

# One-Pot Synthesis of Amphipathic Esters for Demulsification of Water-in-Crude Oil Emulsions

Mahmood M. S. Abdullah, Hamad A. Al-Lohedan, and Basheer Mohammed Al-Maswari\*

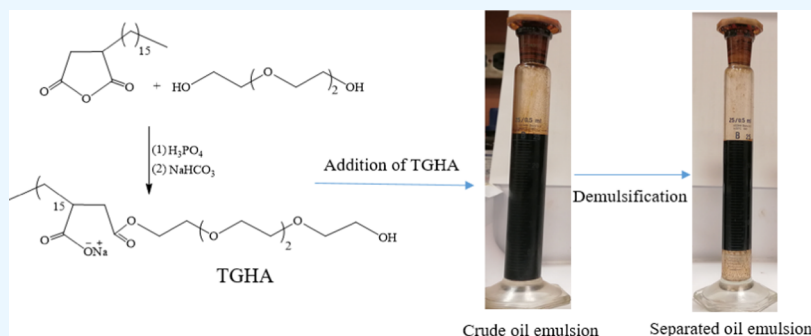
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**ABSTRACT:** The current work aims to synthesize new amphipathic compounds, TGHA and PGHA, and investigate their demulsification performance (DP) in water-in-crude oil emulsions. Their chemical structures, thermal stability, interfacial activity, and micelle formation were investigated by different techniques. The bottle test method was used to investigate the effect of demulsifier concentration, water content, temperature, and demulsification time (DT) on the DP of TGHA and PGHA compared to a commercial demulsifier (CD). The results indicated that these parameters have a noticeable impact on the DP of TGHA and PGHA. The results also showed that TGHA exhibited higher DP than PGHA at all investigated parameters, which could be explained by increasing its hydrophobicity due to lower oxyethylene units in its structure than PGHA. An increase in these units means increased hydrophilicity, which led to obstruction of PGHA molecule diffusion in crude oil as a continuous phase. Moreover, TGHA gave a comparable DP with CD, as it gave a higher DP and shorter DT than CD at a higher water content (50%), while the latter achieved the highest DP and the shortest DT at a low water content (10%).

## 1. INTRODUCTION

An emulsion is a system consisting of an external liquid called the continuous phase, an internal liquid called the dispersed phase, and an emulsifying agent at the liquids' interface. The emulsifying agent is commonly a surface-active compound, which plays a crucial role in emulsion stability.<sup>1,2</sup> Crude oil emulsions are formed spontaneously in crude oil reservoirs. The emulsifying agents, naturally occurring in crude oil, e.g., asphaltene, resin, solid particles, and naphthenic acids, represent the main reason for forming and stabilizing crude oil emulsions.<sup>3–5</sup> The added surface-active chemicals during enhanced oil recovery, in addition to pressure and shear forces, also significantly participate in the increased stability of crude oil emulsions.<sup>6,7</sup> The presence of crude oil in emulsion form makes transportation, storage, and refinery processes difficult. It results in pipeline corrosion, high pumping, and high transportation costs. So, separating these emulsions before starting any of these processes is necessary.<sup>7,8</sup>

Demulsification of crude oil emulsions is an essential process in the refinery and production platforms to remove water from crude oil. Demulsification is commonly categorized as

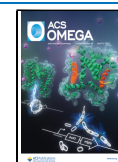
chemical, biological, or physical.<sup>9</sup> Using two of the three techniques is most effective; for instance, using chemical demulsifiers with heat is efficient for the demulsification of crude oil emulsions.<sup>10</sup> Chemical demulsification involves injecting a very low dose of a chemical, commonly known as a demulsifier, into crude oil emulsions. Demulsifiers are commonly surface-active and composed of hydrophobic and hydrophilic moieties that help them interact with aqueous and crude oil phases.<sup>11,12</sup> Demulsifier diffuses through a continuous phase, reaches the naturally occurring interfacial film, and adsorbs on it. The adsorption of demulsifier molecules on this film changes its properties and accelerates its rupture.<sup>13–15</sup> Several surface-active demulsifiers are applied for crude oil

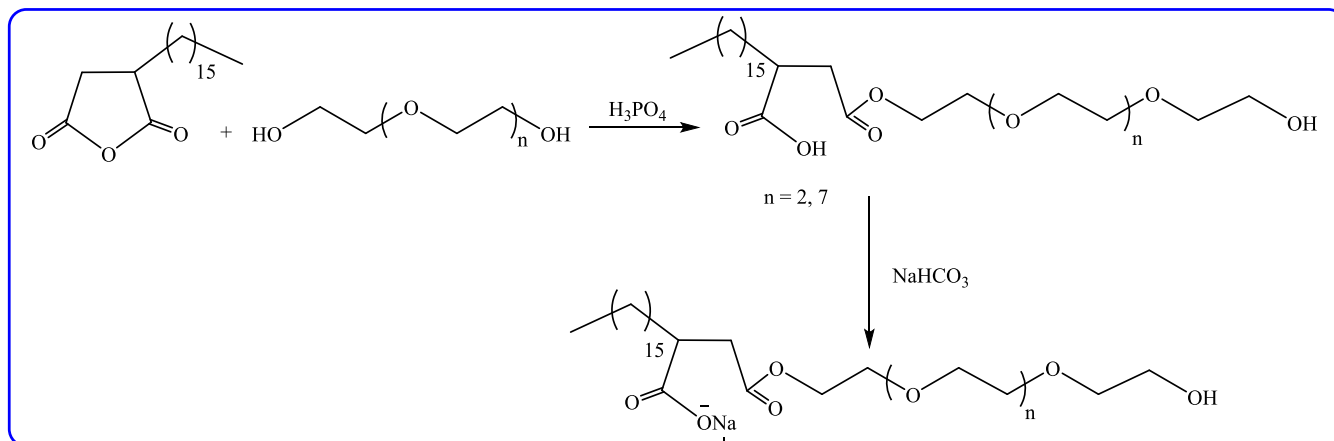
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**Figure 1.** Synthesis preparation route for TGHA and PGHA.

