

Research Article

Performance of Plastic Waste-Based Polyionic Liquid toward the Dehydration of Crude Oil Emulsions

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Polyethylene terephthalate (PET) is one of the most widely used plastics in the world. Due to the large production and use of this plastic, its waste represents one of the most critical environmental problems. The purpose of this study is to convert PET waste into a valuable material. The consumed PET was transformed into a precursor to synthesize a polyionic liquid (PIL) that was used for dehydrating crude oil emulsions. To do so, the consumed PET was converted to bis(2-hydroxyethyl) terephthalate (BHET). First, BHET and tetraethylene glycol were reacted separately with thionyl chloride, obtaining the corresponding alkyl halides, bis(2-chloroethyl) terephthalate, BCET, and TEC, respectively. Next, the obtained alkyl halides, BCET and TEC, were reacted with 1,5-pentanediamine, yielding a polymer (BTP). Finally, BTP was reacted with acetic acid to produce the corresponding PIL (BTP-PIL). The structure and thermal stability of BTP-PIL were characterized using nuclear magnetic resonance spectroscopy and thermal gravimetric analysis. The dehydration performance of PIL and the original polymer was investigated using the bottle test method, including several factors such as demulsifier dose, brine content, temperature, and settling time. Results indicated that PIL achieved high performance in dehydrating crude oil emulsions.

1. Introduction

Plastics are widely used in many different applications and areas of life. There is no doubt that plastics are essential and useful materials today. In 2018, the amount of plastic produced was estimated at 360 ton [1]. With the increase in demand and use of plastic, the amount of waste generated increases. The current disposal methods for plastics still too often hinder the beneficial economics of a more closed material cycle and undoubtedly damage the environment. Polyethylene terephthalate (PET) is one of the most widely produced plastics, and it is used in many applications, such as fibers, soft drink bottles, photographic films, etc. PET represents 8% of the solid waste in the world in terms of weight and 12% in terms of volume [2, 3]. PET generates a large amount of solid waste resistant to environmental degradation, making it a harmful substance that requires recycling or reuse in other products. Recent studies have focused on recycling PET and reusing it in other production [4–13].

Typically, crude oil produced from reservoirs contains brine in emulsion form. Some crude oil components, such

as asphaltene, resins, naphthenic acid, and solid particles, behave as natural emulsifiers. These natural components reduce the interfacial tension (IFT) between crude oil and brine, leading to the formation of stable crude oil emulsions [14–16]. Additionally, adding a surface active agent during enhanced oil recovery increases the stability of these emulsions [13, 17]. However, many operational problems are associated with these emulsions due to the presence of water and salt. For example, the viscosity of crude oil increases, making it difficult to transport. Dissolved salts in water can cause corrosion to equipment such as tanks, pipelines, pumps, etc. In addition, these salts poison the refining catalysts during the refining process [18, 19]. Therefore, water must be removed from these emulsions before starting the storage, transportation, or refining. Chemicals are one of the most effective techniques for breaking crude oil emulsions due to their high efficiency and fast dehydration [20]. Amphiphilic compounds are the most frequently used chemicals for dehydrating crude oil emulsions. As these compounds exhibit surface activity, they can adsorb at the crude oil and brine interface to

rupture the natural interfacial film and change its properties to facilitate phase separation [21].

Recently, surface active ionic liquids (ILs) and polyionic liquids (PILs) have received considerable attention in the dehydration of crude oil emulsions as these materials have surface activity in addition to their capability to work under harsh salinity conditions where conventional compounds cannot work [22–26]. In our earlier work, we successfully prepared different ILs and PILs based on PET waste and natural compounds and employed them to dehydrate crude oil emulsions [11, 12, 22–29]. This work aims to employ bis(2-hydroxyethyl)terephthalate (BHET) obtained from the glycolysis of PET as a precursor to synthesize a new PIL and use it for crude oil emulsion dehydration.

2. Experimental

2.1. Materials. PET waste was collected from consumed drinking bottles. It was chopped into small pieces and washed several times with distilled water first and then acetone. Finally, it was dried in an oven at 80°C until it reached a constant weight. Zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, ethylene glycol (EG), tetraethylene glycol (TEG), thionyl chloride, cesium hydroxide monohydrate ($\text{CeOH} \cdot \text{H}_2\text{O}$), acetic acid (AA), activated powdered 4 Å molecular sieve, sodium hydroxide (NaOH), dimethylformamide (DMF), ethyl acetate, and acetone were obtained from Sigma-Aldrich Co. 1,5-pentanediamine (PA) was obtained from Tokyo Chemical Industry (TCI) Co.

Crude oil was obtained from ARAMCO Co., Riyadh, Saudi Arabia. Its specification was reported in our earlier work [23]. Brine solution (35,000 ppm) was prepared using sodium chloride and distilled water. As reported in our earlier work, water-in-crude oil (W/O) emulsions were prepared with different brine contents (10%, 30%, and 50%). The dehydration performance was calculated using the following equation:

$$\text{DP (\%)} = \frac{\text{Volume of dehydrated water}}{\text{Volume of emulsified water}} \times 100. \quad (1)$$

2.2. Synthesis of PIL, BTP–PIL. The glycolysis of PET was carried out as was reported earlier. A mixture of PET waste (100 g), $\text{Zn}(\text{CH}_3\text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$ (0.2 g), and EG (300 g) was placed in a 1-L three-necked bottom flask supplied with a magnetic stirrer, nitrogen, and thermometer inlets, and a condenser. These components were mixed and refluxed for 8 hr [4, 30]. BHET was obtained after washing it several times using hot water with a yield of 80%. The obtained BHET and TEG were converted to the corresponding alkyl halides, bis(2-chloroethyl) terephthalate (BCET) and TEC, respectively, as was reported in our previous work with thionyl chloride [11].

