Investigation of Dioctyl Sodium Sulfosuccinate in Demulsifying Crude Oil-in-Water Emulsions

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ABSTRACT: This research investigated the performance of dioctyl sodium sulfosuccinate (DSS), a double-chain anionic surfactant, in breaking crude oil-in-water emulsions. The response surface methodology was used to consider the effect of the DSS concentration, oil concentration, and shaking time on demulsification efficiency and obtain optimum demulsification conditions. Further single-factor experiments were conducted to investigate the effects of salinity, crude oil conditions (fresh and weathered), and gravity separation settling time. The results showed that DSS efficiently demulsified stable emulsions under different oil concentrations (500−3000 mg/L) within 15 min shaking time. Increasing DSS concentration to 900 mg/L (critical micelle concentration) increased the demulsification efficiency to 99%.

DSS not only improved the demulsification efficiency but also did not impede the demulsifier interfacial adsorption at the oil−water interface due to the presence of the double-chain structure. The low molecular weight enables the homogeneous distribution of DSS molecules in the emulsion, leading to a high demulsification efficiency within 15 min. Analysis of variance results indicated the importance of considering the interaction of oil concentration and shaking time in demulsification. DSS could reduce the total extractable petroleum hydrocarbons in the separated water to <10 mg/L without gravity separation and could achieve promising demulsification performance at high salinity (36 g/L) and various concentrations of fresh and weathered oil. The demulsification mechanism was explained by analyzing the microscopic images and the transmittance of the emulsion. DSS could be an efficient double-chain anionic surfactant in demulsifying stable oil-in-water emulsions.
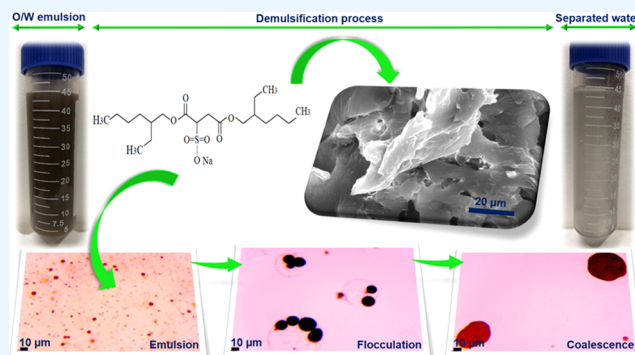
1. INTRODUCTION

A large volume of oily wastewater can be generated from various industrial processes, including oil exploration, enhanced oil recovery, pipeline transportation, and marine oil spill response operation.[1−4] In general, oily wastewater contains tiny oil droplets with sizes varying from about 0.5 μm in diameter to greater than 200 μm, which are categorized as dispersed oil (>10 μm) and emulsified oil (0.1−10 μm).[5] Natural emulsifying agents in crude oil (e.g., resins and asphaltenes) stabilize emulsified oil droplets and form oil-in-water (O/W) emulsions by creating a rigid film around oil droplets.[6,7] The amount of natural emulsifying agents varies with the crude oil type (e.g., light and heavy) and conditions (fresh and weathered) that changes over time after being released into the marine environment. The stability of O/W emulsions mainly depends on the amount of resins and asphaltenes in crude oils and their ratios. A lower resin/asphaltene (R/A) ratio leads to higher emulsion stability.[8,9] Oily wastewater contains toxic materials (e.g., benzene, toluene, and polycyclic aromatic compounds), which can pose severe risks to the aquatic environment if discharged without proper treatment.[3,10] Strict regulations are being implemented in North America to limit the discharge of oil

and grease in oily wastewater to a monthly average of 29 mg/L and a daily maximum of 42 mg/L.[11]

Different oily wastewater treatment processes have been used, including gravity separation, biological treatment, plate coalescence, gas flotation, and filtration. Their efficiency depends on the oil droplet size distribution in wastewater.[12−14] As the oil droplet size decreases (<10 μm), the emulsion stability increases and reduces the efficiency of the treatment processes.[5,15,16] Long settling time, large space requirement, poor efficiency, and fouling are some of the main limitations in demulsifying stable O/W emulsions.[13,17−19] An efficient treatment process is required to break stable O/W emulsions and enhance oil−water separation to meet environmental regulations.

Chemical demulsification has attracted research attention to demulsify stable emulsions because it is a rapid, cost-effective, and easy-to-operate process.[20] Chemical demulsifiers (e.g., ethylcellulose and block polyethers) are surface-active agents (i.e., surfactants) that adsorb at the oil—water interface, reducing the interfacial tension between oil and water phases and break rigid films around oil droplets.[21,22] This process can be combined with gravity separation to demulsify stable emulsions effectively and speed up oil—water separation.[23] Parameters that affect the chemical demulsification process include the type and concentration of the demulsifier, the type and concentration of oil, temperature, shaking time, settling time, and salinity.[24−26]

Different demulsifiers (nonionic and ionic) have been applied in demulsification; however, they have some limitations due to the complexity of the emulsion and industrial restrictions. Nonionic demulsifiers are mainly based on nonionic polyether and are not very effective at demulsifying O/W emulsion containing tiny emulsified oil droplets (≤ 2 μm).[27,28] They are also ineffective at demulsifying heavy crude oil emulsions, where only a 51.95% demulsification efficiency was achieved at high temperatures (e.g., 80 °C).[29] Ionic demulsifiers contain a positive or negative charge known as cationic or anionic demulsifiers, respectively.[30] Cationic demulsifiers are mainly quaternary ammonium salts that can reduce electrostatic repulsion among oil droplets, neutralize the negative charge on the surface of oil droplets, and thus enhance their coalescence.[31] Yonguep et al. investigated the effect of two cationic demulsifiers (cetyltrimethylammonium bromide and trimethyl-tetradecylammonium chloride) on the demulsification of O/W emulsions, and the results showed that above 80% demulsification efficiency was achieved with 10 h of settling.[32] This long settling time restricts cationic demulsifier application in industries like offshore oilfields where the space of offshore platforms is limited.[33] Another research compared the efficiency of different cationic demulsifiers and found that the most effective cationic demulsifier reduced the oil concentration in water to 93 mg/L.[31] This oil concentration in separated water is still too high to discharge into the environment. Dendrimer-based demulsifiers are macromolecules consisting of highly branched polymers emanating from a central core with numerous terminal groups surrounding this core.[22,34] They can be synthesized as ionic demulsifiers and used for O/W demulsification.[22] Synthesis of dendrimer-based demulsifiers is a lengthy and costly process that limits their industrial applications.[35] In addition, dendrimer-based demulsifiers showed poor efficiency in demulsifying O/W emulsions at low oil concentrations (e.g., 3000 mg/L), and thus they are not applicable in the oil and gas industry, where the oil concentration in wastewater is often lower than 10,000 mg/L.[34,36] Also, it has been reported that dendrimer-based demulsifiers have poor demulsification efficiency when the salinity of the water phase is high.[37] Oily wastewaters with high salinity, such as those generated from marine oil spill response operations, would require the application of a salinity-resistant demulsifier.[22,37]