emulsion demulsification, e.g., polymeric surfactants, biosurfactants, and ionic liquids.<sup>16–20</sup> Polymeric surfactants, e.g., poly(propylene oxide-*co*-ethylene oxide), are one of the most applied demulsifiers among all other types due to their high performance and fast demulsification. However, their high cost motivated researchers to look for low-cost and more effective demulsifiers.<sup>21–23</sup> In our earlier works, different surface-active compounds were prepared through a short preparation route using low-cost materials. The prepared compounds were used for crude oil emulsion demulsification.<sup>24–28</sup> In the present work, new surface-active compounds were prepared in the one-pot reaction using low-cost materials via an opening ring of hexadecylsuccinic anhydride (HA) using tetraethylene glycol (TG) or poly(ethylene glycol)-400 (PG-400), yielding the corresponding surface-active compounds TGHA and PGHA. The obtained compounds were characterized using different techniques and applied for crude oil emulsion demulsification. Additionally, their demulsification performance was compared to that of a commercial demulsifier (CD). TGHA and PGHA gave promising results as demulsifiers for crude oil emulsions. Additionally, TGHA achieved a higher demulsification efficiency than that containing PGHA, as its efficiency reached 100% in many cases. This could be explained by increased PGHA hydrophilicity due to increased oxyethylene units compared to TGHA, which hinders the diffusion of PGHA molecules in crude oil (continuous phase). When comparing TGHA and PGHA with CD, TGHA gave a comparable DP with CD, as it gave a higher DP and shorter DT than CD at a higher water content (50%); however, the latter achieved higher DP and shorter DT than TGHA and PGHA at a lower water content (10%).

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Hexadecylsuccinic anhydride (HA), tetraethylene glycol (TG), poly(ethylene glycol)-400 (PG-400), phosphoric acid ( $H_3PO_4$ ), sodium hydrogen carbonate ( $NaHCO_3$ ), and acetonitrile were obtained from SIGMA Co. A commercial demulsifier (CD) was obtained from Baker Petrolite Co. and employed for comparison of its demulsification performance with the synthesized amphipathic compounds TGHA and PGHA.

Seawater containing 35,000 ppm salt was collected from the Arabian Sea coast, Eastern Province, Saudi Arabia. Crude oil was supplied by ARAMCO CO., Riyadh, Saudi Arabia. The specification of crude oil was reported in our previous study.<sup>24</sup>

**2.2. Synthesis of Amphipathic Compounds.** A mixture of either TG or PG-400 (10.30 mmol), HA (10.30 mmol), and  $H_3PO_4$  (1.03 mmol) was mixed in 25 mL of acetonitrile in a two-neck round-bottom flask and heated at 60 °C overnight. After that, the mixture was cooled to an ambient temperature. A saturated  $NaHCO_3$  solution (20 mL of methanol/distilled water 1:4) was added to the reaction mixture to neutralize an excess of  $H_3PO_4$ , with continual stirring for 30 min.<sup>29</sup> The mixture was poured into hexane (100 mL), followed by filtration. The obtained compound was washed with cold distilled water to dispose of excess TG, PG-400, and other inorganic materials. After this, the compound was kept in an oven at 70 °C until it had a constant weight with yields of 96.8 and 95.7%, respectively. The compound obtained from the reaction of TG with HA (sodium 15-heptadecyl-1-hydroxy-13-oxo-3,6,9,12-tetraoxahexadecan-16-oate) was assigned as TGHA, while the one obtained from the reaction of PG-400 with HA (sodium 30-heptadecyl-1-hydroxy-28-oxo-3,6,9,12,15,18,21,24,27-nonaoxahentriacontan-31-oate) was assigned as PGHA. Figure 1 shows the TGHA and PGHA preparation routes.

**2.3. Characterization.** The structures of TGHA and PGHA were elucidated using Fourier transform infrared spectroscopy (FTIR spectrometer, Nexus 6700, Thermo Scientific) and nuclear magnetic resonance spectroscopy (NMR, Avance-400 Bruker spectrometer) using dimethyl sulfoxide- $d_6$  (dms- $d_6$ ) as a solvent. The interfacial tension between crude oil and seawater containing different concentrations of TGHA and PGHA was measured by using a drop shape analyzer (DSA-100, KRUSS, Germany) at ambient temperature. The solubility of TGHA and PGHA was investigated using the relative solubility number (RSN) as the number of milliliters used to treat TGHA and PGHA solutions (1 g of either TGHA and PGHA dissolved in 30 mL of dioxane/toluene (96/4 vol %)) up to the appearance of continuous turbidity is considered as RSN. TGHA and PGHA (1000 ppm) aqueous solutions were used to measure the micelle size at ambient temperature via dynamic light scattering (DLS, Malvern Instrument, Ltd., Malvern, U.K.). In addition, this technique was used to investigate the emulsion droplet size during the demulsification process. For that, an emulsion droplet was taken and diluted with 2 mL of toluene. The dispersed solution was transferred to the cuvette for droplet size measurement at ambient temperature.

**2.4. Crude Oil Emulsion Preparation.** Crude oil emulsions were prepared by mixing crude oil with several seawater ratios (10, 30, and 50%), as reported in our previous work. To do so, the required seawater and crude oil ratios were mixed in a suitable beaker by using a digital homogenizer (T25, IKA, Germany) at 4000 rpm at 25 °C for 20 min. The type of the prepared emulsions was investigated using a drop test, as a drop of a prepared emulsion was dispersed separately in water and other organic solvents. All prepared emulsions exhibited water-in-oil (W/O) emulsion formation, as they dispersed completely in toluene, xylene, and chloroform, while they did not show any dispersion in water.

