

The Influence of Newly Synthesized Demulsifiers on the Interfacial Rheological Properties of a Naturally Occurring Water/Oil Emulsion

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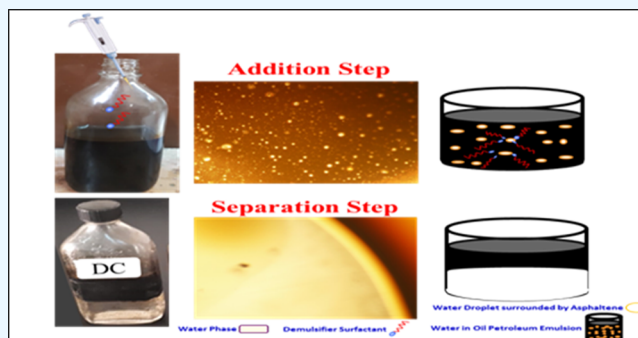
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ABSTRACT: This research aimed to synthesize new polymeric nonionic demulsifiers (DA, DB, and DC) to break 50% of naturally occurring water/oil emulsions. The prepared demulsifiers were synthesized in only two stages utilizing simple techniques. ^1H and ^{13}C NMR, MS, and FTIR spectroscopies were performed to validate the chemical composition of the synthesized demulsifiers. The relative solubility number (RSN) and partition coefficient (K_p) were determined for the three demulsifiers. The interfacial tension (IFT) and dehydration ratios of DA, DB, DC, and their triblock copolymers were investigated. Also, interfacial rheological properties for the three demulsifiers were measured. The findings demonstrate that DB possesses a higher RSN value than DA and DC owing to its hydrophilicity. DC exhibited the lowest IFT value compared to DA, DB, and their corresponding triblock copolymers. DB and DC are more effective in demulsifying than DA and triblock copolymers. DC achieved a 100% dehydration ratio at a low dosage of 75 ppm after 120 min. DC's remarkable performance can be attributed to its aromatic core, molecular weight, and high interfacial activity. According to the rheological data, a higher dehydrating ratio is attained when the demulsifier has a great capacity to lower the viscoelasticity of the W/O emulsion interface. The maximum decrease in G' and G'' values was attained by DC. The mechanism of DC's demulsifying interaction on a naturally occurring W/O emulsion was elucidated.



1. INTRODUCTION

During crude oil production, forms of stable water/oil emulsions were produced.^{1–3} These emulsions were created as a consequence of the presence of formation water as well as natural stabilizers like asphaltenes, resins, carboxylic acids, and solids such as clay and waxes, which induce emulsion stabilization.^{4–6} Interfacial viscoelasticity is an essential property of crude oil emulsions and it is critical for emulsion stability. The emulsion's stability was enhanced by the strong viscoelastic interfacial network of asphaltenes, which hindered droplets' coalescence.⁷ These stable emulsions cause several problems in the petroleum sector, from the production stage through the refinery stage. One of these problems is the difficulty of pumping fluids into the pipelines owing to the increased oil viscosity caused by the existence of emulsified water in the crude oil in addition to corrosion of pipelines, storage tanks, and pumps as well as production and distillation equipment.^{8–10}

There are several methods for demulsifying stable crude oil emulsions, including supersonic demulsification, electro sedimentation, centrifugation, and chemical demulsification.¹¹ The chemical demulsification process is the addition of demulsifiers (surfactants) in small concentrations to stable emulsions to break them down.^{12,13} Surfactants are categorized as ionic,

nonionic, and amphoteric. This variety of surfactants is derived from a surfactant structure with a polar portion and a nonpolar portion. The polar portion might be ionic or nonionic. The polar portion is referred to as the head, while the nonpolar portion, which is a hydrocarbon chain, is referred to as the surfactant chain.^{14,15}

Many researchers found that demulsification was strongly associated with a change in the interfacial rheology from high to low viscoelasticity.^{16–18} The demulsifier's role has been established as changing the interfacial rheological characteristics through reducing the interfacial viscoelasticity and film strength to destabilize the emulsions.^{6,19,20} It is well recognized that storage modulus G' and loss modulus G'' are related to emulsion properties and stability. High G' and G'' values imply stable emulsions. Furthermore, G' is regarded as a reliable indicator of interfacial molecules' interaction and cross-linking.

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When the demulsifier reduces the barrier strength and interfacial viscoelasticity to a certain level, the separation of water from the emulsion would be more easy.^{21,22}

Alves et al. examined and described the demulsification action of a demulsifier based on a synthetic surfactant of castor oil. In a bottled experiment, the demulsifier's highest water separation was around 90%.²³ Ma et al. designed a new oxygen-containing demulsifier, MJTJU-2, for the effective breaking of W/O emulsions. To explore the demulsifying performance, several factors such as demulsifier dose, temperature, and settling time were studied and optimized. Using 400 ppm of MJTJU-2, the emulsions could be completely dehydrated (>97%) in less than 15 min at 60 °C.²⁴ Wei et al. synthesized a multibranch nonanionic polyether demulsifier named FYJP. After 120 min, the maximum dehydration rate of the demulsifier was 94.7% for a dosage of 100 ppm at 85 °C.²⁵

There are a wide variety of commercial demulsifiers, including polymeric surfactants such as copolymers of polypropylene oxide and polyethylene oxide, alkyl phenol formaldehyde resin, and a mixture of various surface-active compounds.^{16,26–28}

In this study, three novel polymeric nonionic surfactants (DA, DB, and DC) were synthesized by reacting 4-hydroxybenzenesulfonic acid with dodecanoyl chloride to produce 4-(dodecanoyloxy)benzenesulfonic acid, which was then esterified by three-block copolymers with different molecular weights (1000, 3000, and 5800). The three-block copolymers have a structure of PEO–PPO–PEO. For the prepared polymeric surfactants, the relative solubility number (RSN) and partition coefficient (K_p) as well as the dynamic interfacial tension were measured. The produced polymeric surfactants were evaluated as demulsifiers for naturally occurring crude oil emulsions (W/O). According to the obtained data, the prepared demulsifier (DC) exhibited good water separation at low concentrations. The influence of the demulsifiers on the interfacial rheology of crude oil emulsions was measured and discussed. Polarizing optical microscopy was applied to study the demulsifying process's interaction mechanisms.

