One-Step Synthesis of Amphiphilic Nonylphenol Polyethyleneimine for Demulsification of Water in Heavy Crude Oil Emulsions

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ABSTRACT: The demulsification of water-in-heavy crude oil emulsion with water droplet size in the microscale has drawn great attention because of their high stability and difficulty of separation. In the present work, a series of ethylene amine-based demulsifiers were prepared in one step through the interaction of pentaethylene hexamine, tetraethylene pentamine, and triethylene tetramine with glycidyl 4-nonylphenyl ether. The amphiphilic polyethyleneimine (APEI) abbreviated as DNPA-6, DNPA-5, and DNPA-4 were prepared to adjust their hydrophile-lipophile balances (HLB) to meet the requirement of the demulsification. 1H NMR, 13C NMR, and FTIR spectra were utilized to verify their chemical structures. The surface properties and zeta potential were also investigated. Demulsifier dose, separation time, and HLB values were taken into account to evaluate the demulsification efficiency of the synthesized APEI. The results suggested that the prepared demulsifiers had high ability to reduce the surface and interfacial tensions and also broke successfully water-in-Arabian heavy crude oil emulsions. The demulsification efficiency of DNPA-5 reached 100% for crude oil/water emulsion (90/10 vol %).

1. INTRODUCTION

Recently the high requirement for utilizing surfactants and polymer-based materials in the enhanced oil recovery leads to the formation of water-in-oil (W/O) or oil-in-water (O/W) emulsions.1,2 Depending on the production scheme, about 80% of the worldwide crude oil is produced in an emulsified form.3 In the crude oil production, W/O emulsion represents the greatest part of the crude oil. The W/O ratio, origin of the emulsion, and natural emulsifier systems are the main factors that affect the emulsion composition.4,5 Also, the heavy crude oil reserves are considered to be more complicated when comparing with light and medium reserves. Heavy crude oil has many undesirable properties such as high viscosity, high acidity, and tendency to form stable emulsions; thus, it represents a major challenge for the oil industry.4,6 In case of heavy crude oil reserves, highly stable W/O emulsions can be produced due to the presence of resins, asphaltenes, naphthenic acids, and fine solids that act as emulsifying agents.8 The petroleum crude oil and water emulsions cause several economic problems such as pipelines corrosion, microorganism’s growth, and oil viscosity increase. Hence, the isolation of water from crude oil before the refining process is required.9 The formed emulsion can be broken down mechanically, electrically, and chemically.9,10 In practice, to get the highest demulsification efficiency, a combination of these techniques should be improved. The combination between heating and chemical demulsifiers is the most broadly used technique.

Demulsifiers have the ability to rapidly separate emulsions into water and oil thanks to their amphiphilic nature with both hydrophobic and hydrophilic moieties. As a result of using demulsifiers, interfacial tension (IFT) between water and oil is reduced and the phase separation is promoted.11,12 Therefore, they can promote the oil flocculation and coalescence.13 Amphiphiles based on anionic, cationic, and nonionic are the three classes of demulsifiers. Nonionic demulsifiers are widely used to break O/W or W/O emulsions. Poly(ethylene oxide)—poly(propylene oxide) (PEO−PPO) block co-polymers, poly ethylene oxide (EO), and poly propylene oxide (PO) are some kinds of nonionic surfactants designed for emulsion breaking purposes.14 Polymeric demulsifiers relied on (PEO) or (PEO−PPO) block copolymers have been widely used due to their good results in the separation of water/oil emulsions, in addition to corrosion reducing.15,16 One of the main significant factors affecting the demulsification performance of (PEO−PPO) block copolymers is the position of EO to PO units in the copolymers. When (EO) as a hydrophilic part presents in the core and (PO) as a hydrophobic part present in the tail, the copolymer showed no efficiency; however, PO core and EO tail polymers display the best demulsification efficiency. Also, it was found that increasing the ethylene oxide contents of these kinds
of polymeric nonionic surfactants increases their demulsification performance.  

The main drawback of using these kind of nonionic polymers is their high production cost.  

Polyethyleneimine (PEI), is an extremely significant polyelectrolyte, with both linear and branched forms. PEI charge is pH dependent with the highest charge density at low pH than any polyelectrolyte.  