To synthesize BTP, an activated powdered 4 Å molecular sieve (2 g) was suspended in anhydrous DMF (35 mL), followed by the addition of $\text{CeOH} \cdot \text{H}_2\text{O}$ (2.28 g, 13.6 mmol). Adding an activated powdered 4 Å molecular sieve accelerates the alkylation process and improves the selectivity. CeOH was found to offer the greatest selectivity in terms

of dialkyl amine, which purportedly minimized polyalkylations as well [31]. The use of DMF and inorganic bases for the alkylation reaction was reported in many studies [32, 33]. The mixture was vigorously stirred for 10 min, PA (0.69 g, 6.8 mmol) was added, and stirred for 30 min. Next, BCET (1 g, 3.4 mmol) and TEC (0.79 g, 3.4 mmol) were added to the mixture with continuous stirring for a further 20 hr at ambient temperature. The mixture was filtrated and washed several times with ethyl acetate [34]. Solvents were evaporated under reduced pressure, and the obtained compound was washed with sodium hydroxide (1 M) to ensure complete conversion of ammonium salt to polyamine, BTP, as sodium hydroxide reacts with ammonium chloride to produce polyamine and ammonium chloride, after drying with the yield of 98.3%. Finally, BTP was heated with a stoichiometric ratio of acetic acid at 100°C for 5 hr, yielding the corresponding PIL, BTP–PIL. Scheme 1 illustrates the preparation route of BTP and BTP–PIL.

2.3. Characterization of PIL, BTP–PIL. The structure of the formed PILs was elucidated by proton nuclear magnetic resonance ($^1\text{H-NMR}$). Their thermal stability was investigated using thermogravimetric analysis. The surface activity of PIL was investigated using a pendant drop technique. The relative solubility number (RSN) was measured by treating the PIL solution (1 g of PIL in 30 mL of dioxane: toluene (96:4 volume%)) using distilled water till getting clear continual turbidity; the amount of consumed water in the titration in milliliters is RSN. The morphology of crude oil emulsion droplets before and during the dehydration process was captured using a polarized light microscope.

3. Results and Discussion

3.1. Chemical Structure of BTP–PIL. The chemical structure of BTP and BTP–PIL was confirmed by Fourier-transform infrared spectroscopy (FTIR) and $^1\text{H-NMR}$ analysis, as presented in Figures 1(a) and 1(b) and 2(a) and 2(b), respectively. As shown in Figure 1(a), several characteristic bands of BTP were noticed. The disappearance of primary amine double bands and the appearance of an N–H vibration band at $3,310 \text{ cm}^{-1}$ affirmed the occurrence of an alkylation reaction. The vibration bands of methylene appeared at $2,928$ and $2,872 \text{ cm}^{-1}$, while the vibration band of carbonyl groups appeared at $1,721 \text{ cm}^{-1}$. The aromatic C=C vibration bands were observed between $1,610$ and $1,460 \text{ cm}^{-1}$, while the C–O–C vibration band was noticed at $1,121 \text{ cm}^{-1}$. The disappearance of the N–H vibration band in the FTIR spectrum of BTP–PIL (Figure 1(b)) indicates the quaternization reaction between BTP and acetic acid. In the $^1\text{H-NMR}$ spectrum of BTP (Figure 2(a)), the protons of methylene diamine appeared between 1.3 and 3.3 ppm. The TEC repeating unit's methylene protons resonated at 1.9 ppm. The phenyl ring's protons were observed at 7.8 ppm. Figure 2(b) presents the $^1\text{H-NMR}$ spectrum of BTP–PIL as the same characteristic peaks can be seen. In this spectrum, two new peaks were noticed at 1.89 and 7.4 ppm, which are linked to the protons of the methyl of acetate and those attached to quaternized nitrogen.