2. EXPERIMENTAL SECTION

2.1. Materials. Hydroxybenzenesulfonic acid was purchased from Sigma-Aldrich and polyoxyethylene–polyoxypropylene–polyoxyethylene (EO–PO–EO), triblock copolymer, was obtained from BASF as Pluronic PE3100 (molar mass = 1000, molar mass of polypropylene glycol = 850, and polyethylene glycol content = 10 wt %); Pluronic PE6400 (molar mass = 3000, molar mass of polypropylene glycol = 1740, and polyethylene glycol content = 40 wt %), and Pluronic P123 (molar mass = 5800, molar mass of polypropylene glycol = 4060, and polyethylene glycol content = 30 wt %). Crude oil emulsion was obtained from Khalda Petroleum Company. Its physicochemical characteristics are listed in Table 1, while Table 2 summarizes the associated formation water properties.

2.2. Preparation. **2.2.1. Preparation of 4-(Dodecanoyloxy)benzenesulfonic Acid.** Dodecanoyl chloride (0.1 mol) was added drop by drop to 4-hydroxybenzenesulfonic acid (4-phenolsulfonic acid) (0.1 mol), which also included *N,N*-diethylethanamine (0.15 mol). For 6 h at 0–5 °C, the reaction mixture was agitated. The white solid product

Table 1. Physicochemical Properties of the Naturally Occurring Crude Oil

specification	method	results
specific gravity at 60/60 °F	ASTM D 1298	0.871
kinematic viscosity at 40 °C (c St)	ASTM D 445	10.88
API ^a gravity at 60 °F	ASTM D 1298	30.8
wax content (wt %)	UOP-46/64	8.42
pour point (°C)	ASTM D 97	18
water content (vol %)	IP 74/70	50
saturates (wt %)		52.53
aromatics (wt %)		16.8
resins (wt %)		25.72
asphaltene (wt %)	IP 143	3.24

^aAPI, American Petroleum Institute.

Table 2. General Characterization of the Formation Water

items	results
total dissolved solids	40,372 mg/L
resistivity	0.01915 Ohm m at 19 °C
conductivity	52.2 μS/m at 19 °C
density	1.0322022 g/mL
pH	7.74 at 19 °C
specific gravity	1.03304
salinity	35,996 mg/L
Na ⁺	12,739 mg/L
Ca ²⁺	745 mg/L
Mg ²⁺	195 mg/L
Cl ⁻	18,938 mg/L
SO ₄ ²⁻	2600 mg/L
HCO ₃ ⁻	779 mg/L

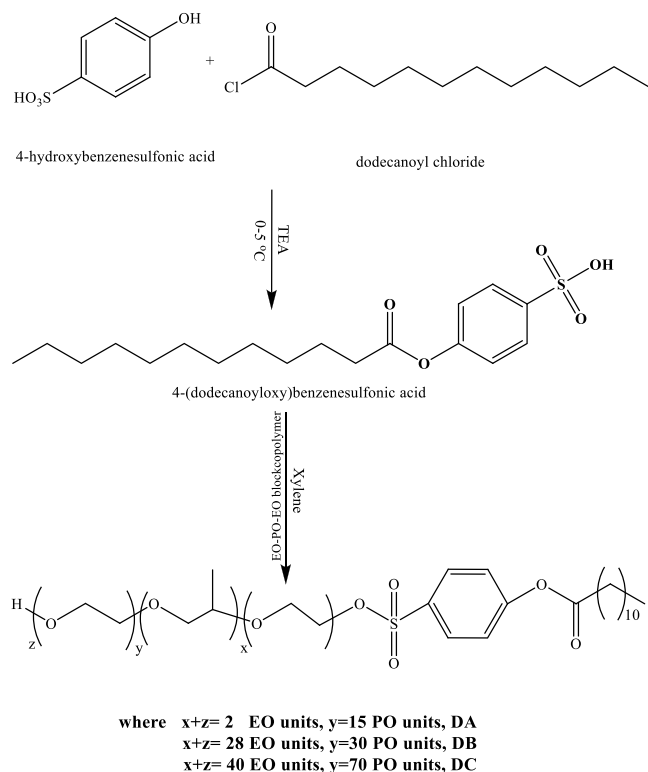
was filtered out. Then it was rinsed with water and methyl alcohol and finally dried in the air.

2.2.2. Synthesis of Polymeric Nonionic Surfactants. To synthesize the nonionic polymeric surfactants, 0.1 mol of 4-(dodecanoyloxy)benzenesulfonic acid, 0.1 mol of EO–PO–EO block copolymers with different molecular weights of 1000, 3000, and 5800, and PTSA as a catalyst with dry xylene were put in a flask that was linked to a condenser and a Dean–Stark trap. The reaction mixture was agitated until the calculated quantity of H₂O was gathered and then cooled down at the ambient temperature. After the reaction was completed, the solvent was removed until dryness; the oily materials were washed with dry diethyl ether several times.²⁹ The three synthesized demulsifiers were abbreviated as DA, DB, and DC as seen in Scheme 1.

2.3. Relative Solubility Number (RSN). RSN was determined in order to assess the hydrophilicity of demulsifiers. A demulsifier sample (1 g) was dissolved in 30 mL of a dioxane/benzene mixture (96 % dioxane:4 % benzene), and the solution was agitated for 30 min at room temperature. The demulsifier solution was titrated with distilled water until the solution became consistently turbid. The titrated water's volume (in mL) was measured to determine RSN.³⁰

2.4. Partition Coefficient (K_p). K_p describes the distribution of a demulsifier between two immiscible solvents. K_p was employed to assess the demulsifier hydrophobicity. The methodology was carried out via dissolving 0.25 g of DA, DB, and DC individually in 25 mL of 1-hydroxy octane (oil phase) followed by adding 25 mL of distilled water. The mixture was

Scheme 1. Synthesis of Polymeric Nonionic Surfactants



agitated for 30 min with a shaker. The flask was then firmly sealed and placed in a water bath at 25 °C for the separation of the mixture into two layers. The 1-hydroxy octane layer was taken off and its UV absorbance was measured. After that, the concentration of the demulsifier in 1-hydroxy octane was estimated using a calibration curve that represented the intensity of the absorbance as a function of concentration. The demulsifier concentration in the aqueous medium (C_w) was calculated by subtracting the concentrations of each DA, DB, and DC in the 1-hydroxy octane phase from the starting concentration. K_p is computed using the formula:

$$K_p = C_w/C_o$$

where C_w is the demulsifier concentration in the water phase and C_o is the demulsifier concentration in the oil phase.

