Article

Surfactant-Enhanced Spontaneous Emulsification Near the Crude Oil−Water Interface

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ABSTRACT: Spontaneous emulsification near the oil−water interface and destabilization of water-in-oil emulsions in the bulk oil phase may affect the efficiency of improved oil recovery. In this study, we investigate the effect of a demulsifier surfactant on spontaneous emulsification near the oil−aqueous phase interface and in the bulk oil phase through imaging. The results show that pronounced spontaneous emulsions may form near the oil−aqueous phase interfaces. The mechanism of diffusion and stranding is believed to dominate spontaneous emulsification. A demulsifier surfactant, which has been used for demulsification of water-in-oil emulsions in the bulk oil phase, is found to enhance spontaneous emulsification near the oil−water interface. The diffusive flux of water through the interface can be enhanced if the demulsifier is added into the aqueous phase, in which the demulsifier may act as a carrier. It can generate a region of local supersaturation combined with hydrated asphaltenes and result in faster and stronger spontaneous emulsification. We also investigate the effect of a viscosifier polymer on emulsion formation. The polymer is used to improve sweep efficiency in oil displacement. In this work, we show that it can inhibit emulsification in the bulk oil phase, but its effect on spontaneous emulsification near the interface is not pronounced.
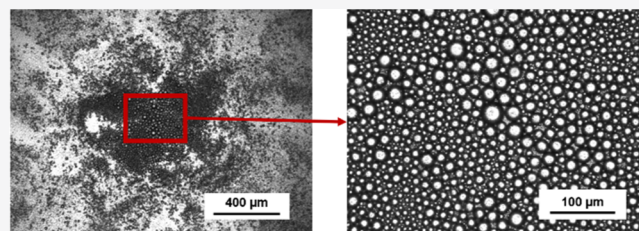
1. INTRODUCTION

Chemical flooding has been used in improved oil recovery (IOR) in the past few decades. In conventional chemical flooding, the two major mechanisms are interfacial tension (IFT) reduction by surfactants and aqueous-phase viscosification by polymers.[1−7] Many surfactants have been used with the primary objective of significantly reducing the IFT. The viscosification of the aqueous phase by polymers is the key technology for mobility control and sweep efficiency improvement. The combinations of surfactant/polymer and alkaline/surfactant/polymer have been considered to improve oil recovery, reduce the amount of surfactant use, and extend the range of effectiveness at high salt concentrations.[8] As an alternative, low salinity water (LSW) injection in IOR has gained growing interest.[9−11] When the low salt concentration is effective, it has been argued that the mechanisms may include wettability alteration,[12,13] reduction in IFT,[14−17] clay migration,[18] and more recently the increase of interfacial elasticity.[10] The technique of adding functional molecules at ultra-low concentrations is highly sought-after for chemicals that are inexpensive, environmentally friendly, and effective at high salt concentrations.[19,20] Recently, we have shown that an ultra-low concentration of the demulsifier in the injection brine may improve oil recovery efficiency, which correlates to the increase in interfacial viscoelasticity.[20] In the new process, interfacial viscoelasticity is dominant. Adsorption of asphaltenes and surfactants at the fluid−fluid interface is related to IFT; the molecular structure at the interface is related to

interfacial viscoelasticity. Direct imaging of the interface may yield an improved understanding of interfacial viscoelasticity.

Emulsion formation in the bulk phase (in vials) generally requires intense mechanical agitation. Spontaneous emulsion formation near the interface has been observed without external energy input.[21,22] Emulsification in the bulk phase may cause ineffective phase separation in crude oil refinery operations and a decrease in flow assurance,[23,24] both of which are undesirable. However, some authors investigating IOR have argued that emulsion formation in LSW injection may lead to efficiency improvement.[12,13,25−27] Emadi and Sohrabi[13] have observed spontaneous microemulsions in oil recovery resulting from low salinity injection. They hypothesize that the microemulsions may contribute to the IOR because of the swelling of connate water and remobilization of the trapped oil. Tagavifar et al.[25] have observed spontaneous emulsion formation and its dynamic behavior in chemical flood microfluidic experiments. Du et al.[12] have reported oil swelling due to water-in-oil emulsions in microfluidic experiments in LSW flooding, which contributes to sweep-efficiency improve-

ment. AlHammadi et al.[28] have reported a correlation between the propensity of microdispersion and oil recovery enhancement based on LSW core flooding.