3.2. Thermal Stability of BTP and BTP–PIL. The thermal stability of BTP and BTP–PIL was measured using TGA,

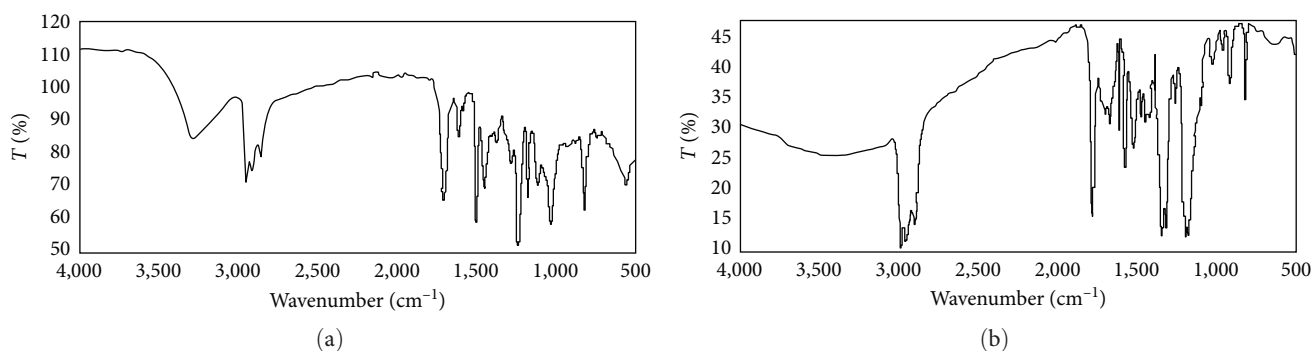
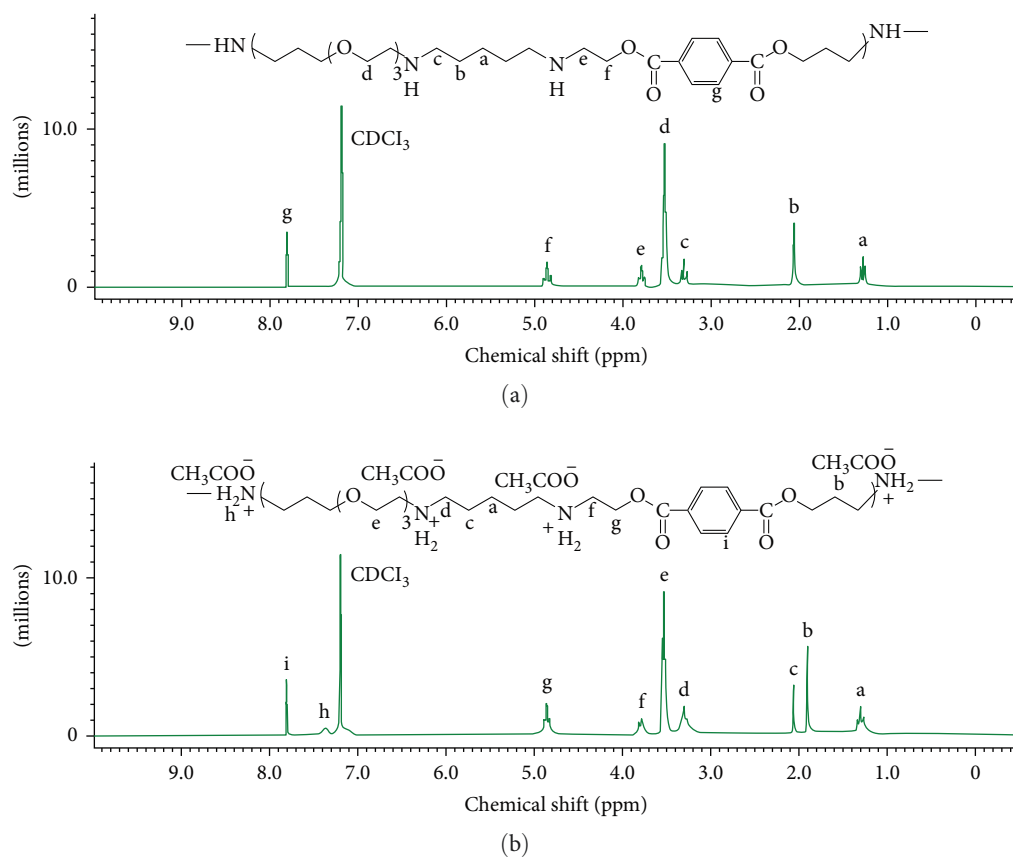


FIGURE 1: FTIR spectra of (a) BTP and (b) BTP-PIL.

FIGURE 2: $^1\text{H-NMR}$ spectra of (a) BTP and (b) BTP-PIL.

as shown in Figure 3. As depicted in Figure 3, up to 100°C , there was no significant weight loss, where the weight loss for BTP and BTP-PIL was 1.5% and 2.1%, respectively. Such loss could be linked to the loss of physisorbed water and other organic solvents. Additionally, the data indicated that the decomposition of BTP took place in two main regions. The first decomposition region was between 135 and 265°C , while the second region started at 305°C up to 420°C . However, BTP-PIL showed decomposition in one region between 336 and 457°C . These data indicated the higher thermal stability of BTP-PIL than BTP, which could result from the ionic nature of BTP-IL [35].

3.3. Interfacial Activity and Solubility of BTP and BTP-PIL. The interfacial activity is the essential criterion for selecting demulsifiers. These materials can adsorb onto the asphaltene rigid film and change its mechanical and physical properties, causing it to rupture. BTP and BTP-PIL have amphiphilic structures, with a hydrophobic part represented by BCET and PA chains and a hydrophilic part consisting of TEC with oxyethylene units. Due to this amphiphilic structure, these compounds are expected to have an interfacial activity. Herein, the IFT of BTP and BTP-PIL at the crude oil and brine interface was evaluated using different concentrations, as shown in Figure 4.