The main difference between (PEO) or (PEO—PPO) block copolymers and PEI is that PEI can form intra- and inter-chain hydrogen bonds between NH groups. Furthermore, it was found that all intra-chain hydrogen bonds are nonlinear and longer than typical H-bonding.  

Low molecular weight (LMW) PEI derivatives were used as low toxic and efficient gene delivery vectors due to their biocompatibility. Biodegradability is one of the most significant characteristics of biocompatible polymers. Biodegradable polymers as environmentally friendly materials have attracted considerable attention for their possible roles as alternatives to nonbiodegradable materials that accumulate in the environment. Also, nonylphenol as a widely used reagent was found that the higher the branching, the lower the biodegradability.  

According to the applications of PEI, ethoxy, hydrophobic, or hydrophilic units can be introduced to its structure. Amiphilic derivatives of PEI using PEO—PPO block copolymers or nonionic surfactants based on lauril acid or nonylphenol with different EO units have been studied and applied as demulsifiers for W/O emulsions. They were used to control the hydrophile—lipophile balance (HLB) and the amphiplicity of demulsifiers to be applied for the W/O emulsion system especially when the oil phase is thick. Most of PEI-based demulsifiers were prepared through multistep procedures and almost most of them used hyper-branched PEI while the method used in our paper is a simple single step reaction using linear LMW PEI. The present work aims to prepare new ethyleneimine-based surfactants that are synthesized through the reaction of LMW PEI series with glycidyl 4-nonyl ether (GNE) and utilized as demulsifiers for water-in-heavy crude oil emulsions. The synthesized surfactants were prepared using a simple one step reaction and their chemical structures were ensured by common spectroscopic tools.

2. RESULTS AND DISCUSSIONS

2.1. Characteristic Properties of DNPA-6, DNPA-5, and DNPA-4. Three amphiphilic polyethyleneimine (APEI) demulsifiers based on glycidyl alkyl benzene and ethyleneimine were synthesized as illustrated in Scheme 1. Fourier transform infrared (FTIR) charts, $^{1}$HNMR, and $^{13}$CNMR spectra were used to verify their chemical structures. The $^{1}$HNMR, $^{13}$C NMR, and FTIR spectra for DNPA-6, DNPA-5, and DNPA-4 surfactants are nearly identical due to the similarity in their structures. The integration of the $^{1}$HNMR peaks assigned for CH$_2$NH groups certainly differ. For brevity, the interpretation of the FTIR, $^{1}$HNMR, and $^{13}$C NMR for DNPA-6 are illustrated in Figures 2, 3 and 4, respectively. The FTIR spectra of DNPA-6 depicted in Figure 2 illustrate that the alcoholic hydroxyl and secondary amine groups of DNPA-6 appeared as broad peak at 3401 cm$^{-1}$. The disappearance of the two stretching bands of NH$_2$ at 3400 cm$^{-1}$ confirmed the interaction of the epoxy ring of glycidyl 4-nonylphenyl ether (GNPE) with the two primary amine groups of pentaethylene hexamine. The stretching bands at 2959 cm$^{-1}$ and 2872 refer to the aliphatic C—H. The stretching band at 1660 cm$^{-1}$ refers to the aromatic C=C bonds. The $^{1}$HNMR spectra (Figure 3) of DNPA-6 confirms the presence of methyl groups as multiplet at 0.30—0.42 ppm, and also methylene groups of the nonyl branch are observed as multiplet at 0.44—0.51, 0.7—0.96, 1.12—1.29, and 1.98—2.16 ppm. The formation of the ethylene amine units in DNPA-6, DNPA-5, and DNPA-4 is confirmed from the appearance of new multiplet peaks in the region between 2.25, and 2.45 ppm. The appearance of new peaks as doublet at 3.82 ppm, and multiplet at 3.97 ppm related to CH$_2$O (methylene oxide) and CH attached to alc. OH, and phenoxy, respectively, confirms the epoxy ring opening. The aromatic protons appeared as doublet at 6.52 ppm, and multiplet at 6.82—6.89 ppm. The $^{13}$C NMR spectra of DNPA-6 (Figure 4) are also used to verify the chemical structures of the prepared APEI demulsifiers. The peaks at 49 and 53 ppm attributed to CH$_2$NH and CH$_3$NHCHOH confirm the interaction of pentaethylene hexamine with GNPE through the epoxy ring opening. Additional details of the other peaks are assigned in the chemical structures of DNPA-6 as illustrated in Figure 4.
2.2. Solubility and Surface Activity of the Prepared APEI. The surface activity and the solubility of surfactants affect strongly their industrial applications. The surface tension measurements were carried out to investigate the impact of the chemical structures of the synthesized surfactants on their surface properties. Also, critical micelle concentration (cmc) and surfactant inter- and intra-molecular interactions in the bulk solution and at air/water interface are investigated.

