and surface area for the particles used in the study are given in Table 1.1.

SNP's	Surface area	SiOH (wt.%)	Carbon content
	$(m^2/g)$		(%)
A200	$200 \pm 25$	100	-

R816	182	68	1.3
R812S	217	10	3.2

Table 1.1: Properties of fumed silica nanoparticles used in this study

An Olympus BX53 cross-polarized optical microscope was used to measure the droplet size of waterin-cyclohexane emulsions. The droplet sizes were quantified using Image J software. More than 500 droplets were counted for each sample and the average of the droplet sizes were reported. The schematic of the microscope stage and the experimental procedure that was adapted to measure the droplet size can be found elsewhere. <sup>50</sup>

# 1.3.1 Preparation of emulsions

The water-in-oil emulsions were prepared using an Ultra-Turrax digital homogenizer operating at 10,000 rpm for 10 minutes. Initially, the non-ionic surfactant was added to the oil phase followed by vigorous shaking to aid complete mixing of Span 80 with the oil phase. The dispersed water phase was added in a drop wise manner to aid homogenous distribution of water droplets.<sup>11, 51, 52</sup> The water-in-cyclohexane emulsion consisted of 69.96 wt. % cyclohexane, 29.96 wt.% water, and 0.08 wt.% Span 80.

#### 1.3.2 Characterization of emulsions

Bottle tests were carried out to macroscopically determine the emulsion stability. In order to ensure that the emulsions did not undergo a structural change at the microscopic level, the droplet sizes were measured for water-in-cyclohexane emulsions before and after the experimental time. Figure 1.2 shows the microphotographs of the surfactant stabilized water-in-cyclohexane emulsion in the absence of silica nanoparticles along with the bottle test images (inset) and also a comparison of the  $0^{\text{th}}$ droplet the experimental average size at hour and after the time.



Figure 1.2: (a) Microphotograph of the water-in-cyclohexane emulsion at the  $0^{th}$  hour (inset: macroscopic appearance of the sample) (b) Microphotograph of the water-in-cyclohexane emulsion after 2 hours (inset: macroscopic appearance of the sample) (c) Comparison of the droplet size distribution of the water-in-cyclohexane emulsion at the  $0^{th}$  hour and after 2 hours.

From the results, it was evident that there was no change in the average droplet size over the experimental time. No bulk phase separation of water from the water-in-oil emulsion was observed from the bottle tests. Thus, it was confirmed that the surfactant stabilized water-in-oil emulsion was stable over the experimental time.

# **1.3.3** The mode of addition of nanoparticles

The nanoparticles were added in either of the following two ways. In pre-mixing, the nanoparticles

were added to the surfactant containing continuous oil phase before emulsion formation. The nanoparticles were completely dispersed in the oil phase by ultra sonication (30 minutes). In post-mixing, the nanoparticles were added to the surfactant-stabilized emulsion. The methodology is illustrated schematically in Figure 1.3. During post-mixing, the nanoparticles were immediately added and gently shaken to mix the silica nanoparticles. The concentrations of the silica nanoparticles were varied from 0.1 wt.% to 1.3 wt.% of the total emulsion.



Figure 1.3: Schematic representation of the mode of addition of nanoparticles

# **1.3.4 Interfacial tension measurements**

Interfacial tension measurements were carried out using an interfacial tensiometer purchased from Core Lab instruments (Tulsa, OK). The pendant drop technique was used to determine the interfacial tension.<sup>53</sup> In order to determine the surfactant adsorption onto the silica nanoparticles, different concentrations of silica nanoparticles were added to the oil phase containing Span 80 and equilibrated for more than 24 hours. The solution containing the surfactant and silica nanoparticles was centrifuged (6,000 rpm for 15 minutes) to remove the silica nanoparticles. The supernatant solution was used for interfacial tension measurements.<sup>40-42</sup> The interfacial tension at the oil-water interface was measured for every second over a period of 5 minutes. Each measurement was repeated at least 5 times and the average interfacial tension is reported.

### **1.3.5** Confocal microscopy

Confocal microscopy experiments were carried out using a Leica TCS SP2 Confocal Microscope.

The silica nanoparticles were fluorescently labeled using 3-aminopropyltriethoxysilane (APTES) and fluorescein isothiocyanate (FITC). The procedure to fluorescently label hydrophobic silica nanoparticles can be found elsewhere. <sup>54</sup>

# 1.3.6 Rheology

The viscoelastic properties of the emulsion along with their rheological flow behavior were measured using a stress controlled Discovery Hybrid Rheometer (DHR-3). The concentric cylinder geometry was used to measure the rheological properties of water-in-oil emulsions in the presence of nanoparticles. A solvent trap was used to prevent evaporation during the experiment. For emulsion viscosity experiments, the shear rate was increased from 1 s-1 to 200 s-1. Dynamic oscillatory experiments were performed to elucidate the emulsion viscoelastic properties. The storage and loss modulus were determined from the amplitude sweep tests (0.01 - 100% strain, 1Hz) and frequency sweep tests (0.2 to 10 Hz).

#### 1.4 Results

## 1.4.1 Effect of nanoparticle wettability and the mode of addition of SNP's on emulsion stability

The following sections describe the effect of SNP wettability on the demulsification efficiency of surfactant-stabilized water-in-oil emulsions. Although our primary objective is to demulsify surfactant-stabilized water-in-oil emulsions using silica nanoparticles (post-mixing), in order to understand the fundamental differences in the interaction between surfactants and nanoparticles, we have also compared the effect of nanoparticles on emulsion stability when nanoparticles were added to the surfactant containing oil phase before emulsion formation (pre-mixing).

# 1.4.1.1Hydrophobic nanoparticles

#### **Post-mixing**

Figure 1.4 shows the fraction of water separated versus the concentration of hydrophobic nanoparticles. Upon post-mixing, no bulk phase separation of water was observed.



Figure 1.4: Fraction of water resolved versus the concentration of hydrophobic nanoparticles

Also, there was no significant change in the droplet size of water-in-oil emulsions upon post-mixing hydrophobic nanoparticles (see Figure 1.5 (i) for droplet size distribution).



Figure 1.5: (a)-(e) Microphotographs of water-in-oil emulsions obtained after post-mixing hydrophobic nanoparticles to the surfactant containing oil phase before emulsion formation (f) Microphotographs of water-in-oil emulsions obtained after pre-mixing 0.1wt.% of hydrophobic nanoparticles (g) Bulk water-in-oil emulsion obtained by pre-mixing hydrophobic nanoparticles (h) Bulk water-in-oil emulsion obtained by post-mixing hydrophobic nanoparticles (i) Average droplet size of water-in-oil emulsions after post-mixing hydrophobic nanoparticles (j) Comparison of the droplet size distribution of the water-in-oil emulsion after pre-mixing and post-mixing 0.1wt.% of hydrophobic nanoparticles

It was observed that the hydrophobic nanoparticles did not aid in destabilization of surfactant stabilized water-in-oil emulsion.

# **Pre-mixing**

From Figure 1.4, phase separation of water was observed upon pre-mixing 0.2 wt.%, 0.3 wt.%, 0.6 wt.% and 1.3 wt.% of hydrophobic nanoparticles. Within the experimental time, the fraction of water

separated was less than 5 % at all the weight fractions investigated. In the presence of hydrophobic nanoparticles at the water-oil interface, the water-in-oil emulsions are unstable to coalescence.<sup>47</sup> Upon the addition of 0.1 wt.% hydrophobic nanoparticles, the droplet sizes of water-in-oil emulsions were larger upon pre-mixing nanoparticles as compared to post-mixing nanoparticles (See Figure 1.5 (a,f,j)). Thus, the mode of addition of nanoparticles influenced the droplet sizes of the resulting water-in-oil emulsions.

#### 1.4.1.2 Partially hydrophobic nanoparticles

# **Post-mixing**

Figure 1.6 shows the fraction of water separated versus the concentration of partially hydrophobic nanoparticles (all the data points were collected 5 minutes after post-mixing nanoparticles).



Figure 1.6: Fraction of water resolved versus the concentration of partially hydrophobic nanoparticles

The partially hydrophobic silica nanoparticles with three dimensional fractal structures (Figure 1.1) led to catastrophic coalescence of water droplets. Upon post-mixing, 0.6 wt.% and 1.3 wt.% of intermediate hydrophobic nanoparticles, due to high concentration of nanoparticles, gelation (at the bottom of the emulsion) was observed (Figure 1.7 (h)). At these higher concentrations, we hypothesize that nanoparticles form a barrier between the water droplets at higher concentration, thereby preventing coalescence of water droplets.<sup>3</sup>



Figure 1.7: (a)-(e) Microphotographs of water-in-oil emulsions obtained after pre-mixing partially hydrophobic nanoparticles to the surfactant containing oil phase before emulsion formation (f) Average droplet size of water-in-oil emulsions after pre-mixing partially hydrophobic nanoparticles (g) Bulk water-in-oil emulsion obtained by pre-mixing partially hydrophobic nanoparticles (h) Bulk water-in-oil emulsion obtained by post-mixing partially hydrophobic nanoparticles

Thus, the extent of demulsification of surfactant stabilized water-in-oil emulsions depended upon the concentration of post-mixed partially hydrophobic nanoparticles.

## **Pre-mixing**

In contrast to post-mixing partially hydrophobic nanoparticles, stable emulsions were formed upon pre-mixing. In addition, no significant change in droplet size was observed with an increase in concentration of nanoparticles (Figure 1.7 (f)). Although, upon pre-mixing, there was a small increase in the droplet size as compared to surfactant stabilized water-in-cyclohexane emulsions in the absence of nanoparticles.

## 1.4.1.3 Hydrophilic nanoparticles

# **Post-mixing**

Figure 1.8 shows the fraction of water separated versus the concentration of hydrophilic nanoparticles (all the data points were collected 5 minutes after post-mixing nanoparticles). Upon addition of hydrophilic nanoparticles, phase separation was observed. The destabilization potential of hydrophilic nanoparticles was lower as compared to partially hydrophobic nanoparticles (from Figure 1.6 and Figure 1.8).



Figure 1.8: Fraction of water resolved (upon post-mixing nanoparticles) versus the concentration of hydrophilic nanoparticles

# **Pre-mixing**

In contrast to post-mixing partially hydrophobic nanoparticles, no stable emulsions were formed.

From the above results, it was clear that upon post-mixing, partially hydrophobic nanoparticles showed higher efficiency to destabilize water-in-oil emulsions as compared to hydrophilic nanoparticles. Upon post-mixing hydrophobic nanoparticles, no demulsification was observed.

Interfacial tension measurements were carried out to probe the fundamental mechanisms that govern the destabilization of surfactant stabilized water-in-oil emulsions upon the addition of silica nanoparticles. Figure 1.9 shows the interfacial tension at the oil-water interface upon the addition of silica nanoparticles of different wettabilities. An increase in the dynamic interfacial tension at the oilwater interface indicates the depletion of surfactant from the bulk oil phase and consequently from the oil-water interface. We observed that hydrophilic silica nanoparticles (A200) have the highest potential of depleting the surfactants from the oil-water interface, which is followed by partially hydrophobic silica nanoparticles. In case of hydrophobic silica nanoparticles, an appreciable increase in interfacial tension was seen only upon the addition of 1.3 wt.% nanoparticles. It was evident that hydrophobic silica nanoparticles did not aid in the depletion of surfactants from the continuous oil phase and consequently from the oil-water interface that in turn led to poor destabilization efficiencies upon post-mixing.



Figure 1.9: Interfacial tension of surfactant supernatant solutions at the oil-water interface upon addition of hydrophilic (A200), partially hydrophobic (R816) and highly hydrophobic (R812S) silica nanoparticles of different wettabilities.

Upon the addition of hydrophilic silica nanoparticles, the polar head of the surfactants form a hydrogen bond with the -OH group at the particle surfaces <sup>42</sup> while the tails orient themselves

towards the oil phase. Hydrophilic silica nanoparticles have higher number of -OH groups at the particle surfaces as compared to the hydrophobic silica nanoparticles (Table 1.1). With an increase in the hydrophobicity of the silica nanoparticles, there is a decrease in the number of -OH groups at the particle surface. Therefore, upon the addition of partially hydrophobic silica nanoparticles, the number of polar heads of the surfactant that bond with the metal oxide surface is fewer as compared to the hydrophilic silica nanoparticles. Hence, hydrophilic silica nanoparticles show a higher potential to adsorb the surfactants as compared to partially hydrophobic silica nanoparticles, which is in accordance with the results in Figure 1.9. The addition of hydrophobic silica nanoparticles could result in either of the following phenomenon - (i) if due to the strong hydrophobic interactions between the tails of the surfactant and silica nanoparticles, the tails of surfactant orient themselves towards the silica nanoparticles then the hydrophilic heads of the surfactant would orient themselves towards the oil phase. This phenomenon would result in depletion of surfactants from the oil-water interface and would eventually result in the movement of surfactants towards the water phase, which in turn would result in destabilization of water-in-oil emulsion (ii) if the hydrophobic interactions between the tails of the surfactant and the nanoparticles are weak then surfactants would remain attached to the oil-water interface (with or without the particles), which in turn will result in stabilization of water-in-oil emulsions. From Figure 1.4, it was observed that the addition of nanoparticles to the surfactant-stabilized emulsions did not result in destabilization of emulsions. Also, from Figure 1.9, it was concluded that the surfactants were not adsorbed by the hydrophobic nanoparticles, which in turn results in poor depletion of surfactants in the bulk oil phase and consequently at the oil-water interface. Therefore, surfactants do not associate strongly with the hydrophobic silica nanoparticles. Hydrophobic silica nanoparticles appear to have high affinity towards the oil phase. Therefore, hydrophobic nanoparticles remains preferentially dispersed in the bulk oil phase as compared to the water phase. Figure 1.10 shows the confocal microscope images of the surfactant-stabilized emulsion upon the addition of 0.2 wt.% hydrophobic silica nanoparticles.



Figure 1.10: Confocal florescence microscope image of the surfactant stabilized water-in-cyclohexane emulsion upon addition of 0.2 wt.% hydrophobic silica nanoparticle (R812S) (a) Optical microscope image of the emulsion (b) Florescence image of the emulsion (with nanoparticles) (c) Overlap of (a) and (b)

It was evident that hydrophobic silica nanoparticles were preferentially distributed in the bulk oil phase.

Although, it was observed from Figure 1.9 that hydrophilic silica nanoparticles have higher potential to adsorb Span 80 as compared to partially hydrophobic silica nanoparticles, the destabilization efficiency of hydrophilic silica nanoparticles is lower as compared to partially hydrophobic silica nanoparticles (from Figures 1.6 and Figure 1.8). Figure 1.11 shows the hypothesized destabilization mechanism for hydrophilic silica nanoparticles.



Figure 1.11: Schematic that shows the demulsification process in surfactant stabilized water-in-oil emulsions upon addition of hydrophilic silica nanoparticles (A200)

Hydrophilic silica nanoparticles are preferentially dispersed in the water phase than in the oil phase. Therefore, when hydrophilic silica nanoparticles are added to the surfactant stabilized water-in-oil emulsion, the nanoparticles have a preferential tendency to move towards the water phase rather than being distributed in the oil phase to promote surfactant adsorption on to the silica nanoparticles that would have caused rapid depletion of surfactants. As hydrophilic silica nanoparticles move towards the water separation i.e., destabilization. Since the hydrophilic silica nanoparticles migrate to the water phase, the demulsified water looks turbid (Figure 1.12) upon the addition of hydrophilic silica nanoparticles to the surfactant stabilized water-in-cyclohexane emulsion due to the presence of silica nanoparticles in bulk water phase.



Figure 1.12: Bulk water-in-oil emulsion after post-mixing hydrophilic nanoparticles (A200).

In order to test this hypothesis, the surfactant stabilized water-in-cyclohexane emulsion, which did not undergo complete phase separation, upon the addition of 0.1 wt.% hydrophilic silica nanoparticles was observed under confocal microscope to elucidate the spatial distribution of hydrophilic silica nanoparticles. Figure 1.13 shows the confocal microscope images of the surfactant-stabilized emulsion upon the addition of 0.1 wt.% hydrophilic silica nanoparticles. It was evident that some of the hydrophilic silica nanoparticles had started moving towards the water phase.



Figure 1.13: Confocal florescence microscope image of the surfactant stabilized water-in-cyclohexane emulsion upon addition of 0.1 wt.% hydrophilic silica nanoparticle (A200) (a) (d) Optical microscope image of the emulsion (b) (e) Florescence image of the emulsion (with nanoparticles) (c) (f) Overlap of (a) (b), and (d) (e). Scale bar: 50 μm

#### 1.4.2 Rheological behavior of emulsions

Rheological and dynamic oscillatory measurements for water-in-oil emulsions cannot be carried out if the water is phase separated from the oil-water mixture upon addition of silica nanoparticles. Therefore, a more concentrated emulsion with a higher concentration of surfactant was prepared in order to avoid instantaneous phase separation of water from the emulsion upon addition of partially hydrophobic silica nanoparticles. The modified surfactant stabilized water-in-oil emulsion consisted of 59.7 wt.% cyclohexane, 40 wt.% water and 0.3 wt.% span 80. Figure 1.14 shows the droplet size distribution of the modified surfactant stabilized water-in-oil emulsion in the absence of nanoparticles. Rheological measurements were carried out by both post-mixing and pre-mixing silica nanoparticles (0.8 wt.%) of varying wettability. A higher concentration of particles was chosen to avoid immediate phase separation of emulsion upon post-mixing partially hydrophobic silica nanoparticles.



Figure 1.14: (a) Microphotograph of the water-in-cyclohexane emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) at the 0<sup>th</sup> hour (inset: macroscopic appearance of the sample) (b) Microphotograph of the water-in-cyclohexane emulsion after experimental time (inset: macroscopic appearance of the sample) (c) Comparison of the droplet size distribution of the water-in-cyclohexane emulsion at the 0<sup>th</sup> hour and after experimental time (d) Comparison of the average droplet size of water-in-cyclohexane emulsion at the 0<sup>th</sup> hour and after experimental time.

Figures 1.15a, 1.15b, and 1.15c show the viscosity versus shear rate for surfactant stabilized water-in-



oil emulsions both in the presence and in the absence of nanoparticles.

Figure 1.15: (a,b,c) Viscosity of surfactant stabilized water-in-oil emulsion versus shear rate - in the absence of SNP's, upon the addition of 0.8 wt.% partially hydrophobic nanoparticle, and upon the addition of 0.8 wt.% hydrophobic nanoparticle respectively (d,e,f) Storage modulus (G') and loss modulus (G') dependence on strain amplitude for surfactant stabilized water-in-oil emulsion - in the absence of SNP's, upon the addition of 0.8 wt.% partially hydrophobic nanoparticle, and upon the addition of 0.8 wt.% hydrophobic nanoparticle respectively (g,h,i) Storage modulus (G') and loss modulus (G') dependence on frequency for surfactant stabilized water-in-oil emulsion - in the addition of 0.8 wt.% hydrophobic nanoparticle respectively (g,h,i) Storage modulus (G') and loss modulus (G'') dependence on frequency for surfactant stabilized water-in-oil emulsion - in the absence of SNP's (strain %=0.03), upon the addition of 0.8 wt.% partially hydrophobic nanoparticle (strain %=0.1), and upon the addition of 0.8 wt.% hydrophobic nanoparticle (strain %=0.03) respectively.

The addition of nanoparticles resulted in an increase in the viscosity of the surfactant-stabilized emulsion. The surfactant stabilized water-in-oil emulsions exhibited shear thinning behavior upon the addition of silica nanoparticles (pre-mixing and post-mixing) of varying wettability, which is in accordance with the literature.<sup>55-58</sup> For water-in-oil emulsions with partially hydrophobic nanoparticles, the viscosities of emulsions were higher upon pre-mixing as compared to post-mixing. This phenomenon can be attributed to the change in droplet size of emulsions upon changing the mode of nanoparticle addition. Fine emulsions have higher viscosities than coarse emulsions.<sup>59</sup> Figure 1.16 shows the microphotographs and the droplet size distribution of water-in-oil emulsions upon premixing and post-mixing nanoparticles of varying wettabilities. Upon pre-mixing partially hydrophobic nanoparticles, the droplet sizes of emulsions were smaller with a narrow size distribution. Upon post-mixing partially hydrophobic nanoparticles, the surfactant stabilized water-in-oil emulsions (indicating destabilization) with a wider size distribution. Therefore, water-in-oil emulsions were more monodispersed upon pre-mixing partially hydrophobic nanoparticles as compared to post-mixing partially hydrophobic nanoparticles.