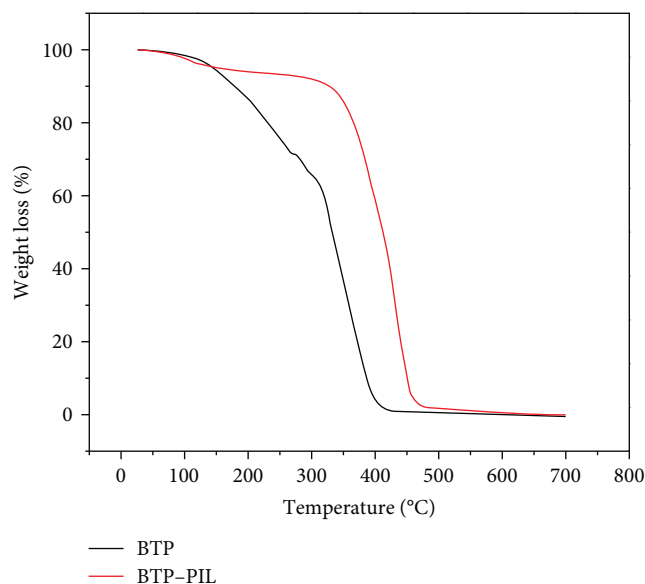


FIGURE 3: TGA thermogram of BTP and BTP-PIL.

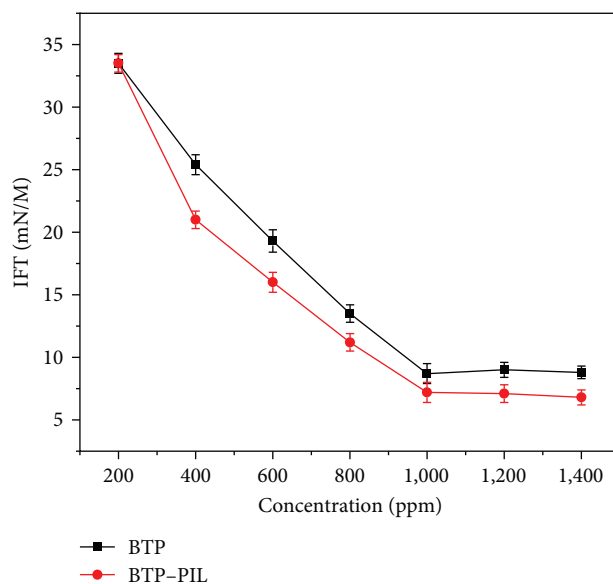


FIGURE 4: IFT at crude oil: brine interface in the presence of BTP and BTP-PIL at different concentrations.

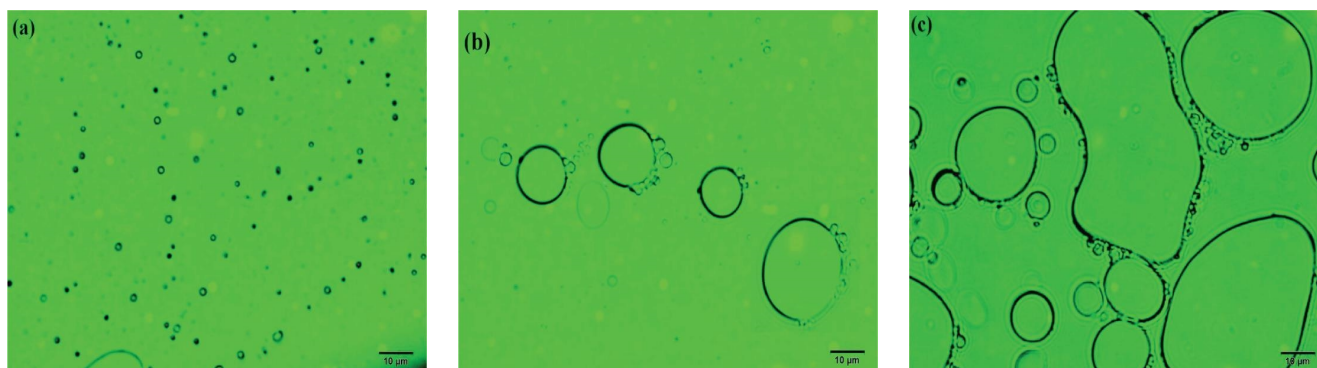


FIGURE 5: Microscopic photos of crude oil emulsion (50% of brine content) at 60°C (a) blank sample after two weeks, (b) sample containing 1,000 ppm of BTP-PIL after 100 min, and (c) sample containing 1,000 ppm of BTP-PIL after 150 min.

The data showed that the performance of these compounds in reducing IFT is related to their concentrations, as their performance improved as their concentrations increased. Additionally, BTP-PIL showed relatively higher performance than BTP, which could be linked to the ability of BTP-PIL to accumulate at the crude oil and brine interface, as the interaction between BTP-PIL ions and oppositely charged ions in brine decreases the repulsion between its molecules at this interface [36]. Furthermore, the results showed that the concentration of 1,000 ppm seems to be optimum for the IFT reduction, where BTP and BTP-PIL reduced IFT from 33.5 to 8.7 and 7.2 mN/M, respectively. However, after that, increased concentration did not result in a significant reduction in IFT.

The solubility of BTP and BTP-PIL was determined using RSN. The RSN values of BTP and BTP-PIL were found to be 16.3 and 17.6 mL, respectively. These values concluded that these compounds were soluble well in organic solvents but had limited solubility in water. Furthermore, BTP-PIL showed a higher RSN value than BTP due to its ionic nature, which makes it more soluble in water.