**2.5. Emulsion Stability Measurement.** The demulsification performance (DP) of TGHA and PGHA was explored by using the traditional bottle test method. Briefly, TGHA and PGHA (500 mg) were dissolved separately in xylene/ethanol (75/15 vol %; 2 mL). After the prepared emulsions were transferred into measuring cylinders (25 mL), they were injected with the required demulsifier dose and shaken 100 times manually to ensure the homogenization of a demulsifier in the prepared crude oil emulsions. Cylinders were shifted to a digital water bath at the measurement temperature. We started recording the demulsification time when the emulsion cylinders were placed in the water bath. DP was calculated using the following equation

$$DP (\%) = \frac{VDW}{VMW} \times 100 \quad (1)$$

where VDW is the volume of demulsified water and VMW is the volume of mixed water for emulsion formation. The blank samples were treated the same way as those containing TGHA or PGHA, except for adding TGHA or PGHA. These samples exhibited no separation for more than 2 weeks, reflecting the prepared emulsion's stability.

### 3. RESULTS AND DISCUSSION

**3.1. Characterization of TGHA and PGHA.** **3.1.1. Chemical Structure.** The opening ring of HA using either TG or PG-400 in the presence of  $H_3PO_4$  to obtain TGHA and PGHA was elucidated using FTIR and  $^1H$  NMR spectroscopy, as illustrated in Figures 2 and 3a,b, respectively. Both compounds showed the same FTIR spectra due to their similar chemical structure. The stretching absorption band of the terminal hydroxyl group was noticed at  $3436\text{ cm}^{-1}$ , while the stretching

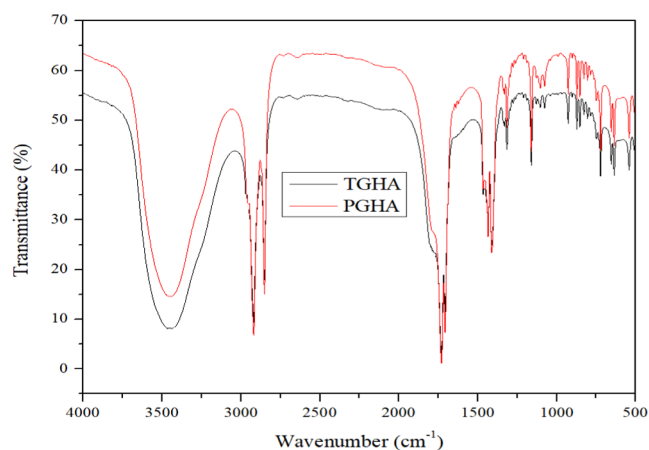


Figure 2. FTIR of TGHA and PGHA.

and bending absorption bands of C–H appeared at 2919, 2851, and  $1466\text{ cm}^{-1}$ . The appearance of the vibrational band of the carbonyl group at  $1742\text{ cm}^{-1}$  indicated ester formation. Additionally, the vibrational absorption band of C–O appeared at  $1160\text{ cm}^{-1}$ . In  $^1H$  NMR spectra, both spectra show remarkable similarity, and this is due to the similarity of TGHA and PGHA in their chemical structures. The main difference is in integrating the protons of oxyethylene units at 3.56 ppm. PGHA showed a higher integrated peak than TGHA due to the higher oxyethylene units in its structure. As depicted in the figure, the alkyl chain protons of HA were noticed at 0.88, 1.26, and 1.56 ppm. The methylene protons of the HA ring appeared at around 2.8 ppm. The appearance of methylene protons of TG and PG-400 at 3.56 ppm verified that the reaction of HA with TG or PG occurred.

**3.1.2. Thermal Gravimetric Analysis.** The thermal stability of TGHA and PGHA was investigated in the range of 25–800 °C under a nitrogen atmosphere, as illustrated in Figure 4. The ionic character of TGHA and PGHA, in addition to the presence of oxyethylene units in their structures, was reflected in their thermal stability,<sup>30,31</sup> as they significantly enhanced their thermal stability. TGHA showed lower thermal stability between 315 and 350 °C, possibly due to the presence of fewer oxyethylene units than PGHA. The participation of the HA alkyl chain in molecular weight increased with a decrease in the number of oxyethylene units, leading to the degradation of TGHA at lower temperatures than PGHA. The primary degradation for both occurred between 450 and 505 °C. The degradation in this region is due to the degradation of oxyethylene units of TG and PG-400.

**3.1.3. Interfacial Activity and Relative Solubility Number.** The compound's performance in reducing the interfacial tension (IFT) between crude oil and seawater is a crucial parameter for selecting it as a demulsifier. The effect of TGHA and PGHA on the IFT between crude oil and seawater was measured using a pendant drop technique, where several TGHA and PGHA concentrations were dissolved in seawater, followed by blowing a drop of crude oil into these aqueous solutions to measure IFT. Table 1 presents the IFT between crude oil and seawater in the presence of TGHA and PGHA at different concentrations. The data showed that the IFT declined with increased concentrations up to a certain concentration. After that, the IFT remained constant, even with increased concentrations. As the concentration of the compound increases, the number of molecules reaching the oil–water interface increases. When the interface becomes wholly covered with compound molecules, the excess molecules begin to collect in the bulk solution to form micelles.

The relative solubility number (RSN) is an alternative practical technique to the hydrophilic–lipophilic balance. It indicates the amphipathic compound's solubility in water and an organic solvent. The higher RSN value, more than 17 mL, indicates compound solubility in water, while the lower RSN value, less than 13 mL, indicates compound solubility in organic solvents. Herein, the RSNs of TGHA and PGHA were determined, as presented in Table 1. The data indicated PGHA's solubility in water. However, PGHA showed an RSN value higher than that of TGHA; the latter can be somewhat soluble in water.