Figure 1.16: (a) Microphotographs of surfactant stabilized water-in-oil emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) upon pre-mixing 0.8 wt.% partially hydrophobic nanoparticle (inset:

macroscopic appearance of the sample) (b) Microphotographs of surfactant stabilized water-in-oil emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) upon pre-mixing 0.8 wt.% hydrophobic nanoparticle (inset: macroscopic appearance of the sample) (c) Microphotographs of surfactant stabilized water-in-oil emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) upon post-mixing 0.8 wt.% partially hydrophobic nanoparticle (inset: macroscopic appearance of the sample) (d) Microphotographs of surfactant stabilized water-in-oil emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) upon post-mixing 0.8 wt.% hydrophobic nanoparticle (inset: macroscopic appearance of the sample) (d) Microphotographs of surfactant stabilized water-in-oil emulsion (59.7 wt.% oil, 0.3 wt.% Span 80, 40 wt.% water) upon post-mixing 0.8 wt.% hydrophobic nanoparticle (inset: macroscopic appearance of the sample) (e) Droplet size distribution of surfactant stabilized water-in-oil emulsion upon post-mixing 0.8 wt.% partially hydrophobic and hydrophobic nanoparticle (f) Droplet size distribution of surfactant stabilized water-in-oil emulsion upon post-mixing 0.8 wt.% partially hydrophobic and hydrophobic nanoparticle (g) Average droplet size of surfactant-stabilized water-in-oil emulsion upon the addition of partially hydrophobic and hydrophobic nanoparticles

The increase in polydispersity of water-in-oil emulsions upon post-mixing partially hydrophobic nanoparticles (due to destabilization) led to a decrease in viscosity as compared to water-in-oil emulsions upon pre-mixing partially hydrophobic nanoparticles. Furthermore, with an increase in the droplet size, the mean distance of separation between the droplets increases that in turn decreases the hydrodynamic interactions and the viscosity.<sup>59</sup> Also, the effective dispersed phase concentration ( $\Phi_e$ ) is given by <sup>59</sup>

$$\Phi_e = \Phi \left( 1 + \frac{\delta}{R} \right)^3 \tag{1}$$

where  $\Phi$  is the true dispersed phase concentration,  $\delta$  is the thickness of the adsorbed layer of surfactant and nanoparticles, and R is the droplet radius. By substituting  $\Phi$ =0.4, R = 4.05 µm for premixing partially hydrophobic nanoparticles and R = 10.85 µm and assuming that the change in  $\delta$  is negligible for pre-mixing and post-mixing partially hydrophobic nanoparticles, we can observe that the effective dispersed phase concentration would be higher upon pre-mixing partially hydrophobic

nanoparticles as compared to post-mixing partially hydrophobic nanoparticles. The decreased effective dispersed phase concentration upon post-mixing led to a decrease in the viscosity of waterin-oil emulsions as compared to pre-mixing partially hydrophobic nanoparticles.

In contrast, upon the addition of hydrophobic nanoparticles, the viscosities of emulsions were higher upon post-mixing as compared to pre-mixing. Upon pre-mixing hydrophobic nanoparticles the droplet sizes were larger than post-mixing (Figure 1.16). Also, water-in-oil emulsions were more polydisperse upon pre-mixing as compared to post-mixing hydrophobic nanoparticles. The increase in polydispersity, effective dispersed phase concentration (from equation 1), and the mean distance of separation between the droplets upon pre-mixing hydrophobic nanoparticles led to a lower viscosity as compared to post-mixing hydrophobic nanoparticles.

The viscosities of emulsions upon the addition of partially hydrophobic nanoparticles were higher than the viscosities of emulsions upon the addition of hydrophobic nanoparticles. Thus, for a fixed concentration of nanoparticles, the flow behavior of emulsions was altered by changing the mode of addition of nanoparticles in addition to wettability.

# **Dynamic oscillatory measurements**

Dynamic oscillatory tests were carried out to elucidate the effect of nanoparticle wettability and the mode of nanoparticle addition on the viscoelastic properties of the emulsions. The elastic (G') and the viscous modulus (G") determine the strength of the network structure in water-in-oil emulsions.<sup>29</sup> Figures 1.15d, 1.15e and 1.15f show the amplitude sweep tests for surfactant stabilized water-in-oil emulsions in the presence and in the absence of nanoparticles of varying wettability. At lower strain range, the elastic modulus and viscous modulus were independent of the applied strain for all the investigated samples, which denoted the linear viscoelastic region. Viscoelastic solid like behavior (G' > G") was observed except for water-in-oil emulsions pre-mixed with hydrophobic nanoparticles. At higher

strain, the reordering of the structure takes place and the emulsions exhibit a viscous liquid like behavior (G">G"). The network strength of the emulsion is determined from the crossover modulus.<sup>29</sup> From Figure 1.15e, it was observed that the post-mixing of partially hydrophobic nanoparticles, which resulted in destabilization of water-in-oil emulsions, had a lower crossover modulus as compared to pre-mixing of partially hydrophobic nanoparticles, which resulted in formation of stable emulsions. Thus, for partially hydrophobic nanoparticles, post-mixing resulted in a weaker network structure as compared to pre-mixing. On the contrary, it was observed that post-mixing of hydrophobic nanoparticles increased the network strength as compared to pre-mixing hydrophobic nanoparticles. The frequency sweeps were conducted to investigate the viscoelastic properties of the emulsions (Figures 1.15g, 1.15h, 1.15i). The elastic modulus was higher than the viscous modulus in the entire frequency range for the emulsions except for water-in-oil emulsions pre-mixed with hydrophobic nanoparticles. Thus, for surfactant stabilized water-in-oil emulsions in the presence of nanoparticles of specific wettability, changing only the mode of nanoparticle addition can alter network strength.

## **1.5 Conclusions**

Demulsification of water-in-oil emulsions were carried out using silica nanoparticles. Surfactant stabilized water-in-oil emulsions were demulsified depending on the mode of nanoparticle addition and nanoparticle wettability. Upon post-mixing, partially hydrophobic nanoparticles demulsified the surfactant stabilized water-in-oil emulsions. In contrast, surfactant stabilized water-in-oil emulsions were not demulsified upon post-mixing hydrophobic nanoparticles due to weak hydrophobic interactions between surfactants and hydrophobic nanoparticles. Upon post-mixing hydrophobic nanoparticles, the preferential distribution of nanoparticles in the water phase led to lower adsorption of surfactants from the oil phase resulting in inefficient destabilization as compared to partially hydrophobic nanoparticles. We have also determined the effect of nanoparticle wettability and the mode of nanoparticle of addition on the rheological and viscoelastic properties of surfactant stabilized

water-in-oil emulsions. We showed that in the presence of nanoparticles of specific wettability, changing only the mode of nanoparticle addition altered the flow behavior and the network strength of emulsions. Furthermore, the efficiency of nanoparticles to demulsify surfactant stabilized emulsions depended on both the nanoparticle and surfactant concentration.

## **1.6 Acknowledgements**

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# CHAPTER II

# INFLUENCE OF NON-IONIC SURFACTANT ADDITION ON THE STABILITY AND RHEOLOGY OF PARTICLE-STABILIZED EMULSIONS

Under review in the Journal of Colloid and Interfacial Science

#### 2.1 Abstract

Nanoparticle wettability is expected to influence the surfactant adsorption onto the oil-water interface, which in turn would affect the structure and rheology of Pickering emulsions. We investigated the influence of non-ionic surfactant (Span 80) addition to Pickering emulsions stabilized by either partially hydrophobic (Aerosil R711) or hydrophobic (Aerosil R812S) nanoparticles under negligible shear conditions. The addition of a non-ionic surfactant to emulsions stabilized by hydrophobic nanoparticles decreased the droplet size of emulsions unlike emulsions stabilized by partially hydrophobic nanoparticles. Even under negligible shear conditions, the addition of a non-ionic surfactant displaced the hydrophobic nanoparticles from the oil-water interface unlike partially hydrophobic nanoparticles. Our results suggested that the displacement of hydrophobic nanoparticles by the addition of a non-ionic surfactant was not due to the change in nanoparticle wettability by surfactant adsorption onto the surface of nanoparticles. Viscosity of emulsions stabilized by partially hydrophobic nanoparticles decreased upon the addition of a non-ionic surfactant. In contrast, the viscosity of emulsions stabilized by hydrophobic nanoparticles increased upon the addition of a non-ionic surfactant. Depending on the nanoparticle wettability, the addition of a non-ionic surfactant influenced the elastic and viscous properties of Pickering emulsions.

# **2.2 Introduction**

Emulsions are ubiquitously encountered in many industrial applications such as those in paints, cosmetics, food, energy, and pharmaceuticals.<sup>2, 60, 61</sup> In addition to surfactants, solid particles can also stabilize emulsions.<sup>3, 11-18</sup> Colloidal particle size and concentration <sup>10, 15, 23, 24, 26, 33, 62-64</sup>, morphology <sup>65-68</sup>, wettability<sup>12, 22, 25, 47, 69</sup>, and density <sup>33, 64</sup> play a critical role in determining the emulsion stability. Once adsorbed to the oil-water interface, solid particles of appropriate wettability, size, and shape are very difficult to desorb from the interface.<sup>47</sup>

In industrial applications, solid particles are usually present along with the surfactants.<sup>70</sup> Stabilization of emulsions in the presence of both surfactants and solid particles has been investigated.<sup>22, 23, 33-39</sup> The extent of particle attachment to the oil-water interface is determined by its wettability. <sup>19, 47</sup> Binks et al. <sup>41</sup> and Lan et al. <sup>38</sup> elucidated the influence of surfactants on particle attachment to the oil-water interface. They observed that surfactant adsorption onto the particles leads to a change in particle hydrophobicity.<sup>23, 64</sup> Lucassen et al. <sup>71</sup>, Binks et al. <sup>40, 41</sup> and Hassander et al. <sup>34</sup> investigated the enhanced stabilization of oil-in-water emulsions in the presence of mixed surfactants and particles. They attributed the enhanced stability of emulsions to particle flocculation in the presence of surfactants. However, few studies have shown that the addition of nanoparticles to surfactant-stabilized emulsions led to destabilization of emulsions.<sup>42, 72</sup>

Fewer investigations were carried out to elucidate the influence of surfactant addition to an existing Pickering emulsion.<sup>40, 70, 73, 74</sup> Alargova et al.<sup>75</sup> and Subramaniam et al.<sup>76</sup> investigated the stability of particle-stabilized foams and bubbles, respectively, upon the addition of a surfactant. They observed a change in wettability of particles upon surfactant addition, which in turn led to particle detachment from the air-liquid interface. Whitby et al.<sup>70</sup> investigated the influence of

addition of an anionic surfactant to oil-in-water emulsions stabilized using silica nanoparticles (Aerosil R816). They concluded that dilution of oil-in-water emulsions using solutions of anionic surfactant did not have appreciable effect on the droplet size. However, at high surfactant concentrations, enhanced rate of creaming and flocculation were observed. Vashisth et al.<sup>73</sup> investigated the influence of addition of an anionic surfactant to oil-in-water emulsions stabilized using silica nanoparticles (Aerosil R816). They concluded that re-emulsification of particle-stabilized emulsions using an anionic surfactant (at high shear rates) led to particle displacement from the oil-water interface.

Our work here highlights, instead, the effect of non-ionic surfactant addition to water-in-oil emulsions stabilized using nanoparticles with different wettability (either partially hydrophobic or hydrophobic silica nanoparticles) under negligible shear conditions. This work will help us elucidate the effect of nanoparticle wettability on the stability and rheology of Pickering emulsions upon the addition of a non-ionic surfactant under negligible shear conditions. We showed that depending on the nanoparticle wettability, the addition of a non-ionic surfactant to particle-stabilized emulsion affected the emulsion morphology and rheology.

# 2.3 Materials and methods

Water-in-oil emulsions were prepared using 1-Bromohexadecane as the continuous phase. 1-Bromohexanedecane ( $\rho = 0.999$  g/ml) was purchased from Fischer Scientific (Assay Percent Range = 97 %). De-ionized (DI) water was used as the dispersed phase. Two types of fumed silica nanoparticles – partially hydrophobic (Aerosil R711 (R711)), and hydrophobic (Aerosil R812S (R812S)) – were used. Fumed silica nanoparticles were provided by Evonik Corporation. Sorbitan monooleate (Span 80, HLB =  $4.3 \pm 1$  (as stated by the vendor)) was used as the surfactant.

#### 2.3.1 Preparation of emulsions

Ultra-Turrax digital homogenizer was used for the preparation of water-in-oil emulsions. Silica nanoparticles (1.5wt.%) were dispersed in 1-Bromohexadecane (68.3 wt.%) and ultrasonicated at 75 % amplitude for 1 minute in order to completely disperse the nanoparticles. DI water (30.15 wt.%) was added in a drop wise manner to the mixture containing 1-Bromohexadecane and silica nanoparticles. The mixture was sheared at 10,000 rpm for 10 minutes. The resulting solid-stabilized emulsion was diluted by adding 1-Bromohexadecane. The diluted emulsion had 70.7 wt.% 1-Bromohexadecane, 27.9 wt.% water, and 1.4 wt.% nanoparticles. The chosen concentration of nanoparticles to stabilize the water-in-oil emulsions was based on bottle tests.

Surfactant was added to the solid-stabilized emulsion at two different concentrations: a) 26% of the nanoparticle concentration (Span 80 (S1)) b) same amount as the nanoparticles (Span 80 (S2)). Surfactant was added to the solid-stabilized emulsion as follows: required amount of surfactant was dispersed in 1-Bromohexadecane (that was used for dilution). Then, 1-Bromohexadecane along with Span 80 was added to the solid-stabilized emulsion and gently shaken (using hand) to mix the oil with the emulsion.

Bottle tests were carried out to test the bulk stability of water-in-oil emulsions over the experimental time. The emulsions were observed before and after the experiment under an Olympus BX53 cross-polarized optical microscope equipped with a high-speed camera in order to ensure structural stability over the experimental time. Image J was used to quantify the droplet size of water-in-oil emulsions.<sup>50</sup>

# 2.3.2 Rheology of emulsions

Discovery Hybrid Rheometer (DHR-3),<sup>51</sup> which was purchased from TA instruments, was used to measure the rheological behavior of water-in-oil emulsions. In order to avoid the sedimentation of water droplets, 1-Bromohexadecane, which has a density similar to that of water, was used as the

continuous phase. The parallel plate geometry was used to measure the viscosity of water-in-oil emulsions. The shear rate was varied from 1 to 200 s<sup>-1</sup>. A solvent trap was used to minimize the loss of sample due to evaporation. The viscoelastic behavior of solid-stabilized water-in-oil emulsions was investigated by performing oscillatory strain measurements at 1 Hz.

# 2.3.3 Confocal microscopy

Confocal microscopy experiments (Leica TCS SP2 confocal microscope) were carried out to understand the spatial distribution of hydrophobic nanoparticles upon surfactant addition. The procedure to fluorescently label hydrophobic silica nanoparticles can be found elsewhere. <sup>54, 72</sup>

## 2.4 Results and Discussion

# 2.4.1 Characterization of emulsions

Figure 2.1 shows the optical microphotographs of water-in-oil emulsions stabilized using partially hydrophobic nanoparticles at the 0<sup>th</sup> hour and after 24 hours.



Figure 2.1: Microphotographs of water-in-oil emulsions stabilized using partially hydrophobic nanoparticles (R711) a) 0<sup>th</sup> hour b) after 24 hours

Figure S1 shows the corresponding droplet size distribution. It was evident from Figures 1 and S1 that there was no significant change in the droplet size of emulsions. Also, the bottle tests showed no bulk phase separation of water and 1-Bromohexadecane. Similar tests were carried out for other systems that were investigated. From the above results, it was concluded that the emulsions under investigation were stable over the experimental time both at the macroscopic and microscopic level.



Figure 2.2: Droplet size distribution for water-in-oil emulsions stabilized by partially hydrophobic nanoparticles (R711) at the 0<sup>th</sup> hour and after 24 hours

# 2.4.2 Influence of surfactant addition on droplet size

Figure 2.3 shows the microphotographs of water-in-oil emulsions stabilized by partially hydrophobic nanoparticles in both the presence and absence of a surfactant. Figure 2.4 shows the corresponding droplet size distribution. It was evident that there was no appreciable change in the droplet size of water-in-oil emulsions upon the addition of a surfactant.



Figure 2.3: Microphotographs of water-in-oil emulsions stabilized using partially hydrophobic nanoparticles (R711) in the a) absence of a surfactant b) upon the addition of Span 80 (S1) c) upon the addition of Span 80 (S2)



Figure 2.4: Droplet size distribution for water-in-oil emulsions stabilized using partially hydrophobic nanoparticles (R711) in the absence of a surfactant, upon the addition of Span 80 (S1) and upon the addition of Span 80 (S2)

Figure 2.5 shows the microphotographs of water-in-oil emulsions stabilized by hydrophobic nanoparticles in both the presence and absence of a surfactant. Figure 2.6 shows the corresponding droplet size distribution. By comparing Figures 2.3 and 2.5, it can be seen that there was a significant effect on the droplet size upon the addition of a surfactant to water-in-oil emulsions stabilized by hydrophobic nanoparticles unlike water-in-oil emulsions stabilized by partially hydrophobic nanoparticles.



Figure 2.5: Microphotographs of water-in-oil emulsions stabilized using hydrophobic nanoparticles (R812S) in the a) absence of a surfactant b) upon the addition of Span 80 (S1) c) upon the addition of Span 80 (S2)



Figure 2.6: Droplet size distribution for water-in-oil emulsions stabilized using hydrophobic nanoparticles (R812S) in the absence of a surfactant, upon the addition of Span 80 (S1) and upon the addition of Span 80 (S2)

The droplets became finer upon the addition of a surfactant to water-in-oil emulsions stabilized by hydrophobic nanoparticles. Under simple shear flow, tip streaming is observed upon surfactant accumulation at the tips of drops.<sup>77</sup> Tip streaming is usually observed when the ratio of the viscosities of dispersed and continuous phase is < 0.1. In our work, the ratio of viscosities of the dispersed phase to continuous phase was 0.15. Hence, in congruence with De Bruijn<sup>77</sup>, we observed the formation of satellite drops upon the addition of a surfactant (from Figures 2.5a and 2.5b). Also, from Figures 2.3a and 2.5a, it was observed that water-in-oil emulsions stabilized by only hydrophobic nanoparticles had a larger droplet size than water-in-oil emulsions stabilized by only partially hydrophobic nanoparticles. This can be attributed to the lower energy of adsorption of hydrophobic nanoparticles to the liquid-liquid interface than partially hydrophobic

nanoparticles.<sup>12</sup> By comparing Figure 2.5 with the droplet size distribution for water-in-oil emulsions stabilized by only a surfactant (Figure 2.7), we observed that upon increasing the addition of a surfactant to water-in-oil emulsions stabilized by hydrophobic nanoparticles, the droplet size is predominantly dictated by surfactants<sup>78</sup> than hydrophobic nanoparticles presumably due to the adsorption of surfactants onto the oil-water interface.



Figure 2.7: Droplet size distribution of surfactant stabilized (1.5 wt.% Span 80) water-in-oil emulsions

In order to further investigate the above-mentioned observations, confocal microscopy experiments were performed. Figure 2.8 shows the confocal microscopy images of water-in-oil

emulsions stabilized by nanoparticles upon the addition of a surfactant. Figures 2.9 and 2.10 show the confocal microscopy image of emulsions stabilized by only nanoparticles.



Figure 2.8: Confocal microscopy images of water-in-oil emulsions upon the addition of Span 80 (S2) to emulsions stabilized using a) hydrophobic nanoparticles (R812S) b) partially hydrophobic nanoparticles (R711) Scale bar: 50 μm


Figure 2.9: Confocal microscopy image of water-in-oil emulsions stabilized by hydrophobic nanoparticles (R812S) in the absence of a surfactant. Scale bar: 50 µm



Figure 2.10: Confocal microscopy image of water-in-oil emulsions stabilized by hydrophobic nanoparticles (R812S) in the absence of a surfactant. Scale bar: 50 µm

In the absence of a surfactant, the hydrophobic particles were located at the oil-water interface (Figure 2.9). In contrast, upon the addition of a surfactant, the hydrophobic nanoparticles tend to be partially dispersed in the continuous phase (Figure 2.8a). Thus, the addition of a non-ionic surfactant to water-in-oil emulsions stabilized using hydrophobic nanoparticles aided in partial displacement of hydrophobic nanoparticles (Figure 2.8a). The surfactant adsorption onto the liquid-liquid interface aided in decreasing the droplet size of emulsions (Figure 2.5). Raman et al.<sup>72</sup> observed that Span 80 did not adsorb strongly onto R812S (hydrophobic) nanoparticles. Therefore, our results indicated that particle detachment from the oil-water interface appeared not

to be linked with the change in hydrophobicity of nanoparticle upon surfactant adsorption, which was in accordance with the observations of Vashisth et al.<sup>73</sup>. On the contrary, from Figure 2.8b, it appeared that the addition of a non-ionic surfactant to water-in-oil emulsions stabilized using partially hydrophobic nanoparticles did not aid in appreciable displacement of partially hydrophobic nanoparticles.

## 2.4.3 Rheology of suspensions and emulsions

## 2.4.3.1 Suspensions

Figure 2.11 shows the viscosity of 1-Bromohexadecane upon the addition of nanoparticles and surfactants. 1-Bromohexadecane exhibited a Newtonian behavior. Even upon the addition of 1.5 wt.% R812S (hydrophobic) nanoparticles, and 1.5 wt.% R812S with Span 80 (S2), 1-Bromohexadecane exhibited a Newtonian behavior.