Anionic surfactants mainly contain fatty acid sodium salt compounds with alkyl sulfonates, and they have been widely used in surfactant flooding for enhanced oil recovery because of their low cost and easy-to-use features.[38] Anionic surfactants have a high surface activity that can efficiently recover residual oil from oil wells by reducing the interfacial tension between

oil and water.[39] However, the demulsification application of anionic surfactants has not been well studied as compared to other types of demulsifiers (e.g., cationic and nonionic). A study showed the poor efficiency of sodium dodecyl sulfate (SDS), an anionic surfactant, in the demulsification of water-in-oil emulsions. The inefficiency of SDS was due to its water solubility, which is not suitable for demulsifying emulsions where the continuous phase is oil.[40] Also, SDS only has one alkyl chain in the structure, which might reduce its homogenous distribution in the emulsion and reduce the adsorption capacity of its molecules at the oil—water interface.[41,42] An anionic surfactant with a double-chain structure is expected to improve the demulsification performance. Such a surfactant would be effective at demulsifying highly saline stable emulsions without requiring a long settling time, as previously reported demulsifiers (e.g., dendrimers, nonionic, and cationic) showed poor efficiency.[28,32,37] In this study, dioctyl sodium sulfosuccinate (DSS) with a double-chain structure is used for chemical demulsification. As a biodegradable anionic surfactant, DSS has a high adsorption capacity at the oil—water interface, which is beneficial for the demulsification process.[41,43] It is expected that the DSS can overcome the drawbacks of single-chain anionic surfactants reported in previous research and the drawbacks of previously reported demulsifier-impeding interfacial adsorption. The response surface methodology (RSM) is used to design experiments and investigate the effect of DSS concentration, oil concentration, shaking time, and their interactions on the demulsification process. Under the optimum conditions, the effects of salinity, crude oil conditions, and settling time are also investigated. The demulsification mechanism of DSS is also explained based on the obtained results.

2. MATERIALS AND METHODS

2.1. Materials. Cold Lake Blend (CLB) heavy crude oil was obtained from Canada's Multi-Partner Research Initiative (MPRI). DSS (96%) was purchased from Fisher Scientific Company, Canada. Its structure is shown in Figure 1. Required
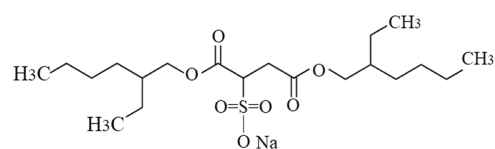

Figure 1. Schematic structure of DSS.

salts to make synthetic ocean water were magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 99.4%), calcium chloride anhydrous ($CaCl_2$, $\geq$96.0%), sodium bicarbonate ($NaHCO_3$, 100.1%), sodium sulfate anhydrous (Na_2SO_4, 99.5%), and sodium hydroxide ($NaOH$, $\geq$97.0%), which were purchased from Fisher Scientific, and strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$, 99.0%), potassium chloride (KCl, 99.0−100.5%), potassium bromide (KBr, $\geq$99.0%), boric acid (H_3BO_3, $\geq$99.5%), sodium fluoride (NaF, $\geq$99.0%), and sodium chloride ($NaCl$, $\geq$99.0%), which were purchased from Sigma-Aldrich, Canada. The chemicals were American Chemical Society (ACS) reagent grade and were used without further purification. Anhydrous silica gel (75−150 μm, 30 Å pore size, Davisil Grade 923), sodium sulfate (granular anhydrous), hexane, and dichloromethane (high-performance liquid chromatography grade) were purchased from Sigma-

Aldrich, Canada. Anhydrous silica gel and sodium sulfate (granular anhydrous) were dried at 200−250 °C for 24 h. Ultrapure water was produced by a water purification system (Milli-Q Advantage A10).

2.2. Methods. *2.2.1. CLB Crude Oil Weathering Process.* Fresh CLB crude oil (7 g) was placed in a fume hood and the cumulative mass loss was monitored for 7 days. As shown in Figure 2, the cumulative CLB mass loss was 15% after 3 days,
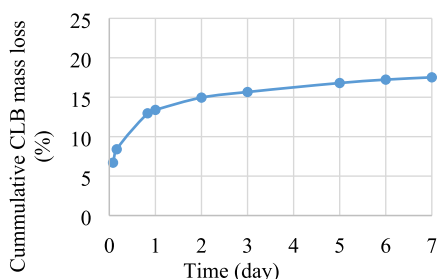

Figure 2. Cumulative CLB mass loss at different times.

and after that, it was insignificant. Thus, CLB crude oil with 15% weathering (i.e., weathered CLB crude oil) was used to prepare O/W emulsions in this research. Table 1 lists the physicochemical properties of fresh and weathered CLB crude oil.

Table 1. Physicochemical Properties of Fresh and Weathered CLB Crude Oil

parameter	value	
	fresh	weathered
API gravity	20.86	12.76
dynamic viscosity at 25 °C (mPa·s)	237.8	12682.0
density at 25 °C (g/cm^3)	0.926	0.978
water content (wt %)	0.041	0.030
saturates (wt %)	45.4	46
aromatics (wt %)	12.0	4.8
resins (wt %)	24.4	28.9
asphaltenes (wt %)	20.0	18.2
ratio of resins/asphaltenes	1.22	1.59

2.2.2. Synthesis of Ocean Water. Ocean water was synthesized by following the ASTM D1141 method.[44] The chemical composition of the substitute ocean water is listed in Table 2. Sodium hydroxide solution (0.1 N) was used to adjust the pH of synthesized ocean water to 8.2 before starting each

Table 2. Chemical Concentration of Synthesized Ocean Water

compound	concentration (g/L)
NaCl	24.53
MgCl$_2$	5.20
Na$_2$SO$_4$	4.09
CaCl$_2$	1.16
KCl	0.695
NaHCO$_3$	0.201
KBr	0.101
H$_3$BO$_3$	0.027
SrCl$_2$	0.025
NaF	0.003

experiment. A Mettler Toledo pH meter was used to measure the pH.