A calibration curve for each demulsifier was obtained by measuring the UV absorbance of various demulsifier concentrations in 1-hydroxy octane (1, 0.8, 0.6, 0.4, 0.2, and 0.1%). A Jenway 6300 UV–visible spectrophotometer was used to measure the absorbance at λ_{\max} of 355 nm.³¹

2.5. Dynamic Interfacial Tension. A theta optical tensiometer (Attension–Biolin Scientific Company, Finland) was used to measure the interfacial tension between crude oil having varying concentrations of the synthesized polymeric surfactants and their corresponding triblock copolymers and formation of H₂O at 25 °C. The measuring theory and operational techniques were stated earlier in ref 31.

2.6. Bottle Test. A bottle test was employed to assess the demulsification performance of DA, DB, DC, and their corresponding triblock copolymers. Each of them was dissolved in xylene (10% active material) and applied to graduated bottles containing 100 mL of a crude oil emulsion. A micropipette was used to inject varied doses of each demulsifier (25, 50, 75, 100, and 200 ppm). After being vigorously shaken for 60 s, the bottles were submerged in a water bath at 60 °C. Based on the performance of the demulsifier under examination, water separation (mL) was recorded at various times.³² By applying the following equation, the demulsification performance can be calculated as below:¹¹

$$\text{water separation\%} = V/V^o \times 100$$

where V denoted the volume of separated water after demulsifier addition and V^o denoted the original water volume in the crude oil emulsion.

2.7. Interfacial Rheology Measurements. The biconical bob geometry of the Physica MCR502 rheometer was used to assess the interfacial viscosity among crude oil and deionized H₂O with and without the addition of demulsifiers. The cell was filled with degassed deionized H₂O. After that, the biconical bob was situated at the horizontal interface and the dehydrated crude oil was poured over it. The formation of the interfacial film was monitored using a strain amplitude of 0.1% and an angular frequency of 1 Hz. G' and G'' values were recorded every 1 min at 60 °C for 120 min under the same conditions as in the bottle test. A Peltier temperature control

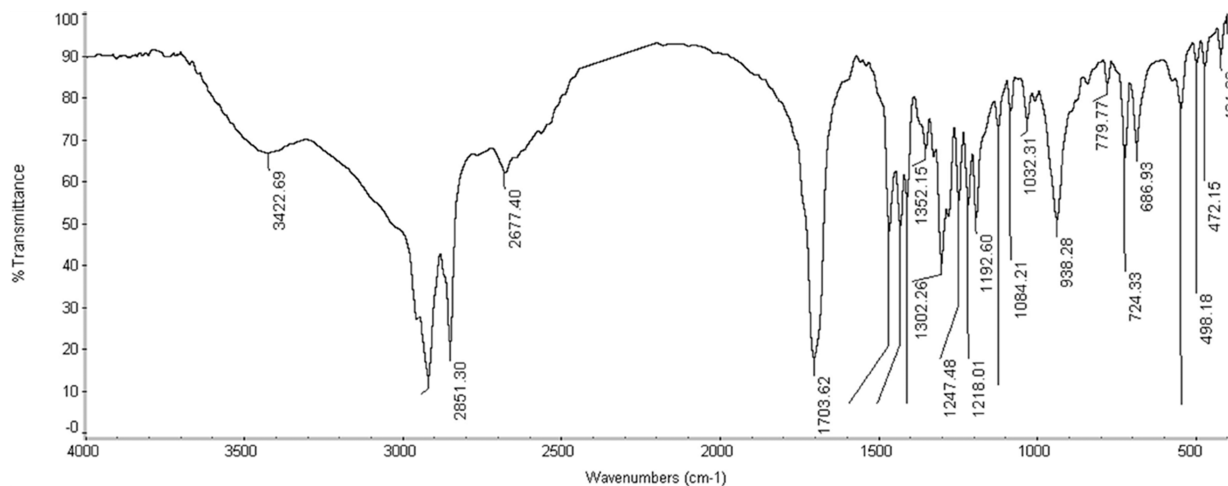


Figure 1. FTIR spectrum of 4-(dodecanoyloxy)benzenesulfonic acid.

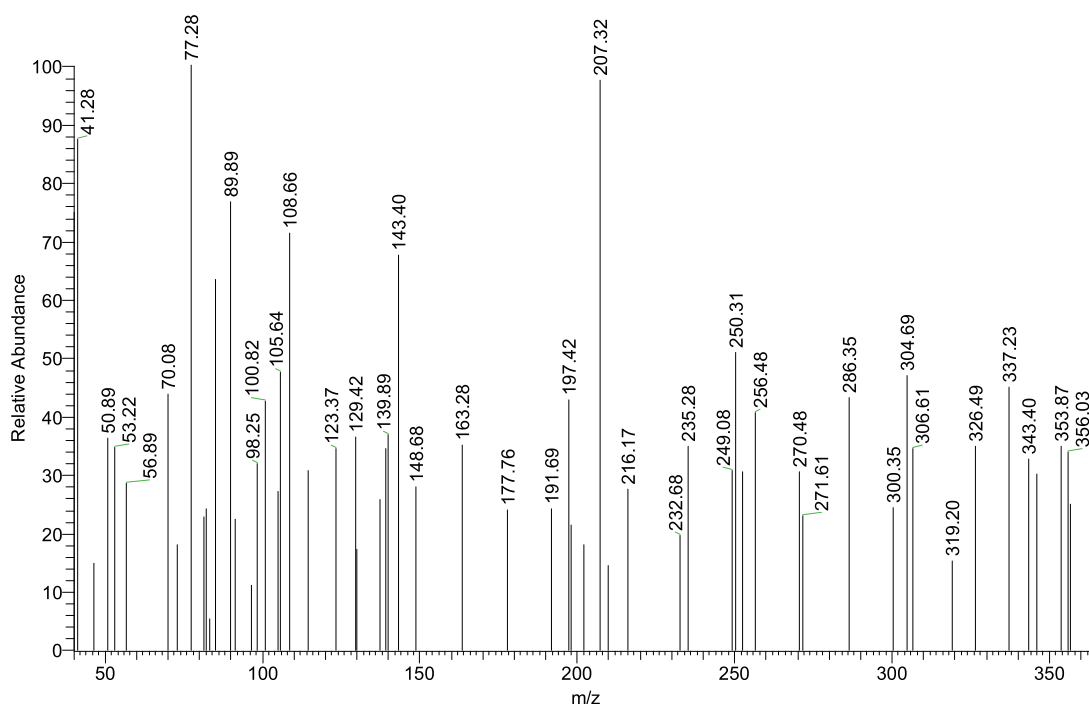


Figure 2. Mass spectrum of 4-(dodecanoyloxy)benzenesulfonic acid.