Figure 2.11: Viscosity versus shear rate for 1-Bromohexadecane upon the addition of nanoparticles and surfactants

Table 2.1 shows the viscosity of suspensions that exhibited Newtonian behavior. Based on our results, it was evident that hydrophobic nanoparticles did not show a stronger tendency for agglomeration<sup>79</sup> in both the presence and absence of Span 80. On the contrary, 1-Bromohexadecane exhibited a shear-thinning behavior upon the addition of partially hydrophobic nanoparticles. Also, the addition of partially hydrophobic nanoparticles significantly increased the viscosity of 1-Bromohexadecane unlike hydrophobic nanoparticles. The number of -OH groups on the surface of hydrophobic nanoparticles are lower than partially hydrophobic nanoparticles. Therefore, the interactions between partially hydrophobic nanoparticles (via hydrogen bonding) are higher than hydrophobic nanoparticles.<sup>80</sup> Thus, our results indicated that the presence of partially hydrophobic nanoparticles led to formation of a stronger 3D network<sup>29</sup> in 1-Bromohexanedecane than hydrophobic nanoparticles. Interestingly, upon the addition of a surfactant, the viscosity of 1-Bromohexadecane containing partially hydrophobic nanoparticles reduced significantly and exhibited a Newtonian behavior. Raman et al. <sup>72</sup> observed that sorbitan monooleate strongly adsorbs onto the surface of partially hydrophobic silica nanoparticles than hydrophobic nanoparticles. Thus, we postulate that the presence of a surfactant breaks the interactions between partially hydrophobic nanoparticles by adsorbing onto the surface of nanoparticles, thereby leading to a decrease in viscosity, which was in accordance with the literature.73

System	Newtonian Viscosity (Pa s)
1-Bromohexadecane	0.0074
1-Bromohexadecane + 1.5wt.% R812S	0.011
1-Bromohexadecane + 1.5wt.% R812S + Span 80 (S2)	0.0106
1-Bromohexadecane + 1.5wt.% R711 + Span 80 (S2)	0.0142

Table 2.1: Viscosity of 1-Bromohexane in the presence of nanoparticles and suspensions

#### 2.4.3.2 Emulsions

Figure 2.12 shows the viscosity of water-in-oil emulsions stabilized using nanoparticles in both the presence and absence of a surfactant. Water-in-oil emulsions stabilized by either partially hydrophobic or hydrophobic nanoparticles showed a shear thinning behavior (Figure 2.12). Even upon the addition of a surfactant, water-in-oil emulsions stabilized using partially hydrophobic nanoparticles showed a shear thinning behavior (Figure 2.12a).



Figure 2.12: Viscosity versus shear rate for Pickering emulsions stabilized using either a) partially hydrophobic nanoparticles (in both the presence and absence of a surfactant) or b) hydrophobic nanoparticles (in both the presence and absence of a surfactant)

Upon the addition of a surfactant, there was a decrease in the viscosity of water-in-oil emulsions stabilized using partially hydrophobic nanoparticles. In contrast, the viscosity of emulsions stabilized by hydrophobic nanoparticles increased upon surfactant addition. This can be attributed to the change in the droplet size. Upon the addition of a surfactant, the droplets became finer that in turn led to an increase in viscosity. Overall, the emulsions that were investigated showed a pseudoplastic behavior.<sup>81,82</sup> The shear thinning behavior was profound for water-in-oil emulsions stabilized using partially hydrophobic nanoparticles than hydrophobic nanoparticles. Water-in-oil emulsions stabilized using partially hydrophobic nanoparticles have higher viscosity than water-in-oil emulsions stabilized using bydrophobic nanoparticles. This can be attributed to the

formation of a stronger 3D network in the continuous phase by partially hydrophobic nanoparticles (as discussed in section 2.4.3.1).

#### 2.4.4 Oscillatory Measurements

The strength of the network structure in water-in-oil emulsions can be characterized from the storage (G') and loss (G") moduli.<sup>83</sup> Figure 2.13a shows the storage and loss moduli of water-in-oil emulsions stabilized by partially hydrophobic nanoparticles upon the addition of a surfactant. Linear viscoelastic region was observed at low strain ranges where the storage and loss moduli were independent of the applied strain.<sup>84</sup>



Figure 2.13: Storage (G') and loss moduli (G") of water-in-oil emulsions stabilized by either partially hydrophobic nanoparticles (a) or hydrophobic nanoparticles (b) in the presence and absence of a surfactant

For water-in-oil emulsions stabilized by partially hydrophobic nanoparticles, both in the presence and absence of a surfactant, viscoelastic solid like behavior was observed (G' > G''). The storage modulus was highest for water-in-oil emulsions stabilized by only partially hydrophobic nanoparticles. Upon increasing the surfactant addition, the storage modulus, which indicated the elastic properties of emulsions, decreased. This result was in congruence with Figure 2.10a; wherein, the addition of a surfactant increased the fluidity of emulsions stabilized using partially hydrophobic nanoparticles. Figure 2.13b shows the storage and loss moduli of water-in-emulsions stabilized by hydrophobic nanoparticles upon the addition of a surfactant. Similar to water-in-oil emulsions stabilized by partially hydrophobic nanoparticles, linear viscoelastic region was observed at low strain ranges for emulsions stabilized by hydrophobic nanoparticles (in both the presence and absence of a surfactant). Viscoelastic solid like behavior (G' > G'') was observed for emulsions stabilized by only hydrophobic nanoparticles and emulsions stabilized by hydrophobic nanoparticles upon the addition of Span 80 (S2).

The storage modulus was decreased upon the addition of Span 80 (S1) to water-in-oil emulsions stabilized by hydrophobic nanoparticles. On the other hand, the storage modulus values were comparable for water-in-oil emulsions stabilized by only hydrophobic nanoparticles, and waterin-oil emulsions stabilized using hydrophobic nanoparticles upon the addition of Span 80 (S2). This can be attributed to the change in the droplet size of water-in-oil emulsions upon the addition of a surfactant. From Figure 2.5, it can be observed that water-in-oil emulsions stabilized using only hydrophobic nanoparticles resulted in coarse emulsions. On the contrary, the addition of Span 80 (S2) resulted in fine emulsions. The addition of Span 80 (S1) resulted in emulsions containing a mixture of coarse and fine emulsion droplets. Pal et al. <sup>59</sup> investigated the effect of droplet size on the rheology of emulsions. They observed that the storage modulus of coarse emulsions were higher than the storage modulus of emulsions containing a mixture of coarse and fine emulsion droplets. Also, they observed that fine emulsions had higher storage modulus than coarse emulsions. In congruence with results of Pal et al.<sup>59</sup>, we observed that the addition of Span 80 (S1) to water-in-oil emulsions stabilized using hydrophobic nanoparticles lowered the storage modulus, since it resulted in a mixture of fine and coarse emulsion droplets. Also, from the work of Pal et al.,<sup>59</sup> we would expect that upon the addition of Span 80 (S2) to water-in-oil emulsions stabilized by hydrophobic nanoparticles (which resulted in fine emulsions), the storage modulus would be higher than water-in-oil emulsions stabilized by only hydrophobic nanoparticles (coarse

emulsions). However, we observed that the storage modulus values were comparable. We postulate that the surfactants can act as plasticizing agent in the presence of nanoparticles, which can lead to lower storage modulus values than emulsions stabilized by only nanoparticles.<sup>85</sup> Although the water-in-oil emulsions stabilized by only hydrophobic nanoparticles had coarse droplets, the presence of a 3D network in the continuous phase presumably resulted in storage modulus values comparable to that of water-in-oil emulsions stabilized using hydrophobic nanoparticles upon the addition of Span 80 (S2) (which resulted in fine droplets).

## **2.5 Conclusions**

We investigated the effect of surfactant addition to water-in-oil emulsions stabilized by either partially hydrophobic or hydrophobic silica nanoparticles under negligible shear conditions. Depending upon the nanoparticle wettability, the addition of a non-ionic surfactant to a particlestabilized emulsion affected the emulsion morphology and rheology. Our results showed the addition of a surfactant to a Pickering emulsion stabilized by partially hydrophobic nanoparticle did not affect the droplet size of emulsions. <sup>70, 74</sup> On the contrary, we found that surfactant addition to emulsions stabilized by hydrophobic nanoparticles resulted in the transition of a coarse emulsion to a fine emulsion, which in turn affected the strength of the network structure of the emulsions. At the investigated surfactant concentrations, even under negligible shear conditions, surfactant addition to emulsions stabilized by hydrophobic nanoparticles resulted in the displacement of nanoparticles from the oil-water interface unlike emulsions stabilized by partially hydrophobic nanoparticles. Our results showed that the displacement of hydrophobic nanoparticles from the oil-water interface was not due to the change in nanoparticle wettability upon surfactant adsorption, which was in accordance with Vashisth et al.<sup>73</sup> Suspensions containing partially hydrophobic nanoparticles showed a shear thinning behavior unlike suspensions with hydrophobic nanoparticles. However, upon the addition of a surfactant, the suspension with partially hydrophobic nanoparticles displayed Newtonian behavior. Emulsions

stabilized using either hydrophobic or partially hydrophobic nanoparticles showed a shear thinning behavior in both the presence and absence of a surfactant.

Our results suggest that, depending on the nanoparticle wettability, the morphology and rheology of Pickering emulsions can be modified by non-ionic surfactant addition, even under negligible shear conditions. These results have implications in drug delivery, recycling of particles that are used as encapsulates, and separation of particles from the oil-water interface.<sup>73,70,86,87</sup>

#### 2.6 Acknowledgments

We thank Dr. Victor Lifton of Evonik for donating the silica nanoparticles and providing consultation. We thank Brent Johnson of Oklahoma State University for helping us with confocal microscopy. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## CHAPTER III

# INFLUENCE OF SURFACTANTS AND NANOPARTICLES ON THE FORMATION AND RHEOLOGY OF OIL-IN-OIL EMULSIONS

Under review in Langmuir

#### 3.1 Abstract

Surfactant-nanoparticle interactions are expected to influence the type and stability of emulsions. In this work, we investigated the influence of mixed surfactant/nanoparticle emulsifier system on the behavior of oil-in-oil (O/O) emulsions. Vegetable (soybean) oil and silicone oils (50 cSt and 100 cSt) were used to form oil-in-oil emulsions. Surfactants with varying HLB values (Span 80/Triton X-100) and hydrophobic silica nanoparticles were used as emulsifiers. Simultaneous emulsification using hydrophobic nanoparticles and a surfactant (either Span 80 or Triton X-100) resulted in a single-step formation of multiple oil-in-oil-in-oil (O/O/O) emulsions. Regardless of the initial phase to which the surfactant was added, simultaneous emulsification using surfactants and hydrophobic nanoparticles led to the formation of multiple emulsions. The addition of Span 80 to a vegetable oil-in-PDMS oil (VO/PDMS) emulsion stabilized by only hydrophobic nanoparticles resulted in the formation of a multiple PDMS/VO/PDMS emulsion. Multiple O/O/O emulsions had lower viscosity when compared to simple O/O emulsions. Simple O/O emulsions had a lower degree of shear thinning behavior when compared to multiple O/O/O emulsions.

## **3.2 Introduction**

Oil-water Pickering emulsions,<sup>12</sup> air-water foams,<sup>88</sup> and air-oil foams<sup>89</sup> can be stabilized by the adsorption of particles at the fluid-fluid interface. Particle adsorption at the oil-water interface is well studied.<sup>90</sup> On the contrary, there is very limited understanding on particle adsorption at the non-aqueous interfaces especially at the oil-oil interface.<sup>91</sup> Water-free or non-aqueous system refers to a system in which the water phase in a water-oil system is replaced by either a polar solvent, or a liquid polymer.<sup>91</sup> Although, there have been some studies in the literature where water in a water-oil system has been replaced by a polar solvent,<sup>92-94</sup> liquid polymer oil,<sup>95-98</sup> or immiscible polymer blends<sup>99-101</sup> due to wide industrial applications, literature studies on true oiloil emulsions (oils with low dielectric constant < 3) is deficient.<sup>91</sup> A summary of literature studies on true oil-in-oil emulsions can be found elsewhere.<sup>80</sup> Oil-in-oil emulsions have wide applications in cosmetics<sup>102-104</sup>, drug delivery<sup>105-107</sup>, catalysis<sup>108</sup>, electronics<sup>109-111</sup> and personal care.<sup>102, 112-114</sup> Formation of stable oil-in-oil emulsions using surfactants are extremely difficult.<sup>115</sup> Recently, Binks et al.<sup>80</sup> performed a systematic investigation on the stabilization of oil-in-oil emulsions by using only solid particles. They concluded that wettability of particles play a significant role in determining the type of emulsions (vegetable-in-silicone oil or silicone oil-in-vegetable oil). Increasing the hydrophobicity of the particles favored the formation of vegetable oil-in-silicone oil emulsions. They also observed that multiple oil-in-oil emulsions can be formed by a two-step procedure using particles of different wettability.<sup>80, 115</sup>

To the best of our knowledge, the influence of mixed emulsifier (surfactant and nanoparticles) systems on oil-in-oil emulsion behavior has not been investigated. Our work elucidates the influence of combined interactions between surfactants and nanoparticles on the formation of oil-in-oil emulsions. Single-step formation of multiple oil-in-oil-in-oil (O/O/O) emulsions was observed upon simultaneous emulsification using hydrophobic nanoparticles and a surfactant. We also investigated the influence of combined interactions between surfactants between surfactants and nanoparticles on

the rheological behavior of oil-in-oil emulsions.

#### 3.3 Materials and methods

For the preparation of oil-in-oil emulsions, Polydimethylsiloxane (PDMS) silicone oils of viscosity 50 cSt ( $\rho = 0.959$  g/cc) and 100 cSt ( $\rho = 0.964$  g/cc) were used as the continuous phase. Vegetable (soybean) oil ( $\rho = 0.917$  g/cc) was used as the dispersed phase. Both the silicone oils and vegetable oil had a low dielectric constant ( $\varepsilon < 3$ ).<sup>80, 116</sup> The oil densities were measured using Metler Toledo DA – 100M density meter. Hydrophobic fumed silica nanoparticles (Aerosil R812S) were received from Evonik Corporation. The surface substitution of silanol (3 - 4 %) by hexamethyldisiloxane made Aerosil R812S hydrophobic .<sup>30</sup> In this work, two surfactants – Sorbitan monooleate (Span 80) and Octylphenol Ethoxylate (Triton X-100, TX-100) – with varying HLB values were purchased from Sigma Aldrich and used as received. Span 80 is a non-ionic surfactant with an HLB value of  $4.3 \pm 1$  (commonly used to stabilize water-in-oil emulsions). Triton X-100 (TX-100) is a non-ionic surfactant with an HLB value of 13.4 (commonly used to stabilize oil-in-water emulsions).

## 3.3.1 Preparation of emulsions

For the preparation of solid-stabilized emulsions, hydrophobic silica nanoparticles (1.5 wt.%) were first dispersed in either 50 cSt or 100 cSt PDMS oil (68.33 wt.%). In order to uniformly disperse the nanoparticles, PDMS oil containing hydrophobic nanoparticles was ultrasonicated at 75 % amplitude for 1 minute. Then, the vegetable oil (30.14 wt.%) was added to the PDMS oil containing nanoparticles in a drop-wise manner, while shearing the mixture at 10,000 rpm. The mixture was sheared for 10 minutes. Then, the emulsion was diluted by adding the PDMS oil. After dilution, the emulsion contained 70.68 wt.% PDMS oil, 1.41 wt.% nanoparticles and 27.9 wt.% vegetable oil.

For the preparation of surfactant-solid stabilized emulsions, two cases were considered: (i) simultaneous emulsification using surfactants and nanoparticles, and (ii) the addition of a surfactant to a Pickering emulsion. Case (i) – for simultaneous emulsification, the surfactant was added either to the vegetable oil or PDMS oil before emulsion formation and no surfactant was added during the dilution of emulsion with the PDMS oil. Case (ii) – the surfactant was added to the Pickering emulsion as follows: the required amount of surfactant (Span 80 or Triton X-100) was added to the PDMS oil (that was used for dilution). The mixture was shaken to mix the surfactant with the PDMS oil. Then, the PDMS oil containing a surfactant was added to the Pickering emulsion and gently shaken (using hand) to mix the oil with the Pickering emulsion. In both the cases, surfactant concentration was kept similar to the particle concentration.

Bottle tests were carried out to investigate the macroscopic stability of the emulsion during the experimental time. Furthermore, in order to ensure that the structure of emulsions were not altered during the experimental time, the emulsions were observed before and after the experiments using an Olympus BX53 cross-polarized optical microscope equipped with a high speed camera. Image J was used to quantify the droplet size distribution.<sup>50</sup>

#### 3.3.2 Rheology

The rheology of emulsions was investigated using a stress-controlled Discovery Hybrid Rheometer (DHR-3). The parallel plate geometry with a solvent trap was used to measure the viscosity of suspensions and emulsions. The shear rate was varied from 1 to  $200 \text{ s}^{-1}$ .

## 3.3.3 Confocal microscopy

The hydrophobic nanoparticles were dyed using 3-aminopropyltriethoxysilane (APTES) and fluorescein isothiocyanate (FITC).<sup>72</sup> The procedure to fluorescently label hydrophobic silica nanoparticles can be found elsewhere. <sup>54</sup>

#### **3.4 Results and Discussion**

## 3.4.1 Characterization of emulsions

The mutual solubility of vegetable (soybean) oil and PDMS oil was assessed to ensure that the oils were immiscible.<sup>80</sup> Equal volumes of vegetable oil and PDMS oil were placed in a glass vial and vigorously shaken. The volume of the separated phases was observed after one day (Fig 3.1). It was evident that vegetable oil and PDMS oil were immiscible.



Figure 3.1: Vial containing equal volumes of 50 cSt PDMS oil and vegetable (soybean) oil (after 24 hours).

Figure 3.2 shows the microphotographs of vegetable oil-in-50 cSt PDMS oil emulsion at the 0<sup>th</sup> hour and after the experimental time along with the droplet size distribution. From Figure 3.2, it was evident that there was no significant change in the droplet size of the emulsion during the experimental time and there was no bulk phase separation of vegetable oil and 50 cSt PDMS oil. Similar tests were carried out for all the emulsions that were investigated in this study. From the

results, it was concluded that all the emulsions that were investigated in this work were stable both at the microscopic and macroscopic level.



Figure 3.2: Microphotographs of vegetable oil-in-50 cSt PDMS oil emulsion at the 0<sup>th</sup> hour (a) and after the experimental time (b) along with the corresponding droplet size distribution (c).

In order to understand the synergistic interactions between surfactants and hydrophobic nanoparticles on emulsion formation, it is critical to first understand the formation of emulsions solely stabilized by either nanoparticles or surfactants.

## 3.4.2 Emulsions stabilized solely by hydrophobic nanoparticles

In congruence with Binks et al.<sup>80</sup>, highly hydrophobic nanoparticles led to formation of stable vegetable (soybean) oil-in-PDMS oil (VO/PDMS) emulsion. Figure 3.3 shows the microphotographs of vegetable oil-in-50 cSt PDMS oil (VO/PDMS (50 cSt)) emulsion and vegetable oil-in-100 cSt PDMS oil (VO/PDMS (100 cSt)) emulsion stabilized using hydrophobic nanoparticles along with the droplet size distribution.



Figure 3.3: Microphotographs of a) vegetable oil-in-50 cSt PDMS oil (VO/PDMS (50 cSt)) emulsions stabilized by only hydrophobic nanoparticles b) vegetable oil-in-100 cSt PDMS oil

(VO/PDMS (100 cSt)) emulsions stabilized by only hydrophobic nanoparticles c) corresponding droplet size distribution.

From Figure 3.3, it was observed that the droplet size was slightly smaller for emulsions with 50 cSt PDMS oil as the continuous phase when compared to emulsions with 100 cSt PDMS oil as the continuous phase. This can be attributed to lower homogenization efficiency with an increase in the viscosity of the continuous phase.<sup>117</sup> Figure 3.4 shows the confocal microscopy image of VO/PDMS emulsion stabilized by only hydrophobic nanoparticles. From Figure 3.4, it was evident that the hydrophobic nanoparticles were predominantly located at the oil-oil interface.



Figure 3.4: Confocal microscopy image of vegetable oil-in-PDMS oil (VO/PDMS) emulsion stabilized by only hydrophobic nanoparticles with 50 cSt PDMS oil (a) and 100 cSt PDMS oil (b) as the continuous phase

## 3.4.3 Emulsions solely stabilized by surfactants

Surfactant-stabilized (using either Span 80 or Triton X-100) VO/PDMS emulsions were unstable to coalescence at the investigated surfactant concentration (1.5 wt.%). We observed that both the

surfactants were preferentially more soluble in vegetable oil as compared to the silicone oils (Figures 3.5 and 3.6). Bancroft's rule states that the phase in which the emulsifier is soluble constitutes the continuous phase.<sup>118</sup> Since the surfactants were not soluble in the PDMS oil (which constituted to 70.68 wt.% of the total emulsion), stable VO/PDMS emulsions could not be formed with Span 80 or Triton X-100.



Figure 3.5: Addition of Span 80 to PDMS oil (50 cSt and 100 cSt) and vegetable oil a) immediately after the addition of Span 80 b) after 24 hours



Figure 3.6: Addition of Triton X-100 to PDMS oil (50 cSt and 100 cSt) and vegetable oil a) immediately after the addition of Span 80 b) after 24 hours

## 3.4.4 Surfactant-solid stabilized emulsions

## 3.4.4.1 Simultaneous emulsification of surfactants and nanoparticles

Figures 3.7 and 3.8 show the microphotographs of PDMS/VO/PDMS emulsions stabilized using hydrophobic nanoparticles and a surfactant (either span 80 or Triton X-100). Upon simultaneous emulsification of a surfactant (either Span 80 or Triton X-100) with the hydrophobic nanoparticles, multiple emulsions of PDMS oil-in-vegetable oil-in-PDMS oil (PDMS/VO/PDMS) were formed (Figures 3.7 and 3.8). To the best of our knowledge, this work is the first to report single-step formation of oil-in-oil multiple emulsions.