At cmc, the surfactant molecules adsorbed on the solution surface reach equilibrium and at the same time form aggregates (micelles) in the solution bulk. In order to determine cmc, the relation between (ln c; mol/L) and the surfactant surface

Figure 1. Droplet sizes of the different water/oil emulsions (a) 50/50, (b) 70/30, and (c) 90/10.

Figure 2. FTIR spectra of DNPA-6.
tensions in aqueous solutions is plotted as shown in Figure 5. The values of cmc (mol. L\(^{-1}\)) and surface tensions at cmc (\(\gamma_{\text{cac}}\) mN m\(^{-1}\)) of DNPA-6, DNPA-5 and DNPA-4 surfactants are indicated from Figure 5 and listed in Table 1. The data showed that DNPA-6 has the highest cmc value, whereas DNPA-4 has the lowest one. This is attributed to the relatively highest hydrophilic part in DNPA-6, and the lowest in DNPA-4 while DNPA-5 was in between. Furthermore, DNPA-6 had the greatest ability to reduce water surface tension due to the strong hydrogen bond between water and the highest number of amino groups, which decrease the interaction between water molecules and that between surfactant molecules.\(^{35}\)

Figure 3. \(^1\)H NMR spectra of DNPA-6 in CDCl\(_3\) solvent.

Figure 4. \(^{13}\)C NMR spectra of DNPA-6 in CDCl\(_3\) solvent.
The theoretical solubility of the prepared surfactants can be evaluated by calculating the hydrophilic–lipophilic balance (HLB).36 The HLB of surfactant can be easily calculated using Griffin and Davies equations.7 Also, by calculating the HLB values of surfactants, we can easily expect their potential applications.39 For nonionic surfactants having HLB below 8, values of surfactants, we can easily expect their potential applications.40 As displayed in (Figure 7a), the charges of the surfactant aggregates can be also determined from where DNPA-5 and DNPA-4 need lower one. The surface average minimum surface area per molecule (Dh; nm) and polydispersity index (PDI) values were measured con

Table 1. Surface Activity Parameters, HLB, and Zeta Potential of DNPA-6, DNPA-5, and DNPA-4 at 25 °C

| compound | cmc (mM) | (∂γ/∂ ln c)T | γcmc (mN/m) | Γmax × 10^-6 (mol/m²) | Amin, (nm²/molecule) | HLB | zeta potential (mV) |
|----------|----------|----------------|-------------|-------------------------|---------------------|-----|---------------------|
| DNPA-6   | 0.32     | 15.06          | 34 ± 0.5    | 6.08                    | 0.27                | 9.58 | 56.8 ± 0.7          |
| DNPA-5   | 0.19     | 16.1           | 37 ± 0.5    | 6.5                     | 0.25                | 8.98 | 70.60 ± 1           |
| DNPA-4   | 0.091    | 18.7           | 39 ± 0.5    | 7.5                     | 0.22                | 8.29 | 74.6 ± 1            |