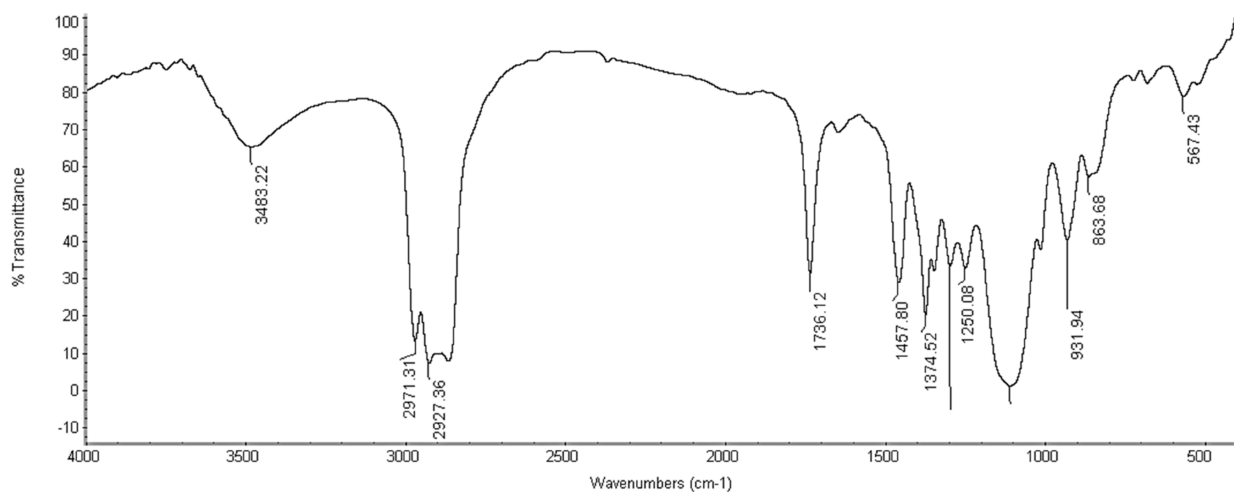


Figure 3. FTIR spectrum of DC.

device with an accuracy of ± 0.5 °C was used to regulate the temperature.²¹

2.8. Photographic Studies of the Demulsification Process. Photographic microscopy investigations were conducted for both untreated and treated crude oil emulsions. The untreated and treated specimens were collected at varying periods to be analyzed. On a glass slide, an emulsion droplet was spread. The samples were imaged using an Olympus optical polarizing microscope (Germany) equipped with a camera.³³

3. RESULTS AND DISCUSSION

3.1. Validation of the Chemical Structure. Fourier transform infrared (FTIR) spectroscopy, mass spectrometry (MS), and 1H nuclear magnetic resonance (NMR) and ^{13}C NMR spectroscopies were used to verify the chemical structure of the produced compounds.

3.1.1. Chemical Structure of 4-(Dodecanoyloxy)benzenesulfonic Acid. FTIR (ν in cm^{-1}) (Figure 1): 2851.3, 2919.9 (ν_{C-H} sym. and asym. stretch), 724.3 ($\nu_{(CH_2)_n}$ rock), 1247.4, 1703.6 (ν_{C-O-C} , $\nu_{C=O}$, ester), 1032.3, 1123.4 ($\nu_{S=O}$ sym. and asym. stretch), 686.9 (ν_{S-O} stretch), 1467.1 ($\nu_{C=C}$ aromatic).

Mass spectrum (m/z) (Figure 2): 356.03 (M^+ , 33.89% $C_{18}H_{28}SO_5$), 250.31 (50.85% $C_{10}H_{18}SO_5$), 207.32 (97.46% $C_8H_{15}SO_4$), 143.40 (67.51% $C_8H_{15}O_2$), 108.66 (71.35% C_8H_{12}), 77.28 (100.00% C_6H_5), 91.34 (22.35% C_7H_7). The mass spectrum findings affirmed the chemical composition of the synthesized 4-(dodecanoyloxy)benzenesulfonic acid.

3.1.2. Chemical Structure of the Polymeric Surfactant (DC). FTIR (ν in cm^{-1}) (Figure 3): 3483.2 (ν_{OH} stretch), 2859.5, 2927.3, 2971.3 (ν_{C-H} sym. and asym. stretch), 1250.0, 1736.1 (ν_{C-O-C} , $\nu_{C=O}$, ester), 1109.6 (ν_{C-O-C} etheral band,

asym. stretch), 1348.3 ($\nu_{\text{S=O}}$ asym. stretch), 1457.8 ($\nu_{\text{C=C}}$ aromatic).

The ^1H NMR spectrum is shown in Figure 4; new sigma shifts appeared at $\delta = 0.83$ ppm due to protons of (CH_3); $\delta =$

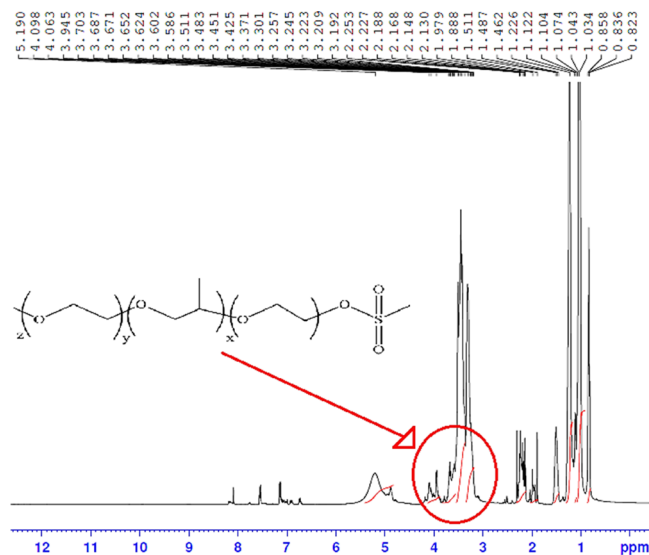


Figure 4. ^1H NMR spectrum of DC.