2.2.3. Demulsifier Characterization. Water solubility of DSS was evaluated by dissolving 1 g of DSS in 99 g of Milli-Q water following the previous research method.[31] The morphology and thermal stability of pure DSS were investigated by scanning electron microscopy (SEM) (Philips XL30) and thermogravimetric analysis (TGA) (TA Instruments Discovery TGA), respectively. TGA analysis was conducted under a nitrogen atmosphere from room temperature (28 °C) to 600 °C at a heating rate of 20 °C/min.

2.2.4. O/W Emulsion Preparation. The crude CLB O/W emulsion was prepared using a Q700 sonicator (Qsonica, 20 kHz, solid titanium probe diameter = 12.7 mm) following the method based on our previous research.[45] A given amount of CLB crude oil was poured on the surface of 100 mL of synthesized ocean water according to the desired oil concentration (500−3000 mg/L), and then the sonicator probe was submerged in the middle of the sample. The Q700 Sonicator sonicated the sample to make a stable emulsion. Sonication was conducted at an amplitude of 70% (power of 76−80 W) for 16 min at a 20:20 second on:off pulse. When the pulse was on, the probe passed ultrasound waves through the sample and generated high shear forces and shock waves in the sample, leading to stable emulsion formation. The on:off pulse was used to prevent the increase of the emulsion temperature. There was no significant sign of emulsion breaking after 24 h.

2.2.5. Demulsification Process. The demulsification process was conducted in a batch system. About 45 mL of the O/W emulsion was added to a 50 mL centrifugal tube. A given amount of pure DSS was added to the emulsion at the desired demulsifier concentration, and the mixture was shaken at 100 rpm on a Talboy 3500 Orbital Shaker for different shaking times. Then the solution was subjected to gravity separation at room temperature (∼25 °C) for 45 min to allow oil−water separation. Gravity separation of the emulsion (45 mL) without adding a demulsifier was considered as a control experiment. The transmittance value of separated water was measured at different shaking times.[36,37] Measurements were conducted at a wavelength of 235 nm using a UV-Vis Spectrophotometer 8100 (Orion AquaMate UV-Vis spectrophotometer, Perkin Elmer). After mixing the demulsifier and emulsion, the size and shape of the oil droplets in water were monitored using a compound microscope (Fisher Scientific AX800) with a 200× objective magnification.[31] The images were captured by a digital camera (Fisher Scientific C-Mount Digital Camera) and analyzed using SeBaView software (version 4.7).

2.2.6. Experimental Design. Important experimental parameters on demulsification efficiency, including demulsifier concentration, oil concentration, and shaking time, were selected based on previous studies.[26,34,46] Table 3 lists the

Table 3. Experimental Parameters and Levels in RSM

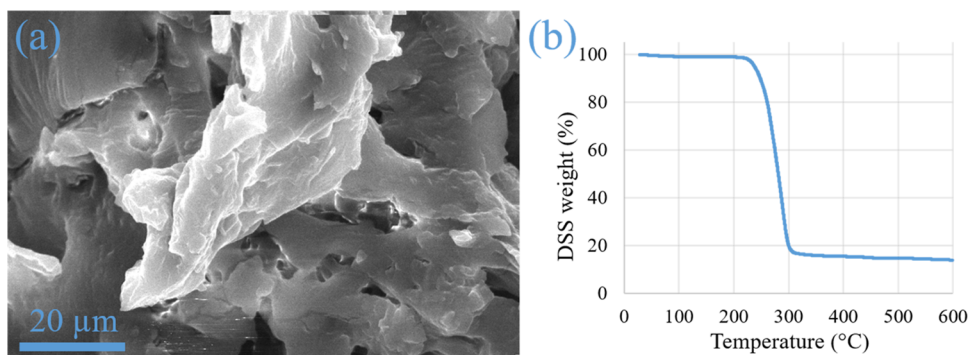| parameter	unit	coded levels				
		−α	−1	0	+1	+α
DSS concentration	mg/L	300	500	800	1100	1300
weathered CLB oil concentration	mg/L	500	1000	1750	2500	3000
shaking time	min	8	10	13	16	18

Figure 3. Characterization of DSS (a) SEM image and (b) the TGA curve.

Table 4. CCD Matrix in the DSS Demulsification Process and the Obtained Results

	experimental parameters			EPH in separated water			
run	DSS concentration (mg/L)	weathered CLB oil concentration (mg/L)	shaking time (min)	TEPH (C_{10}–C_{50}) concentration (mg/L)	EPH (C_{10}–C_{19}) fraction (%)	EPH (C_{19}–C_{32}) fraction (%)	EPH (C_{32}–C_{50}) fraction (%)
1	300	1750	13	519.2	36.3	51.3	12.4
2	500	1000	10	233.7	35.9	52.7	11.4
3	500	1000	16	66.6	37.8	52.1	10.1
4	500	2500	10	54.2	41.1	46.0	12.9
5	500	2500	16	62.9	38.6	51.0	10.4
6	800	500	13	2.3	98.8	1.2	ND[a]
7	800	3000	13	22.5	46.3	53.7	ND
8	800	1750	8	26.7	49.9	50.1	ND
9	800	1750	13	2.0	62.0	38.0	ND
10	800	1750	13	3.4	84.9	15.1	ND
11	800	1750	13	16.8	47.2	52.8	ND
12	800	1750	13	14.3	51.0	49.0	ND
13	800	1750	13	35.6	50.3	49.7	ND
14	800	1750	13	37.4	43.9	56.1	ND
15	800	1750	18	13.3	50.8	49.2	ND
16	1100	1000	10	25.1	53.5	46.5	ND
17	1100	1000	16	6.4	68.5	31.5	ND
18	1100	2500	10	5.3	78.4	21.6	ND
19	1100	2500	16	8.6	70.5	29.5	ND
20	1300	1750	13	7.5	17.0	83.0	ND