R812S + TX-100 (premix in PDMS) R812S + TX-100 (premix in VO)



Figure 3.7: Microphotographs of PDMS/VO/PDMS emulsions stabilized using hydrophobic

nanoparticles and a surfactant (either span 80 or Triton X-100). PDMS oil viscosity = 50 cSt. Premix refers to the addition of a surfactant to the oil phase before emulsion formation.

R812S + S80 (premix in PDMS) R812S + S80 (premix in VO)

R812S + TX-100 (premix in PDMS) R812S + TX-100 (premix in VO)



Figure 3.8: Microphotographs of PDMS/VO/PDMS emulsions stabilized using hydrophobic nanoparticles and a surfactant (either span 80 or Triton X-100). PDMS oil viscosity = 100 cSt. Premix refers to the addition of a surfactant to the oil phase before emulsion formation.

Also, multiple oil-in-oil emulsions using both surfactants and solid particles have not been reported elsewhere to the best of our knowledge. Multiple emulsions are usually formed using two surfactants that have very different HLB values (in case of surfactant stabilized multiple emulsions<sup>119</sup>) or two particles that have very different wettability (in case of particle stabilized

multiple emulsions<sup>115</sup>). We postulate that since the surfactants were preferentially miscible with the vegetable oil (Figures 3.5 and 3.6) and the hydrophobic nanoparticles favor the formation of VO/PDMS emulsion, simultaneous emulsification of both surfactant and nanoparticles led to formation of multiple oil-in-oil-in-oil (PDMS/VO/PDMS) emulsions. Both 50 cSt and 100 cSt PDMS oils showed similar behavior.

## 3.4.4.2 Surfactant addition to a Pickering emulsion

Figure 3.9 shows the microphotographs of emulsions upon the addition of a surfactant (either Span 80 or Triton X-100) to an existing vegetable oil-in-PDMS oil emulsion stabilized by hydrophobic nanoparticles. Upon the addition of Triton X-100, even under negligible shear conditions, multiple oil-in-oil-in-oil (PDMS/VO/PDMS) emulsions were formed. In contrast, the addition of Span 80 to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles did not result in the formation of a multiple emulsion.



Figure 3.9: a) Microphotograph of emulsion upon the addition of Triton X-100 to an existing VO/PDMS (50 cSt) emulsion stabilized by only hydrophobic nanoparticles b) microphotograph of emulsion upon the addition of Span 80 to an existing VO/PDMS (50 cSt) emulsion stabilized by only hydrophobic nanoparticles c) microphotograph of emulsion upon the addition of Triton X-100 to an existing VO/PDMS (100 cSt) emulsion stabilized by only hydrophobic nanoparticles b) microphotograph of emulsion upon the addition of Span 80 to an existing VO/PDMS (100 cSt) emulsion stabilized by only hydrophobic nanoparticles b) microphotograph of emulsion upon the addition of Span 80 to an existing VO/PDMS (100 cSt) emulsion stabilized by only hydrophobic nanoparticles

Furthermore, the addition of span 80 did not have a significant influence on the droplet size of VO/PDMS emulsion stabilized using hydrophobic nanoparticle (by comparing Figures 3.3, 3.10 and 3.11).



Figure 3.10: Droplet size distribution of VO/PDMS (50 cSt) emulsion stabilized by hydrophobic nanoparticles upon the addition of Span 80. Postmix (in legend) refers to the addition of a surfactant to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles.



Figure 3.11: Droplet size distribution of VO/PDMS (100 cSt) emulsion stabilized by hydrophobic nanoparticles upon the addition of Span 80. Postmix (in legend) refers to the addition of a surfactant to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles.

Figure 3.12 shows the confocal microscopy images for VO/PDMS emulsions stabilized by hydrophobic nanoparticles upon the addition of Span 80. It can be observed that the addition of Span 80 did not displace the nanoparticles from the oil-oil interface presumably due to the higher desorption energy of hydrophobic nanoparticles from the oil-oil interface. Thus, no change in the droplet size of VO/PDMS emulsions stabilized by hydrophobic nanoparticles was observed upon the addition of Span 80. Both 50 cSt and 100 cSt PDMS oils showed similar behavior.



Figure 3.12: Confocal microscopy images upon the addition of Span 80 to an existing VO/PDMS (50 cSt) emulsion (a) and VO/PDMS (100 cSt) emulsion (b) stabilized by hydrophobic nanoparticles

# 3.4.5 Rheology of suspensions and emulsions

## 3.4.5.1 Suspensions

Figure 3.13 shows the viscosity versus shear rate for the oils under investigation in both the presence and absence of either a surfactant or hydrophobic nanoparticles. Pure vegetable oil and the silicone oils showed a Newtonian behavior.



Figure 3.13: Viscosity versus shear rate for the oils under investigation in both the presence and absence of either a surfactant or hydrophobic nanoparticles

Vegetable oil exhibited a Newtonian behavior and showed no significant change in viscosity upon the addition of a surfactant (Span 80 or Triton X-100). However, the viscosity of 50 cSt PDMS oil and 100 cSt PDMS oil increased (by > 50%) upon the addition of hydrophobic nanoparticles possibly due to the formation of branched, agglomerated structures.<sup>79</sup> Both the silicone oils exhibited Newtonian behavior even in the presence of 1.5 wt.% hydrophobic nanoparticles.

#### 3.4.5.2 Emulsions

Figure 3.14 shows the viscosity versus shear rate for both simple (VO/PDMS) and multiple (PDMS/VO/PDMS) emulsions. From the results, it was observed that VO/PDMS emulsion stabilized by only hydrophobic nanoparticles had the highest viscosity. The addition of Span 80 to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles decreased the

emulsion viscosity. The simple (VO/PDMS) emulsions had higher viscosity than multiple (PDMS/VO/PDMS) emulsions.



Figure 3.14: Viscosity versus shear rate for both simple (VO/PDMS) and multiple (PDMS/VO/PDMS) emulsions. Premix refers to the addition of a surfactant to the oil phase before emulsion formation. Postmix refers to the addition of a surfactant to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles.

The degree of shear thinning was lower for simple emulsions as compared to multiple emulsions. This can be attributed to larger deformation of multiple emulsion droplets under shear flow.<sup>120</sup> Simple emulsions had smaller droplet diameter as compared to multiple emulsions. Hence, the deformation of simple emulsion droplets will be lower when compared to multiple emulsion droplets under shear flow.<sup>120</sup> It was also observed that the multiple emulsions had similar viscosity irrespective of the initial phase to which the surfactant was added and the mode of surfactant addition. Furthermore, multiple emulsions formed using either Span 80 or Triton X-100 had similar viscosity. Thus, the type of surfactant did not affect the viscosity of multiple O/O/O emulsions.

#### **3.5 Conclusions**

We investigated the influence of mixed surfactant/nanoparticle emulsifier system on the behavior of oil-in-oil (O/O) emulsions. Polydimethylsiloxane (PDMS) oil (with two different viscosities – 50 cSt and 100 cSt) and vegetable (soybean) oil were used to form oil-in-oil emulsions. Hydrophobic silica nanoparticles and two surfactants (Span 80 and Triton X-100) with varying HLB values were used as stabilizers.

Multiple oil-in-oil (O/O/O) emulsions were formed in a single-step upon simultaneous emulsification using hydrophobic nanoparticles and a surfactant (either Span 80 or Triton X-100). During simultaneous emulsification, the initial phase to which the surfactant was added did not influence the formation of multiple O/O/O emulsions. To the best of our knowledge, this is the first time such single-step formation of multiple O/O/O emulsions is reported. In congruence with Binks et al.<sup>80</sup>, we observed that using only hydrophobic nanoparticles as a stabilizer resulted in the formation of stable vegetable oil-in-PDMS oil emulsions. We observed that the hydrophobic nanoparticles were not displaced from the oil-oil interface upon the addition of Span 80 to an existing simple VO/PDMS emulsion stabilized by hydrophobic nanoparticles. Hence, no significant influence on droplet size was observed upon the addition of Span 80 to an existing VO/PDMS emulsion stabilized by hydrophobic nanoparticles. In contrast, the addition of Triton X-100 to an existing simple VO/PDMS emulsion stabilized by hydrophobic nanoparticles resulted in the formation of a multiple PDMS/VO/PDMS emulsion. Multiple oil-in-oil-in-oil emulsions had a higher degree of shear thinning behavior when compared to simple oil-in-oil emulsions. Also, multiple O/O/O emulsions formed by simultaneous emulsification using hydrophobic nanoparticles and a surfactant had similar viscosities regardless of the initial oil phase to which the surfactant was added. These results can have significant implications in numerous applications<sup>80, 115</sup> including cosmetics<sup>102-104</sup>, drug delivery<sup>105-107</sup>, catalysis<sup>108</sup>, electronics<sup>109-111</sup> and personal care<sup>102, 112-114</sup>.

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## CHAPTER IV

# A COMPARISON OF THE RHEOLOGICAL BEHAVIOR OF HYDRATE FORMING EMULSIONS STABILIZED USING EITHER SOLID PARTICLES OR A SURFACTANT

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#### 4.1 Abstract

Simple clathrate hydrates are non-stoichiometric, ice-like crystalline compounds that can, among other things, cause blockages of oil and gas pipelines. More challenging exploration and development has emphasized the need to investigate the rheological behavior of hydrates in order to ensure continuous production of crude oil through pipelines especially for solid stabilized emulsions. Therefore, a difference in the rheological behavior of hydrate forming water-in-oil emulsions stabilized using either solid particles (aerosil R974, fumed silica particles) or a surfactant (Span 80, a non-ionic surfactant) over a range of water cuts is investigated. A rheometer with helical ribbon geometry was used to investigate the rheological behavior of hydrate slurries as opposed to conventional standard geometries. Cyclopentane was used as the hydrate-forming component. The results showed that hydrate formation was rapid in the presence of solid particles as compared to surfactant. We hypothesize that solid particles act as nucleation sites and reduce the induction time required for hydrate formation. In addition, the viscosity of water-in-oil emulsions increased with an increase in water cut. Hydrate forming emulsions formed using solid particles had a higher viscosity than emulsions formed using surfactant.

### 4.2 Introduction

Flow assurance problems are a major concern to offshore energy development <sup>121</sup>. Some of the flow assurance problems include formation of hydrates, waxes, asphaltenes, and corrosion of pipelines. Of all the flow assurance problems, hydrate formation is the most critical to address <sup>122</sup> because hydrate formation takes place within hours unlike waxes or asphaltenes that takes weeks or months to form. Simple clathrate hydrates are ice-like crystalline solid compounds. Hydrate structures have repetitive crystal units, which are made up of asymmetric and spherical-like cages of hydrogen bonded water molecules <sup>123</sup>. Hydrates consists of two components – host and guest molecules. In simple clathrate hydrates, the host molecule is water, whereas, the guest molecules are low molecular weight hydrocarbons such as methane, ethane, propane, and also gases such as carbon-di-oxide, nitrogen, oxygen, hydrogen sulphide etc. They are formed when guest molecules are completely enclosed inside the host molecules at suitable conditions. Based on the cage size and guest molecule, simple clathrate hydrates are classified into three predominant structures namely structure I, structure II, and structure H<sup>123</sup>. The cubic structure I, consists of 46 water molecules, arranged in such a way that two pentagonal dodecahedron  $(5^{12})$  and six tetrakaidecahedra (5<sup>12</sup>6<sup>2</sup>) are formed <sup>123, 124</sup>. The cubic structure II, predominantly man-made, consists of 136 water molecules, arranged in such a way that sixteen pentagonal dodecahedron  $(5^{12})$  and eight hexakaidecahedron  $(5^{12}6^4)$  are formed <sup>123, 124</sup>. Structure H hydrates, which consists of 34 water molecules, is formed by both large and small guest molecules <sup>123</sup>.

Hydrate formation, in an oil-dominated system (higher oil content), is an interfacial phenomenon that takes place when gas/hydrocarbon (guest) molecules that are dissolved in the oil phase come in contact with the water phase (host molecules) under suitable conditions. Hydrates are generally formed at high pressure and low temperatures <sup>123</sup>. However, cyclopentane and tetrahydrofuran (THF) hydrates are formed at atmospheric pressure. Although, THF hydrates are formed at atmospheric pressures, THF is miscible with water that restricts the mass transfer limitation that

is found to occur in gas hydrate forming emulsions in crude oil pipelines. Cyclopentane is a useful guest molecule for studying hydrates since both cyclopentane and natural gases form structure II hydrates. Cyclopentane hydrates have a dissociation temperature of 7°C <sup>125</sup>. Hence, in this study cyclopentane is used as the guest molecule to form hydrates.

Exploration of oil at more challenging conditions has emphasized the need to study hydrate formation in water-in-oil emulsions. Hydrate formation depends on crude oil properties. Crude oils have natural surfactants such as asphaltenes, resins, carboxylic acids that aid in formation of stable emulsions <sup>126, 127</sup>. These natural surfactants that adsorb on to the oil-water interface have both polar and non-polar ends that stabilize water droplets in crude oil. Also, twin-tailed or bulk tail surfactants are present in the crude oil to stabilize the water droplets. Thus, formation of water-in-oil emulsions becomes inevitable in crude oil production. Surfactants play an important role in formation of emulsions. Although, thermodynamics of hydrate formation is well understood, kinetics of hydrate formation <sup>128, 129</sup>. Hence, type of emulsion stabilizers used plays an important role in the process of hydrate formation.

Hydrate formation in crude oil pipelines leads to a decrease in effective flow path of crude oil and thereby leads to an increase in the pressure drop along the pipe. Also, during hydrate formation, the capillary forces between hydrate particles cause binding of water droplets leading to agglomeration that in turn increases the flow resistance. Hydrate formation generally causes an increase in pressure drop and can lead to blockage of the flow line. The phase transformation that takes place due to hydrate formation can alter the flow properties of a mixture that in turn affects the rheological behavior of the mixture. Viscosity of the mixture is essential in determining the pressure drop. Hence, knowledge of rheological behavior of hydrate systems will help in enhancing the design of multiphase pipelines. Hydrate management measures are typically more economically feasible than hydrate avoidance measures <sup>122</sup>. Also, hydrate remediation measures such as depressurization, thermal, and electrical heating methods become difficult to implement in subsea pipelines. Also, depressurization involves multiple safety concerns. Consequently, knowledge of rheological behavior of hydrates and the influence of surfactants and solid particles on flow properties becomes important for efficient hydrate management measures.

Karanjkar <sup>130</sup> studied the rheology of water-in-oil emulsions formed using Span 80 surfactant over varying water cuts. To extend this work, we focused on solid stabilized emulsions. Recent work by Ahuja <sup>131, 132</sup> showed the dependence of hydrate formation and rheology on particles concentration by adding solid particles to water-in-cyclopentane emulsions stabilized using Span 80. The objective of our work was to compare the rheological behavior of hydrate forming water-in-oil emulsions that are formed using either solid particles or a surfactant over a range of water fractions. In addition, a non-standard rheometer geometry (i.e., helical geometry) was used to characterize the rheology of hydrate forming water-in-oil emulsions as opposed to standard rheometer geometries.

## 4.3 Materials

The emulsions used in this study were formed using deionized water (resistivity of 17.3 m $\Omega$  cm<sup>-1</sup>), light mineral oil (+99% purity, Sigma Aldrich) and cyclopentane and iso-octane (+99% purity, Sigma Aldrich). The model oil emulsions were stabilized using Span 80 (Sorbitan Monooleate) and a hydrophobic silica nanoparticle (aerosil R974, provided by Evonik). Span 80 is an oil soluble, non-ionic surfactant with an HLB value <sup>2</sup> of  $4.3\pm1.0$  (as stated by vendor). Lachance et al. <sup>133</sup> have successfully used Span 80 molecules that are smaller than asphaltene molecules to resemble the surface activity of asphaltenes in crude oil. Hence, Span 80 was used as the surfactant in this study. Aerosil R974 is a hydrophobic fumed silica. The physical properties of

the components are given in Table 1. All materials used in this study were used without further purification.

This paper focuses on the rheology of oil continuous emulsions formed using either a surfactant or solid particles. The water cuts were varied from 10 Vol. % to 40 Vol. %. The Span 80/aerosil R974 concentration was fixed at 0.1 Vol. % based on the total volume. The critical micelle concentration (CMC) of Span 80 is 0.03 (%v/v)<sup>134, 135</sup>. Thus, the concentration of Span 80 was well above the CMC value. The oil phase was a mixture of light mineral oil and cyclopentane/Iso-Octane (50:50 by volume). The amount of cyclopentane was in excess of the stoichiometric requirement for formation of cyclopentane hydrates, which is one mole of cyclopentane to 17 moles of water. In this paper, hydrate forming water-in-oil emulsions refers to emulsions that contain light mineral oil and cyclopentane in the oil phase. The control system refers to water-in-oil emulsions in which the oil phase consists of light mineral oil and iso-octane. Cyclopentane was used as the hydrate-forming component.

# 4.3.1. Preparation of emulsions

All emulsions were prepared using an IKA T25 digital Ultra-Turrax homogenizer operating at 20,000 rpm for 20 minutes. The dispenser had a rotor diameter of 17mm and a stator diameter of 25mm. First, the cyclopentane/iso-octane was added to light mineral oil followed by the addition of the surfactant/solid particles. Then, the mixture was vigorously shaken so that the surfactant/solid particles was well mixed with the oil phase. In order to achieve homogeneous distribution of the droplet phase, water was added in a drop wise manner to the oil phase <sup>52</sup>. The droplet diameters for all systems investigated were less than 20µm due to high mixing speed. The control system consists of 40 Vol. % water, 0.1 Vol. % aerosil R974, 29.95 Vol. % light mineral oil and 29.95 Vol. % iso-octane.

#### 4.3.2 Emulsion characterization

Prior to investigating the rheology of hydrate forming water-in-oil emulsions, it must be ensured that the emulsions were stable during the phase of experiment in order to predict the rheological behavior. In order to ensure that the emulsions did not undergo a significant structural change, microscopic investigations were carried out.

The emulsions were characterized using an Olympus BX53 polarized optical microscope equipped with a Linkam temperature controlled shear stage and a high-speed camera. It is well equipped to characterize concentrated water-in-oil emulsions. The mean droplet size of the water-in-oil emulsions was observed immediately after preparation of the sample and after 12 hours. Images obtained from the microscope were analyzed using the ImageJ software. Figure 4.1 shows micrographs at the 0<sup>th</sup> hour and after 12 hours for 30 Vol.% water-in-oil emulsion stabilized using 0.1 Vol.% Aerosil R974.



Figure 4.1: Microphotographs of the 30 Vol.% water-in-oil emulsion stabilized using 0.1 Vol.% Aerosil R974 at different time periods (a)  $0^{\text{th}}$  hour, (b) after 12 hours.

Figure 4.2 and 4.3 shows the mean droplet size for water-in-oil emulsions stabilized using 0.1 Vol.% Span 80 and 0.1 Vol.% Aerosil R974 respectively at the 0<sup>th</sup> hour and after 12 hours. A statistical analysis was carried out to ensure that there is no statistical difference in droplet size between the 0<sup>th</sup> hour and the 12<sup>th</sup> hour. From the results, it was confirmed that the water-in-oil

emulsions were stable through out the experimental time. In addition, the settling of droplets in emulsions during the phase of the experiment, due to density difference, was avoided by use of a helical ribbon, which is discussed in detail in the sections below.



Figure 4.2: Comparison between the mean droplet sizes at the 0<sup>th</sup> hour and after 12 hours for water-in-oil emulsions stabilized using 0.1 Vol.% Span 80.


Figure 4.3: Comparison between the mean droplet sizes at the 0<sup>th</sup> hour and after 12 hours for water-in-oil emulsions stabilized using 0.1 Vol.% Aerosil R974.

# 4.4 Equipment

The rheology data was obtained using a stress-controlled Discovery Hybrid Rheometer (DHR-3 Rheometer) equipped with peltier temperature control, which can be varied from -20°C to 150°C, for rapid heating and cooling. The rheometer used in our study is shown in Figure 4.4.



Figure 4.4: Discovery Hybrid Rheometer -3 (DHR-3).

# 4.4.1 Experimental Protocol

The hydrate forming water-in-oil emulsions that were prepared using the IKA T25 digital ultraturrax homogenizer was placed in the rheometer that was pre-cooled to 15°C. Once the sample was placed, the temperature inside the rheometer was reduced to  $-2^{\circ}C$  after which ice crystals were added in order to reduce the long induction time required for hydrate formation to take place <sup>130</sup>. Once the ice crystals were added, the sample was maintained at  $-2^{\circ}C$  for 10 to 15 minutes before the experiment was set to run. This was done in order to reduce temperature fluctuation after the addition of ice crystals. Flow peak hold experiments were done at a fixed temperature of  $-2^{\circ}C$ , where the viscosity of sample is measured over time with constant shear rate of 10 s<sup>-1</sup>. In order to minimize the losses due to evaporation the sample was partially sealed during the experiment.