**3.1.4. Micelle Size (MS).** Micelle formation is a crucial characteristic of amphipathic compounds as their molecules' self-assembly forms these micelles. Herein, the ability of

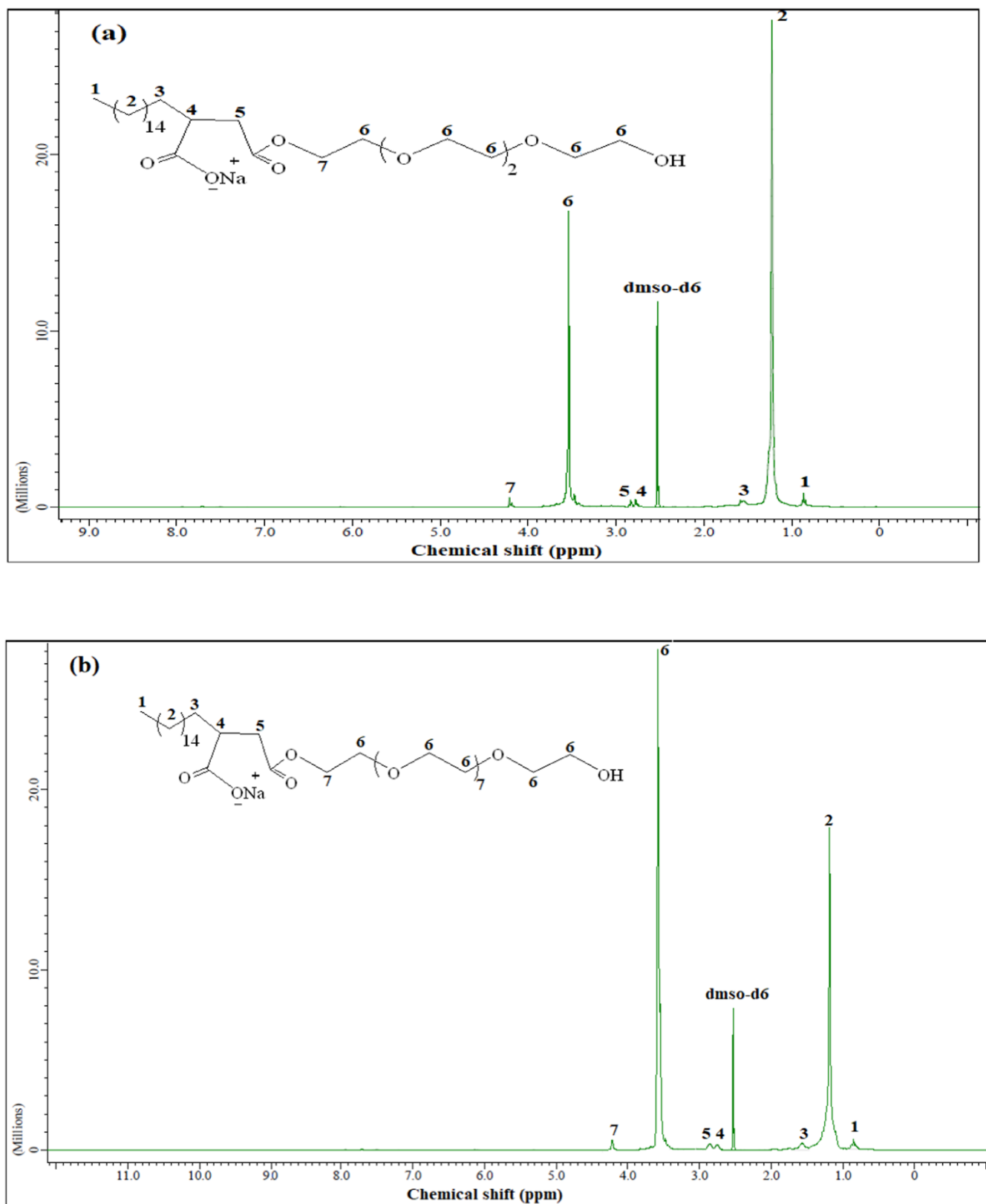


Figure 3. Proton nuclear magnetic resonances of (a) TGHA and (b) PGHA.

TGHA and PGHA to form micelles was investigated using DLS, as presented in Figure 5. The data showed that the MSs of TGHA and PGHA were 188.8 and 225.1 nm, respectively, while the polydispersity index (PDI) values of TGHA and PGHA were 0.135 and 0.156, respectively. These data

confirmed the ability of TGHA and PGHA to form micelles. The low polydispersity index values reflect the ability of TGHA and PGHA to form uniform micelles.

**3.2. Demulsification Performance (DP) of TGHA and PGHA.** The interfacial activity of TGHA and PGHA

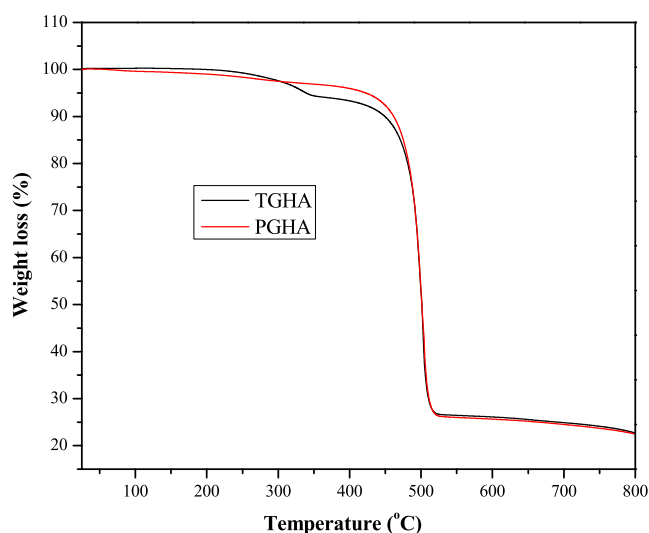


Figure 4. TGA of TGHA and PGHA.