3.4. Dehydration Performance of BTP and BTP-PIL. This study used the bottle test as a simple and effective method for investigating the performance of BTP and BTP-PIL. The dehydration performance of these compounds was examined with various influencing factors, e.g., demulsifier dose, brine content, temperature, and settling time. Blank samples showed high stability, where these samples did not show any separation when placed in a water bath at measurement temperatures for more than 2 weeks, indicating the stability of the prepared emulsions. Additionally, the small droplet sizes of a blank sample (brine content of 50%) with an average diameter of 1.5 μm after 2 weeks (Figure 5(a)) demonstrated the stability of these emulsions. Based on the drop test method, all the prepared emulsions showed significant dispersion in organic solvents, e.g., chloroform and toluene, but no dispersion in water, confirming the formation of W/O emulsions.

3.4.1. Effect of BTP and BTP-PIL Dose. Figure 6 depicts the effect of the demulsifier dose on dehydration performance at 50% of brine content and a settling time of 200 min. The data showed a direct relationship between BTP and BTP-PIL

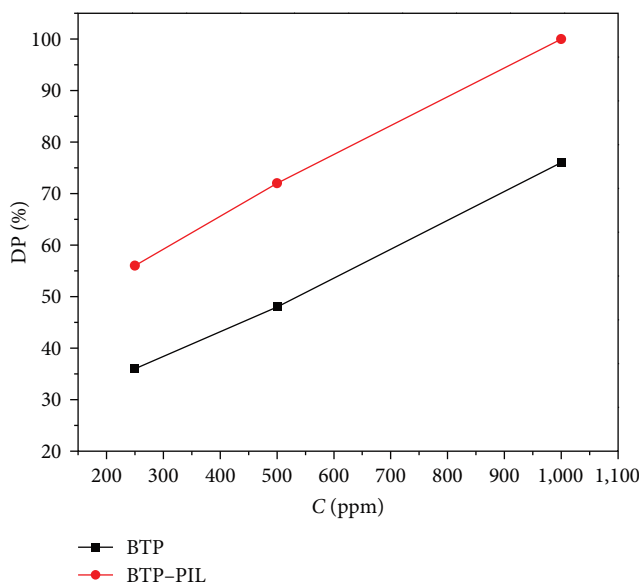


FIGURE 6: Dehydration performance (DP) against BTP and BTP-PIL dose at 60°C.

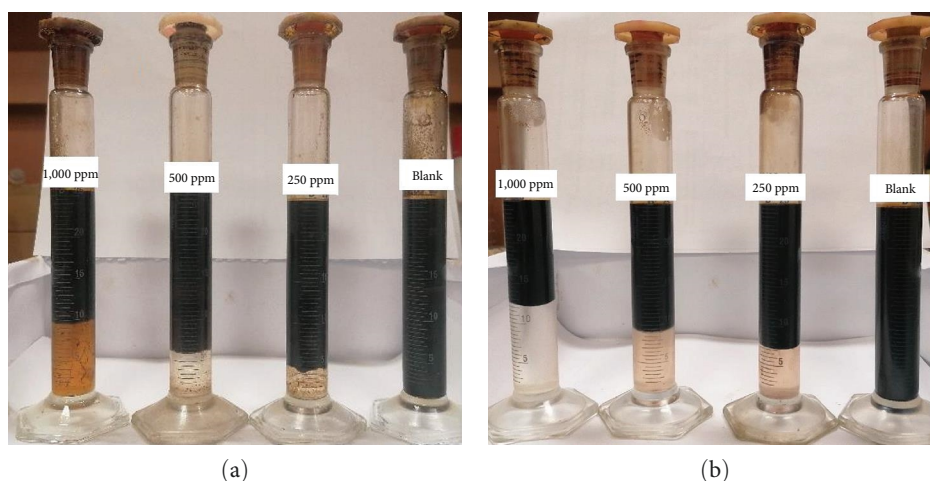


FIGURE 7: Optical photos of separated brine using different doses of (a) BTP and (b) BTP-PIL at 60°C.

doses and dehydration performance, as performance increased with increasing doses. Based on the results, the dehydration performance rises to 76% for BTP and 100% for BTP-PIL with an increase in dose from 250 to 1,000 ppm. Figure 7 displays the optical photos of separated brine using different doses of BTP and BTP-PIL. With an increase in the demulsifier dose in the prepared emulsion, the number of its molecules adsorbed onto the natural interfacial film increases, weakening this film till it ruptures, facilitating the coalescence of water droplets [37]. Furthermore, BTP-PIL showed higher dehydration performance than BTP. This can be linked to the ionic nature of BTP-PIL, where its ions interact with oppositely charged ions of brine, reducing the repulsion between BTP-PIL molecules and allowing them to accumulate, thus reducing IFT at this interface.

3.4.2. Effect of Brine Content. Brine content in W/O oil emulsions is one of the most significant factors influencing the dehydration of these emulsions. Besides asphaltene, resin, naphthenic acids, and solid particles, the amount of brine also determines the stability of these emulsions. Commonly, a higher brine content in W/O emulsions facilitates dehydration, whereas emulsions containing more brine content require less settling time and fewer demulsifier doses for water separation [38]. The effect of brine content on the dehydration performance of BTP and BTP-PIL using different doses at 60°C, a settling time of 200 min, and 1,000 ppm is presented in Figure 8. The data showed that the dehydration performance improved with increasing the brine content in the prepared emulsions. As the brine content was increased from 10% to 50%, the dehydration performance improved from 32% to 76% for BTP and from 38% to 100%