There have been a number of investigations on spontaneous emulsification at or near the interface. Various authors relate the phenomena to three mechanisms: (1) interfacial turbulence, (2) interfacial bending, and (3) diffusion and stranding.[24,29,30] Ultra-low IFT is a prerequisite of interfacial turbulence. Spontaneous emulsification has been observed predominantly when surfactants are used for IFT reduction.[24,31,32] At a relatively high IFT (e.g., >1 mN/m), spontaneous emulsions can also form due to different mechanisms. Duboué et al.[33] investigate the mechanism for spontaneous emulsification near the interface of asphaltene—toluene and the water phase. They suggest that a mechanism akin to diffusion and stranding leads to the formation of water-in-oil emulsions. Rodríguez-Hakim et al.[24] present a comprehensive analysis of the asphaltene—toluene—water fluid system to confirm the mechanism of diffusion and stranding in spontaneous emulsification and rule out the other two mechanisms. Duboué et al.[33] and Rodríguez-Hakim et al.[24] observe spontaneous emulsification mainly near the interface. The process is dominated by asphaltenes. Without asphaltenes, there is no emulsion at the interface of the toluene and aqueous phases. Others also report that oil-in-water emulsion can also form spontaneously if surfactants (e.g., Span 80 for flow assurance) are added in the oil phase.[34−36] The effect of different types of chemicals on spontaneous emulsification near the crude oil—aqueous phase interface is largely unknown. Advancing the knowledge of spontaneous emulsification may give insight into the IOR process from chemical flooding.

In this study, we use imaging to investigate the effect of functional molecules on the formation of emulsions near the oil—aqueous phase interface in relation to potential mechanisms for the new IOR method using ultra-low-concentration demulsifiers. We employ three different aqueous phases: deionized water, LSW, and seawater. Two types of chemicals, a surfactant for demulsification in the bulk oil phase and a polymer for aqueous-phase viscosification, and their mixtures, are added into the aqueous phase. The effect of the demulsifier surfactant on polymers is important in industrial applications. Based on imaging, we perform a comprehensive study of spontaneous emulsification. The effectiveness of the emulsion destabilization in the bulk oil phase is also examined for reference. The interfacial viscoelasticity, bulk water viscosity, and IFT measurements are included for completeness.

2. EXPERIMENTAL SECTION

2.1. Materials. A crude oil sample is used for the imaging of the bulk oil phase and the interface. The initial water content of the crude oil sample is about 20%, part of which is in the form of water-in-oil emulsions. It is centrifuged at 2000 rpm for 8 h to remove the water phase and the water-in-oil emulsions. The separated oil phase is then sonicated for 20 min before being used in measurements. The basic properties of the crude oil sample are listed in Table 1. Generally,

Table 1. Basic Properties of the Crude Oil Sample at 25 °C

property	value
density (g/cm^3)	0.899 ± 0.004
viscosity (mP·s)	45.6 ± 0.2
TAN (mg$_{KOH}$/g)	0.27 ± 0.03
TBN (mg$_{KOH}$/g)	6.28 ± 0.06

crude oil samples are not transparent, and the fluid—fluid interface cannot be observed through the oil phase using an optical microscope. We dilute the crude oil with toluene by a volume ratio of 1:20 (oil/toluene) to facilitate a transparent view. The properties are also measured for the mixture of crude oil and toluene. We refer to the mixture as the oil phase in the rest of this paper.

We select a series of representative oil—aqueous phase systems in IOR based on chemical flooding to examine the effect of chemicals on spontaneous emulsification. Three different types of aqueous phases are employed: deionized water (DIW), LSW, and seawater (SW). SW is often used for waterflooding and is available for injection in many oil fields. The composition of the SW is listed in Table 2. The LSW is