1.48 ppm for (CH_2CH_3); $\delta = 1.12$ ppm for (CH_2)₈ of alkyl chain; $\delta = 1.88$ ppm for ($\text{COOCH}_2\text{CH}_2$); $\delta = 2.22$ ppm for (COOCH_2); $\delta = 1.22$ ppm due to protons of propylene oxide's (CH_3); $\delta = 3.20$ ppm for ($\text{CH}_3\text{CHCH}_2\text{O}$); $\delta = 3.37$ ppm for ($\text{CH}_3\text{CH}_2\text{O}$); $\delta = 3.70$ ppm for (CH_2OH); $\delta = 3.62$ ppm for ($\text{CH}_2\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OSO}_2$); $\delta = 4.06$ ppm for (CH_2OSO_2); $\delta = 5.19$ ppm for terminal (OH), and $\delta = 6.73$ – 8.08 ppm for (aromatic- H protons).

The ^{13}C NMR ($\text{DMSO-}d_6$) spectrum (Figure 5) exhibits the characteristic chemical shifts for CH_3 at 14.1 and 17.3 ppm, the

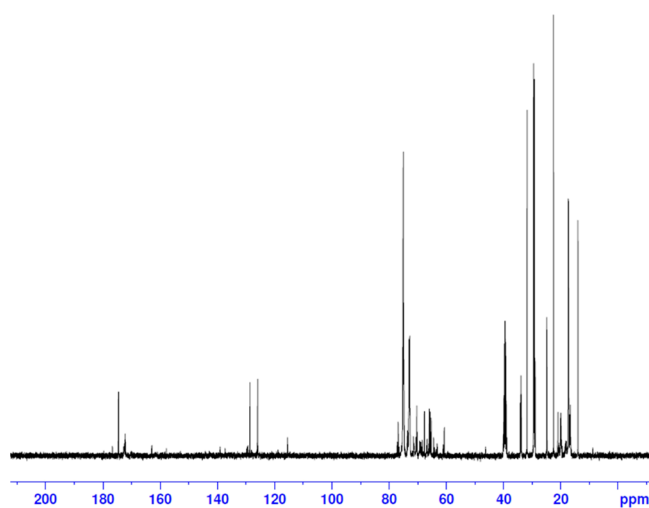


Figure 5. ^{13}C NMR spectrum of DC.

first for the terminal CH_3 of the long alkyl chain and the latter for the CH_3 of propylene oxide. Chemical shifts appeared at $\delta = 22.6$ ppm for $-\text{CH}_2\text{CH}_3$; $\delta = 31.8$ ppm for $-\text{CH}_2\text{CH}_2\text{CH}_3$; $\delta = 28.9$ – 29.5 ppm for $-(\text{CH}_2)_6$; $\delta = 24.9$ ppm for $\text{CH}_2\text{CH}_2\text{OCO}$ –, and $\delta = 33.9$ ppm for $\text{CH}_2\text{CH}_2\text{OCO}$ –. The chemical shift of carbonyl carbon appeared at 174.6 ppm.

Chemical shifts appeared at $\delta = 69.2$ and 67.7 ppm for $\text{OCH}_2\text{CH}_2\text{OS}=\text{O}$ and that of CH & CH_2 of propylene oxide appeared at $\delta = 75.2$ and 77.1 ppm. The chemical shifts of the carbon of the ethylene oxide part ($-\text{OCH}_2\text{CH}_2\text{OH}$) appeared at $\delta = 60.7$ and 70.5 ppm and $\delta = 115.0$ – 162.9 ppm for (aromatic- C), respectively.

3.2. Relative Solubility Number (RSN). The RSN values for the three polymeric surfactants (DA, DB, and DC) are obvious in Table 3. According to the data, the RSN increases

Table 3. Molecular Weight, RSN, HLB, and K_p for the Prepared Polymeric Surfactants

surfactants	molecular weight	EO %	RSN	K_p
DA	1338	6.57	10.5	0.17
DB	3338	36.90	15.5	0.64
DC	6138	28.67	13.2	0.35

as the EO percent increases, implying that the RSN values increase with the increasing hydrophilic content.³⁴ These results are reliable to other studies.^{35,36} It has been stated that a surfactant with RSN less than 13 is hydrophobic, a surfactant with RSN more than 17 is hydrophilic, and RSN between 13 and 17 suggests that the surfactant is dispersed.³⁷ As a result, DB and DC are partially water dispersible, while DA is hydrophobic. The order of increasing RSN values is $10.2 < 13.2 < 15.5$ for $\text{DA} < \text{DC} < \text{DB}$ increase as the hydrophilicity increased.

3.3. K_p . K_p is the surfactant distribution between the aqueous and oily media, and therefore, indirectly illustrates the demulsifier's ability to permeate the interface film. The demulsifier's partition is usually diffusion-controlled and is primarily dependent on the diffusion rate and adsorption from the oil phase to the interface.³⁸ According to Table 3, DC and DB have K_p values of 0.35 and 0.64, respectively, whereas DA has a K_p value of 0.17. This indicates that DB and DC have a high capacity to diffuse and be adsorbed, which may cause damage to the interfacial film.