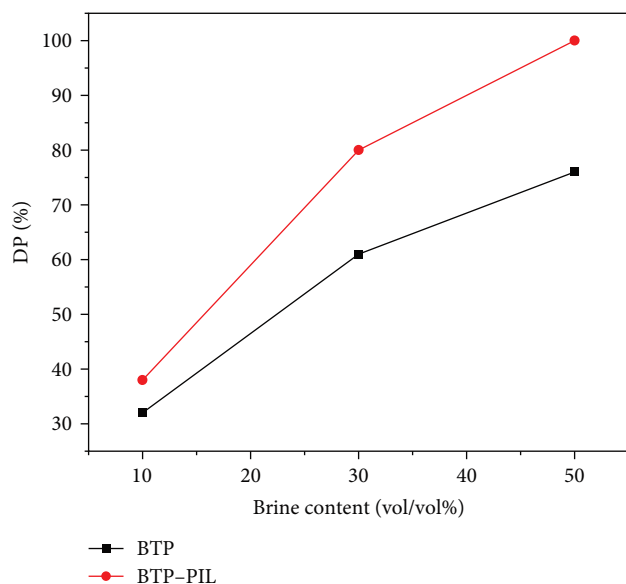


FIGURE 8: Dehydration performance of BTP and BTP-PIL against brine content at 60°C and 1,000 ppm of demulsifier dose.

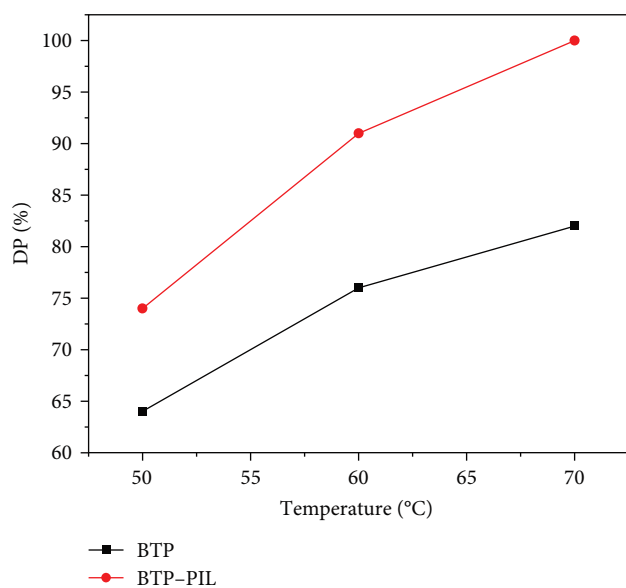


FIGURE 9: Dehydration performance of BTP and BTP-PIL (1,000 ppm) against temperature.

for BTP-PIL. When the brine content increases, the number of droplets increases, and the distance between water droplets decreases. This quickens the agglomeration and coalescence of water droplets in less time and enhances water separation [39].

3.4.3. Effect of Temperature. The dehydration performance of BTP and BTP-PIL (1,000 ppm) against temperature at a brine content of 50% and a settling time of 200 min is presented in Figure 9. By raising the temperature from 50 to 70°C, the dehydration performance jumped from 64% to 82% for BTP and from 64% to 100% for BTP-PIL. Several factors may contribute to improving dehydration performance with

rising temperature: (i) the viscosity of the emulsion decreases as the temperature rises, thereby improving the ability of water droplets to move and making coalescence faster; (ii) increased kinetic energy of water droplets; and (iii) encouraging the interfacial layer rupturing process, which plays an essential role in the dehydration process [40]. As the temperature rises, the asphaltene rigid film's mechanical strength decreases, decreasing emulsion stability. Additionally, the movement of demulsifier molecules increases with increasing temperature, accelerating the diffusion of these molecules to reach the crude oil and brine interface and adsorb there.

3.4.4. Effect of Settling Time. A dehydration process requires time for demulsifier molecules to diffuse and adsorb to weaken and rupture the interface between crude oil and brine, causing phase separation. Therefore, dehydration performance improves with increasing settling time. The effect of settling time on the dehydration performance of BTP and BTP-PIL for 50% brine content emulsions at 60°C is presented in Figure 10. It was observed that dehydration performance increased with increasing settling time, reaching its maximum capacity. Afterward, dehydration performance remained unchanged.

Additionally, BTP-PIL achieved higher dehydration performance and shorter settling times than BTP, which can be linked to its higher ability to reduce IFT than BTP. As the demulsifier is injected, the water droplets agglomerate and fuse, forming bigger droplets. The tiny droplets condense much faster as the coalescence of the droplets increases. Increasing time allows the demulsifier molecules to weaken and break the asphaltene interfacial film, facilitating the agglomeration and coalescence of water and improving water separation [39].

3.5. Dehydration Mechanism. Dehydration of crude oil emulsions requires breaking the natural emulsifier film around droplets to allow water droplets to coalesce and fuse. Different steps are involved in the dehydration process: diffusion of demulsifier molecules in the continuous phase, their adsorption into the natural emulsifier interfacial film, modification of the interfacial film behavior to be easy for rupture, water droplets coalescence, and sedimentation [41]. The presence of naturally occurring emulsifying agents as components of crude oil forms an interfacial film at the crude oil and brine interface. This film obstructs the aggregation and separation of water droplets, enhancing emulsion stability [14].