[a]ND: Not detected.

parameters and their levels. Design Expert (version 12.0.11.0, Stat-Ease, Inc.) was used to design experiments. RSM was used to evaluate the effect of each independent parameter and their interactions and identify the optimum conditions for the demulsification process. Central composite design (CCD) as a comprehensive design of RSM was used in this study. For each independent numeric parameter, five levels (coded with ±1, ±α, 0) were considered in CCD. Experimental data from CCD were fitted using eq 1.[47]

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} i \sum_{j} \beta_{ij} X_i X_j \tag{1}$$

where Y represents the predicted response, β_0 is a constant coefficient, β_i is the linear effect of X_i variable, β_{ii} is the second-order effect of variable X_i, and β_{ij} is the effect of the linear interaction between parameters X_i and X_j. Analysis of variance (ANOVA) was performed to determine the significance of parameters.

Further single-factor experiments were conducted under the optimum conditions suggested by RSM to investigate the effect

of salinity (0 and 36 g/L) and crude oil conditions (fresh and weathered) on DSS performance. The effect of settling time of gravity separation on the demulsification efficiency was investigated to determine when the demulsification process reaches equilibrium. Single-factor experiments were repeated three times, and the average was reported.

2.2.7. Analysis of Total Extractable Petroleum Hydrocarbons in Water and Emulsion. Total extractable petroleum hydrocarbons (TEPH) that remained in separated water were extracted following the liquid–liquid extraction method using hexane/dichloromethane (1:1 vol) in the British Columbia Laboratory Manual.[48] This was conducted by taking 40 mL of sample from separated water and mixing it with 2 mL of the solvent in a 50 mL vial (solvent:sample volume ratio was 1:20). The mixture of the solvent and sample was shaken on an orbital shaker for 30 min at 70 rpm. After that, solvent and water were allowed to separate, and then the solvent was passed through activated anhydrous sodium sulfate and silica gel to remove moisture and polar organic compounds. Then, 1 mL of the fresh solvent was poured to elute sodium sulfate and silica gel. The whole extract was collected in a gas
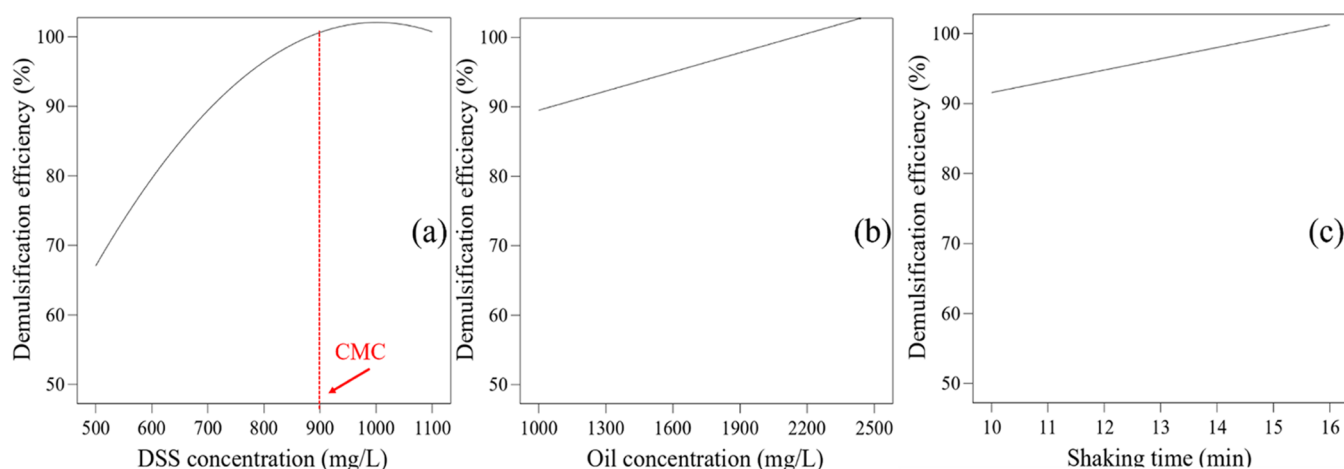
Figure 4. Predicted effect of a single parameter on demulsification efficiency, (a) oil concentration: 1750 mg/L; shaking time: 13 min; (b) DSS concentration: 800 mg/L; shaking time: 13 min; and (c) DSS concentration: 800 mg/L; oil concentration: 1750 mg/L.

chromatography vial. Then, a portion of that was taken for analysis of TEPH using an Agilent 6890 gas chromatograph with a flame ionization detector (GC−FID). The hydrocarbon mixtures were grouped in (nC_{10}−nC_{19}), (nC_{19}−nC_{32}), and (nC_{32}−nC_{50}). Decane (nC_{10}), nonadecane (nC_{19}), eicosane (nC_{20}), dotriacontane (nC_{32}), tetracontane (nC_{34}), and pentacontane (nC_{50}) were used as the external standards. The ZB-1HT INFERNO capillary column (Phenomenex) with a length of 30 m, an inner diameter of 0.32 mm, and a film thickness of 0.25 μm was used. The carrier gas was helium at a rate of 1.6 mL/min. TEPH extract (1 μL) was injected into the system, and a split ratio of 10:1 was used for each run. During analysis, the injector and detector temperatures were kept at 290 and 320 °C, respectively. The initial temperature of the oven was at 130 °C, then increased to 310 and 340 °C at 20 and 5 °C/min, respectively, and held at 340 °C for 8 min. The procedures to determine TEPH in the emulsion were the same as that for the measurement of TEPH in separated water.

Demulsification efficiency (DE) was calculated using eq 2.[49]

$$DE = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

where C_i and C_f are initial and final TEPH concentrations in the emulsion and separated water, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of DSS. The water solubility test of DSS showed that DSS was a water-soluble demulsifier that dissolved in water completely. The morphological structure of DSS was determined by SEM analysis. As shown in Figure 3a, DSS has a flaky and thin structure involving different macropores, which are responsible for its lightweight. Thermal stability is one of the characteristics of demulsifiers that plays a crucial role in their application in industries. The TGA result of DSS is shown in Figure 3b. The initial 2.5% weight loss of DSS is due to water evaporation. DSS remained thermally stable up to around 250 °C as a result of the higher decomposition temperature of dioctyl sulfosuccinate as the anion in the chemical structure. DSS decomposed and significantly lost weight at a temperature >250 °C. Based on the TGA curve, it is concluded that DSS is relatively thermally stable and can be used in a wide range of applications (e.g., where the oily wastewater temperature is high).