Table 2. Composition of the SW

| composition	content (mg/L)
Na$^+$	14,000.00
K$^+$	450.00
Ca^{2+}	485.00
Mg^{2+}	1370.00
Ba^{2+}	0.05
Sr^{2+}	8.00
Fe^{2+}	0.01
Cl$^-$	23,860.00
SO$_4^{2-}$	3190.00
HCO$_3^-$	115.00
CO$_3^{2-}$	2.20
total salinity	43,480.00

prepared with diluted SW to the salinity of 0.1 wt %. Two types of chemicals are added into the aqueous phases: a surfactant for demulsification of water-in-oil emulsions in the oil phase and a polymer for aqueous-phase viscosification. The surfactant is a demulsifier (DEM), which is a non-ionic functional molecule provided by Nalco Champion, EcoLab, USA. It mainly consists of ethoxylated resins. The concentration of the demulsifier in the aqueous phase is 100 ppm. The hydrolyzed-polyacrylamide (HPAM, FP 3630S) polymer is provided by SNF, USA, which is used for aqueous-phase viscosification. The average molecular weight is about 20 million g/mol, and the hydrolysis degree is about 25−30%. The pure polymer is in dry powder. The concentration in the aqueous phase is 2000 ppm. Our interest in polymers is mainly driven by their widespread use in improving the sweep efficiency for IOR and the potential for the synergistic effect from combined polymers and demulsifier surfactants. To examine the synergy effect, we use a mixture of 2000 ppm HPAM and 100 ppm DEM in the aqueous phase. The effects on interfacial viscoelasticity and IFT are provided in the Supporting Information, S1−S2. The viscosity measurements are provided in the Supporting Information, S3. In order to have a pronounced aqueous-phase viscosity increase, the concentration of HPAM should be generally high, about 20 times higher than that of DEM.

2.2. Imaging of the Interface. Glass slides with concavity are used for the imaging of the interface. The diameter of the concavity is about 16 mm. The depth is 1.5 mm. The slide and cover glass are pre-cleaned with ethanol and DIW and then air-dried. All the liquids are sonicated for 20 min before the tests to keep uniformity. The sketch map for observing the interface is illustrated in Figure 1. One droplet of the aqueous phase is placed in the center of the concavity. The volume of the droplet is around 40−60 μL. The concavity is then carefully filled with the oil phase without disturbance and sealed with a cover glass. The volume of the oil phase is about 100−120 μL. We use a Leica DM 2700 M microscope and an Infinity 2 camera for imaging. The top region of the droplet is observed to have a relatively flat interface. Magnifications of 5×, 20×, and 100× are applied.

2.3. Emulsion by Agitation in the Bulk Oil Phase. Demulsifiers can destabilize the emulsions already formed or inhibit emulsion formation in the bulk oil phase. To examine the
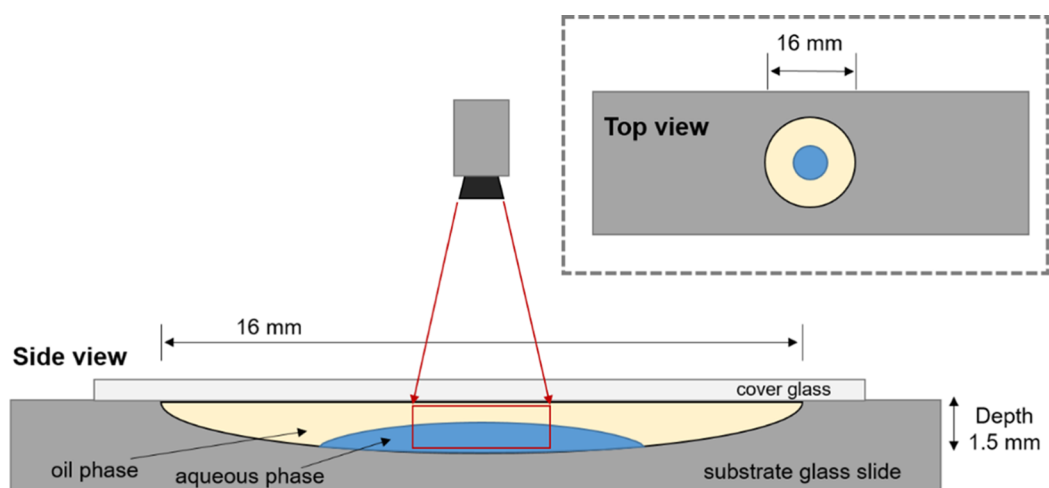
Figure 1. Sketch of the setup and the method for observing the oil–aqueous phase interface. The red box in the bottom panel represents the area observed through the microscope.
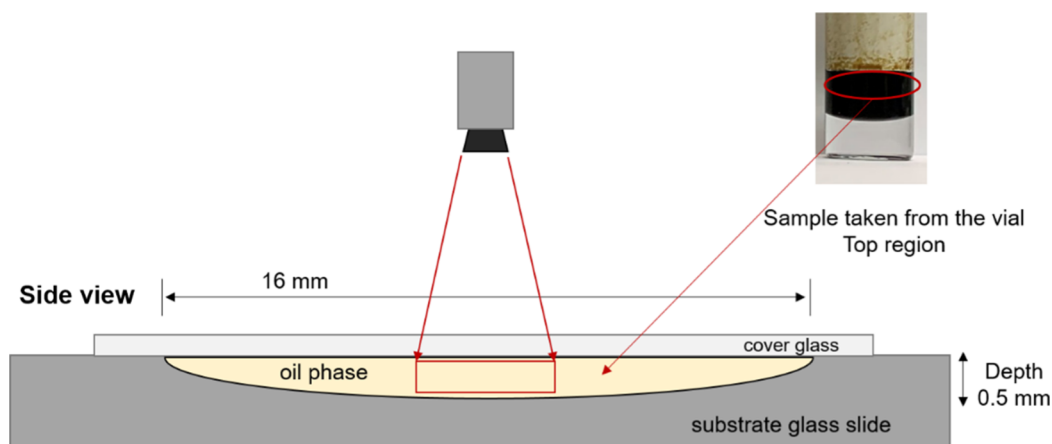