Table 1. IFT between Crude Oil and Seawater in the Presence of TGHA and PGHA at Different Concentrations

compound	concentration (ppm)	IFT (mN/m)	RSN (mL)
TGHA	0	33.5	16.6
	250	25.2	
	500	21.4	
	750	12.2	
	1000	5.2	
	1250	5.1	
PGHA	0	33.5	20.4
	250	28.2	
	500	24.7	
	750	14.2	
	1000	7.5	
	1250	7.5	

recommended their application as demulsifiers for breaking crude oil emulsions. Different influencing parameters were investigated, including the concentration, water content, temperature, and demulsification time (DT). The bottle test method was used to investigate the effect of these parameters on the DP of TGHA and PGHA compared to CD.

**3.2.1. Concentration Effect.** The concentration effect of TGHA, PGHA, and CD on the DP was investigated using W/O emulsion containing 10 and 50% seawater at 60 °C and a DT of 340 min, as presented in Figure 6a,b. As depicted in the figure, the concentration effect was related to water content. The concentration effect was clear with W/O emulsions containing 10% seawater. The DP increased from 25% at 250 ppm to 55% at 1000 ppm for TGHA, while it increased from 18% to 46% for PGHA at these concentrations, respectively; in contrast, the DP of CD improved from 41 to 94%. However, in emulsions containing the highest percentage of seawater (50%), the effect of concentration was minimal. Concentration's limited effect with increased seawater content could be linked to the lower emulsions' stability than those containing lower water contents.<sup>1</sup> When comparing the DP of TGHA and PGHA with CD, the latter achieved the highest DP at a lower seawater content (10%), which could be explained by the terminal ionic group of TGHA and PGHA, which can hinder their diffusion in crude oil as a continuous phase<sup>32</sup> compared to CD, which is commonly composed of

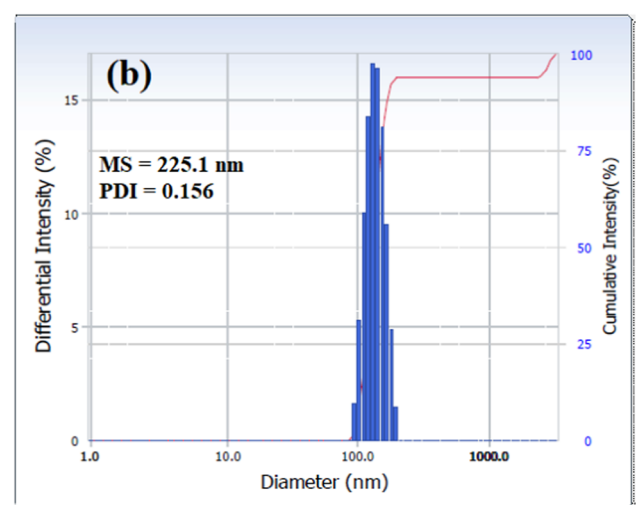
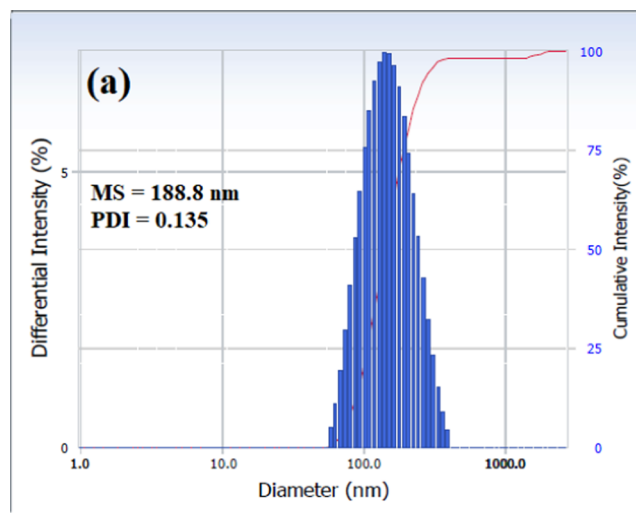
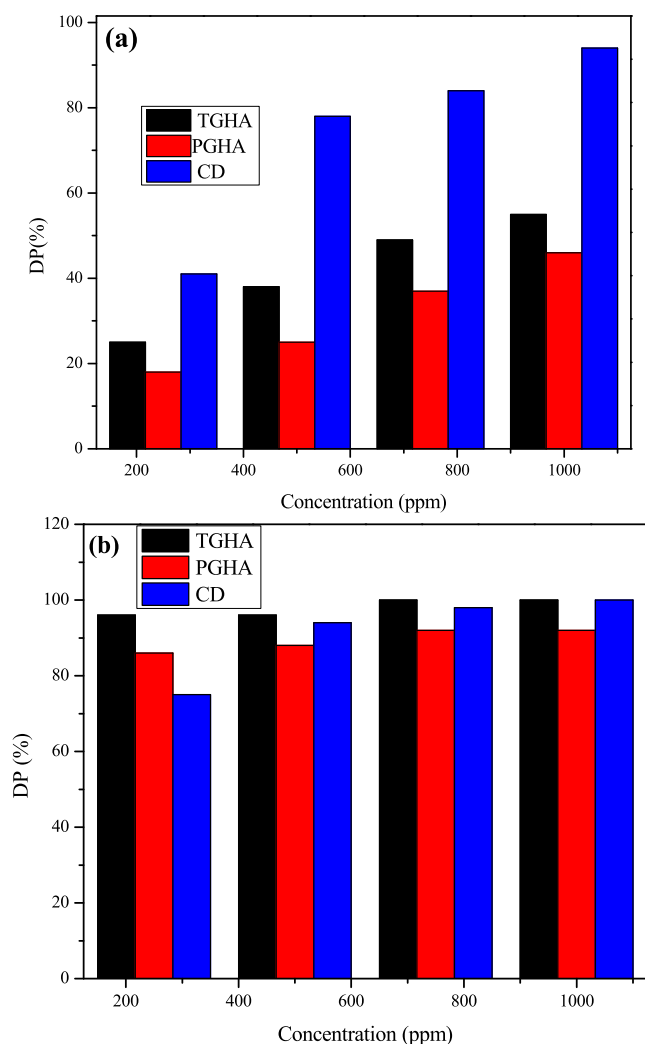