3.2. Demulsification Results. *3.2.1. RSM Experimental Results.* Considering DSS concentration, oil concentration, and shaking time as experimental parameters, 20 experiments were designed by CCD design. Table 4 shows the parameters and the experimental results.

A quadratic model was developed for the demulsification process, as shown below:

$$DE = -204.37 + 0.34X_1 + 0.08X_2 + 7.68X_3$$
$$- 4 \times 10^{-5}X_1X_2 - 3.50 \times 10^{-3}X_2X_3$$
$$- 1.36 \times 10^{-4}X_1^2 \qquad (3)$$

where DE is the demulsification efficiency (%), X_1 represents the DSS concentration (mg/L), X_2 represents the oil concentration (mg/L), and X_3 represents the shaking time (min). The ranges of experimental parameters are listed in Table 3.

ANOVA was used to confirm the adequacy of the model and the importance of the effect of each independent parameter, and the results are shown in Table S1. ANOVA showed that the developed quadratic model was significant (*F*-value: 12.40, *P*-value: 0.0001) in determining the demulsification efficiency. X_1, X_2, X_1X_2, X_2X_3, and X_1^2 were significant parameters (*P*-values < 0.05) in this model to predict the demulsification efficiency. Model summary statistics for the generated quadratic model by RSM are listed in Table S2.

3.2.1.1. DSS Concentration. Based on ANOVA, the DSS concentration was one of the critical parameters in the demulsification process (F-value: 34.83, P-value < 0.0001). Demulsification efficiency reached around 70% (Figure 4a), and the TEPH in the separated water was reduced to <70 mg/L (Table 4) when the DSS concentration was 500 mg/L (except for run #2). DSS is a low molecular weight demulsifier (444.56 Da), and a low molecular weight demulsifier often requires a high concentration to effectively demulsify an O/W emulsion.[26] However, it is readily biodegradable and less toxic than high-molecular-weight demulsifiers with complex structures that may be effective at a lower concentration. Additional merits of DSS over other demulsifiers are its easy-to-use feature, readily available, and stable physicochemical properties. As shown in Figure 4a, increasing DSS concentration to 900 mg/L increased the demulsification efficiency, and beyond this concentration, the improvement in demulsification
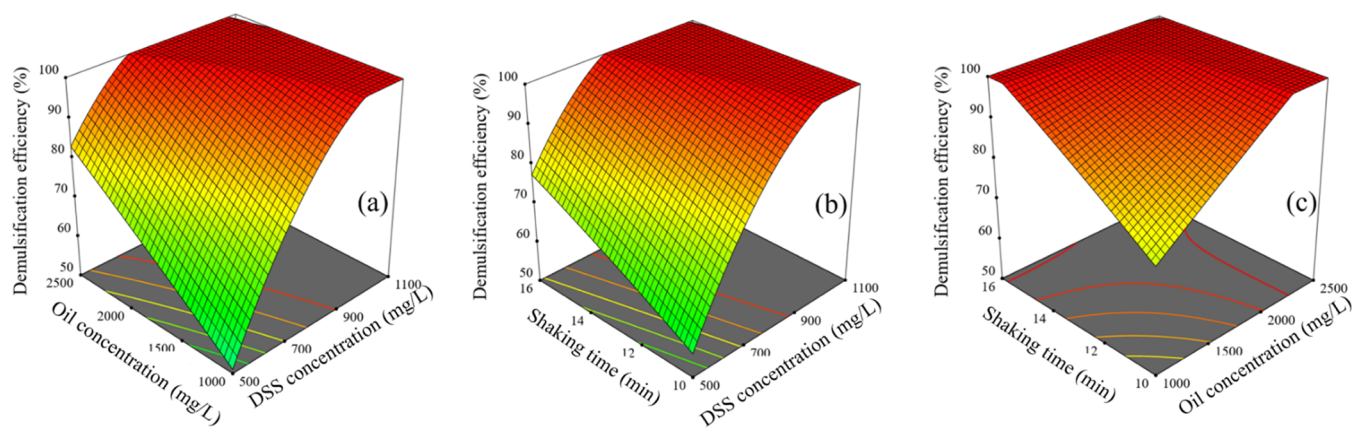
Figure 5. Effect of interactions of different parameters on demulsification efficiency at (a) a shaking time of 13 min, (b) oil concentration of 1750 mg/L, and (c) DSS concentration of 800 mg/L.

efficiency was insignificant. It can be concluded that the critical micelle concentration (CMC) of DSS for O/W demulsification is 900 mg/L.[50,51] As listed in Table 4, increasing DSS concentration from 300 mg/L to 1300 mg/L reduced TEPH in separated water to <10 mg/L. This high demulsification efficiency of DSS may be because the double-chain structure facilitated the homogeneous distribution of DSS in the emulsion. Also, the double-chain structure did not impede DSS interfacial adsorption at the oil–water interface as opposed to the double-chain cationic demulsifier, the efficiency of which was reduced notably due to interfacial adsorption restriction.[52]

3.2.1.2. Oil Concentration. Oil concentration is one of the essential parameters for evaluating demulsification performance. The ANOVA results suggest that oil concentration significantly affected the demulsification efficiency (*P*-value: 0.03). The effect of oil concentration on demulsification efficiency is shown in Figure 4b. DSS efficiently demulsified emulsions containing different oil concentrations (demulsification efficiency ≥ 90%). By increasing oil concentration, higher demulsification efficiencies were achieved. The reason is the high probability of collision of emulsified oil droplets and formation of bigger ones at high oil concentrations compared to lower ones. Results of the same experimental conditions (experimental runs #2 and #4 in Table 4) showed that increasing the oil concentration in the emulsion from 1000 to 2500 mg/L helped in coalescence and then settling of oil droplets which resulted in a significant reduction of TEPH from 233.7 to 54.2 mg/L, respectively. At low oil concentrations (e.g., 500 mg/L), tiny emulsified oil droplets are far away from each other, and thus the chance of their coalescence is low. These persistent emulsified oil droplets required a higher DSS concentration (800 mg/L) to demulsify them (Table 4). This concentration is still lower than the CMC, which reduced TEPH in separated water to 2.3 mg/L. The significant reduction in TEPH indicated that the demulsification efficiency of DSS was not affected by the initial oil concentration. This is an advantage of DSS over other demulsifiers (e.g., dendrimers), which have low efficiency for emulsions with low oil concentrations.[34] DSS is widely applicable to various oil concentrations in emulsions, even when the oil concentration is as low as 500 mg/L.