#### 4.4.2 Rheometer Geometry

Parallel-plate, cone-plate or concentric cylinder geometries are commonly used to characterize systems in the linear visco elastic regions. However, complex fluids are often difficult to measure under these conditions. Also, the rheology results of complex fluids are greatly influenced by the level of sedimentation during testing or slippage at the sample tool interface. Thus, measuring viscosity becomes a challenge. However, vane geometries have been used to study density matched water-in-oil emulsions <sup>131, 132, 136</sup>. Vane geometry is effective for measuring the yield stress of the samples and for localized structure disruption around the vane. The problem with using vane geometry for the systems in this study is that pockets of unmixed zones are created due to continuous settling which leads to inhomogeneous samples. This leads to the vane coring into the fluid, thereby separating the solids from the liquids <sup>137, 138</sup>. In order to avoid discrepancies associated with standard geometries for investigating the rheological behavior of complex fluids, a non-standard geometry is preferred. The benefits of using a non-standard geometry include measurement of apparent viscosity of complex fluids, continuous study of systems with large particles, and avoiding sedimentation. In addition, use of non-standard geometry helps in measuring the rheology of complex fluids under process-like conditions. Both the mixing time and power consumption during addition of solids or liquids can be studied. Thus, non-standard geometries can be used after adequate calibration based on the couette analogy to characterize complex fluid systems in transient and oscillatory testing regimes. Helical ribbon type fixtures are preferable since the mixing device with a complex geometry rotating inside a complex fluid can be used to resolve rheological characterization problems associated with standard geometries <sup>139</sup>. Helical ribbon is specifically designed to overcome the difficulties of measuring the viscosity of slurries. In addition, Aït-Kadi et al.<sup>140</sup> found that among various non-standard geometries helical

ribbon could produce reliable data. Helical ribbon geometry has large local spacing, providing continuous mixing, thereby preventing the solid particles from settling down <sup>140</sup>. In order to justify the above statements, an experiment was performed using both helical ribbon and vane geometry for 40 vol. % hydrate forming water-in-oil emulsions stabilized using Span 80. Figure 4.5 shows the relative viscosity versus time data obtained using helical ribbon geometry and vane geometry for 40 Vol. % hydrate forming water-in-oil emulsions stabilized using Span 80.



Figure 4.5: Viscosity vs. time plot for hydrate forming water-in-oil emulsions (40 Vol. % water) stabilized using Span 80 as the surfactant measured using helical ribbon and vane geometry. (Relative viscosity is defined as the ratio of viscosity of the emulsion to the viscosity of the oil phase)

The relative viscosity is defined as the viscosity of the emulsion to the viscosity of the oil phase. From the figure 5, it could be seen that the time for an increase in viscosity due to formation of hydrate crystals was higher using vane geometry due to inhomogeneous distribution of droplets. Also, after a certain point, there was accumulation of solids between the vane blades unlike helical ribbon fixtures where there was homogeneous distribution of hydrate crystals and hence the viscosity measurements become inappropriate using vane geometry for the systems under our study. The helical ribbon prevented phase separation between the solid and fluid creating a 3 dimensional flow pattern. In helical ribbon fixture, settling of droplets was also prevented. Thus in this study helical ribbon geometry supplied by TA instruments as shown in Figure 4.6 was used. The diameter of the helical ribbon used in this study is 2.33cm.



Figure 4.6: Helical geometry used for carrying out rheological measurements (D – diameter, L – length)

#### 4.4.3 Calibration of the helical ribbon

Based on the couette analogy, an analytical method was used to quantitatively analyze torque rotational speed in order to obtain viscosity shear rate data from a helical ribbon geometry <sup>140</sup>. Initially the viscosity of standard oil (Newtonian fluid) was found using the couette geometry. Then inner cylinder was replaced with a new mixing element and torque measurements were made at the same angular rotation speed that was used to measure viscosity of the standard oil. The couette analogy consists of determining an equivalent inner radius  $R_i$  of a couette inner cylinder having the same height as the impeller that produces the same rotational speed and torque in a cylindrical vessel of external radius  $R_e$ . The determination of radius  $R_i$  is based on the assumption of a power law fluid.

For a power law fluid

 $\eta = m \gamma^{n-1}.$ 

Where m is the fluid consistency index, n is the flow behavior index and  $\eta$  is the apparent viscosity. Stress and strain constants were obtained after determining the shear rate and shear stress as a function of radius. Calibration of helical ribbon was done using Cannon S60 oil.

### 4.5 Results and discussion

Figure 4.7 shows the effect of water cut on hydrate formation in hydrate forming water-in-oil emulsions formed using solid particles (Aerosil R974) as the emulsion stabilizer. The temperature was held constant at -2°C at a constant shear rate of 10s<sup>-1</sup>. Higher subcooling promotes rapid hydrate growth <sup>123, 134</sup> and thus the temperature was reduced to -2°C to promote rapid hydrate nucleation and thereby reducing the long induction times required for hydrate formation. In order to confirm that there is no ice formation taking place in emulsions as the temperature is reduced

to -2°C, we ran the control sample containing 40 Vol. % water by following the same experimental protocol that was followed to run hydrate forming water-in-oil emulsions.



Figure 4.7: Viscosity vs. time for water-in-oil emulsions formed using 0.1 Vol.% Aerosil R974 as the emulsion stabilizer at variable water cuts.  $T = -2^{\circ}C$ , shear rate = 10 s<sup>-1</sup>. (Relative viscosity is defined as the ratio of viscosity of the emulsion to the viscosity of the oil phase)

We tested the control system at the highest water fraction used in this paper. It can be seen that the viscosity of the control sample fairly remained constant throughout the experiment. Thus, we confirmed that there was no ice formation in emulsions at the experimental conditions. Figure 4.7 shows that the rise in viscosity of the hydrate forming water-in-oil emulsions was slow at the initial stages followed by a rapid increase in viscosity leading to jamming of the helical ribbon fixture. Figure 4.8a shows the solid hydrate formation in 40 Vol. % water-in-oil emulsions, which led to jamming of the rheometer fixture. This jamming of the fixture was caused by rapid growth of hydrate crystals for which yield stress was greater than the applied shear stress.



Figure 4.8: a) Rheometer jamming caused by water-in-oil emulsion (40 Vol. % water) formed using Aerosil R974 b) Rheometer jamming caused by water-in-oil emulsion (20 Vol. % water) formed using Aerosil R974.

The abrupt rise in viscosity was very rapid for hydrate forming water-in-oil emulsions formed using higher water cuts. Thus, induction time for hydrate formation was quicker for higher water cut emulsions compared to lower water cut emulsions. The viscosity of the emulsions increased with an increase in water cut. This observation was in accordance with Webb et al. <sup>141</sup>, Camargo et al. <sup>142</sup> and Sinquin et al. <sup>143</sup> in which they observed an increase in relative viscosity and yield stress with an increase in water cut.

Figure 4.9 shows the effect of water cut on hydrate formation in hydrate forming water-in-oil emulsions formed using Span 80 as the surfactant. Similar to hydrate forming water-in-oil emulsions formed using aerosil R974, hydrate forming water-in-oil emulsions formed using Span 80 showed an increase in viscosity with an increase in water cut. Also, the abrupt rise in viscosity due to hydrate formation, which in turn led to jamming in rheometer fixture (as shown in Figure 4.10), was rapid at higher water fractions than at lower water fractions.



Figure 4.9: Viscosity vs. time for water-in-oil emulsions formed using 0.1 Vol.% Span 80 as the surfactant at variable water cuts.  $T = -2^{\circ}C$ , shear rate = 10 s<sup>-1</sup>. (Relative viscosity is defined as the ratio of viscosity of the emulsion to the viscosity of the oil phase)



Figure 4.10: Rheometer jamming caused by water-in-oil emulsion (40 Vol. % water) formed using Span 80.

The rise in viscosity of hydrate forming water-in-oil emulsions with an increase in water cut is attributed to the fact that during hydrate formation, the hydrophilic nature of the hydrate surface leads to the rise of the capillary forces which tends to create adhesion forces between the hydrate particles <sup>144</sup>. Although dispersion forces cause adhesion between the hydrate particles, capillary forces are mainly responsible for causing adhesion between the hydrates particles <sup>145</sup>. The capillary bridge that is formed between the hydrate particles due to free water film causes agglomeration <sup>146, 147</sup> which in turn leads to hydrate plug formation. McCulfor et al. <sup>148</sup> stated that addition of small amounts of water increases the viscosity due to formation of water bridges between particles. Agglomeration results in an increase in effective volume fraction of the hydrate system. As the effective volume fraction is increased, the relative viscosity is also increased.

The comparison of rheological behavior of hydrates formed from emulsions stabilized using solid particles (aerosil R974) and Span 80 as the surfactant emerges as an interesting question. The key variables of interest to observe were induction time, viscosity and time required to jam the rheometer. Although exact induction time for hydrate formation cannot be predicted from the viscosity versus time plot, a qualitative observation can be made by monitoring the time at which there is an abrupt rise in viscosity. For emulsions formed with 40 Vol. % water cut, an abrupt increase in viscosity was observed at ~53.13 minutes and ~3.01 minutes when Span 80 and solid particles (aerosil R974) were used respectively as the emulsion stabilizers. For emulsions with 30 Vol. % water cut, an abrupt increase in viscosity was observed at ~54.67 minutes for Span 80 and ~6.67 minutes for aerosil R974. For emulsions with 10 Vol. % water cut, an abrupt rise in viscosity was observed at ~48 minutes when aerosil R974 was used. For emulsion with 20 Vol. % water cut formed using aerosil R974, the viscosity could not be measured because of hydrate formation at the top of the helical ribbon (as shown in Figure 4.8b) rather than the formation through out the cell. The experiment was repeated three times, but no change in results was observed. We hypothesize that as the droplets were brought to the top of the cell by rotation of helical ribbon, induction time for hydrate formation is reached and crystallization of the dispersed phase takes place before the droplets could move to the bottom of the cell. For emulsions formed using Span 80 with 10 Vol. % and 20 Vol. % water cuts there was a gradual rather than an abrupt increase in viscosity. It was clear that solid particles enhanced hydrate formation to a greater extent than surfactants and this phenomenon was profound at higher water fractions. Though the exact mechanism for promotion of hydrate formation by solid particles needs to be investigated, we hypothesize that solid particles act as nucleation sites for rapid hydrate formation to take place and hence reduce the induction time for hydrate formation. Thus the risk of hydrate plug formation appears to increase in the presence of solid particles. This result was in accordance with the observations of Mohammadi et al.<sup>149</sup> where they observed an increase in hydrate formation in the presence of wax.

Though initially the rise in viscosity was slower for emulsions formed using both aerosil R974 and Span 80, after a certain point, emulsions formed using solid particles as emulsion stabilizers showed a more abrupt rise in viscosity than emulsions formed using Span 80 due to rapid growth of hydrate crystals. Thus, transporting water-in-oil emulsions becomes difficult in the presence of solid particles compared to transporting it in the presence of surfactants especially under hydrate forming conditions since the presence of solid particles intensifies hydrate formation.

For emulsions formed using Span 80 as the surfactant, weakly thixotropic behavior was observed at lower water cuts. These observations are in accordance with the literature <sup>119, 130, 141, 142, 150-152</sup> where a shear thinning and thixotropic behavior for hydrate slurries was observed. Complete hydrate plugging did not take place for hydrate forming water-in-oil emulsions stabilized using Span 80 with 10 Vol.% and 20 Vol.% water cut. Dieker et al <sup>153</sup> stated that by decreasing water concentration the adhesion forces between hydrate particles were decreased. Hence, we believe that the adhesion forces were decreased for 10 Vol.% and 20 Vol.% water-in-oil emulsions stabilized using Span 80. Also, we believe that, at lower cuts, the repulsive forces between the surfactants that are adsorbed on to the hydrate is greater than the adhesion forces between the hydrate particles. Hence, hydrate particles did not tend to adhere to each other, thereby, did not cause complete plugging. Also, Aman et al. <sup>154</sup> stated that the adsorption of surfactants on to the hydrate-oil interface reduced the cyclopentane hydrate cohesive force. In addition, Aman et al.<sup>155</sup> found that higher concentrations of Span 80 (~1 Wt.%) reduced the average hydrate inter-particle adhesion force only by 37%. Thus, hydrate agglomeration that in turn leads to abrupt rise in viscosity is not completely suppressed for 10 Vol.% and 20 Vol.% water-in-oil emulsions stabilized using Span 80 rather it is suppressed to an extent that the system could be flown as a slurry. For higher water-cut emulsions, stabilized using Span 80, the capillary cohesive force between the hydrate particles is more than the repulsion force between surfactants that are

adsorbed on to the hydrates thereby leading to agglomeration. Hence, hydrate particles agglomerate and cause complete plugging.

In case of water-in-oil emulsions stabilized using Aerosil R974, hydrate plugging took place even at low water cuts. We hypothesize that in the presence of solid particles the capillary cohesive force between the hydrate particles, even at lower water cuts, is more than the steric repulsive force between the particles that stabilize the water droplets. Therefore, agglomeration between the hydrate particles take place and ultimately leads to plugging for water-in-oil emulsions with lower water cuts. Further, the capillary cohesive force increases with an increase in water cut. Therefore, at higher water cuts, the plugging tendency is much more faster than at lower water cuts. Figure 4.11 is drawn to explain the above-mentioned hypothesized phenomena pictographically.



Figure 4.11: Proposed conceptual mechanism for observed difference in rheological behavior between solid stabilized emulsions and surfactant stabilized emulsions.

Although relative viscosity gives a qualitative view on the build up of hydrates and subsequent plugging tendency, it would be more quantitative to determine the amount of hydrate particles in the system over time.

Albert Einstein, in 1906, proposed an equation that relates the viscosity to the volume fraction of solids in the system <sup>156</sup>. The equation is ideally applied for extremely low concentrations of spherical particles. Einstein's equation of viscosity is given by

$$\eta_{\rm r} = 1 + 2.5\phi \tag{4.1}$$

Where  $\eta_r$  is the relative viscosity defined as the ratio of viscosity of the suspension of spherical solid particles to the viscosity of the dispersion medium and  $\phi$  is the volume fraction of suspended spherical solid particles.

Toda et al. <sup>157</sup> extended the Einstein's viscosity equation to determine the viscosity of concentrated dispersions. The equation is given by

$$\eta_{\rm r} = \frac{1 - 0.5\phi}{(1 - \phi)^3} \tag{4.2}$$

The usage of above equation to predict the amount of hydrate particles from relative viscosity suffers from serious disadvantages. The above equations assume that the particles are completely spherical but Karanjkar et al. <sup>134</sup> described the conical nature of hydrate crystals. Also, the interaction between hydrate crystals during agglomeration is a complex phenomenon, which cannot be described with the help of equation 4.2. Despite the above disadvantages, equation 4.2 would help us in determining a rough estimation of the amount of hydrate particles, which in turn would help us in understanding the rise in relative viscosity of the system. Also, in equation 4.2, the viscosity of slurry is relative to the viscosity of the dispersion medium at the start of experiment rather than viscosity of the oil phase. This procedure eliminates the concentration of solid particles that was initially present in the emulsion before the start of the experiment. Hence,

the volume fraction of solid particles obtained from equation 4.2 does not account for the solid particles that were initially present in the system before the start of the experiment.

The volume fraction of solid (hydrate) particles was calculated using equation 4.2. Figure 4.12 shows the plot of volume fraction of hydrate particles versus time for water-in-oil emulsions stabilized using Aerosil R974. From figure 4.12, it can be seen that the fraction of hydrate particles increases rapidly with time for higher water cut emulsions as compared to lower water cut emulsions. Hence, hydrate plugging was faster at higher water cuts.



Figure 4.12: Volume fraction of solids versus time for water-in-oil emulsions stabilized using 0.1 Vol.% Aerosil R974.

Figure 4.13 shows the plot of volume fraction of hydrate particles versus time for water-in-oil emulsions stabilized using Span 80. Similar to water-in-oil emulsions stabilized using Aerosil R974, the volume fraction of hydrate particles rapidly increased with time with an increase in water cut.



Figure 4.13: Volume fraction of solids versus time for water-in-oil emulsions stabilized using 0.1 Vol.% Span 80.

From figures 4.12 and 4.13 once can see that the time for build up of hydrate particles is much shorter for water-in-oil emulsions stabilized using a solid particle as compared to water-in-oil emulsions stabilized using a surfactant. Hence, hydrate formation is rapid in the presence of solid particles as compared to a surfactant. The authors would like to emphasize that further modeling is required for accurate prediction of the fraction of hydrate particles from the relative viscosity of the system.

# 4.6 Conclusions

Rheological studies were carried out for hydrate forming water-in-oil emulsions. We utilized a rheometer with non-standard geometry to investigate hydrate formation in water-in-oil emulsions because our data showed that standard geometries do not accurately characterize the systems that were investigated. Hydrates forming water-in-oil emulsions were investigated at various water

cuts. In order to examine the effect of either solid particles or a surfactant on hydrate formation, hydrates forming water-in-oil emulsions were formed using solid particles (Aerosil R974) and Span 80 as the surfactant. From the experiments, it was concluded that hydrate formation was rapid in the presence of solid particles as compared to the surfactant. Solid particles act as nucleation sites to enhance the process of hydrate formation and reduce the induction time required for hydrate formation to take place. It was observed that complete hydrate plugging did not take place for water-in-oil emulsions stabilized using Span 80 at lower water cuts; whereas, complete hydrate plugging was observed for water-in-oil emulsions stabilized using Aerosil R974 at all investigated water cuts. A conceptual mechanism was proposed for hydrate formation and plugging in solid stabilized water-in-oil emulsions that would aid in understanding the observed difference in rheological behavior between solid-stabilized using solid particles was higher than the viscosity of water-in-oil emulsions formed using Span 80 as the surfactant. In addition, it was observed that viscosity of water-in-oil emulsions increased with an increase in water cut.

Rheological characterization of water dominant systems using solid particles would be the next step in order to gain better insight into hydrate formation processes and their rheological behavior. Due to the influence of particles on hydrate formation that was illustrated in this work, future work will focus on investigating hydrate formation using solid particles of varying hydrophobicity.

#### 4.7 Acknowledgement

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# CHAPTER V

# EMULSION STABILITY OF SURFACTANT AND SOLID STABILIZED WATER-IN-OIL EMULSIONS AFTER HYDRATE FORMATION AND DISSOCIATION

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### 5.1 Abstract

Hydrates are ice-like crystalline compounds that can cause plugging of crude oil pipelines. Stable water-in-oil emulsions aid in preventing hydrate particle agglomeration and hydrate plug formation in crude oil pipelines. The type of stabilizers present in water-in-crude oil emulsions also influences hydrate formation. Therefore, the effect of hydrate formation and dissociation on the stability of water-in-oil emulsions stabilized using either surfactants or solid particles was investigated. In addition, the difference in the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using solid particles of varying hydrophobicity was investigated. Furthermore, the effect of hydrate formation and dissociation on the droplet size of the water-in-oil emulsions was quantified. The results showed that, the water-in-oil emulsions stabilized using moderately hydrophobic solid particles resisted emulsion destabilization, after hydrate formation and dissociation, unlike water-in-oil emulsions that were stabilized using either surfactant stabilized emulsions, the droplet size of water in the residual emulsion increased by more than 85% as compared to the droplet size before hydrate formation. On the contrary, for solid stabilized emulsions, no significant change in the droplet size of the residual emulsion was observed after

hydrate dissociation as compared to the water-in-oil emulsion before hydrate formation. A conceptual mechanism was proposed to explain the observed difference in the stability of solid stabilized water-in-oil emulsions when subjected to hydrate formation and dissociation. Additionally, dynamic interfacial tension measurements were carried out to explain the difference in the initial droplet size of solid stabilized and surfactant stabilized water-in-oil emulsions.

## **5.2 Introduction**

Emulsions are in general colloidal dispersions of a liquid in another immiscible liquid stabilized using surfactant and/or solid particles. Emulsions have a wide variety of industrial applications such as those in energy, cosmetics, pharmaceuticals, and agriculture. In the energy industry, emulsions are ubiquitously encountered in nearly every stage of production, transportation, and operation.<sup>158</sup> Naturally occurring surfactants such as clay, silica, and inorganic particles present in crude oil systems have been shown to affect the hydrate formation and its characteristics resulting into the flow assurance issues.<sup>159-161</sup> Gas hydrates (also known as clathrates/clathrate hydrates) are non-stoichiometric, ice-like crystalline structures formed from host water molecules and low molecular weight guest gas molecules such as methane, ethane, and propane at low temperatures and at high pressures prevalent in subsea conditions.<sup>162</sup> Hydrate formation is one of the most important flow assurance problems since hydrate formation occurs more rapidly as compared to formation of wax and asphaltenes. Furthermore, huge amount of money is spent in managing and mitigating pipeline blockages due to hydrate formation.<sup>162</sup> Hydrate formation may occur during operations such as start-up, restart, shut in, and in places in the pipeline where there is a change in flow geometry, across valves, risers, and offshore/subsea systems.<sup>163</sup>

Hydrates are classified as either structure I, II, or H depending on the cage size and guest gas molecule.<sup>124</sup> Structure I hydrates are composed of twelve pentagonal (5<sup>12</sup>) and two hexagonal (6<sup>2</sup>) cavities occupied by guest molecules such as methane, ethane, and carbon-dioxide.<sup>124</sup> Structure II

hydrates are the most common type in the oil and gas industry, and are composed of 5<sup>12</sup>6<sup>4</sup> cavities and occupied by guest molecules such as propane and iso-butane. Structure H hydrates are composed of high molecular gas compounds and are the least common type.<sup>124</sup> This paper focuses on the investigation of structure II hydrates. Although, hydrates are generally formed at high pressure and low temperature conditions, cyclopentane hydrates and tetrahydrofuran (THF) hydrates are formed at atmospheric conditions. Tetrahydrofuran is miscible with water and hence does not provide mass transfer limitations that is generally observed with natural gas hydrates. Hence, tetrahydrofuran was not used as the hydrate forming guest molecule. Cyclopentane is a useful guest molecule to investigate structure II hydrates since cyclopentane forms structure II hydrates, which is similar to natural gas hydrates. In addition cyclopentane hydrates can be formed at atmospheric pressures and at a temperature of around 7 <sup>o</sup>C.<sup>125</sup> Thus, cyclopentane was used the hydrate forming guest molecule.