Figure 5. Surface tension isotherm of DNPA-4, DNPA-5, and DNPA-6.
of the emulsion. DNPA-6, DNPA-5, DNPA-4, and a commercial demulsifier (ARBREAK 8846) were dissolved separately in toluene/ethanol (75/25 wt %) and then injected to 25 mL of the previously prepared emulsion at different concentrations ranging from 250 to 1000 ppm. The demulsification performance as a function of time was observed. The emulsion breaking process is depicted in Scheme 2. Oil was the continuous phase of the synthesized emulsions while water was the dispersed phase and that was confirmed by the drop test method. The emulsion droplet sizes were noticed using the optical microscopy photographs as represented in Figure 9a, which indicate the formation of microscaled emulsion. A blank bottle, without the addition of any demulsifier and with the equivalent volume of the toluene/ethanol solvent, was used to observe the emulsion stability at the same demulsification conditions (60 °C). The demulsification efficiencies (η %) with different concentrations of DNPA-6, DNPA-5, DNPA-4, and ARBREAK 8846 and at various time intervals are listed in Table 3. As shown in Figure 9b,c, optical microscopy photographs were taken for crude oil/water separation at different time intervals. The effect of several factors including HLB value, demulsifier concentration, effect of water content, and effect of contact time on demulsification efficiency were studied. Water separation photos of W/O emulsions (50:50 vol %) are shown in Figure 10 to ensure the ability of the prepared APEIs to act as demulsifiers.

2.6. Hydrophile–Lipophile Balance “HLB” Effect. Studying the HLB values gives a strong indication to the surfactant solubility and the demulsification performance. As shown in Table 1, the HLB values of DNPA-6, DNPA-5, and DNPA-4 are 9.58, 8.98, and 8.29, respectively. Surfactants with high HLB values have longer hydrophilic parts and are more soluble in aqueous phase (dispersed phase) than those with low HLB values. After the addition of demulsifiers to the prepared emulsion, those with high HLB will move toward the water/oil interface and will have more thermodynamic stability at the interface of the water droplets than those with low HLB. As a consequence of such stability, demulsifier molecules arrange a continuous hydrophilic pathway among the dispersed water droplets, and as a result, the interfacial film surrounding the water droplets is removed. Therefore, DNPA-6 with longer ethylene amine hydrophilic part is the best demulsifying agent while DNPA-4 shows the worst performance as shown in Table 3.

2.7. Influence of the Demulsifier Concentration. The demulsifier dose is one of the most notable parameters managing the adsorption of demulsifiers at the interface. The applied commercial and prepared demulsifier doses were 250, 500, and 1000 ppm. The increase in the demulsifier concentrations lead to big enhancement in the demulsification process and as a result big amount water was separated from the emulsion. The demulsification efficiencies of DNPA-6, DNPA-5, DNPA-4, and ARBREAK with different concentrations are shown in Table 3. For the commercial demulsifier, ARBREAK 8141, the demulsification efficiencies increased with the increasing concentration in only crude oil/water emulsion (90/10 vol %) while showing the same efficiency for other emulsion compositions with different concentrations. It reached 100% demulsification efficiencies for crude oil/water emulsion (50/50 and 70/30 vol %), although it took more time to reach equilibrium than that taken by the synthesized demulsifiers. The
synthesized DNPA-6 and DNPA-5 showed higher demulsification rate and efficiency for the crude oil/water emulsion (90/10 vol %) than that for the commercial demulsifier. Increasing the demulsifier dose for all synthesized demulsifiers, from 250 to 1000 ppm leads to a remarkable increment in the demulsification efficiency. This can be assigned to the increment in the demulsifier adsorption on the W/O interface which progressively substitute the asphaltene (native emulsifiers) and reduce the mechanical stability of the interfacial film which eventually result in its displacement and then water droplets collapsing.