3.2.1.3. Shaking Time. Sufficient shaking time is required for DSS dissolution and dispersion in the emulsion to reach the oil–water interface. The effect of shaking time on demulsifi-

cation efficiency was investigated (Figure 4c). The required shaking time to demulsify the crude O/W emulsion by DSS was low (<16 min), which made DSS a suitable demulsifier for industrial applications. DSS was a water-soluble demulsifier with low molecular weight (<3000 Da), which brought about the quick diffusion of the demulsifier in the continuous water phase.[26] Table 4 shows the remaining TEPH in the water and their fractions at different shaking times. The high interfacial activity and adsorption capacity of DSS because of two long tails in its structure caused it to weaken and then break the rigid film at the oil–water interface within low shaking time (<16 min). It is worth noting that the solid form of DSS was used in this study and this did not affect the demulsifier efficiency (98%). Hence, applying pure solid DSS rather than dissolving it in an organic solvent, a common method for applying demulsifiers that are in the solid form, can reduce the toxicity of the demulsification system and the generation volume of hazardous liquid wastes.

3.2.1.4. Interaction of Parameters. The effect of the interaction of different experimental parameters on the efficiency of the demulsification process was investigated. As shown in Figure 5a, at a high oil concentration in the emulsion (e.g., 2500 mg/L), a lower DSS concentration (500 mg/L) could achieve a high demulsification efficiency (~80%). A higher DSS concentration was required to achieve similar results when the oil concentration was low. The effect of the interaction of the DSS concentration and shaking time on demulsification efficiency is shown in Figure 5b. It was found that increasing shaking time led to higher demulsification efficiency at lower DSS concentrations, and this was due to sufficient time for dissolution and dispersion of DSS in the emulsion to reach the oil–water interface and break the rigid film. Figure 5c indicates that when oil concentration was high, a lower shaking time (10 min) was sufficient to achieve high demulsification efficiency, because many oil droplets in the emulsion at high oil concentration coalesced quickly and increased the demulsification efficiency. It is crucial to consider the effect of the interaction of parameters on demulsification efficiency, which may bring benefits of applying demulsifiers at lower concentrations.

The optimum conditions of different parameters for achieving maximum demulsification were obtained (Table 4), and it was at the oil concentration of 1000 mg/L, a DSS concentration of 900 mg/L, and a shaking time of 15 min, respectively. The effects of salinity, gravity separation settling

time, and crude oil conditions on demulsification efficiency were then investigated under these optimum conditions.

3.2.2. Single-Factor Experimental Results. 3.2.2.1. Salinity. Figure 6a illustrates the effect of the presence of salts in the
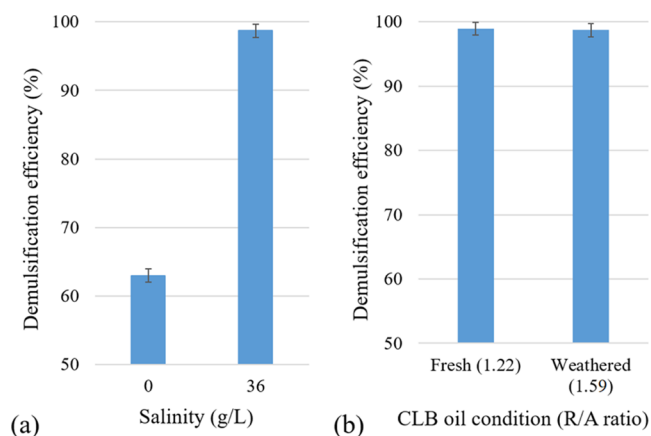
Figure 6. Effect of (a) salinity and (b) CLB oil condition (R/A ratio) on demulsification efficiency.

water phase on the demulsification efficiency. Asphaltenes are crude oil's polar fraction with a negative surface charge in the aqueous solutions where pH is above 4.[53] Asphaltenes create a rigid film around the emulsified oil droplets in water and form droplets with a negative surface charge. Also, DSS is an anionic demulsifier, in which the molecules have a negative surface charge. Without salts in water, repulsive electrical force among the DSS molecules and asphaltenes reduced the number of DSS molecules present at the oil−water interface. This phenomenon led to low demulsification efficiency by DSS (around 63%). However, salts in the water increased the DSS performance significantly and reduced TEPH in separated water notably (Table 5). This is a merit of DSS over other demulsifiers such as dendrimers, whose efficiency was highly reduced in highly saline emulsions.[37] Salt cations in the water phase (e.g., Na^+, Mg^{2+}, Ca^{2+}) neutralized the repulsive electrical force among the DSS molecules and emulsified oil droplets, facilitating the DSS molecules to reach and saturate the oil−water interface.[53] Hence, it is concluded that for an anionic demulsifier in a demulsifying O/W emulsion, the combination of destabilization of the rigid film around emulsified oil droplets due to the high surface activity of the demulsifier and the electrostatic force among molecules in the emulsion brings about the highest demulsification efficiency.