When a demulsifier is added to the emulsion, its molecules diffuse through the continuous phase and adsorb at the crude oil and brine interface. By interacting with an interfacial film, demulsifier molecules weaken and rupture it, destabilizing the emulsion droplets. Consequently, with time, larger water droplets are formed due to the aggregation and coalescence of tiny water droplets. Figures 5(b) and 5(c) exhibited the coalescence of small droplets becoming larger over time. Coalescence of droplets results in droplet sedimentation, resulting in the eventual separation of water from the emulsion. Schemes 1 and 2 illustrate the proposed dehydration mechanism using BTP-PIL.

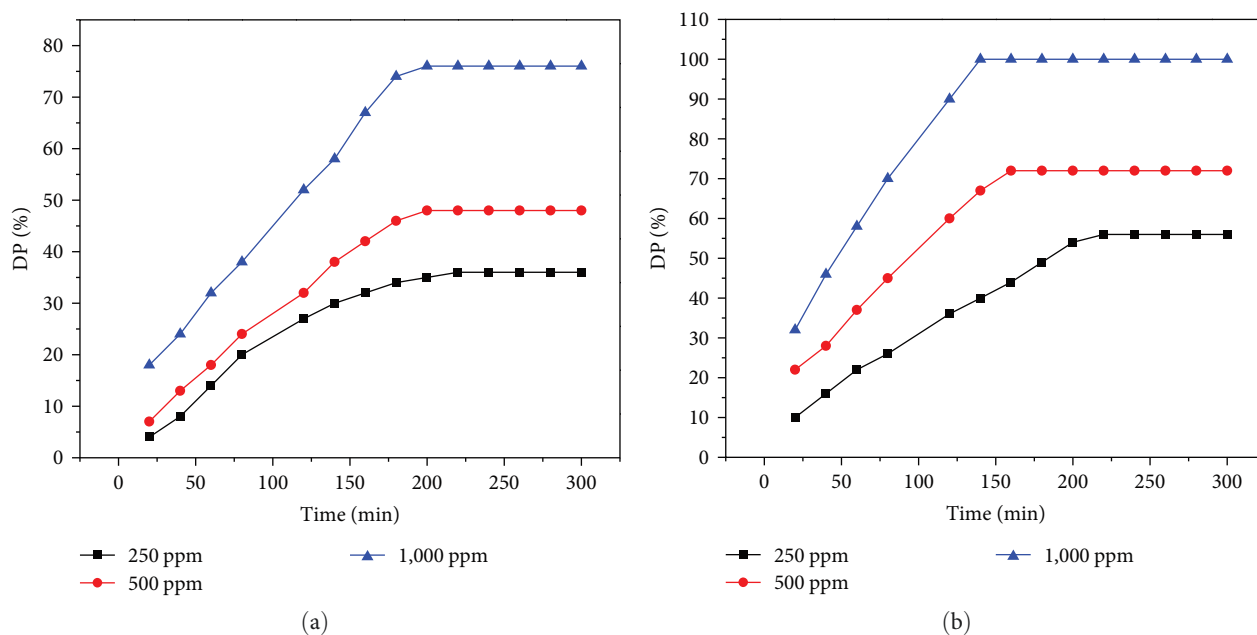
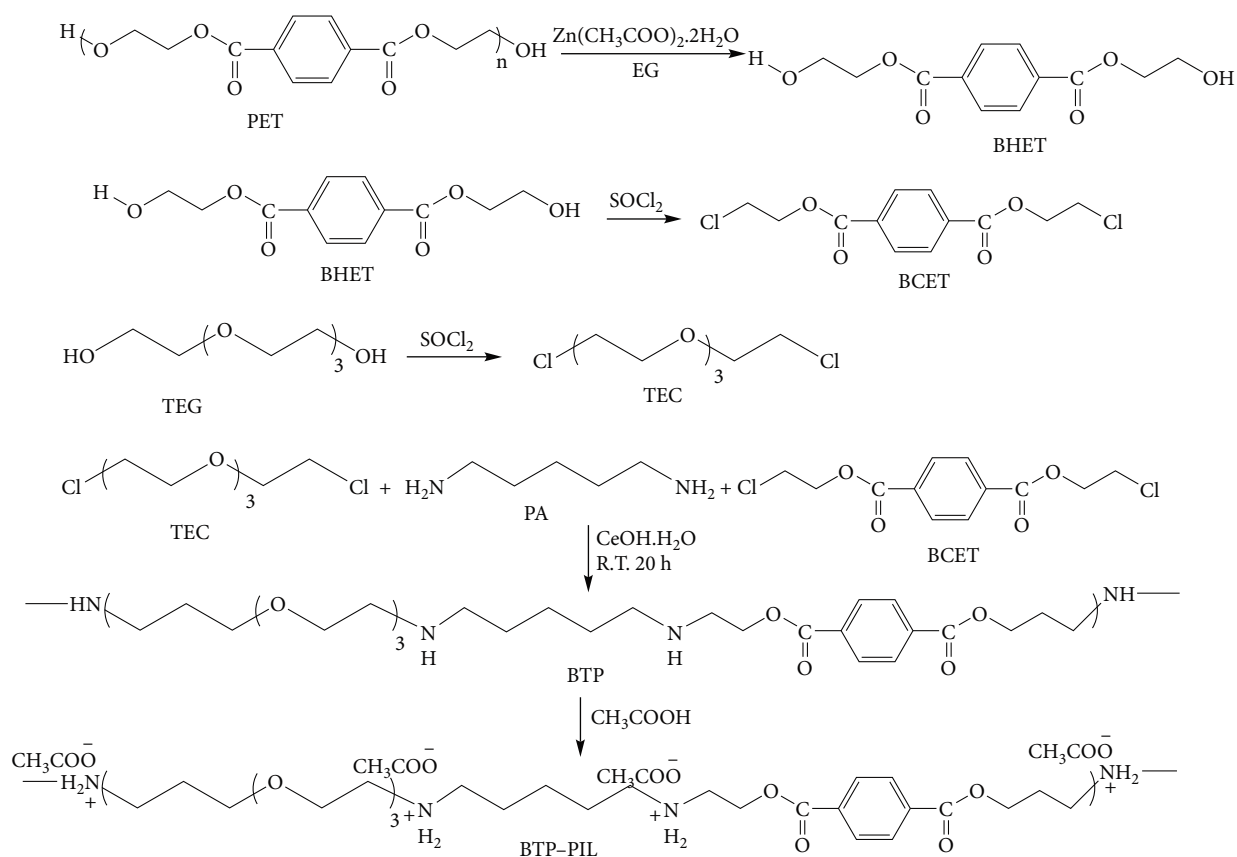
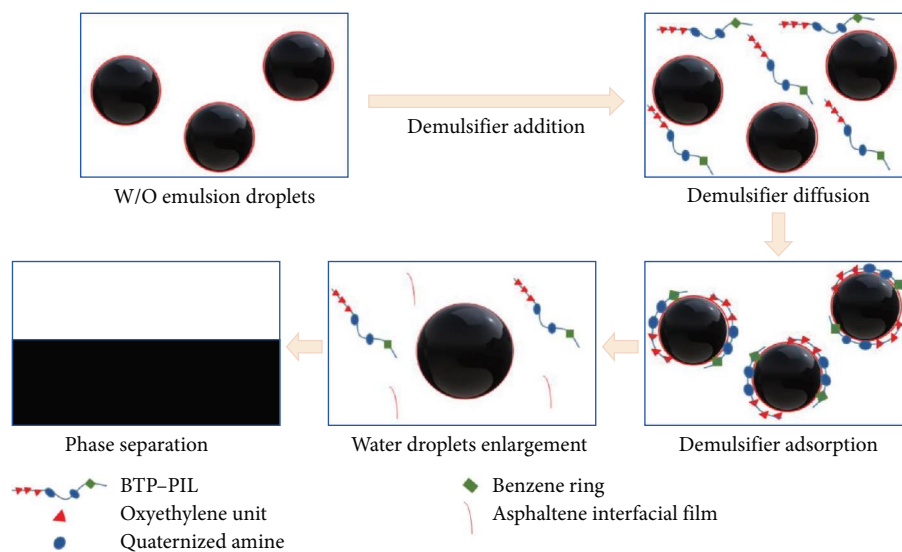