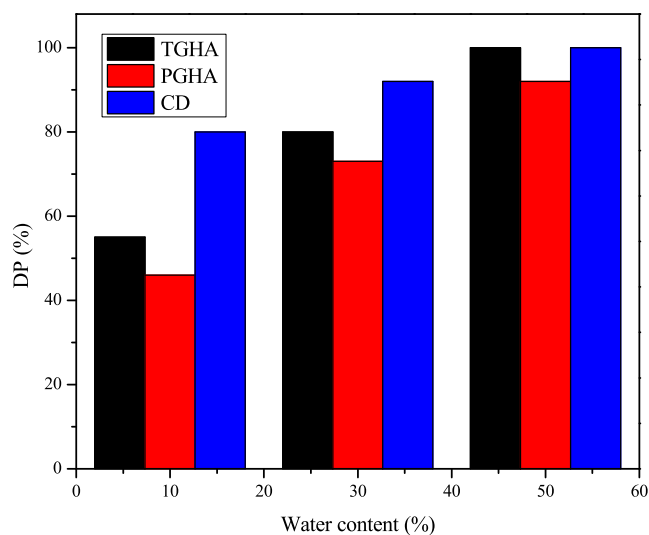
Figure 5. MS and PDI of (a) TGHA and (b) PGHA.

nonionic surfactants. With increased seawater contents (50%), TGHA gave DP higher than CD, especially at low concentrations, which could be related to the same reason, as increased seawater content could facilitate diffusion of TGHA and PGHA due to the ionic group.

**3.2.2. Water Content Effect.** The water content of crude oil emulsions plays a crucial role in their stability. Commonly, increasing the water content decreases oil emulsion stability.<sup>33</sup> Herein, the water content effect was evaluated using W/O emulsions containing 10, 30, and 50% seawater, 1000 ppm TGHA, PGHA, and CD, 60 °C, and a DT of 340 min, as illustrated in Figure 7. As depicted in the figure, the DP improved with an increase in water content as it increased from 55% at a water content of 10% to 100% at 50% for TGHA. In contrast, it increased from 46 to 92% for PGHA and from 80 to 100% for CD at 10 and 50%, respectively. The number of emulsion droplets increases with an increase in water content, which reduces the distance between droplets, resulting in an increased collision probability between these droplets.<sup>16,34</sup> By comparing the DP of CD with TGHA and PGHA at a high water content (50%), CD and TGHA achieved the same DP; however, at a low water content (10%), CD gave the highest DP. These data indicate that TGHA can be used effectively as a demulsifier at high water contents.



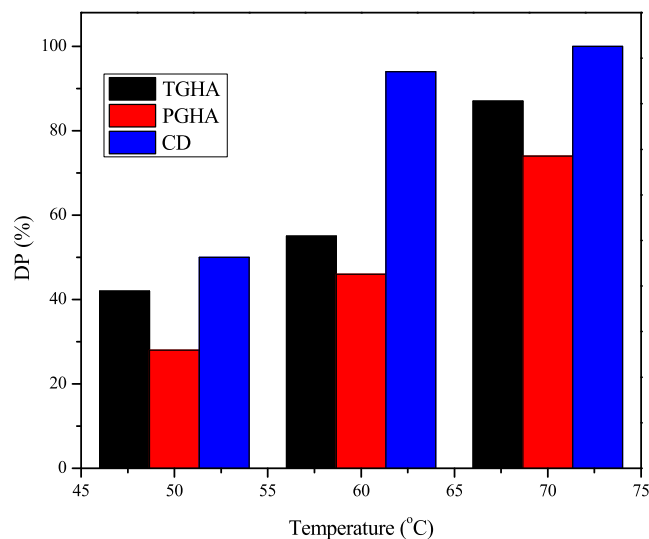
**Figure 6.** DP of TGHA, PGHA, and CD at different concentrations for W/O emulsion containing (a) 10% and (b) 50% of seawater.



**Figure 7.** DP of TGHA, PGHA, and CD (1000 ppm) at different water content ratios.

**3.2.3. Temperature Effect.** Temperature is one of the most essential parameters in the demulsification process. Using a

demulsifier in combination with heat commonly gives higher performance.<sup>26,35</sup> Herein, the DP of TGHA, PGHA, and CD was investigated at different temperatures in the range of 50–70 °C using 1000 ppm TGHA, PGHA, and CD, W/O emulsion containing 10% water content, and a settling time of 340 min, as shown in Figure 8. Results showed that the DP of