2.8. Effect of Contact Time. As mentioned before, the demulsifiers break the emulsion either by combining with asphaltene molecules surrounding the water droplets or by replacing them.\textsuperscript{50,51} First, the demulsifier molecules move from the solution bulk toward the oil/water interface. Then, they arrange themselves to break the rigid film. As a result, coalescence of water droplets occurs.\textsuperscript{52,53} Thus, the coalescence process of the emulsion begins to happen prior to the phase separation. Therefore, the amount of water separated from the emulsion for the synthesized and the commercial demulsifiers increases with time as shown in Table 3. DNPA-6, DNPA-5, and DNPA-4 showed a relatively high demulsification rate than the commercial demulsifier. In Figure 8, the contact time is plotted against the demulsification efficiencies of different doses of all of the synthesized demulsifiers using crude oil/water emulsion (90/10 vol %). It is indicated from Figure 8 that the water separation time of crude oil/water emulsion (90/10 vol %) was nearly the same for DNPA-6 and DNPA-5 (100 min), while it was longer for DNPA-4 (140 min). Also, it was found that as the demulsifier concentration increases, the separation time decreases and the separation efficiency increases for all synthesized demulsifiers. DNPA-5 reached 100% demulsification efficiency when injected with a concentration 1000 ppm. The difference in the demulsification rate and efficiency between the prepared demulsifiers may be due to the number of ethylene amine units in the chemical structure of each demulsifier which plays a great role in the adsorption of demulsifier molecules on the water/oil interface\textsuperscript{54} ARBREAK 8141 (Figure 8d) took more time to reach equilibrium than DNPA-6, DNPA-5 (100 ppm) and DNPA-4 (250 ppm).

Table 2. IFT of the Heavy Crude Oil/Water Interface with Different Demulsifier Concentrations in the Aqueous Phase at 25 °C

| demulsifier | concentration (mg L$^{-1}$) | IFT (mN/m) |
|-------------|---------------------------|------------|
| DNPA-6      | 0                         | 33.5 ± 1   |
|             | 250                       | 23.5 ± 0.8 |
|             | 500                       | 19 ± 0.5   |
|             | 1000                      | 11 ± 0.1   |
| DNPA-5      | 0                         | 33.5 ± 1   |
|             | 250                       | 23.3 ± 0.8 |
|             | 500                       | 20.2 ± 0.5 |
|             | 1000                      | 11.7 ± 0.1 |
| DNPA-4      | 0                         | 33.5 ± 1   |
|             | 250                       | 26 ± 0.5   |
|             | 500                       | 21.5 ± 0.5 |
|             | 1000                      | 15 ± 0.4   |

Figure 7. Zeta potential of (a) DNPA-6, (b) DNPA-5, and (c) DNPA-4 at their cmc and 25 °C.

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DNPA-5 showed the highest demulsification rate and efficiency among the synthesized and the commercial demulsifiers for crude oil/water emulsion (90/10 vol %) (Figure 8b).

3. CONCLUSIONS

In this paper, we studied the demulsification efficiencies of three novel APEI. They were synthesized by the reaction of Pentaethylen hexamine, tetraethylene pentamine, and triethylene tetramine with GNPE in a single step reaction through epoxy ring opening mechanism to give DNPA-6, DNPA-5, and DNPA-4, respectively. Their chemical structures were ensured by common spectroscopic tools including FTIR, 1HNMR, and 13CNMR. The prepared surfactants successfully declined the surface tension and the IFT of water/heavy crude oil interface. At cmc, the particle size and zeta potential were determined to investigate the agglomeration size and the charge on the formed micelles. The potential of DNPA-6, DNPA-5, and DNPA-4 to lower IFT and the positive surface charge on their surfaces demonstrated that they can be utilized as demulsifiers for water/heavy crude oil emulsions and their behavior was examined. The demulsification conditions were optimized to reach the maximum water removal ratio with the shortest settling time. The demulsification performance reached 100% for DNPA-5 for crude oil water emulsion (90/10 vol %) in 100 min. The demulsification performance data indicate the potential application of DNPA-6, DNPA-5, and DNPA-4 as demulsifiers in oilfields.

4. EXPERIMENTAL SECTION

4.1. Materials. Pentaethylene hexamine, tetraethylene pentamine, and GNPE were purchased from Aldrich company and used without further purification. Xylene (99.5%) was purchased from Sinpharm Chemical Reagent Corporation. ARBREAK 8846 is a commercial demulsifier produced by Baker Petrolite Corporation. Chemically, ARBREAK 8846 is mainly based on a high-molecular weight oxyalkylated alkylphenolic resin. Riyadh refinery unit; Aramco Co. was the supplier for Arabian heavy crude oil with specifications listed in Table 5. The heavy crude oil and sea water, gathered from Arabian Gulf at Dammam coast, were utilized to prepare synthetic emulsions with the ratios of (90/10, 70/30, and 50/50 vol %) heavy crude oil/water.