Hydrate management is economically feasible and favorable when compared to complete avoidance due to excessive capital and operating costs involved in completely preventing hydrate formation.<sup>122</sup> Formation of water-in-oil emulsions (water dispersed in continuous oil phase) is one of the most predominant multiphase flow situation encountered in petroleum industry. The key objective of this manuscript is to investigate the influence of hydrate formation and dissociation on water-in-oil emulsions. Lachance et al. <sup>133</sup> studied the effect of hydrate formation and dissociation on the stability of water-in-crude oil emulsions. They concluded that hydrate formation and dissociation led to destabilization of emulsions. Hydrate formation is generally dependent on the crude oil properties. Crude oils contains various natural surfactants such asphaltenes, resins and carboxylic acids. Furthermore, the type of surfactant and the concentration of surfactant in crude oil affects hydrate formation.<sup>128, 129</sup> Raman et al. <sup>51</sup> studied the effect of stabilizers on hydrate formation and their rheological behavior in hydrate forming water-in-oil

emulsions. They concluded that the solid particles promote hydrate formation to a greater extent as compared to surfactants. Thus, the type of stabilizer affects hydrate formation.

For effective hydrate management strategies in water-in-oil emulsions, the amount of water present in the emulsion plays a crucial role.<sup>164</sup> Finely dispersed water-in-oil emulsions help in mitigating the hydrate blockages.<sup>163</sup> Thus, droplet size of water-in-oil emulsion plays an important role in hydrate management strategies. In addition, droplet size affects the rheological properties of water-in-oil emulsions. Furthermore, the stability of emulsion influences the flow friction factor.<sup>119, 165-167</sup> Unstable emulsions leads to a drag-reduction behavior unlike surfactant-stabilized emulsions. Thus, investigating the effect of hydrate formation and dissociation on emulsion stability and on the droplet size of water-in-oil emulsions would provide a better insight on the flow behavior of water-in-oil emulsions before hydrate formation and after hydrate dissociation.

Hydrate formation is an interfacial phenomenon that takes place when hydrocarbons dissolved in the oil phase come in contact with the water phase.<sup>163</sup> Thus, interfacial characterization of oil-water interface in the presence of various stabilizers becomes critical.

The objective of this paper was to investigate and compare the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using either surfactants or solid particles. Different types of stabilizers were used to investigate the effect of hydrophobicity of solid particles on the stability of water-in-oil emulsions upon hydrate formation and dissociation. In addition, our objective was to quantify the effect of hydrate formation and dissociation on droplet size of the water-in-oil emulsions stabilized using either surfactants or solid particles. Furthermore, interfacial tension measurements were carried out to elucidate the effect of stabilizers on the interfacial properties of water-in-oil emulsions.

#### 5.3 Materials and methods

## 5.3.1 Materials used

Water-in-oil emulsions were investigated in order to gain insight on the effect of hydrate formation and dissociation on emulsion stability. Deionized water with a resistivity of 18.2 m $\Omega$ cm-1 was used to form the internal phase. The continuous oil phase consisted of light mineral oil (+99% purity, sigma Aldrich), and either cyclopentane (+95% purity, Alfa Aesar) or iso-octane (+99.48%, Honeywell). Cyclopentane was used as the hydrate-forming component. Sorbitan monooleate (Span 80), an oil soluble, non-ionic surfactant was used to stabilize the water-in-oil emulsions. The HLB <sup>2</sup> value of Span 80 is 4.3±1.0 (as stated by the vendor). Span 80, though, a smaller molecule as compared to asphaltenes, can resemble the surface activity of asphaltenes.<sup>133</sup> Hence, for investigation of surfactant stabilized water-in-oil emulsions, Span 80 was used as the surfactant. For preparation of solid stabilized water-in-oil emulsions, two types of solid particles with different hydrophobicity were chosen. Solid stabilized water-in-oil emulsions were either stabilized using Aerosil R974 (moderately hydrophobic solid nanoparticle, provided by Evonik Inc.) or Aerosil R104 (solid nanoparticle with higher hydrophobicity, provided by Evonik Inc.).

Water-in-oil emulsions were investigated at two different water cuts viz. at 20 Vol.% and 40 Vol.% water cut. The concentration of the emulsifiers (Span 80, Aerosil R974 and Aerosil R104) were kept constant at 0.1 Vol.% (based on total volume) for all water fractions. The critical micelle concentration (CMC) of Span 80 is 0.03(%v/v).<sup>134, 135</sup> Thus, under the current study, for the water-in-oil emulsion stabilized using surfactant, the surfactant concentration was well above the critical micelle concentration. The oil phase of the hydrate forming water-in-oil emulsions constituted equal volumes of light mineral oil and cyclopentane (50:50 by volume). The quantity of cyclopentane was higher than the stoichiometric requirement for formation of cyclopentane

hydrates, which is one mole of cyclopentane to 17 moles of water. For control samples, the cyclopentane in the oil phase was replaced by iso-octane.

In this manuscript, water-in-oil emulsions, in general, refers to hydrate forming water-in-oil emulsions (emulsions with cyclopentane in oil phase rather than iso-octane). Water-in-oil emulsions containing iso-octane will be explicitly stated whenever required.

## 5.3.2 Preparation of emulsions

The emulsions were prepared using an IKA T25 digital Ultra-Turrax homogenizer operating at 20,000 rpm for 20 min. The rotor and stator diameter of the dispenser were 17mm and 25mm respectively. Initially, the oil phase that consisted of equal volumes of light mineral oil and cyclopentane were mixed together followed by the addition of either solid particles or surfactant. The mixture was then sheared using the homogenizer for 1 min at 20,000 rpm to ensure complete mixing of the oil phase and the stabilizer. Once the oil phase and the stabilizers were mixed, water (internal phase) was added in a drop wise manner to ensure homogeneous distribution of the internal phase.<sup>52</sup> Since the mixing was done at high shear rate, the emulsion samples were sealed using a parafilm to prevent the evaporation of volatile components. All emulsions were prepared using the same protocol. During the preparation of the control sample, the cyclopentane (hydrate forming component) was replaced by iso-octane.

## 5.3.3 Emulsion characterization

Emulsion stability is essential for investigation of hydrate formation and dissociation on the stability of water-in-oil emulsions. If the emulsions are inherently unstable, then probing the effect of hydrates on emulsion stability becomes impossible. In order to ensure that the emulsions, which were used for investigation, were stable over the experimental time, microscopic investigations were carried out.

For macroscopic investigation, bottle tests were carried out to ensure that there was no bulk phase separation during the experimental time. Figure 5.1 shows the visual appearance of the 40 Vol.% water-in-emulsion stabilized using 0.1 Vol.% Aerosil R974. It can be visually seen that the emulsion was stable over a period of 4 hours.



Figure 5.1: Visual or macroscopic appearance of 40 vol.% Water-in-oil emulsion stabilized using 0.1 vol.% Aerosil R974. a) Emulsion at the 0<sup>th</sup> hour b) Emulsion after 4 hours

In order to ensure that there was no significant structural change, microscopic characterization of the emulsions were carried out. For microscopic investigation, an Olympus BX53 polarized optical microscope equipped with a high-speed camera was used. Figure 5.2 shows the schematic of the microscope used for measuring the droplet size of the emulsion. The droplet sizes were measured at the 0<sup>th</sup> hour and after 4 hours.



Microscope Specifications	
Sample Diameter	30 mm
Viewing Diameter	2.8mm
Temperature range	-45°C to 450°C



Figure 5.2: Schematic of the microscope stage and the visualization setup used for experiments.

In order to avoid sampling discrepancies, multiple images of the same emulsion sample were taken both at the 0<sup>th</sup> hour and after 4 hours. Figure 5.3 shows the photomicrographs of the 40 Vol. % water-in-oil emulsion that was stabilized using 0.1 Vol.% Aerosil R974. Image J software was used to analyze the images that were captured by the microscope.



Figure 5.3: Photomicrographs of the 40 vol.% water-in-oil emulsion stabilized using 0.1 vol.% Aerosil R974 a)  $0^{\text{th}}$  hour b) after 4 hours

A similar procedure was carried out to characterize all the water-in-oil emulsions that were used for the investigation. Figure 5.4 and 5.5 shows the comparison of the mean droplet size for water-in-oil emulsions with 20 vol.% and 40 vol.% water fraction respectively at the 0<sup>th</sup> hour and after 4 hours. It was observed that the droplet size did not change significantly after 4 hours. From the above macroscopic and microscopic characterizations, it can be concluded that the emulsions were stable during the entire experimental time.



Figure 5.4: Comparison of the mean droplet size at the 0<sup>th</sup> hour and after 4 hours for 20 vol.% water-in-oil emulsions.



Figure 5.5: Comparison of the mean droplet size at the 0<sup>th</sup> hour and after 4 hours for 40 vol.% water-in-oil emulsions. Inset: sample photomicrograph taken during image J processing.

# 5.3.4 Experimental protocol

The experimental procedure that was used in this work is outlined below

1. Water-in-oil emulsions were prepared using an IKA T25 digital Ultra-Turrax homogenizer. The emulsions were sheared for 20 min at 20,000 rpm. Once the emulsions were prepared, macroscopic and microscopic characterization of the emulsions were carried out. A small portion of the sample was placed inside a glass vial for visual observation of the emulsion over the experimental time. Also, a small sample of the emulsion was placed in the sample area of the microscope as shown in Figure 5.2. At the 0<sup>th</sup> hour, multiple images of the sample were taken to avoid sampling discrepancies.

2. The entire water-in-oil emulsion sample, which was prepared using the homogenizer, was placed in the chiller (HAAKE N8-C41 chiller). The chiller temperature was maintained between  $2 \, {}^{0}$ C to  $3 \, {}^{0}$ C. Ethylene Glycol was used as the coolant.

3. Once the sample temperature reaches 2  $^{0}$ C to 3  $^{0}$ C, then ice crystals were added to the sample to aid nucleation.  $^{130}$ 

4. After the addition of ice crystals, the sample was sheared using an IKA T25 digital Ultra-Turrax homogenizer at a shear rate of 2,800 rpm for 3 hours. The sample was sealed to avoid evaporation of volatile components.

5. After 3 hours, the water-in-oil emulsion, which experienced hydrate formation, was taken out of the chiller. The sample was allowed to reach room temperature.

6. Once the hydrates were dissociated at room temperature, a sample of the residual emulsion was observed under the microscope to detect the effect of hydrate formation and dissociation on the droplet size of the water-in-oil emulsion. Multiple images of the residual water-in-oil emulsion were taken using the microscope.

7. The photomicrographs, which were taken at the  $0^{th}$  hour and after hydrate dissociation, were analyzed using Image J to quantify the droplet size distribution.

8. In addition, images of the bulk sample that was not subjected to hydrate formation were taken to determine the emulsion stability over time.

#### 5.4 Results and discussion

The objective of this study was to observe the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using either a surfactant or solid particle. In addition, the effect of hydrate formation and dissociation on water-in-oil emulsions stabilized using solid particles of

different wettability was also investigated. Our method of investigation was divided into two parts 1) Effect of hydrate formation and dissociation on macroscopic stability of the water-in-oil emulsions 2) Effect of hydrate formation and dissociation on droplet size (microscopic characterization) of the water-in-oil emulsions. This work is critical for developing effective flow assurance strategies because the droplet size of the emulsion plays a crucial role in determining pressure drop along the pipeline and in predicting the rate of conversion of water drops to hydrate particles.

#### 5.4.1 Effect of stabilizer on droplet size of water-in-oil emulsions

Droplet size plays an important role in determining the stability and rheological properties of the emulsions. Figure 5.4 and 5.5 illustrates the effect of stabilizer on droplet size of the water-in-oil emulsion at two different water fractions. It can be seen that the presence of surfactant reduces the droplet size of the water-in-oil emulsions as compared to the solid stabilized water-in-oil emulsions. In addition, Figures 5.4 and 5.5 show that the water-in-oil emulsions stabilized using highly hydrophobic solid particles (Aerosil R104) had a larger droplet size as compared to the water-in-oil emulsions stabilized using solid particles that were moderately hydrophobic (Aerosil R974) which in accordance with observations of Binks et al.<sup>47</sup>

Dynamic interfacial tension measurements were carried out to gain insight on this phenomenon. A high pressure, interfacial tensiometer (IFT) model # IFT-10-OS purchased from Core Lab Instruments (Tulsa, OK) was used for conducting dynamic interfacial tension measurements. The pendant drop method was used for measuring the dynamic interfacial tension.<sup>53</sup> The interfacial tension value at the oil-water interface was observed over a period of 500 seconds until a steady state was reached as shown in Figure 5.6.



Figure 5.6: Dynamic interfacial tension at the oil-water interface in the presence of Aerosil R104. Oil here consists of an equal volume mixture of light mineral oil and cyclopentane along with Aerosil R104. Inset - an oil droplet dispersed in the water phase.

Table 5.1 shows the dynamic interfacial tension values at the oil-water interface in the presence of either a surfactant or a solid particle. It can be seen the presence of surfactant tends to reduce the dynamic interfacial tension at the oil-water interface unlike solid particles, which do not reduce the interfacial tension at the oil-water interface. These observations were in accordance with Drelich et al.<sup>74</sup>

System	Dynamic Interfacial
	Tension (mN/m)
Oil -water	48.36 ±0.06
Oil+ 0.1 vol% Span 80 - water	3.04 ±0.02
Oil+ 0.1 vol% Aerosil R104 - water	50.5 ±0.05
Oil+ 0.1 vol% Aerosil R974 - water	50.16 ±0.05

Table 5.1: Summary of dynamic interfacial tension at the oil-water interface in the absence and presence of stabilizer. Oil here represents an equal volume mixture of light mineral oil and cyclopentane.

Figure 5.7 shows the schematic of the hypothesized mechanism describing the effect of solid particles and surfactant on the interfacial tension at the oil-water interface. For clean water-oil interface (in the absence of surfactant or solid particles), tension is caused at the water-oil interface because of the inequality in the cohesive force of water/oil molecules at the interface.



Figure 5.7: A sketch of the hypothesized mechanism describing the effect of solid particles and surfactant on the interfacial tension at the oil-water interface.

A surfactant binds the water and oil molecules together since they are amphiphilic. In the presence of surfactant, the adhesive force between the water and oil molecules balances the inequality in the cohesive force of water/oil molecules at the interface, which causes the net force to tend to zero, thereby, leading to a reduced interfacial tension. Solid particles are not amphiphilic. They adsorb at the water/oil interface depending on the wettability of particles and prevent coalescence by steric repulsion. In the presence of solid particles, the adhesive force between the water and oil molecules at the interface does not balance the inequality in the cohesive force of water/oil molecules. The net force at the interface does not tend to zero but rather remains the same as a clean interface. Thus, the presence of solid particles does not reduce the interfacial tension.

#### 5.4.2 Effect of hydrate formation and dissociation on emulsion stability

#### 5.4.2.1 Microscopic characterization of water-in-oil emulsions

Figures 5.8 -5.13 show the photomicrographs of the water-in-oil emulsions that were taken before hydrate formation and after hydrate dissociation along with the droplet size distributions. In addition, these pictures show the corresponding visual observation of the bulk water-in-oil emulsion at each stage. The photomicrographs of the water-in-oil emulsions that were taken after hydrate dissociation correspond to the residual emulsion.



Figure 5.8: Water-in-oil emulsion stabilized using surfactant (Span 80) at 20 vol.% water fraction a) Before hydrate formation b) photomicrograph of the emulsion at the 0<sup>th</sup> hour c) macroscopic visualization of emulsion after conversion to hydrate particles d) macroscopic visualization of emulsion after hydrate dissociation e) photomicrograph of the residual emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.


Figure 5.9: Water-in-oil emulsion stabilized using moderately hydrophobic solid particles (Aerosil R974) at 20 vol.% water fraction a) Before hydrate formation b) photomicrograph of the emulsion at the 0<sup>th</sup> hour c) macroscopic visualization of emulsion after conversion to hydrate particles d) macroscopic visualization of emulsion after hydrate dissociation (no free water layer

is observed) e) photomicrograph of the emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.



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Figure 5.10: Water-in-oil emulsion stabilized using highly hydrophobic solid particles (Aerosil R104) at 20 vol.% water fraction a) Before hydrate formation b) photomicrograph of the emulsion at the 0<sup>th</sup> hour c) macroscopic visualization of emulsion after conversion to hydrate particles d) macroscopic visualization of emulsion after hydrate dissociation e) photomicrograph of the residual emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.



Figure 5.11: Water-in-oil emulsion stabilized using surfactant (Span 80) at 40 vol.% water fraction a) Before hydrate formation b) macroscopic visualization of emulsion after conversion to hydrate particles c) macroscopic visualization of emulsion after hydrate dissociation d)

photomicrograph of the emulsion at the 0<sup>th</sup> hour e) photomicrograph of the residual emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.



Figure 5.12: Water-in-oil emulsion stabilized using moderately hydrophobic solid particles (Aerosil R974) at 40 vol.% water fraction a) Before hydrate formation b) macroscopic visualization of emulsion after conversion to hydrate particles c) macroscopic visualization of emulsion after hydrate dissociation d) photomicrograph of the emulsion at the 0<sup>th</sup> hour e)

photomicrograph of the residual emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.



Figure 5.13: Water-in-oil emulsion stabilized using highly hydrophobic solid particles (Aerosil R104) at 40 vol.% water fraction a) Before hydrate formation b) photomicrograph of the emulsion at the 0<sup>th</sup> hour c) and d) macroscopic visualization of emulsion after conversion to hydrate particles e) macroscopic visualization of emulsion after hydrate dissociation f) photomicrograph of the residual emulsion after hydrate dissociation g) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.

From the photomicrographs, it can be seen that the droplet size of the water-in-oil emulsion stabilized using a surfactant increased after hydrate dissociation. Thus, hydrate formation and dissociation caused an increase in the droplet size of the surfactant stabilized water-in-oil emulsions. On the contrary, hydrate formation and dissociation did not significantly affect the droplet size of the water-in-oil emulsions stabilized using solid particles. The difference in the mean droplet size of the water-in-oil emulsions, before hydrate formation and after hydrate dissociation, is shown in Table 5.2. Table 5.2 shows that the droplet size of the surfactant stabilized emulsion increased by approximately more than 85% after hydrate dissociation unlike solid stabilized emulsion, which did not exhibit a significant change in the droplet size of the residual emulsion after hydrate dissociation.

Water-in-oil emulsion with 40 vol.% water cut				
	Mean droplet size (µm)			
Stabilizers	Before Hydrate formation	After Hydrate		
		Dissociation		
		(From residual emulsion)		
Span 80	10.1±3.2	18.9±14.9		
R974	21.6±6.5	16.6±7.6		
R104	35.1±13.0	29.2±10.4		
Water-in-oil emulsion with 20 Vol.% water cut				
Span 80	4.4±2.1	8.9±3.5		
R974	11.0±2.9	11.2±3.3		
R104	17.9±4.5	15.1±4.5		

Table 5.2: Effect of hydrate formation and dissociation on mean droplet size of water-in-oil

#### emulsions

# 5.4.2.2. Macroscopic characterization of water-in-oil emulsions

Figure 5.14 shows the effect of hydrate formation and dissociation on the stability of water-in-oil emulsions with 40 vol.% water cut. It can be clearly seen that hydrate formation and dissociation destabilized water-in-oil emulsions which is in accordance with the observation of Lachance et al.



Figure 5.14: Effect of hydrate formation and dissociation on stability of water-in-oil emulsions with 40 vol.% water cut.

Figure 5.15 shows the effect of hydrate formation and dissociation on the stability of water-in-oil emulsions with 20 vol.% water cut. Hydrate formation and dissociation causes destabilization of water-in-oil emulsions stabilized using a surfactant or highly hydrophobic solid particles. Hydrate formation and dissociation did not cause destabilization of water-in-oil emulsions stabilized using solid particles that are moderately hydrophobic. Thus, moderately hydrophobic solid particles resist destabilization to a greater extent as compared to highly hydrophobic solid particles.



Figure 5.15: Effect of hydrate formation and dissociation on stability of water-in-oil emulsions with 20 Vol.% water cut.

Figure 5.16 provides the schematic of the hypothesized mechanism explaining the phenomenon for the observed difference in stability of water-in-oil emulsions, stabilized using solid particles, upon hydrate dissociation. We hypothesize that, during hydrate dissociation, for water-in-oil emulsions stabilized using moderately hydrophobic solid particles, the steric repulsion between the particles at the interface overcomes the capillary attraction between the water droplets, thereby, inhibiting coalescence.



Figure 5.16: The schematic of the hypothesized mechanism explaining the phenomenon for the observed difference in stability of water-in-oil emulsions, stabilized using solid particles, upon hydrate dissociation.