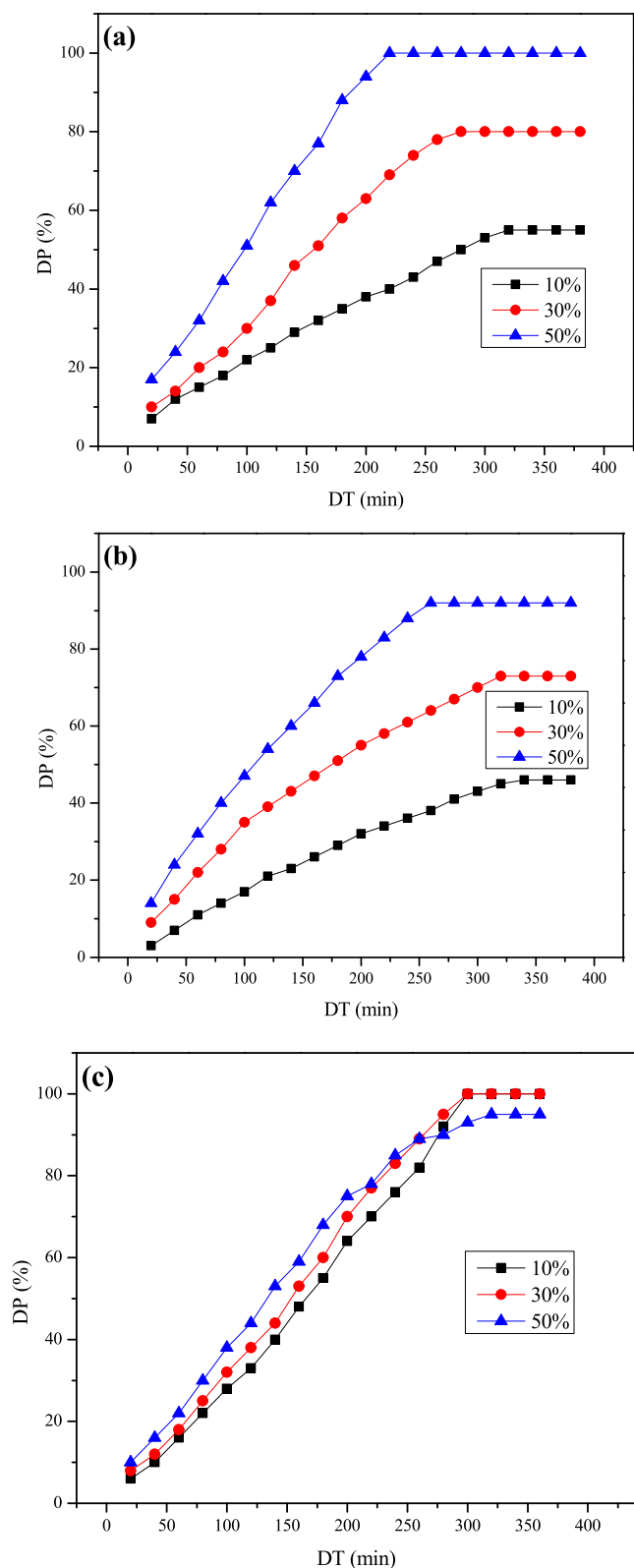


**Figure 8.** DP of TGHA, PGHA, and CD (1000 ppm) at different temperatures.

TGHA, PGHA, and CD improved significantly with increased temperature. When the temperature increased from 50 to 70 °C, the DP increased from 42 to 87%, respectively, for TGHA, while it improved from 28 to 74% for PGHA at these temperatures.

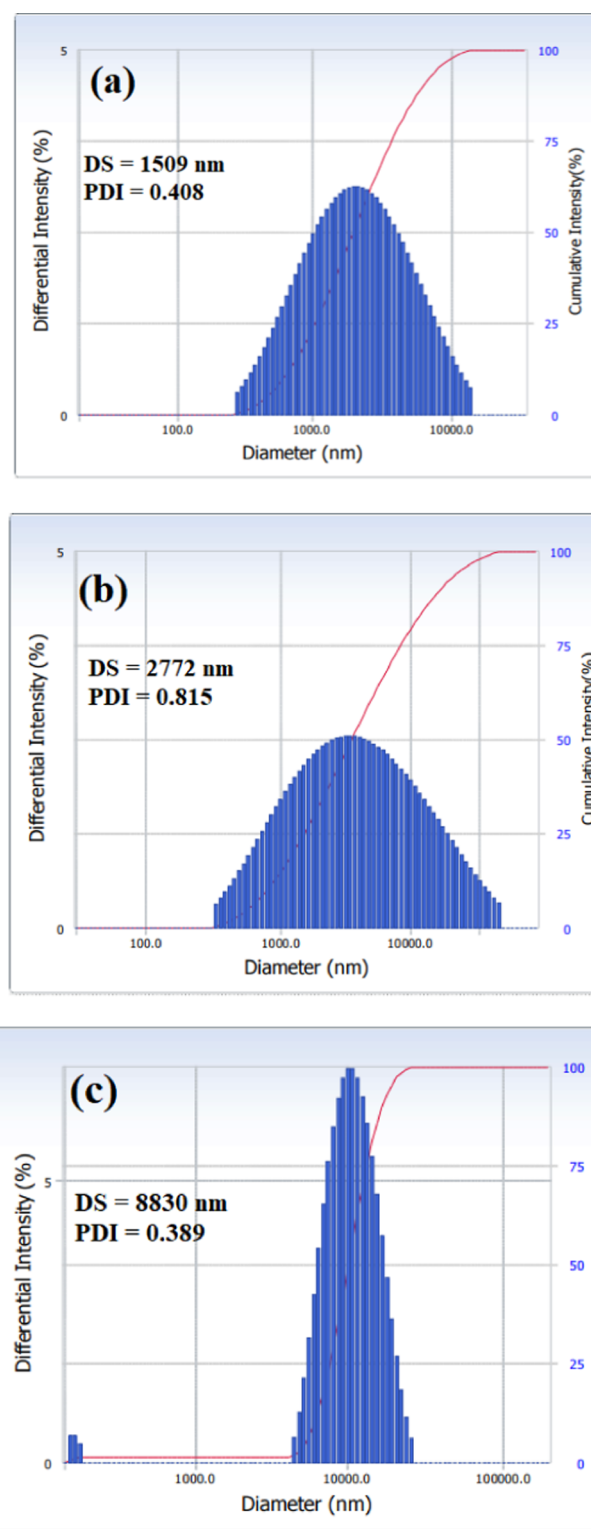
In contrast, the DP of CD improved from 50 to 100% at these temperatures. These data indicated that TGHA gave a higher DP than PGHA, while CD achieved the highest DP. An increase in temperature causes viscosity reduction, enhancing the kinetic energy of droplets and increasing the difference in the density of water and crude oil, contributing to effective coalescence and aggregation of water droplets and phase separation.<sup>36</sup>

**3.2.4. Demulsification Time (DT) Effect.** DT also represents a critical parameter during the demulsification process; after demulsifier injection into an oil emulsion, it needs time to diffuse throughout a continuous phase, reach the oil and water interface, penetrate and rupture this rigid film. The DT effect on the DP of TGHA, PGHA, and CD was evaluated using a concentration of 1000 ppm at 60 °C, as shown in Figure 9a–c. The data indicated that there was a direct relationship between DP and DT. The results also showed that emulsions with a lower water content took longer to DT than those with a higher water content. This is because it is difficult to separate emulsions containing a smaller amount of water than those containing a higher water content, as mentioned previously. In addition, PGHA showed longer DT than TGHA, which could be explained by increased PGHA hydrophilicity due to increased oxyethylene units compared to TGHA. Increased hydrophilicity hinders the diffusion of PGHA molecules in crude oil (continuous phase), requiring more DT. However, CD achieved the highest DP and the shortest DT at a low water content (10%); it gave a lower DP than TGHA and the longest DT among all at a high water content (50%).