4.2. Synthesis of Demulsifiers. Three APEI were synthesized in a single-step reaction by mixing pentaethylene hexamine (10 mmol, 2.32 g) or tetraethylene pentamine (10 mmol, 1.89 g) or triethylene tetramine (10 mmol, 1.46 g) -dissolved separately in 50 mL of xylene- with GNPE (20 mmol, 500 ppm) at different concentrations.

Table 3. Demulsification Efficiency for DNPA-6, DNPA-5, and DNPA-4 at 60 °C

| compound   | dosage (ppm) | crude oil/water composition | η (%) | t (min) | η (%) | t (min) | η (%) | t (min) |
|------------|--------------|----------------------------|-------|---------|-------|---------|-------|---------|
|            |              | 90/10                      |       |         |       |         |       |         |
| DNPA-6     | 250          | 10                         | 140   | 13      | 180   | 40      | 60    |         |
|            | 500          | 60                         | 120   | 13      | 150   | 48      | 45    |         |
|            | 1000         | 80                         | 100   | 33      | 130   | 80      | 40    |         |
| DNPA-5     | 250          | 10                         | 120   | 25      | 170   | 20      | 75    |         |
|            | 500          | 80                         | 120   | 33      | 150   | 44      | 60    |         |
|            | 1000         | 100                        | 100   | 33      | 120   | 76      | 50    |         |
| DNPA-4     | 250          | 5                          | 140   | 33      | 150   | 10      | 90    |         |
|            | 500          | 12                         | 120   | 33      | 120   | 24      | 75    |         |
|            | 1000         | 25                         | 120   | 46      | 100   | 56      | 65    |         |
| ARBREAK 8846 | 250       | 35                         | 400   | 100     | 380   | 100     | 300   |         |
|            | 500          | 48                         | 370   | 100     | 350   | 100     | 240   |         |
|            | 1000         | 62                         | 350   | 100     | 300   | 100     | 190   |         |

The blank sample (at 0 ppm of demulsifier) showed no water separation for more than 2 weeks at 60 °C.

Table 4. DLS Data for APEI Interaction With Asphaltene at Different Concentrations

| compound   | conc. (ppm) | APEI | asphaltene | asphaltene/APEI |
|------------|-------------|------|------------|-----------------|
| DNPA-6     | 250         | 56.8 ± 0.7 | 27.74 ± 0.3 |                  |
|            | 500         | 27.74 ± 0.3 |          |                  |
|            | 1000        | 27.74 ± 0.3 |          |                  |
| DNPA-5     | 250         | 70.6 ± 1 | -43.35 ± 0.5 | 30.79 ± 0.32 |
|            | 500         | 30.79 ± 0.32 | 30.79 ± 0.32 |                  |
|            | 1000        | 30.79 ± 0.32 | 30.79 ± 0.32 |                  |
| DNPA-4     | 250         | 74.6 ± 1 | 33.25 ± 0.35 | 33.25 ± 0.35 |
|            | 500         | 33.25 ± 0.35 | 33.25 ± 0.35 |                  |
|            | 1000        | 33.25 ± 0.35 | 33.25 ± 0.35 |                  |

Scheme 2. Possible Demulsification Mechanism Using DNPA-6, DNPA-5, and DNPA-4 Demulsifiers
Figure 8. Demulsification efficiencies of different concentrations of (a) DNPA-6, (b) DNPA-5, (c) DNPA-4, and (d) ARBREAK 8846 against time for crude oil/water emulsion (90/10 vol %) at 60 °C.