Figure 2. Sketch of the setup for observation of the bulk oil phase. The oil sample is taken from the top of the vial after agitation (top right). The red box in the bottom panel represents the area observed through the microscope.
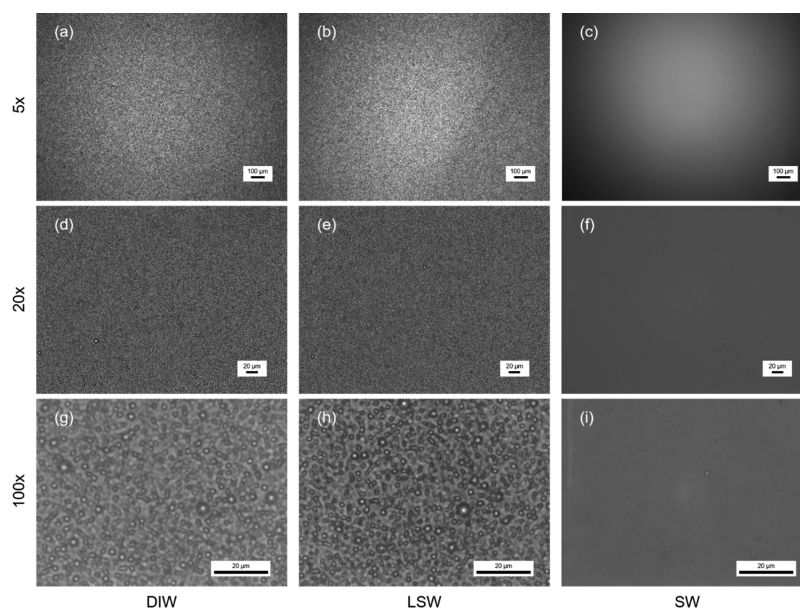

Figure 3. Images of the oil–aqueous phase interface without chemicals. The images are taken 1 h after the oil is placed on the top of the aqueous phase. The magnifications are 5×, 20×, and 100×.
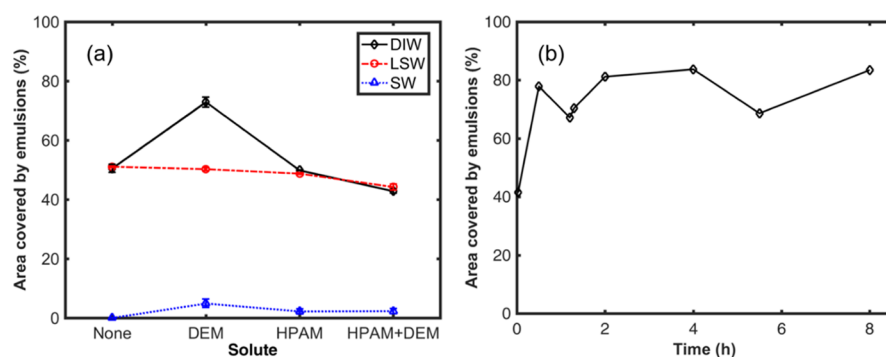
Figure 4. Interfacial area covered by emulsions near the interface of the oil−aqueous phase. (a) Intensity of emulsification with and without the two chemicals in the aqueous phase. The results are based on the images taken 1 h after the oil is placed on the top of the aqueous phase. (b) Evolution of the enhanced emulsification near the oil−DIW interface with DEM. The results are calculated based on images with a 5× magnification.