3.4. Interfacial Tension (IFT). IFT gives information on the diffusion and adsorption of demulsifier molecules at the W/O interface and indicates their capacity to permeate the interfacial layer and cause emulsion breaking.^{28,39} IFT is illustrated in Figures 6 and 7. Figure 6 depicts the influence of the three-block copolymers and their corresponding demulsifier concentrations on IFT at the crude oil–water interface. It

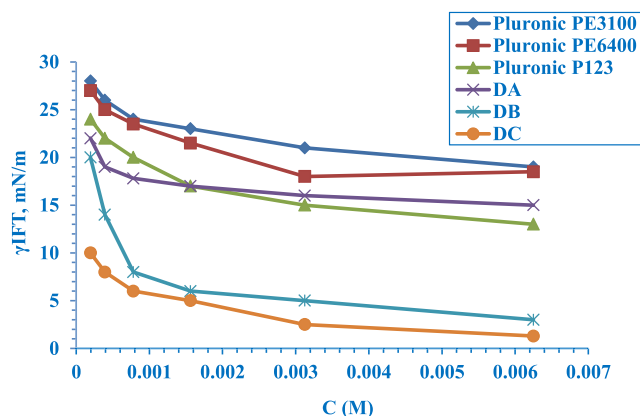


Figure 6. Effect of concentrations of the triblock copolymers and demulsifiers on the IFTs between the crude oil–water interface.

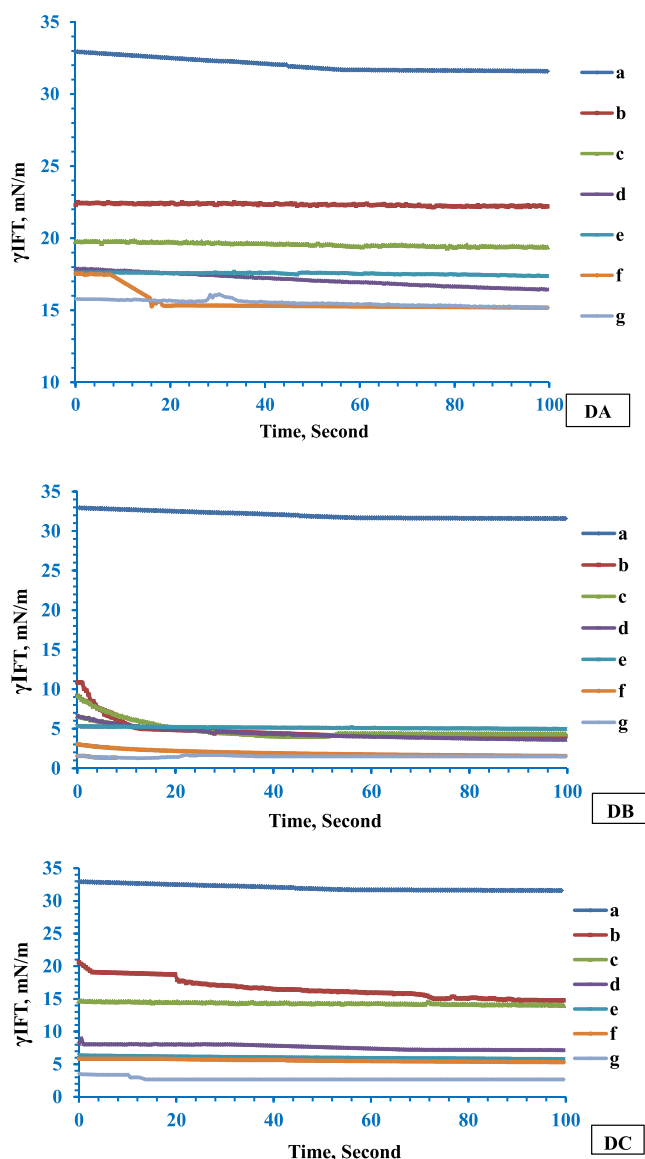


Figure 7. IFT as a function of time for crude oil with and without different concentrations of DA, DB, and DC. (a) Blank, (b) 1.95×10^{-5} , (c) 3.91×10^{-5} , (d) 7.81×10^{-5} , (e) 1.56×10^{-4} , (f) 3.13×10^{-4} , and (g) 6.25×10^{-4} M.

can be noticed that the IFT dropped as the concentration of the triblock copolymers and their corresponding demulsifiers increased. The prepared demulsifiers decrease the IFT more than their corresponding block copolymers. This implies that the surfactant molecules have a high capacity to permeate and damage the interfacial film.^{22,40} Figure 7 demonstrates the dynamic IFTs for surfactants DA, DB, and DC. For DA and DC, the IFT lines are stable at most concentrations, which may be attributed to the rapid adsorption of the surfactant molecules on the W/O interface. This behavior may be related to the hydrophobic moiety as well as the solubility power for each surfactant in the continuous (oil) phase. In the case of DB, γ_{IFT} declined gradually with time until it reached a constant value. This may be due to an increase in the surfactant's adsorptive ability in dispersed water molecules, which results from an almost equal ratio of ethylene oxide and propylene oxide in its structure.

3.5. Demulsification Effectiveness. 3.5.1. Influence of the Demulsifier's Molecular Structure.

Table 4. Separated Water Amount and the Demulsification Efficiency of Crude Oil Emulsion (50%) in the Presence of Different Concentrations of the Three Triblock Copolymers and Prepared Demulsifiers at 60 °C for 120 min

demulsifier	concentration ppm	water separated, mL	dehydration ratio
control	0	0	0
Pluronic PE3100	25	0	0
	50	0	0
	75	0	0
	100	0	0
	200	2	4
DA	25	0	0
	50	0	0
	75	0	0
	100	0	0
	200	0	0
Pluronic PE6400	25	5	10
	50	5	10
	75	10	20
	100	15	30
	200	17	34
DB	25	20	40
	50	30	60
	75	35	70
	100	40	80
	200	50	100
Pluronic P123	25	5	10
	50	5	10
	75	10	20
	100	16	32
	200	20	40
DC	25	30	60
	50	40	80
	75	50	100
	100	40	80
	200	30	60

demulsification efficiencies of the prepared demulsifiers and their triblock copolymers at different concentrations for 50% naturally occurring crude oil emulsions at 60 °C for 120 min. As predicted, no water separation has been detected for the blank sample, pointing toward the high stability of the tested emulsion. By comparing the efficiencies, it can be noticed that the prepared demulsifiers showed higher efficiencies than the corresponding triblock copolymers except DA and Pluronic PE3100, which gave zero performance. The high efficiencies of the prepared demulsifiers are due to the presence of a phenyl ring in their molecular structures, which interacts with the polyaromatic structure of asphaltene by the π - π interaction and enhanced their affinities toward asphaltene molecules.⁴¹ Regarding the demulsifiers' molecular weights, increasing EO and PO moieties increases the molecular weight of the demulsifier as in DC and DB and hence improves the demulsifier properties. The higher adsorption tendency, contact area, and stronger interaction with the interface film for DB and DC promote better film rupture and water droplet coalescence.⁴² DC with the highest molecular weight of all demulsifiers has the highest efficiency (100% at 75 ppm).