3.2.2.2. CLB Oil Conditions (R/A ratio). Natural emulsifying agents (e.g., resins and asphaltenes) of crude oils vary greatly.[29]

The physicochemical composition of crude oils affects the emulsion stability, affecting the demulsifier efficiency.[54] The performance of DSS in demulsifying emulsions containing different natural emulsifying amounts was investigated using different crude oil conditions (Figure 6b). DSS was effective at demulsifying both fresh and weathered emulsions (different R/A ratios) which proved that DSS performance was not affected by the physicochemical composition of crude oils. The R/A ratio determines the stability of the emulsion, where a lower ratio increases emulsion stability.[55] Fresh CLB had a lower R/A ratio (1.22) than the weathered one (1.59), as listed in Table 1, and thus had higher emulsion stability. This is also supported by the emulsified oil droplet size distribution in the emulsion generated by fresh and weathered CLB (Figure 7). The average oil droplets size for the fresh and weathered CLB emulsions were 4.6 and 6.1 μm, respectively. Based on the oil droplets' size distribution and their average size, and TEPH remaining in separated water (Table 5), it can be concluded that DSS can effectively demulsify O/W emulsion, where the average size of oil droplets is <10 μm. This is another advantage of DSS to nonionic demulsifiers, which showed poor efficiency in demulsifying heavy crude oil emulsions containing emulsified oil droplets (<10 μm).[28,29]

3.2.2.3. Settling Time. The settling time of gravity separation is one of the critical parameters in the demulsification process, which affects the processing time and settling tank size.[56] After 15 min of shaking time, different gravity separation settling times (0, 15, 30, and 45 min) were considered to settle the oil droplets in water. The effect of settling time on demulsification efficiency is shown in Figure 8, and the TEPH remaining in water and their fractions at different settling times are listed in Table 5. As shown, the application of a demulsifier significantly broke the O/W emulsion and promoted the separation of oil from water, and thus the gravity separation settling time had an insignificant effect on further oil/water separation. The demulsification efficiency was higher than 96% for all settling times. The remaining TEPH in separated water was lower than 10 mg/L for all investigated settling times (0, 15, 30, 45 min). The results indicated that DSS efficiently demulsified the O/W emulsion without the need for a long settling time under gravity separation, thus reducing the demulsification process time significantly. This is quite a remarkable result over other demulsifiers (e.g., cationic), which have been reported to require a long settling time (e.g., 10 h) to achieve desirable results.[32] As no settling time is required for DSS demulsification, it is an efficient demulsifier for application in oil and gas industries and offshore oil spill response operations.

Table 5. Effect of Salinity, CLB Crude Oil Conditions, and Settling Time on the Demulsification Process[a]

	experimental parameters			EPH in separated water			
run	salinity (g/L)	CLB oil condition	settling time (min)	TEPH (C_{10}−C_{50}) concentration (mg/L)	EPH (C_{10}−C_{19}) fraction (%)	EPH (C_{19}−C_{32}) fraction (%)	EPH (C_{32}−C_{50}) fraction (%)
1	0	weathered	45	111.5	29.6	55.9	14.5
2	36	weathered	45	3.9	56.4	28.6	15.0
3	36	weathered	30	8.1	75.8	12.5	11.7
4	36	weathered	15	2.7	36.4	12.7	50.9
5	36	weathered	0	7.8	18.6	10.1	71.3
6	36	fresh	45	3.1	67.5	17.1	15.4

[a]DSS concentration of 900 mg/L, oil concentration of 1000 mg/L, shaking time of 15 min, and shaking speed of 100 rpm.
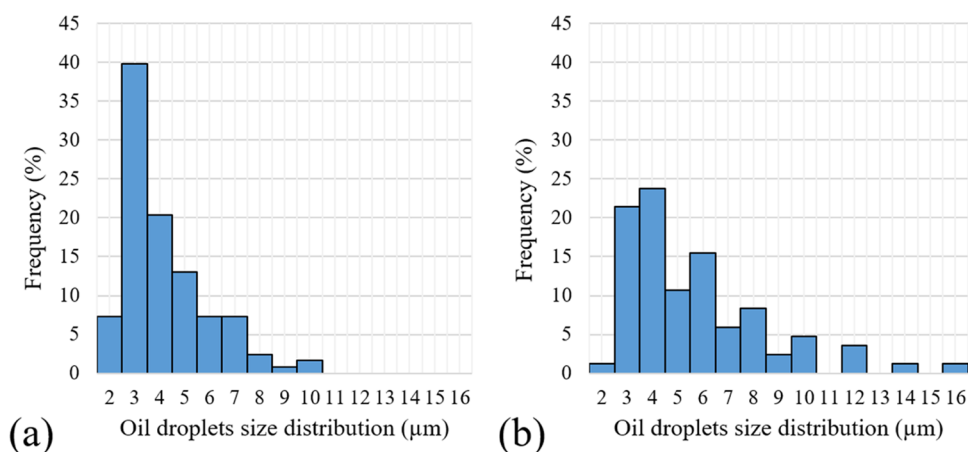
Figure 7. Oil droplets size distribution in the generated O/W emulsion (a) fresh CLB O/W emulsion, (b) weathered CLB O/W emulsion.
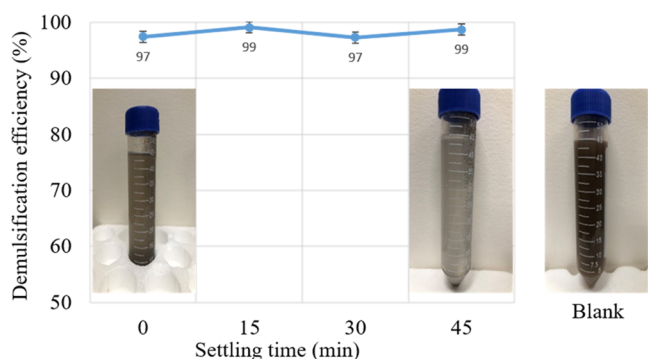
Figure 8. Effect of settling time on demulsification efficiency at a DSS concentration of 900 mg/L, an oil concentration of 1000 mg/L, a shaking time of 15 min, and a salinity of 36 g/L.