Magnification: 5x   20x   100x
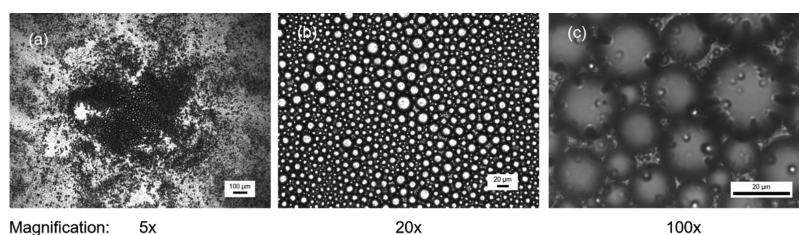
Figure 5. Images of the oil−DIW interface at different magnifications with DEM in the aqueous phase. The images are taken 1 h after the oil is placed on the top of the aqueous phase. (b,c) are taken around the central region of panel (a).
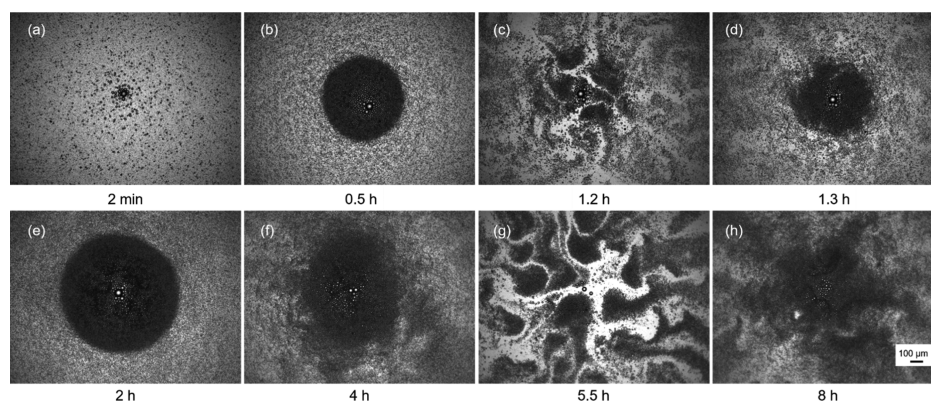
Figure 6. Evolution of the oil−DIW interface with DEM in the aqueous phase at a 5× magnification. Due to the effect of gravity, the large emulsions concentrate in the center at the top of the interface and form a dark circular region.

effectiveness of the demulsifiers, we carry out a series of tests in vials and captured images of the bulk oil phase with emulsification by agitation. The sketch map is presented in Figure 2. First, 1.5 mL of the oil phase and 1.5 mL of the aqueous phase are placed into a vial. Then, we shake the vial for 10 s to mix the oil and aqueous phases. Emulsions may form in this process. In general, the bulk oil phase may contain macroemulsions after agitation of the oil and water mixture. The emulsions may gradually fall onto the interface due to gravity and coalesce with the aqueous phase. Only stable emulsions remain in the bulk oil phase for a long time. The samples from the top of the oil phase are taken at 1 h after shaking and then placed into the concavity with a depth of about 0.5 mm and sealed with a cover glass. We use the same microscopy system to observe the interface and the bulk oil phase. All the measurements are conducted at room temperature.

3. RESULTS AND DISCUSSION

3.1. Imaging. The images of the interface of the oil−aqueous phase without chemicals are presented in Figure 3. We take the percentage of the interfacial area covered by

emulsions as an indicator of emulsification intensity (see Figure 4). The indicator is calculated based on the images in a binary form. We generate binary images from the original gray scale by assigning a threshold under the same brightness. The threshold is selected empirically to maintain the shape of the emulsions. The percentage of the area covered by emulsions is obtained by the number of pixels for emulsions over the total number of pixels. The error bars are from three images for each point.