Moreover, higher interfacial activities of DB and DC than DA are also considered vital characteristics for obtaining higher demulsification performances. High interfacial activity is achieved when the demulsifier molecules' diffusion speed and adsorption at the interface are rapid. This leads to the production of a thinner interfacial layer that is more elastic and susceptible to rupture. The demulsification process, which consists of replacing asphaltene aggregates at the W/O interface with demulsifier additives, generates films with reduced elastic modulus, encouraging coalescence of the dispersed water droplets.³¹

The hydrophilicity of the demulsifier is critical for demulsification efficiency, which can be expressed as the RSN value. An increased RSN value is beneficial for enhancing the demulsification efficiency. As demonstrated in Table 3, DB and DC have higher RSN values than DA. As shown in Figure 8, the demulsifier DA did not provide any demulsification

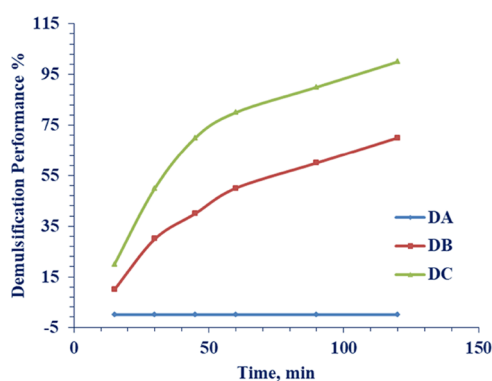


Figure 8. Demulsification performance of the prepared demulsifiers (DA, DB, and DC) at different times, a dose of 75 ppm, and a temperature of 60 °C.

efficiency, whereas DB and DC exhibited high demulsification effectiveness. The high hydrophobicity character of demulsifier DA which lowered its RSN value is a possible explanation for this observation. On the other hand, the hydrophilicity character of DB and DC increased on increasing the EO moiety, which increased their RSN values. Due to the hydrophobic effect of the oil phase, the demulsifier molecules with higher hydrophilic character have a stronger driving force to penetrate and damage the interfacial film.

3.5.2. Influence of the Demulsifier Dose. As summarized in Table 4, both DA and its corresponding block polymer Pluronic PE3100 have no demulsification efficiencies at different concentrations, whereas the demulsification efficiencies of DB, Pluronic PE6400, and Pluronic P123 increased as their concentration increased as seen in Table 4 and Figure 9. For DC, the demulsification efficiency increased on increasing its concentration and then decreased again as shown in Figure 10 and Table 4; when the concentration was 75 ppm, the dehydrating ratio approached 100%, but when the concentration was 200 ppm, the dehydrating ratio declined to 60%. As the concentration of DC increased from 25 to 75 ppm, more demulsifier molecules were adsorbed at the W/O interface, which coalesce water droplets faster and enhance the dehydrating ratio. Over 100 ppm, a high molecular weight demulsifier at high concentrations may impede migration from the bulk phase to the W/O interface, resulting in a decrease in the demulsification effectiveness.^{42,43} Also, the surplus molecules may be adsorbed at the W/O interface, producing

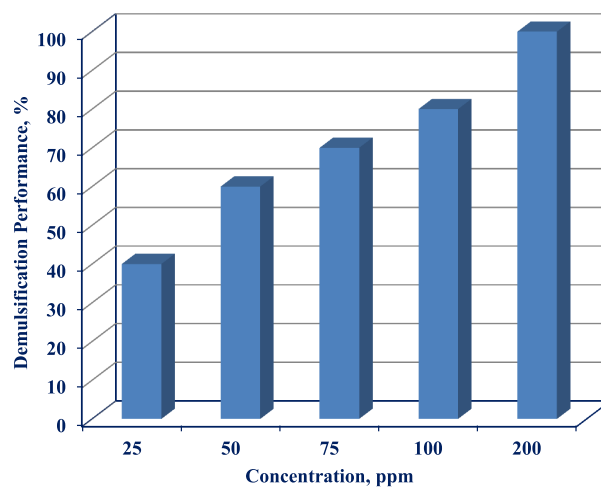


Figure 9. Demulsification performance of the demulsifier (DB) for different concentrations at 120 min and a temperature of 60 °C.

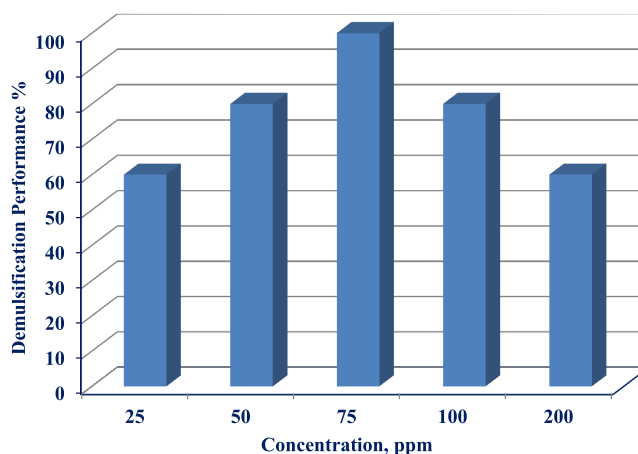


Figure 10. Demulsification performance of the demulsifier (DC) for different concentrations at 120 min and a temperature of 60 °C.

a demulsifier molecular layer that prevented the water droplets from coalescing and reducing the demulsification effectiveness.^{44,45} Furthermore, the excess demulsifier molecules may combine to create micelles, which may possess a negative impact on the demulsification efficiency.⁴⁶

3.6. Interfacial Rheology. It is widely recognized that the existence of surface-active compounds in crude oil, like resins, waxes, asphaltenes, and naphthenic acids, generates a mechanically rigid or viscoelastic interfacial barrier that develops around water droplets, contributing to the high petroleum emulsion stability. Asphaltenes get the greatest attention among all these components because of their critical role in emulsion stability. As a result, the interfacial film generated via asphaltenes at the W/O interface exhibits an extremely viscoelastic behavior.⁴⁷ Therefore, the effect of adding different demulsifiers (DA, DB, and DC) at 60 °C on the interfacial rheology was studied as shown in Figure 11a,b. It is obvious that the interface between water and blank crude oil (dehydrated crude oil) was altered from comparatively viscous ($G' < G''$) to more stiff ($G' > G''$), with both G' and G'' increasing with time. After 120 min, G' and G'' were nearly constant, as shown in Figure 11a,b.²¹ After adding DA, the values of G' and G'' for DA slightly decreased from 0.002828 and 0.002229 Pa to 0.002607 and 0.002007 Pa, respectively.