In addition, it is known that the energy required to desorb a moderately hydrophobic particle from the water-oil interface is much higher as compared to a highly hydrophobic solid particle.<sup>47</sup> Thus, moderately hydrophobic solid particles remain at the water-oil interface even after hydrate dissociation. For water-in-oil emulsions stabilized using highly hydrophobic solid particles, the steric repulsion between the particles at the interface is less than the capillary attraction between the water droplets, which in turn leads to destabilization. Furthermore, the energy required to desorb highly hydrophobic solid particle from the water-oil interface is less as compared to the energy required to desorb a moderately hydrophobic solid particle. After hydrate dissociation, highly hydrophobic solid particles are desorbed from the water-oil interface that in turn leads to destabilization. At 40 vol.% water fraction, a free water layer is seen for water-in-oil emulsions stabilized using moderately hydrophobic particle unlike water-in-oil emulsions at 20 vol.% water fraction. This observation can be attributed to the fact that, at 40 vol.% water cut, the droplet size of the water-in-oil emulsion stabilized using moderately hydrophobic particle is twice as large as

compared to that of the water-in-oil emulsion stabilized using moderately hydrophobic solid particle with 20 vol.% water cut. Consequently, the number of particles covering the interface at 40 vol.% water cut is less as compared to the water-in-oil emulsion with 20 vol.% water cut (since the particle concentration is kept constant across all the water fractions under investigation). Furthermore, increase of water fraction would lead to an increase in capillary force between the particles.<sup>148</sup> Hence, for water-in-oil emulsions stabilized using moderately hydrophobic solid particles, at 40 vol.% water fraction, the capillary attraction between the water molecules overcomes the steric repulsion between the particles at the interface, thereby, leading to destabilization.

In order to test the hypothesis, for water-in-oil emulsion stabilized using moderately hydrophobic particles (Aerosil R974) with 40 vol.% water fraction, the concentration of the solid particles were increased from 0.1 vol.% to 0.2 vol.%. Figure 5.17 shows the photomicrographs of the water-in-oil emulsion that was taken before hydrate formation and after hydrate dissociation along with the pictures showing the corresponding visual observation of the bulk water-in-oil emulsion at each stage.



Figure 5.17: Water-in-oil emulsion stabilized using moderately hydrophobic solid particles 0.2 vol.% Aerosil R974 at 40 vol.% water fraction a) Before hydrate formation b) photomicrograph of the emulsion at the 0<sup>th</sup> hour c) macroscopic visualization of emulsion after conversion to

hydrate particles d) macroscopic visualization of emulsion after hydrate dissociation (no free water layer is observed) e) photomicrograph of the emulsion after hydrate dissociation f) droplet size distribution in the emulsion before hydrate formation and after hydrate dissociation.

It was observed that hydrate formation and dissociation did not cause destabilization of the waterin-oil emulsion, which is similar to the observations for water-in-oil emulsion stabilized using 0.1 vol.% of moderately hydrophobic solid particle with 20 vol.% water fraction. The mean droplet size before hydrate formation and after hydrate dissociation for 40 vol.% water cut emulsion stabilized using 0.2 vol.% Aerosil R974 was  $27.5\pm10.8$  µm and  $21\pm8.9$  µm respectively.

Thus, water-in-oil emulsions stabilized using moderately hydrophobic particles resist destabilization due to hydrate formation and hydrate dissociation unlike water-in-oil emulsions stabilized using highly hydrophobic solid particles. Figure 5.18 shows the effect of hydrate formation and dissociation on stability of water-in-oil emulsions stabilized using moderately hydrophobic solid particles.



Figure 5.18: The effect of hydrate formation and dissociation on stability of water-in-oil emulsions stabilized using moderately hydrophobic solid particles.

In addition, for water-in-oil emulsions, stabilized using surfactants, the capillary attraction between the hydrate particles upon dissociation is greater than the repulsive force between the surfactants adsorbed at the interface. Hence, coalescence of droplets takes place, which in turn leads to destabilization of the water-in-oil emulsion which is in accordance with the observations of Lachance et al.<sup>133</sup>

# 5.4.2.3 Control experiments to determine the effect of shear on destabilization

Control experiments were performed to ensure that the amount of shear applied to water-in-oil emulsions during the period of experiment did not contribute to evolution or reduction in droplet

size, thereby, avoiding the effect of shear induced destabilization.<sup>168</sup> In the control experiments, the cyclopentane was replaced by iso-octane in order to study the effect of shear on water-in-oil emulsions without hydrate formation. In addition, it would help in de-convoluting the effect of shear and hydrate formation on droplet size.

The experimental protocol was similar to that of the hydrate forming water-in-oil emulsions. The experimental temperature, time and shear were similar to that for hydrate formation and dissociation experiments. For control samples, after the experimental time, no free water layer in the emulsion was visually observed. In order to determine the effect of shear on the control system at a microscopic level, the droplet size was measured at the 0<sup>th</sup> hour and after application of shear. Figure 5.19 shows the comparison of the mean droplet size for the control system with 40 vol.% water cut at the 0<sup>th</sup> hour and after application of shear. It can seen that, shear induced destabilization was not observed for the systems under investigation. Thus, it was ensured that the difference in the droplet size for hydrate forming water-in-oil emulsions was due to hydrate formation and dissociation.



Figure 5.19: The comparison of the mean droplet size for control water-in-oil emulsions with 40 vol.% water cut at the 0<sup>th</sup> hour and after application of shear.

# 5.4.3 Predicting the influence of droplet size on flow behavior

Based on the above-mentioned discussions, Fig. 5.20 depicts a representative sketch that shows the effect of hydrate formation and dissociation on the stability of water-in-oil emulsions. In general, destabilization of the emulsion tends to show a drag reduction behavior.<sup>165, 167</sup> Thus, hydrate formation and dissociation favors the drag reduction behavior for water-in-oil emulsions. Further, experiments under flowing conditions are necessary in order to predict the quantitative difference in the magnitude of the drag reduction behavior between the solid stabilized and surfactant stabilized water-in-oil emulsions. Although, no experiments were performed to characterize the difference in rheological behavior between the solid stabilized and surfactant stabilized water-in-oil emulsions after hydrate dissociation, qualitative predictions could be made depending on the droplet size of the residual water-in-oil emulsions.



Figure 5.20: A representative sketch illustrating the effect of hydrate formation and dissociation on stability of water-in-oil emulsions.

Hinze <sup>169</sup> developed an equation that relates the maximum droplet size  $(d_{max})$  and the friction factor along the pipe. The equation is given as

$$d_{max} \left(\frac{\rho_c}{\sigma}\right)^{3/5} \varepsilon^{2/5} = C \tag{5.1}$$

Where  $\varepsilon$  is the mean energy dissipation rate given by  $\varepsilon = \left(\frac{fU_c}{2D}\right)^{2/5}$ , f is the friction factor, U<sub>c</sub> is the continuous phase velocity, D is the diameter of the pipe,  $\rho_c$  is the continuous phase density,  $\sigma$  is the interfacial tension and C is a constant. Assuming that the diameter of the pipeline (through which the emulsion flows), velocity of the continuous phase and the density of the continuous phase are kept constant, then equation 1 can be rewritten as

$$\frac{d_{max}}{\sigma^{0.6}} = \frac{A}{f^{0.4}} \tag{5.2}$$

Where, A is a constant and it is a function of diameter of the pipeline, velocity of the continuous phase and the density of the continuous phase. Thus, the friction factor along the pipe before hydrate formation and after hydrate dissociation could be calculated by substituting the maximum diameter of the water droplet before hydrate formation, maximum diameter of the water droplet before hydrate dissociation, and the interfacial tension. Due to the separation of free water after hydrate dissociation, which leads to drag reduction behavior, the calculation of friction factor for the residual water-in-oil emulsions after hydrate dissociation would be further less than the predicted value of friction factor.

From equation 5.2, it can be seen that, for surfactant stabilized water-in-oil emulsions, the formation of larger droplets, in the residual emulsion, after hydrate dissociation tends to decrease the interfacial stress on the droplets, which in turn would reduce the friction factor along the pipe, thereby, reducing the effective emulsion viscosity. For solid stabilized water-in-oil emulsions, the formation of smaller (or same droplet size as the original emulsion) droplets, in the residual emulsion, after hydrate dissociation tends to increase the interfacial stresses on the droplets, which in turn would lead to an increase in friction factor along the pipe, thereby, increasing the effective emulsion viscosity. In addition, for water-in-oil emulsions stabilized using moderately hydrophobic solid particles, hydrate dissociation did not destabilize the emulsion when the surface coverage of particles on the droplets is higher. Thus, water-in-oil emulsion stabilized using moderately hydrophobic solid particles, would either show a decreased drag reduction behavior (for emulsion with 40 vol.% water fraction stabilized using 0.1 vol.% Aerosil R974) or no drag reduction behavior (for emulsion with 20 vol.% water fraction stabilized using 0.1 vol.% Aerosil R974 and for emulsion with 40 vol.% water fraction stabilized using 0.2 vol.% Aerosil R974), since stable emulsions do not show a drag reduction behavior. Thus, the pressure drop would be lower for flow of surfactant stabilized water-in-oil emulsions after hydrate dissociation as compared to solid stabilized water-in-oil emulsions. The pressure drop would be higher for water-in-oil emulsions with 20 vol.% water cut stabilized using 0.1 vol.% moderately hydrophobic solid particles and for water-in-oil emulsions with 40 vol.% water cut stabilized using 0.2 vol.% moderately hydrophobic solid particles, even after hydrate dissociation.

# **5.5 Conclusions**

This work quantifies the impact of hydrate formation and dissociation on emulsion stability of surfactant stabilized water-in-oil emulsions and solid stabilized water-in-oil emulsions. In addition, two types of solid particles, with varying wettability, were used to stabilize water-in-oil emulsions to investigate the influence of particle hydrophobicity on the effect of hydrate formation/dissociation on emulsion stability. Microscopic and macroscopic characterizations were carried out for water-in-oil emulsions before hydrate formation and after hydrate dissociation. Furthermore, dynamic interfacial tension measurements were carried out to explain the effect of stabilizer type on interfacial properties.

In general, it was observed that initial droplet size of the water-in-oil emulsions was greater for solid stabilized emulsions as compared to the surfactant-stabilized emulsions. This phenomenon was explained using the results obtained from dynamic interfacial tension measurements. Solid particles do not change the dynamic interfacial tension at the water-oil interface unlike surfactants, which drastically reduced the water-oil interfacial tension.

For surfactant stabilized water-in-oil emulsions, hydrate formation and dissociation destabilized the emulsion at both 20 Vol.% and 40 Vol.% water fraction. A free water layer was seen after hydrate dissociation which was in accordance with the observations of Lachance et al.<sup>133</sup> In addition, a residual emulsion was seen after hydrate dissociation above the free water layer at the bottom. Water-in-oil emulsions stabilized using highly hydrophobic solid particles were also destabilized upon hydrate formation and dissociation at both water fractions. Similar to

surfactant-stabilized emulsion, a residual emulsion was observed above the free water layer at the bottom for water-in-oil emulsions stabilized using Aerosil R104.

On the contrary, for water-in-oil emulsions stabilized using a sufficient amount of moderately hydrophobic solid particles, no free water layer was seen after hydrate dissociation for water-in-oil emulsions. Thus, it was concluded that moderately hydrophobic solid particles resisted emulsion destabilization to a greater extent than the surfactant and highly hydrophobic solid particles.

Microscopic characterizations of the residual emulsion after hydrate dissociation showed that the droplet size for water-in-oil emulsions stabilized using surfactant increased by approximately two folds as compared to the droplet size before hydrate formation; Whereas, the droplet size for the residual water-in-oil emulsions stabilized using solid particles did not show a significant change as compared to the droplet size before hydrate formation. This phenomenon would have a significant effect on the flow behavior of water-in-oil emulsions after hydrate dissociation.

Investigation of rheological behavior of hydrate forming water-in-oil emulsions after hydrate dissociation will be carried out to gain better insight on the flow behavior of these emulsions. In addition, further studies will be carried out to elucidate the effect of concentration of solid particles on emulsion stability upon hydrate dissociation.

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# CHAPTER VI

# THE EFFECT OF PARTICLE HYDROPHOBICITY ON HYDRATE FORMATION IN WATER-IN-OIL EMULSIONS IN THE PRESENCE OF WAX

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## 6.1 Abstract

Clathrate hydrates are non-stoichiometric, ice like crystalline solids that can lead to plugging of crude oil pipelines. In addition, wax deposition leads to partial or complete blockage of crude oil pipelines. Crude oil is a complex hydrocarbon mixture that includes asphaltenes, aromatics, naphthenes, resins, and paraffins. De-convoluting the effects of solid particles and surfactants that are present in crude oil on hydrate and wax formation would improve the hydrate and wax prediction strategies. A fundamental investigation using model oil was carried out in order to (i) de-convolute the effect of hydrophobicity of solid particles, surfactants, and water on hydrate and wax formation in water-in-oil emulsions, (ii) investigate the relationship between hydrates and wax in silica stabilized and surfactant stabilized water-in-oil emulsions. The results showed that the presence of silica and water did not have a significant effect on Wax Appearance Temperature (WAT). In addition, the amount of hydrate formation decreased with an increase in hydrophobicity of silica nanoparticles at the water-oil interface. The presence of wax promoted hydrate formation in water-in-oil emulsions stabilized using either highly hydrophobic silica nanoparticles or a surfactant. On the contrary, the presence of wax did not promote hydrate formation in water-in-oil emulsions stabilized using the least hydrophobic silica nanoparticles.

Our data indicate that wax did not exist at the water/oil interface; therefore, wax did not serve as nucleation sites for hydrate formation. The addition of wax affected the droplet size of water-in-oil emulsions stabilized by highly hydrophobic silica nanoparticles, which in turn influenced hydrate formation. Also, hydrate dissociation led to destabilization of water-in-oil emulsions in the presence of wax that led to changes in the WAT.

# **6.2 Introduction**

The formation of hydrates and waxes in crude oil pipelines are major flow assurance problems facing the offshore energy industry. Hydrates are non-stoichiometric, ice like crystalline structures that can cause complete blockage of crude oil pipelines.<sup>123</sup> Hydrate formation is an interfacial phenomenon that takes place when hydrocarbons (guest molecules) come in contact with water (host molecules) at suitable conditions.<sup>123</sup> In general, gas hydrate formation takes place at low temperature and high-pressure conditions. The formation of hydrates is considered to be the most important deepwater flow assurance problem.<sup>122</sup> Wax formation and deposition on crude oil pipelines can also lead to partial or complete blockage of pipelines.<sup>170,171</sup>

The formation of water-in-oil emulsions is one of the commonly encountered multiphase flow situations in the petroleum industry and can directly impact hydrate formation. The extent of emulsion stability impacts hydrate plug formation.<sup>172,173</sup> Crude oil naturally contains several water and oil-wet fine solid particles, such as inorganic scales, clays, sand, rust particles produced from corrosion, precipitated asphaltenes, and wax; these dispersed particles not only have the potential to stabilize the emulsions, but also promote hydrate formation by introducing nucleation sites. Thus, quantifying the effect of solid particles (with different wettability), surfactants, and wax on hydrate formation would help in accurately predicting hydrate formation in crude oil pipelines.

The presence of surfactants can promote hydrate formation.<sup>174</sup> In addition to surfactants, Raman et al.<sup>51</sup> observed that solid nanoparticles that stabilize the water-in-oil emulsions promote hydrate

formation in water-in-oil emulsions more than surfactants. Although solid particles promote hydrate formation in water-in-oil emulsions, the effect of hydrophobicity of solid particles on hydrate formation is as yet unknown.

The objective of the current investigation is to quantify the effect of hydrophobicity of solid (silica) particles, which are used to stabilize water-in-oil emulsions, on hydrate formation in water-in-oil emulsions, and to compare the extent of hydrate formation in water-in-oil emulsions stabilized using solid particles of different wettability/hydrophobicity and surfactants in the presence and in the absence of wax. Also, the effect of water, silica, and hydrate forming component on Wax Appearance Temperature (WAT) was quantified. Furthermore, the effect of hydrate dissociation in surfactant and solid stabilized water-in-oil emulsions on WAT was investigated. This manuscript focuses on de-convoluting the effect of hydrophobicity of solid particles (silica nanoparticles), surfactants, and water on hydrate and wax formation in water-in-oil emulsions, and on investigating the inter-relation of hydrates and wax in solid stabilized and surfactant stabilized water-in-oil emulsions.

# 6.3 Materials and Methods

Hydrate formation in water-in-oil emulsions was investigated both in the presence and in the absence of wax. The continuous oil phase consisted of light mineral oil (+99% purity, Sigma Aldrich) and/or cyclopentane (+95% purity, Alfa Aesar). Water-in-oil emulsions were stabilized using either silica nanoparticles or a surfactant. Evonik Inc. provided the fumed silica nanoparticles that were used to stabilize the water-in-oil emulsions. Three different silica nanoparticles were used to stabilize water-in-oil emulsions – silica nanoparticles with the least hydrophobicity (H1), silica nanoparticles with intermediate hydrophobicity (H2), and highly hydrophobic silica nanoparticles (H3). Table 6.1 provides the carbon content for the silica nanoparticles that were used to stabilize the water-in-oil emulsions. Methanol wettability and

carbon content were used to determine the level of hydrophobicity of the silica nanoparticles.<sup>47, 48</sup> Sorbitan monooleate (Span 80) was used as the surfactant. Span 80 is an oil soluble, non-ionic surfactant with an HLB<sup>2</sup> value of  $4.3\pm1.0$  (as stated by the vendor). Paraffin wax (product number - 327204) was purchased from Sigma Aldrich. The detailed analysis of this wax can be found in the paper by Alcazar-Vara et al.<sup>175</sup> The droplet phase consisted of deionized water with a resistivity of 18.2 m $\Omega$  cm<sup>-1</sup>.

The weight fraction of the stabilizers (silica nanoparticles or surfactants) and wax were kept constant at 0.3 wt.% and 5 wt.% respectively. The critical micelle concentration of Span 80 is 0.03 (% v/v).<sup>135,134</sup> Thus, the concentration of the surfactant that was used to stabilize the water-in-oil emulsion was above the critical micelle concentration. For hydrate forming water-in-oil emulsions, the continuous oil phase consisted of an equal amount of light mineral oil and cyclopentane (50:50 by weight). The amount of cyclopentane was in excess of the stoichiometric requirement for formation of cyclopentane hydrates. Investigations of hydrate formation in water-in-oil emulsions were carried out with a water concentration equal to 10 wt.% unless otherwise stated.

silica nanoparticle	Carbon content (%)
H1	0.92
H2	1.2
Н3	3.2

Table 6.1: Carbon content (%) for the solid particles that were used to stabilize the water-in-oil emulsions.

A TA Q2000 Differential scanning calorimeter (DSC) (with a temperature accuracy of +/- 0.1 °C) was used for carrying out calorimetric studies in water-in-oil emulsions. The thermocouples in the DSC measure the temperature of the sample and the reference. The heat required to achieve a

zero difference in the temperature between the reference and the sample is recorded.<sup>176</sup> In the current paper, an exothermic process is denoted by a negative heat flow and an endothermic process is denoted by a positive heat flow. The DSC was used to find the Wax Appearance Temperature (WAT).

An Olympus BX53 cross-polarized optical microscope equipped with a high-speed camera was used for measuring the droplet size of water-in-oil emulsions both in the presence and in the absence of wax. Image J was used to determine the droplet size distribution in water-in-oil emulsions. The schematic of the microscope stage and the image analysis procedure to determine the droplet size of water-in-oil emulsions can be found elsewhere.<sup>50</sup>

## 6.3.1 Preparation of emulsions

All water-in-oil emulsions were prepared using the Ultra-Turrax digital homogenizer operating at 10,000 rpm for 10 minutes. The dispenser had a rotor diameter of 17 mm and a stator diameter of 25 mm. The internal phase was added in a drop wise manner in order to ensure homogeneous distribution of the water droplets.<sup>52</sup>

# 6.3.2 Preparation of hydrate forming emulsion in the absence of wax

Initially, the stabilizers (silica nanoparticles or surfactant) were added to the oil phase consisting of light mineral oil and cyclopentane. The mixture was shaken vigorously to ensure complete mixing of the stabilizer with the oil phase. Then the water was added in a drop wise manner to the continuous oil phase. All steps were performed at room temperature.

# 6.3.3 Preparation of non-hydrate forming emulsion in the presence of wax

Initially, the oil phase consisting of light mineral oil, stabilizer (silica nanoparticles or a surfactant), and wax were heated at 80 °C for two hours in order to eliminate the thermal history of the wax.<sup>177</sup> The Wax Appearance Temperature (WAT) was measured for the oil phase

consisting of light mineral oil, wax, and the stabilizer. For preparation of water-in-oil emulsions, hot water (at 80 °C) was added in a drop wise manner to the continuous oil phase (at 80 °C).

#### 6.3.4 Preparation of hydrate forming emulsion in the presence of wax

Similar to the procedure for preparing the non-hydrate forming emulsions, the oil phase consisting of light mineral oil, stabilizer (silica nanoparticles or a surfactant), and wax were heated at 80 °C for two hours. The temperature of the system was then lowered to 45 °C before the addition of cyclopentane in order to avoid evaporation of cyclopentane (boiling point of cyclopentane – 49 °C) from the water-in-oil emulsion. This was followed by the addition of cyclopentane and hot water (at 45 °C) to the continuous oil phase.

#### 6.3.5 Characterization of emulsions

In order to ensure that the water-in-oil emulsions under investigation were stable over the experimental time, macroscopic and microscopic investigations were carried out. Bottle tests were used to macroscopically characterize the stability of water-in-oil emulsions over the experimental time. Figure 6.1 shows the water-in-oil emulsion stabilized using the least hydrophobic silica nanoparticle with 5 wt.% water fraction (in the presence of wax). From the figure, it can be seen that the emulsion was stable over the experimental time. Similarly, bottle tests were conducted for all the water-in-oil emulsions used in this study. The water-in-oil emulsions showed no phase separation, which indicated that the emulsions were stable during the experimental time.