**Figure 9.** DP of (a) TGHA, (b) PGHA, and (c) CD (1000 ppm) at different settling times at 60 °C.

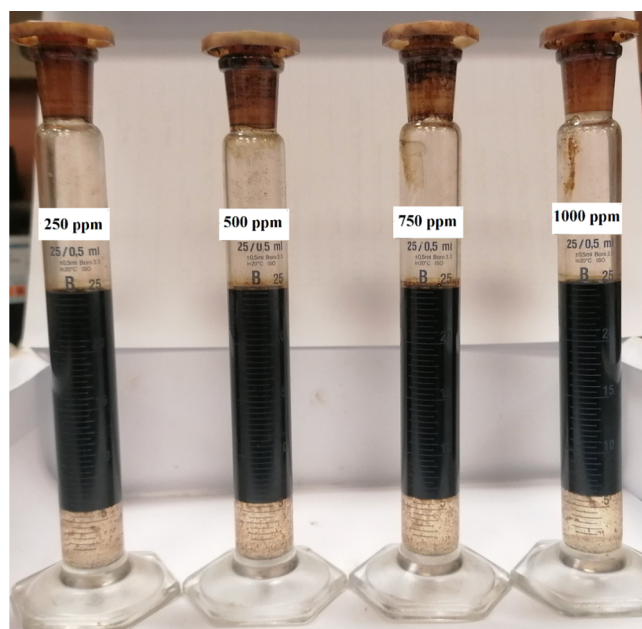
**3.3. Emulsion Droplet Size during the Demulsification Process.** The droplet size (DS) of the W/O emulsion containing 30% seawater in the presence of TGHA (500 ppm) was evaluated with the DLS technique at different DTs, as shown in Figure 10a–c. The measurements were taken at



**Figure 10.** DS of W/O emulsion containing a water content of 30% in the presence of TGHA (500 ppm) at (a) 0 min, (b) 80 min, and (c) 160 min.

different DTs, 0, 80, and 160 min. The figure shows that the average droplet size was 1.5  $\mu\text{m}$  at 0 min (Figure 10a). DS increased with time (Figure 10b,c), as an increased time gives TGHA enough time to diffuse and penetrate the rigid asphaltene interface to rupture it, which causes the tiny droplets to assemble into larger droplets. The heaviness of the

droplets increases with their size until, if they reach a certain weight, these droplets move downward to settle at the bottom of the cylinder, causing phase separation. Figure 11 shows an optical image of settled-down demulsified water using THE at different concentrations.



**Figure 11.** Optical images of demulsified water using TGHA at different concentrations at 60 °C and 280 min of DT.

#### 4. CONCLUSIONS

New amphipathic compounds were synthesized via an opening-ring reaction of HA with TG or PG-400 in the presence of  $H_3PO_4$  as a catalyst, followed by neutralization of an excess of  $H_3PO_4$  and the obtained acid with  $NaHCO_3$ , producing the corresponding amphipathic compounds TGHA and PGHA. The chemical structures, thermal stability, interfacial activity, RSN, and MS of TGHA and PGHA were evaluated using different techniques. These measurements confirmed these compounds' formation, thermal stability, interfacial activity, and ability to form micelles. Based on the cumulative analysis, TGHA and PGHA were recommended to serve as demulsifiers of W/O emulsions using different factors such as demulsifier concentration, water content, temperature, and DT. Additionally, the DP of TGHA and PGHA was compared with the DP of CD. The results indicated that the DP of TGHA and PGHA improved with increased concentration, water content, temperature, and DT. The results also revealed a higher DP of TGHA than PGHA at all investigated parameters. These data reflect the ability of TGHA to serve as an effective demulsifier for crude oil emulsions containing high water contents at 70 °C.

When comparing the DP of TGHA and PGHA with CD, the latter achieved lower DP and longer DT than TGHA at a higher water content (50%), while it gave the highest DP and the shortest DT among all at a low water content (10%). A decrease in the water content hinders TGHA molecules from diffusing in crude oil (continuous phase) due to ionic groups in its structure. This means that TGHA can be applied as an effective demulsifier for W/O containing a higher water content (50%).

The emulsion droplet size measurements confirmed increased droplet sizes with an increase in time as tiny droplets fused into big ones. When the droplet size reaches a certain weight, these droplets move downward to settle at the bottom of the cylinder, causing phase separation.

#### AUTHOR INFORMATION

##### Corresponding Author

**Basheer Mohammed Al-Maswari** – Department of Chemistry, Yuvaraja's College, University of Mysore, Mysore, Karnataka 570005, India; [orcid.org/0000-0002-2503-208X](https://orcid.org/0000-0002-2503-208X); Email: [basheer.almaswari@gmail.com](mailto:basheer.almaswari@gmail.com)

##### Authors

**Mahmood M. S. Abdullah** – Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; [orcid.org/0000-0002-8057-8376](https://orcid.org/0000-0002-8057-8376)

**Hamad A. Al-Lohedan** – Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

Complete contact information is available at:

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##### Notes

The authors declare no competing financial interest.

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