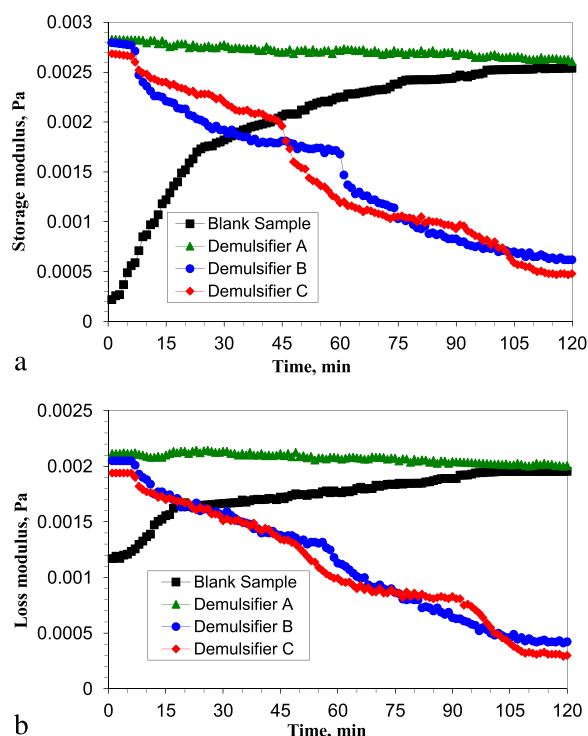


Figure 11. (a) Storage modulus G' against sweep time for DA, DB, and DC. (b) Loss modulus G'' against sweep time for DA, DB, and DC.

This small reduction in the G' and G'' values, which were slightly higher than the values of blank crude oil where the barrier between droplets was still high, was probably because of the creation of a new viscoelastic interfacial barrier via the interaction, diffusion, adsorption, and rearrangement of DA molecules and asphaltenes.⁴⁸ This inability to lower G' and G'' values had an impact on its demulsification capability, as demonstrated by the bottle test. When 200 ppm of DB and 75 ppm of DC were applied, their potential to influence the interfacial shear rheology characteristics was observed as shown in Figure 11a,b. After about 5 min, both DB and DC abruptly lowered the G' and G'' values and then stabilized with fluctuation, where G' values were higher than G'' . This is because both demulsifier molecules diffused and permeated the interface, breaking the cohesive asphaltene network. The interfacial rheology parameters were dramatically impacted via the adsorbed interface film, with extra from both demulsifiers adsorbed and rearranged when the network was broken.²¹ G' and G'' values for both demulsifiers decreased again and became steady after about 100 and 110 min. For DB, G' and G'' lowered to around 0.00062 and 0.00042 Pa, respectively, while for DC, G' and G'' reduced to around 0.00048 and 0.00030 Pa, respectively. They both exhibited rapid and efficient demulsification performance; however, DC had the benefit of requiring less dose compared to DB.

3.7. Microscopic Inspection of the Demulsification Mechanism. Water droplets are very ultrastable in an oil emulsion when protected by a viscoelastic interface layer produced by asphaltenes and other additives.^{38,49} Following the addition of the demulsifier, it competed with asphaltenes for adsorbing at the W/O interface, as shown in Figure 12. Because of the demulsifier molecules' great competitiveness, the emulsifier molecules present at the interfacial film are



Figure 12. Microscopic inspection of the demulsification mechanism.

displaced, resulting in the interfacial film's weakening. This action allows adjacent water droplets to coalesce, as illustrated in the micrograph (Figure 12, coalescence step). A greater decrease in the viscoelasticity of the interfacial layer facilitates the coalescence of water droplets, channel creation, and water separation, resulting in an improved demulsification performance. Meanwhile, high interfacial properties, an appropriate molecular weight, and high hydrophilicity may increase the demulsifier's adsorption and penetration into the interfacial film, allowing for even better demulsification results. Furthermore, the demulsifier's capacity to permeate the interfacial layer is further enhanced by a virtually uniform partition coefficient. Because of the advantages mentioned above, DB and DC demulsifiers provide superior demulsification efficiency for oil emulsions.

4. CONCLUSIONS

New polymeric nonionic demulsifiers based on hydroxybenzenesulfonic acid were synthesized. ¹H NMR, ¹³C NMR, MS, and FTIR spectroscopies were performed to validate the chemical composition of the prepared demulsifiers. To comprehend the behavior of the synthesized materials at the interface, RSN, K_p , and IFT were studied. The IFT measurement revealed that DA, DB, and DC had significant interfacial activity and can effectively lower the IFT. The analysis of the K_p and RSN values indicated that hydrophobicity and hydrophilicity of the synthesized demulsifiers influenced the overall dehydration rate and demulsification efficiency. The demulsification test demonstrated that DB and DC demulsifiers provide superior demulsification efficiency for naturally occurring oil emulsions than the corresponding triblock copolymers, whereas DA did not provide any water separation. This is owing to DB and DC having rapid diffusion and adsorption at the water/oil interface. DC achieved a remarkable demulsification performance at a low dosage of 75

ppm for 120 min. DC has a greater capacity to reduce the viscoelasticity of the W/O emulsion at a lower dosage compared to DB. Polarizing optical microscopy was performed to discuss the demulsifying mechanisms. Adsorption and flocculation, coalescence and channel formation, and finally separation were observed to represent the three phases of the demulsifying mechanism.

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Notes

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