FIGURE 10: Dehydration performance of (a) BTP and (b) BTP-PIL for 50% brine content emulsions against time at 60°C.



SCHEME 1: Synthesis route of BTP-PIL.



SCHEME 2: Proposed dehydration mechanism using BTP–PIL.

4. Conclusion

A novel PIL was synthesized based on PET waste and employed for W/O emulsion dehydration. First, the obtained BHET from the glycolysis of PET and TEG were converted to the respective alkyl halides, BCET and TEC. Afterward, BCET and TEC were reacted with PA, yielding the corresponding polyamine, BTP. Finally, the latter was reacted with AA to obtain the corresponding PIL, BTP–PIL. This study was conducted to determine the chemical structure, thermal stability, and interfacial activity of BTP–PIL. Compared to BTP, BTP–PIL showed higher thermal stability and interfacial activity, which is due to the ionic nature of BTP–PIL. The higher thermal stability of BTP–PIL is due to its composition, consisting of repeating units of organic salts. Consequently, the ions can interact with the ions of brine, which reduces the repulsion between BTP–PIL, facilitating the accumulation of its molecules at the crude oil and brine interface, thereby reducing IFT.

Due to the performance of BTP and BTP–PIL in the reduction of IFT at the crude oil and brine interface, their performance in dehydrating W/O emulsion was investigated using different influencing factors, e.g., demulsifier dose, brine content, temperature, and settling time. The results indicated that BTP–PIL exhibited higher dehydration performance than BTP. Furthermore, the data showed that the dehydration performance improved as the demulsifier dose, brine content, temperature, and settling time increased. Increasing the demulsifier dose results in more molecules reaching the crude oil and brine interface, weakening and rupturing the asphaltene interfacial film and destabilizing emulsions. At rising temperatures, the emulsion viscosity decreases, improving the mobility of water droplets. Additionally, rising temperatures enhance the kinetic energy of water droplets and encourage the asphaltene interfacial film rupturing. By increasing the settling time, the demulsifier molecules take their time to diffuse, adsorb, and interact with the asphaltene interfacial film, causing its rupture.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Mahmood M. S. Abdullah was responsible for the investigation and methodology, writing—original draft, writing—review, and editing of the paper; Hamad A. Al-Lohedan was responsible for the methodology, review, editing, and resources; and Mohd Sajid Ali was responsible for the conceptualization, investigation, reviewing, and editing of the paper.

Acknowledgments

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