In the oil−DIW and oil−LSW systems, we observe a large number of emulsions forming spontaneously near the interface, which cover up to 50% or more of the interfacial area. In the oil−SW system, there is no emulsion formation. The spontaneous emulsification at the aqueous−oil interface may be affected by salinity. The emulsions decrease with a salinity increase. This observation is in agreement with the findings in the literature from the interface of water and the mixture of asphaltene and toluene.[25,33]
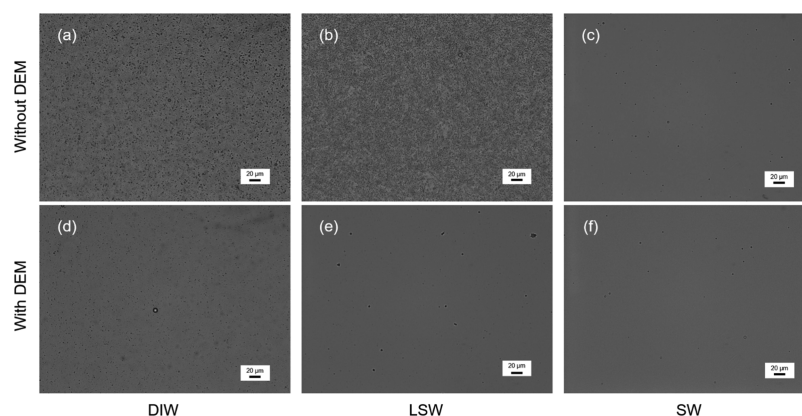
Figure 7. Emulsification in the bulk oil phase after agitation with and without DEM. The images are taken 1 h after agitation. The demulsifier is added into the aqueous phase initially. The magnification is 20×.

The addition of DEM in DIW has a significant effect on emulsion formation near the interface. There is more pronounced spontaneous emulsion formation; the size and intensity increase compared to the condition without DEM. Up to 70% or more of the interfacial area is covered by spontaneous emulsions (see Figure 4). The size of the emulsions in the central region approaches 10−30 μm (Figure 5). We monitor the evolution of the emulsions for 8 h (see Figure 6). The enhanced emulsion formation and accumulation are highly unstable, especially for large emulsions around the center. The emulsions tend to coalesce with each other and accumulate at the center gradually. Then, some of the large droplets coalesce with the aqueous phase suddenly. The incident may disturb the interface and lead to disordered patterns of emulsion clusters. After that, the emulsions resume accumulating at the center of the interface. The process occurs periodically, which leads to the fluctuation of the area covered by emulsions with time (see Figures 4b and 6).

When HPAM and the mixture of DEM and HPAM are added to the aqueous phase, the images of the interface show a similar intensity of spontaneous emulsification to DEM alone except in oil−DIW (Figures 4 and S4).

We take the percentage of the image generated from the setup in Figure 2 for the bulk oil phase that is covered by emulsions as an indicator of the intensity of emulsification. We observe pronounced emulsion formation in the bulk oil phase when mixed with DIW and LSW after agitation. No appreciable emulsion is found in the oil phase mixed with SW. The intensity of emulsion in the bulk oil phase decreases with a salinity increase. DEM, HPAM, and their mixture are very effective in inhibiting emulsion formation in the bulk oil phase after mixing with the aqueous phases, especially by DEM (see Figures 7 and 8). The mixture of DEM and HPAM is significantly less effective in demulsification from DIW, where some aggregates appear (Figures S4 and S5).