Figure 9. Optical microscopy images of crude oil/water emulsion (90/10 vol %) in (a) blank after 3 weeks, (b) after 30 min 500 ppm of DNPA-5 and (c) after 60 min.
5.52 g) in three-necked flasks. The reaction mixtures were heated to 120 °C under vigorous stirring under a nitrogen atmosphere for 4 h. Then, the reaction mixtures were cooled down, and the solvent was distilled off using rotary evaporator. The remaining product was dissolved in isopropanol and then separated and the unreacted ethyleneimine. The organic layer was separated and the remaining product was dissolved in isopropanol and then precipitated with diethyl ether. The precipitated solid was dried under vacuum to provide the crude product. The crude product was further purified by column chromatography on silica gel and recrystallization from xylene/ethanol mixture (75/25 vol %). Different concentrations of APEI demulsifiers were prepared under the same conditions for DNPA-6, DNPA-5, and DNPA-4 in order to compare the demulsification performance. Each demulsifier solution was prepared by dissolving each demulsifier at different concentrations (in ppm) of (a) DNPA-6, (b) DNPA-5, and (c) DNPA-4.

4.4. Preparation of Water/Crude Oil Emulsion. In a 500 mL beaker, the crude oil was homogenized at 5000 rpm and 25 °C while adding water gradually to the oil. After adding the calculated amount of seawater, the emulsion was left for 30 min under homogenization to ensure the formation of one phase emulsion. Different ratios of crude oil to water emulsions were prepared (50:50, 70:30, and 90:10). The droplet sizes of the prepared emulsions were measured by dispersing 50 mg of each prepared (50:50, 70:30, and 90:10). The droplet sizes of the prepared emulsions were measured by dispersing 50 mg of each emulsion in 10 mL of toluene, and the data were displayed in Figure 1. The emulsion droplet diameters were 576.8, 487.7, and 455.5 nm for 50:50, 70:30, and 90:10 W/O emulsions, respectively. The prepared emulsions showed high stability at 60 °C for more than 2 weeks.

4.5. Hydrophile–Lipophile Balance (HLB). In order to calculate the HLB of the synthesized APEI, the following equation was utilized: $HLB = 20 \times M_H/(M_H + M_L)$, where $M_H$ and $M_L$ are the formula weight of the hydrophilic and lipophilic (hydrophobic) portions of the molecule.

4.6. Demulsification Performance Study. To study the demulsification efficiency for each emulsion used in this study, 25 mL quick-fit measuring cylinders were used. The demulsifiers’ solutions were prepared by dissolving each demulsifier in xylene/ethanol mixture (75/25 vol %). Different concentrations of ARBREAK 8846 as a commercial demulsifier were prepared under the same conditions for DNPA-6, DNPA-5, and DNPA-4 in order to compare the demulsification performance. Each demulsifier with different concentrations were then injected into the 25 mL cylinders containing different emulsion types. To ensure the complete homogeneity of the demulsifiers and the emulsion solution, the mixture was shaken vigorously for 1 min. The demulsification process was then noticed and studied at different time intervals after placing the bottles in a water bath at 60 °C. In each set of experiments, a blank sample was considered in order to ensure the stability of the prepared emulsions at 60 °C. The demulsification

Table 5. Arabian Heavy Crude Oil Specifications

| Test                        | Method      | Results |
|-----------------------------|-------------|---------|
| API gravity                 | calculated  | 20.8    |
| Specific gravity 60/60 (°F) | IP 160/87   | 0.929   |
| Wax content, (wt %)         | UOP 46/64   | 2.3     |
| Asphalten content, (wt %)   | IP 143/84   | 8.3     |
| $M_w$ (g/mol)               | determined from gel permeation chromatography | 6350 |
| Heteroatoms (w/w %)         |             | 6.5     |
| Aromatic carbon (mol %)     |             | 49.0    |
| Determined from $^{13}$C{NMR} |          |         |
| Aromatic hydrogen (mol %)   |             | 7.81    |
| Determined from $^1$HN{NMR} |             |         |
| Saturates (wt %)            |             | 16.3    |
| Aromatics (wt %)            |             | 25.3    |
| Resins (wt %)               |             | 48.1    |

Figure 10. Water separation Photographs of crude oil/water emulsions (50:50 vol %) for different concentrations (in ppm) of (a) DNPA-6, (b) DNPA-5, and (c) DNPA-4.
efficiencies (η%) for different compositions of crude oil and water emulsions at 60 °C were determined as described in the former work.  The η% was determined according to the relation η% = Vf/ Ve, where Vf is the water volume separated at a specific time and Ve is the total emulsified water.

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**Notes**

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