Figure 6.1: Visual appearance of the water-in-oil emulsion stabilized using least hydrophobic silica nanoparticle with 5wt.% water cut, which was used to investigate the effect of water cut on WAT. (a)  $0^{th}$  hour (b) after the experimental time

In order to ensure that the water-in-oil emulsions did not undergo any structural changes over time at the microscopic level, the droplet sizes were measured for all water-in-oil emulsions immediately after preparation, and also after the experimental time. Figure 6.2 shows the microphotographs of hydrate forming water-in-oil emulsions stabilized using intermediate hydrophobic silica nanoparticles in the absence of wax.



Figure 6.2: Microphotographs of hydrate forming water-in-oil emulsions stabilized using intermediate hydrophobic silica nanoparticles in the absence of wax. (a)  $0^{th}$  hour (b) after the experimental time

Figures 6.3-6.5 show the comparison of the average droplet size (along with the standard deviations) for all the water-in-oil emulsions before and after the experimental time. From the figures, it can be seen that there was no significant change in the droplet size before and after the experimental time.



Figure 6.3: Comparison of the mean droplet size for the non-hydrate forming water-in-oil emulsions (absence of cyclopentane in the oil phase) at the 0<sup>th</sup> hour and after the experimental time. The two vertical bars under each sample represent the mean droplet size of the water-in-oil emulsion at the 0<sup>th</sup> hour (left vertical bar) and after experimental time (right vertical bar) respectively.



Hydrate forming water-in-oil emulsions in the absence of wax

Figure 6.4: Comparison of the mean droplet size for the hydrate forming water-in-oil emulsions (in the absence of wax) at the 0<sup>th</sup> hour and after the experimental time. The two vertical bars under each sample represent the mean droplet size of the water-in-oil emulsion at the 0<sup>th</sup> hour (left vertical bar) and after experimental time (right vertical bar) respectively.



Hydrate forming water-in-oil emulsions in the presence of wax

Figure 6.5: Comparison of the mean droplet size for the hydrate forming water-in-oil emulsions (in the presence of wax) at the 0<sup>th</sup> hour and after the experimental time. The two vertical bars under each sample represent the mean droplet size of the water-in-oil emulsion at the 0<sup>th</sup> hour (left vertical bar) and after experimental time (right vertical bar) respectively.

Thus, it was concluded that the water-in-oil emulsions, which were used in the study, were stable during the entire experimental time. Interestingly, Figure 6.4 shows that the average droplet size increased with an increase in hydrophobicity of the solid particles, which is in accordance with the observations of Binks et al.<sup>47</sup> and Raman et al.<sup>50</sup>

#### 6.3.6 Experimental protocol for DSC measurements

## 6.3.6.1 Hydrate forming water-in-oil emulsions in the absence of wax

The temperature of the system was decreased from 25 °C to -45 °C at the rate of 1 °C/min. Next, the temperature of the system was increased back to 25 °C at the rate of 1 °C/min.

#### 6.3.6.2 Non-hydrate forming water-in-oil emulsions in the presence of wax

The temperature of the sample was decreased from 60 °C to -5 °C at the rate of 1 °C/min. The same procedure was followed to determine the WAT for systems containing a mixture of light mineral oil and either solid particles or a surfactant in the absence of water.

## 6.3.6.3 Hydrate forming water-in-oil emulsions in the presence of wax

For hydrate forming water-in-oil emulsions, the temperature of the system was held at 48 °C for 30 minutes and then the temperature was reduced to -45 °C at the rate of 1 °C/min. Next, the temperature was ramped up to 48 °C at the rate of 1 °C/min. The procedure was repeated consecutively for three times in order to study the effect of hydrate dissociation on emulsion stability in the presence of wax.

# **6.4 Results and Discussion**

The key objective of this paper was to investigate the effect of hydrophobicity of solid particles on hydrate forming water-in-oil emulsions both in the presence and in the absence of wax. In addition, a comparison of the extent of hydrate formation in solid stabilized water-in-oil emulsions and surfactant stabilized water-in-oil emulsions both in the presence and in the absence of wax was carried out. To de-convolute the effect of wax on hydrate formation, we first quantified the effect of water and particle hydrophobicity on wax appearance temperature (WAT).

#### 6.4.1 Effect of water and particle hydrophobicity on wax appearance temperature (WAT)

The effect of water on WAT is shown in Table 6.2. From the results, it can be seen that the presence of water did not have a significant effect on WAT at the investigated water fractions. The wax appearance temperature increased by 1.8 °C on addition of 20 wt.% water. This phenomenon could be attributed to the presence of crystal nucleation sites, which was provided by the emulsified water.<sup>178</sup>

Systems	WAT (°C)
Light mineral oil + Wax	25.8
Light mineral oil + wax + H1	25.5
Light mineral oil + wax + H1 + 5wt% water	26
Light mineral oil + wax + H1 + 10wt% water	26.5
Light mineral oil + wax + H1 + 20wt% water	27.3

Table 6.2: Effect of water on WAT in water-in-oil emulsions

The effect of hydrophobicity of silica nanoparticles and Span 80 on WAT in water-in-oil emulsions is shown in Table 3. No effect on WAT was observed in the presence of silica nanoparticles of different hydrophobicities (at the investigated weight fraction [0.3 wt.%]).

Systems	WAT (°C)
Light mineral oil + wax + H1+ 10wt% water	26.5
Light mineral oil + wax + H2 + 10wt% water	26.3
Light mineral oil + wax + H3 + 10wt% water	26.3
Light mineral oil + wax + Span 80 + 10wt% water	26.2

Table 6.3: Effect of hydrophobicity of solid particles on WAT in water-in-oil emulsions

# 6.4.2 Effect of cyclopentane on wax appearance temperature

Table 6.4 shows the effect of cyclopentane on WAT. The presence of cyclopentane reduced the WAT in all cases.

Systems	WAT (°C)
Light mineral oil + Cyclopentane + wax + H1 + water	20.7
Light mineral oil + Cyclopentane + wax + H2 + water	23
Light mineral oil + Cyclopentane + wax + H3 + water	22.2
Light mineral oil + Cyclopentane + wax + Span 80 + water	21

Table 6.4: Effect of cyclopentane (lighter hydrocarbon) on WAT

# 6.4.3 Effect of particle hydrophobicity on hydrate formation

The emulsion stability can be determined by the shape and temperature at which the exothermic peak for ice nucleation is observed. A symmetric peak during ice nucleation characterizes a stable emulsion.<sup>179,180</sup> Figure 6.6 shows the heat flow curves in DSC during hydrate formation and dissociation in water-in-oil emulsion stabilized using the least hydrophobic particle (H1). During cooling, an exothermic peak was observed at -38 °C, which corresponds to the homogeneous ice nucleation temperature.<sup>181</sup>



Figure 6.6: Thermogram for water-in-oil emulsion stabilized using least hydrophobic silica nanoparticle

The exothermic peak observed during ice nucleation point was symmetrical, which indicated that the emulsion was highly stable. Figure 6.7 shows the cooling and heating cycles in a DSC for hydrate forming water-in-oil emulsions stabilized using either solid particles of different hydrophobicities (least hydrophobic [H1], intermediate hydrophobicity [H2], highly hydrophobic [H3] or a surfactant [Span 80]. The freezing point of ice decreases with a decrease in droplet size.<sup>180</sup> Therefore, Figure 6.7a shows that an increase in hydrophobicity of the solid particles led to an increase in the freezing point of ice. Thus, an increase in hydrophobicity of solid particles caused an increase in droplet size in water-in-oil emulsions.<sup>47</sup> From the cooling curves (Figure
6.7a), it can also be concluded that all the water-in-oil emulsions in the current study, which were either stabilized using solid particles of different hydrophobicities or a surfactant were stable.



Figure 6.7: Thermograms for water-in-oil emulsions stabilized using either solid particles of different hydrophobicities or a surfactant a) Cooling cycle b) Heating cycle.

Both ice and hydrate dissociation is an endothermic process. The thermograms for water-in-oil emulsions stabilized using either solid particles of different hydrophobicities or surfactants were characterized by the presence of two dissociation peaks (ice and hydrate dissociation) (Figure 6.7b). The first dissociation peak which is close to 0 °C corresponds to ice dissociation and the small endothermic peak after ice dissociation corresponds to hydrate dissociation.<sup>182</sup> From the heating curves (Figure 6.7b), it can be concluded that the amount of hydrate formation decreased with an increase in hydrophobicity of solid particles. This phenomenon can be attributed to the fact that an increase in particle hydrophobicity caused an increase in the size of water droplets, which resulted in a reduction in available surface area for hydrate formation. Consequently, the amount of hydrate formation is reduced in water-in-oil emulsions stabilized using highly hydrophobic silica nanoparticles (water-in-oil emulsions with larger droplets) as compared to water-in-oil emulsions stabilized using least hydrophobic silica nanoparticles (water-in-oil emulsions with smaller droplets).

Furthermore, it can be seen that solid particles promote hydrate formation to a greater extent than a surfactant, which is in accordance with the observations of Raman et al.<sup>51</sup> In the presence of surfactant, the ice dissociation peak was not immediately followed by the hydrate dissociation peak, unlike solid stabilized water-in-oil emulsions. This phenomenon was attributed to the fact that solid particles at the oil-water interface served as nucleation sites and thereby reduced the induction time for hydrate formation to a greater extent than a surfactant.<sup>51, 183, 184</sup> Although solid particles serve as nucleation sites to enhance hydrated formation, in the case of water-in-oil emulsions stabilized using highly hydrophobic silica nanoparticles, the mass transfer limitation as a result in a reduction in surface area was considerably high and hence the extent of hydrate formation was lower than the surfactant stabilized water-in-oil emulsions.

## 6.4.4 Effect of wax on hydrate formation in water-in-oil emulsions

The effect of wax on the extent of hydrate formation in water-in-oil emulsions stabilized using either silica particles of different hydrophobicities or a surfactant can be seen from the heat flow curves in DSC shown in Figure 6.8.



Figure 6.8: Thermograms for hydrate forming water-in-oil emulsions in the presence of wax

The area under heat flow versus time provides the heat associated with the process. Table 6.5 shows the amount of heat absorbed during the hydrate dissociation process for water-in-oil emulsions stabilized using either solid particles or a surfactant, both in the presence and in the absence of wax. From Table 6.5 and Figures 6.7 and 6.8, it can be seen that the presence of wax enhanced hydrate formation in water-in-oil emulsions stabilized using intermediate hydrophobic solid particles, highly hydrophobic solid particles, and a surfactant. At the water fractions investigated in this work, wax did not promote hydrate formation in water-in-oil emulsions stabilized using the least hydrophobic particles.

Stabilizers	Q (J)*10^-3						
that were used to stabilize water-in- oil emulsions	Absence of wax	Presence of wax	Increase or decrease in Q in the presence of wax (%)	Does presence of wax promote hydrate formation			
H1	38.5	16.1	-58.1	No			
H2	10.5	13.1	24.4	Yes			
Н3	2.6	10.3	288.9	Yes			
Span80	3.7	13.8	271.3	Yes			

Table 6.5: Heat absorbed during the hydrate dissociation process for water-in-oil emulsions stabilized using either solid particles or a surfactant, both in the presence and in the absence of wax.

In the case of hydrate forming solid stabilized water-in-oil emulsions that were prepared in the absence of wax, the solid particles reside at the water-oil interface and hence promote hydrate formation to a greater extent than the surfactants by providing nucleation sites at the water-oil interface (region of hydrate formation). It is believed that wax formation might provide nucleation sites that could enhance hydrate formation.<sup>149</sup> In order to test this hypothesis, water-in-oil emulsions stabilized using either solid particles of different hydrophobicities or a surfactant in the presence of wax were observed under the cross-polarized microscope. Figure 6.9 shows the microphotographs of water-in-oil emulsions that were stabilized either using solid particles of different hydrophobicities or a surfactant in the presence of wax.



Figure 6.9: Microphotographs of water-in-oil emulsions that were stabilized in the presence of wax using (a) H1 (b) H2 (c) H3 (d) Span 80. Images were taken at the 0<sup>th</sup> hour (at room temperature). The white streaks represent the wax crystals in the continuous oil phase.

The white streaks in the microphotographs indicated the presence of wax. From the microphotographs, it can be seen that wax was distributed in the continuous oil phase and does not completely reside at the oil-water interface. Wax – a highly hydrophobic compound – remains preferentially dispersed in the bulk oil phase rather than at the oil-water interface. Consequently, this work indicates that wax does not likely serve as nucleation sites for hydrate formation. In order to find the mechanism by which hydrate formation was enhanced in the presence of wax, droplet size measurements of water-in-oil emulsions in the presence and in the absence of wax were carried out. From Table 6.6, it can be seen that in the presence of wax, the droplet size

decreased for water-in-oil emulsions stabilized using intermediate and highly hydrophobic solid particles and surfactant stabilized water-in-oil emulsions, thereby, increasing the interfacial contact area between the host and the guest molecules. However, the droplet size increased for water-in-oil emulsions stabilized using least hydrophobic solid particles in the presence of wax, which in turn decreases the interfacial contact area of host and guest molecules. Thus, the modification in the interfacial properties of water-in-oil emulsions in the presence of wax led to enhanced hydrate formation in surfactant stabilized water-in-oil emulsions and in water-in-oil emulsions stabilized using intermediate and highly hydrophobic solid particles.

Hydrate forming	Average droplet diameter (μm)		Increase or decrease in	Does presence of wax
water-in-oil emulsions stabilized using	In the absence of wax	In the presence of wax	droplet diameter in the presence of wax (%)	promote hydrate formation
H1	5.8±1.7	8.5±2	46.6	No
H2	16.3±3.3	12.9±4.4	-20.9	Yes
Н3	18.9±4	12±4	-36.5	Yes
Span 80	4.5±1.1	2.3±0.8	-48.9	Yes

Table 6.6: Average droplet diameter for water-in-oil emulsions in the presence and in the absence

## of wax.

In order to be certain that the enhanced temperature at which the water-in-oil emulsions containing wax were prepared did not contribute to the reduction in droplet size, both surfactant stabilized and solid stabilized water-in-oil emulsions, in the absence of wax, were prepared at elevated temperature (45 °C). Table 6.7 gives the comparison of the average droplet size for solid and surfactant stabilized water-in-oil emulsions that were prepared at room temperature and at elevated temperature (45 °C) in the absence of wax. It can be seen that the enhanced temperature led to an increase in droplet size <sup>185</sup> unlike water-in-oil emulsions in the presence of wax, which

led to a decrease in droplet size. These experiments show that it is the presence of wax that modifies the droplet size of water-in-oil emulsions, which led to increased oil-water interfacial contact area between the dispersed and the continuous phase that in turn led to an increase in hydrate formation.

Hydrate forming water-in-oil	Average droplet diameter (μm)		
emulsions stabilized using	At room temperature	At elevated temperature	
H1	5.8±1.7	9.8±2.8	
H2	16.3±3.3	19.5±3.8	
НЗ	18.9±4	19.3±7.2	
Span 80	4.5±1.1	6±1.5	

Table 6.7: Comparison of average droplet diameter for hydrate forming water-in-oil emulsions (in the absence of wax) prepared at normal room temperatures and at elevated temperatures (at the 0<sup>th</sup> hour).

# 6.4.5 Effect of hydrate dissociation in water-in-oil emulsions in the presence of wax

Hydrate dissociation in water-in-oil emulsions led to destabilization of water-in-oil emulsions..<sup>50,</sup> <sup>133</sup> Our interest was to investigate the effect of hydrate dissociation on emulsion stability in the presence of wax. Figure 6.10 shows the hydrate dissociation trends for water-in-oil emulsions stabilized using either silica nanoparticles of different hydrophobicities or surfactants in the presence of wax. The results showed significant reduction in hydrate formation after each consecutive cycle, which indicated emulsion destabilization.<sup>133</sup>



Figure 6.10: Hydrate dissociation peaks for water-in-oil emulsions stabilized using a) least hydrophobic solid particles (H1) b) intermediate hydrophobic solid particles (H2) c) highly hydrophobic solid particles (H3) d) Span 80 for three consecutive runs.

The decrease in the interfacial contact area between water and oil after emulsion destabilization led to significant reduction in hydrate formation. In addition, it can be seen that emulsion destabilization is very significant in the presence of surfactants compared to solid stabilized water-in-oil emulsions. Furthermore, water-in-oil emulsions stabilized using least hydrophobic particles showed only a little destabilization after hydrate dissociation as compared to water-in-oil emulsions stabilized using solid particles of higher hydrophobicity, which is in accordance with the observations of Raman et al.<sup>50</sup> From the above results, it can be concluded that the presence of wax did not mitigate emulsion destabilization after hydrate dissociation in water-in-oil emulsions.

#### 6.4.6 Effect of hydrate dissociation on wax appearance temperature

Hydrate formation in water-in-oil emulsions in the presence of wax led to destabilization of emulsions. Figure 6.11 shows the WAT for three consecutive cycles in hydrate forming water-in-oil emulsions stabilized using either silica nanoparticles of different hydrophobicities or surfactants in the presence of wax. As mentioned in the last section, emulsion destabilization takes places as we proceed from cycle 1 to cycle 3. Therefore, WAT increased sharply with emulsion destabilization (larger droplet size).



Figure 6.11: The Wax Appearance Temperature (WAT) for hydrate forming water-in-oil emulsions stabilized in the presence of wax using a) least hydrophobic solid particles (H1) b) intermediate hydrophobic solid particles (H2) c) highly hydrophobic solid particles (H3) d) Span 80 for three consecutive cycles.

Pirrozian et al.<sup>178</sup> observed an increase in WAT with a decrease in droplet size (produced by varying the shear rate). These results contradict the results observed in this study. Thus, an investigation was carried out to determine the observed difference in the WAT with destabilization of hydrate forming water-in-oil emulsions. The likely reason for the observed difference hinges on the fact that hydrate dissociation is accompanied with an increase in pressure due to the release of hydrate forming guest molecule into the gas phase.<sup>147</sup> In order to test if the hydrate dissociation in the current study aided in removal of cyclopentane from the oil phase, the weight of the surfactant stabilized water-in-oil emulsion in the presence of wax that was used for the DSC experiments was measured before hydrate formation and after hydrate dissociation (after three consecutive runs). The results showed more than 75% reduction in cyclopentane from the sample. Hence, we believe that the removal of cyclopentane from the oil phase due to hydrate dissociation decreased the solubility of wax in the continuous phase that in turn led to increase in the WAT. Therefore, hydrate dissociation would lead to a significant increase on the WAT of oil since hydrate dissociation is always accompanied with the release of hydrate forming guest molecule<sup>147</sup> (lighter hydrocarbon, typically smaller than n-pentane) that in turn reduces the solubility of wax in the continuous oil phase.

## **6.5** Conclusions

Hydrate and wax formation in water-in-oil emulsions were investigated in the presence of silica nanoparticles (of different hydrophobicities), surfactant, and cyclopentane. The effect of wax on the extent of hydrate formation was quantified. It was concluded that

• The presence of water did not show a significant effect on WAT (at the investigated weight fractions [up to 20 wt%]). In addition, the silica nanoparticles of different hydrophobicities did not have an effect on WAT at the investigated weight fractions.

- The presence of cyclopentane (hydrate forming component) in the continuous oil phase reduced the WAT significantly by increasing the solubility of wax in the continuous oil phase.
- The hydrophobicity of solid particles at the water-oil interface had a profound effect on the extent of hydrate formation. Highly hydrophobic silica nanoparticles at the oil-water interface reduced the extent of hydrate formation to a greater extent as compared to least hydrophobic silica nanoparticles at the oilwater interface.
- In general, solid stabilized water-in-oil emulsions enhanced hydrate formation to a greater extent than surfactant stabilized water-in-oil emulsions, which is in accordance with the observations of Raman et al.<sup>51</sup>
- The presence of wax promoted hydrate formation in water-in-oil emulsions stabilized using either highly hydrophobic and intermediate hydrophobic silica nanoparticles or a surfactant.
- On the contrary, the presence of wax did not promote hydrate formation in waterin-oil emulsions stabilized using the least hydrophobic silica nanoparticles. This phenomenon was attributed to the change in the droplet size of emulsions due to the presence of wax rather than the creation of additional nucleation sites for hydrate formation in the presence of wax.
- Hydrate formation in water-in-oil emulsions in the presence of wax led to destabilization of water-in-oil emulsions.
- The destabilization of water-in-oil emulsions led to a significant increase in WAT for the water-in-oil emulsions. This phenomenon was attributed to the release of hydrate forming component (cyclopentane) from the continuous oil phase due to hydrate dissociation. Thus, it was found that hydrate dissociation led

to a significant increase in WAT in addition to destabilization of the water-in-oil emulsion.

Further investigations will be carried out to examine the potential use of hydrophobic silica nanoparticles in hydrate mitigation strategies. Also, the relationship between the droplet size and hydrate conversion in the presence of wax could be investigated. In addition, investigations will be carried out to quantify the combined effect of both solid particles and surfactants in water-in-oil emulsions in the presence of wax.

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# **APPENDICES**

## Determination of Droplet Size of Emulsions

Image J software was used to measure the droplet size of emulsions. The following procedure was adopted to measure the droplet size of emulsions from the microphotographs that were obtained from the Olympus BX53 optical microscope.



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