3.2. Mechanisms. Based on the imaging of the interface and the bulk oil phase, we observe contrasting functionality of DEM in the bulk and at the interface. As expected, DEM destabilizes the emulsions or inhibits emulsion formation in the bulk oil phase. In this work, we find that DEM enhances spontaneous emulsification near the interface.
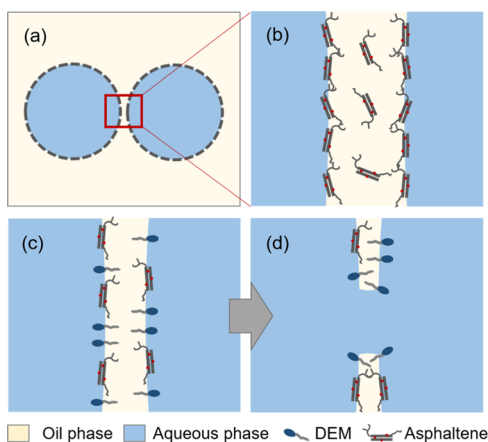
In the bulk oil phase, without DEM in the aqueous phase, the emulsions formed by agitation are due to the accumulation of asphaltenes at the interface of the water-in-oil emulsions. Asphaltenes promote the formation of the viscoelastic interface
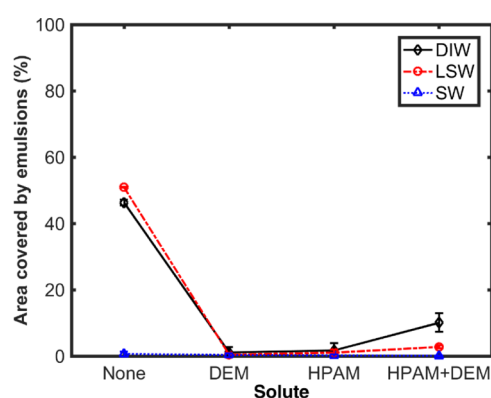
Figure 8. Area of the image covered by emulsions in the bulk oil phase after agitation with an aqueous phase containing different functional molecules. The calculations are based on the images taken 1 h after agitation. The results are based on the images with a 5× magnification.

and inhibit droplet coalescence and therefore stabilize the emulsions (see Figure 9a,b).[24] The mechanism of demulsification by DEM in the bulk oil phase may vary with the type of the functional molecules. For water-in-oil emulsions, the oil film between the two water droplets must break to allow the coalescence and formation of macroemulsions, which may lead to eventual separation of the aqueous phase in the emulsion from the oil phase. The water-in-oil macroemulsions generally have a higher density than the oil phase. Gravity causes them to fall onto the interface and coalesce with the bulk aqueous phase at the bottom, which subsequently results in phase separation. Non-ionic demulsifiers can also adsorb at the interface similar to asphaltene molecules and change the composition of the interface.[37,38] The DEM molecules used in this study contain resin functionality, so they have a high affinity with asphaltenes. The solubility of asphaltene in the bulk oil phase can also increase with the addition of DEM molecules. The DEM molecules in the aqueous phase and its diffusion may destabilize the oil film between the two neighboring microemulsions because of the dissolution of asphaltenes from the interfaces into the bulk oil phase. The process may result in destabilization of water-in-oil emulsions and facilitate droplet coalescence. Figure 9c,d presents a schematic of the process.

Rodríguez-Hakim, et al.[24] suggest that asphaltene-induced spontaneous emulsion formation is primarily due to diffusion

Figure 9. Diagram of the mechanisms of demulsification in the bulk oil phase by DEM. (a) Water-in-oil emulsions without DEM molecules in the bulk oil phase. (b) Details of the magnified region from the rectangular area in (a). The stable film between water droplets may form due to the accumulation of asphaltene molecules at the interface. (c,d) Oil film thinning of water-in-oil emulsions due to DEM. DEM can replace some asphaltenes at the interface, which can lead to water droplet coalescence through oil film thinning.

and stranding. The high IFT in this study (Table S1) may rule out interfacial turbulence. In the oil−aqueous phase system, water molecules may bind to the polar sites of asphaltene molecules which are surface-active.[39] As a result, the concentration of asphaltenes at the interface is significantly higher than that in the bulk oil phase. In an experiment, we dissolved the demulsifier surfactant in the oil phase at a concentration of 100 ppm and have measured the viscoelasticity of the oil−water interface. The measurements indicate that the demulsifier molecules prefer the interface to either of the bulk phases. Asphaltene heteroatom molecules may accumulate at the interface and form clusters with water molecules of the aqueous phase. The hydrated asphaltene clusters may then form aggregates.[33]

The process can create a region of local supersaturation near the interface, where spontaneous emulsification may occur.[22] From aging, the asphaltenes may form a viscoelastic interface, which can further stabilize the emulsions. The emulsions may also form a stable layer, which is similar to the condition of a "brownish" phase described in the literature.[33]