3.3. Demulsification Mechanism by DSS. Figure 9 shows the schematic diagram of the demulsification process by DSS. After adding DSS to the emulsion and mixing, DSS molecules dissolved in the emulsion and reached the oil–water interface quickly due to its low molecular weight. Then, DSS molecules saturated the oil–water interface. DSS is an anionic surfactant with a negative surface charge. Asphaltenes of crude oil that formed the rigid film at the oil–water interface also have a negative surface charge at pH > 4.[53] The presence of positive ions (e.g., Na^+, Mg^{2+}, and Ca^{2+}) in the emulsion contributed to DSS saturation of the oil–water interface by reducing the repulsive force among the negative surface charge molecules. This was confirmed by the high demulsification efficiency when the water phase had high salinity. DSS possesses high surface activity and adsorption capacity due to its double-chain structure, which displaced natural emulsifying agents of crude oil like asphaltenes and resins and ruptured the rigid film at the oil–water interface. Hence, the unstable emulsion flocculated and coalesced, as shown in Figure 10, leading to oil and water separation. The transmittance of the emulsion at different shaking times was measured (Figure 11). The transmittance of the emulsion increased within short shaking times (<15 min), which also proved the quick aggregation and coalescence of emulsified oil in water. At 15 min, coalesced oil droplets were still suspended in the separated water phase, resulting in 60% transmittance in separated water. The low TEPH concentration in separated
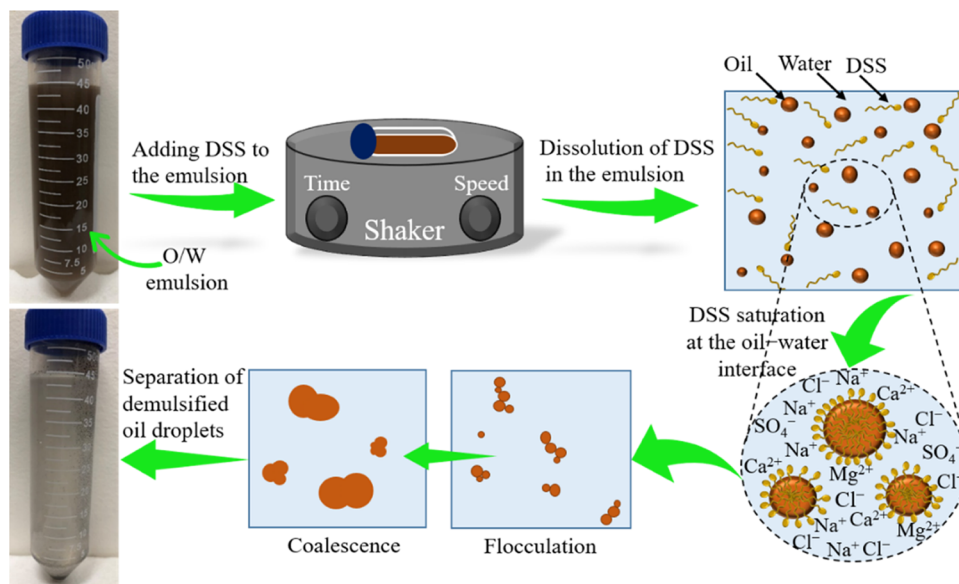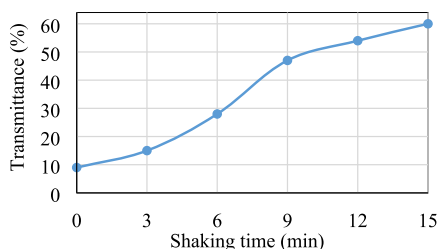

Figure 9. Schematic diagram of the demulsification process by DSS.
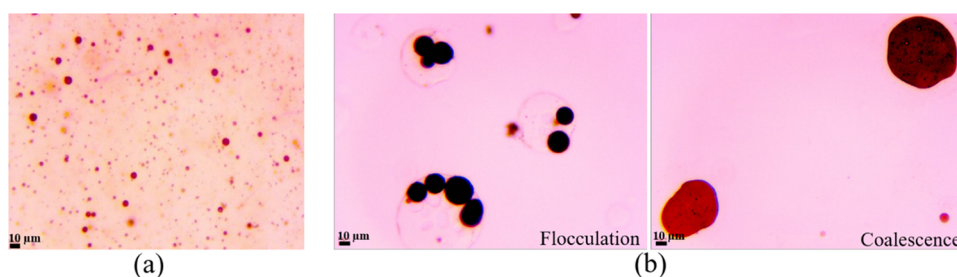
Figure 10. Microscopy images of (a) emulsified O/W (1000 mg/L), (b) demulsified O/W (1000 mg/L) by DSS (flocculation and coalescence of oil droplets) under optimum conditions of the demulsification process by DSS.

Figure 11. Transmittance of the O/W emulsion against shaking time under optimum conditions of the demulsification process by DSS.

water (7.8 mg/L) without gravity separation (0 min settling time) indicated that although turbidity reached 60%, the efficiency of the demulsification process reached 97%. After 45 min of gravity separation, the suspended oil droplets settled, and TEPH was reduced to 3.9 mg/L (demulsification efficiency reached 99%).

4. CONCLUSIONS

The performance of DSS as a new anionic surfactant in the demulsification of crude O/W emulsions was investigated. Effects of the DSS concentration, crude oil concentration, and shaking time were investigated, and the optimum conditions were obtained. DSS is a low molecular weight demulsifier that diffuses in the emulsion quickly and demulsifies the emulsion within a short time. The optimum conditions of DSS concentration and shaking time were 900 mg/L and 15 min, respectively, when the oil concentration was 1000 mg/L. Under these optimum conditions, the effect of salinity, crude oil conditions (fresh and weathered oil with different R/A ratios), and settling time of gravity separation were investigated. Since DSS is an anionic surfactant, it was more efficient at demulsifying O/W emulsions when salt ions (e.g., Na^+, Mg^{2+}, Ca^{2+}) were in the emulsion (98% demulsification efficiency) compared to when there was no salt (63% demulsification efficiency). Demulsification efficiency was not affected by the crude oil conditions and different R/A ratios of crude oils (i.e., emulsion stability). DSS demulsified the emulsion effectively even when the R/A ratio was low (demulsification efficiency > 98%, TEPH = 3.1 mg/L), which proved that the surface activity of DSS was higher than asphaltenes and resins (natural emulsifying agents). DSS demulsification significantly reduced the settling time of gravity separation. The demulsification mechanism by DSS was the displacement of natural emulsifying agents and weakening of the rigid film at the oil−water interface. This led to aggregation, flocculation, and then coalescence of oil droplets which were shown by capturing microscopic images and measuring the transmittance of emulsion. This research investigated the application of DSS in the demulsification process as a reliable demulsifier for different industrial applications.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04022.

ANOVA and model summary statistics for the response surface quadratic model for demulsification by DSS (PDF)

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Notes

The authors declare no competing financial interest.

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