By adding DEM to the aqueous phase, the diffusion and stranding processes may be enhanced by DEM from the aqueous phase (see Figure 10). DEM has a hydrophilic head promoting its binding with water molecules. The DEM tail prefers the oil side of the interface. DEM in the aqueous phase may diffuse toward the interface due to the chemical potential difference between the aqueous phase and the interface. In this process, DEM can act as a carrier to provide a considerable flux of water molecules through the interface and generate the region of local supersaturation combined with hydrated asphaltenes (see Figure 10b). As a result, emulsification near the interface is enhanced by DEM. Because the diffusive flux is much higher with DEM, the rate of emulsion formation and the size increase are faster. The process of fast growth is unstable, and the large-size droplet may coalesce with the bulk water phase in turn. DEM can also facilitate coalescence. The incident of coalescence can disturb the interface and the pattern of the emulsions, which relates to Figure 6. The process can occur periodically and may persist until the chemical potential difference of DEM between the bulk aqueous phase and the interface becomes low. Smaller emulsions may remain thermodynamically stable and reach a balance in a region near the interface.

4. CONCLUSIONS

We may draw the following main conclusions from this investigation:

(1) As expected, the DEM surfactant destabilizes the emulsions or inhibits emulsion formation in the bulk oil phase. It may also enhance spontaneous emulsification near the interface when added to the bulk aqueous phase.
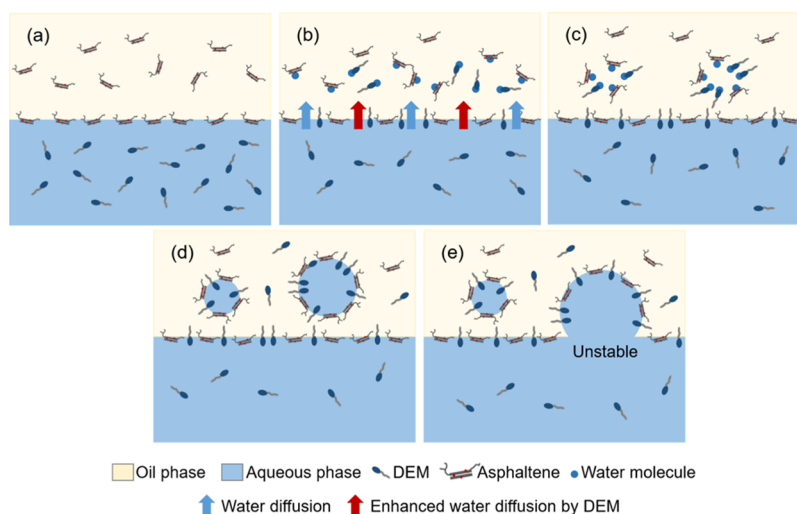
Figure 10. Evolution of DEM surfactant-enhanced spontaneous emulsification near the oil−aqueous phase interface. (a) The oil phase is in contact with the aqueous phase without disturbance. DEM is in the aqueous phase initially. (b) DEM acts as a carrier of water molecules and leads to a higher total diffusive flux of water. (c,d) The process of diffusion and stranding is stronger with DEM, which may enhance emulsification near the interface. (e) The large emulsions may be unstable and coalesce with the aqueous phase in turn. This process can occur periodically.

(2) The mechanism of surfactant-enhanced spontaneous emulsification near the interface is likely from diffusion and stranding. The DEM surfactant may serve as a carrier of water molecules to the interface and generate a region of local supersaturation combined with hydrated asphaltenes.

(3) DEM may adsorb at the interface similar to asphaltene molecules and change the composition of the interface. DEM may facilitate droplet coalescence in the bulk oil phase because of oil film thinning between water droplets.

In the experiments presented in this work, the crude oil is diluted with toluene by a factor of 20. Observations from a diluted crude may be in the same direction as an undiluted crude. Experiments in an undiluted crude oil may help with further observations. The work has set the stage for further investigations.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c00725.

> Methods and experimental results of interfacial viscoelasticity, IFT, and viscosity and images of the oil—aqueous phase interface and the bulk oil phase for the effect of HPAM and the mixture of HPAM and DEM (PDF)

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Notes

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