ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

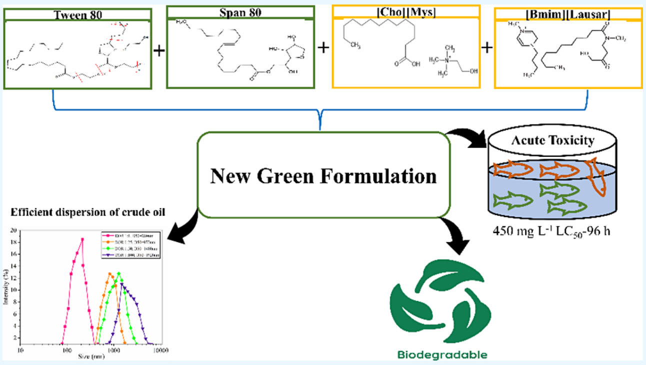
Formulation and Optimization of Effective Oil Spill Dispersants Composed of Surface-Active Ionic Liquids and Nonionic Surfactants

Masooma Nazar, Aqeel Ahmad, Syed Muhammad Shakil Hussain,* and Muhammad Moniruzzaman*

Cite This: *ACS Omega* 2024, 9, 30636−30644

Read Online

ABSTRACT: The use of chemical dispersants to remove oil spills in aquatic environments raises serious concerns, including heightened toxicity and limited biodegradability, which diminish their effectiveness. This study aimed to develop an environmentally friendly formulation by combining two nonionic surfactants (Tween 80, Span 80) with two surface-active ionic liquids (SAILs): 1-butyl-3-methylimidazolium lauroyl sarcosinate [Bmim][Lausar] and choline myristate [Cho][Mys], to remediate crude oil spill. The performance of the formulation was evaluated by its emulsion stability, surface tension, interfacial tension (IFT), and effectiveness. The toxicity and biodegradability of the formulation were also assessed to ensure their safe application in aquatic environments. The formulation (F9) exhibited the most stable emulsion, maintaining stability even after 5 h with a critical micelle concentration (CMC) of 3.52 mM. The efficiency of the formulation in dispersing various crude oils (Arab, Ratawi, and Doba) ranged from 70.12 to 93.72%. Acute toxicity tests conducted on zebrafish demonstrated that the formulation, with an LC_{50} value of 450 mg L^{-1}, exhibited practically nontoxicity after 96 h. The formulation showed rapid biodegradability, exceeding 60% within a 28-day testing period. This research presents a promising approach for synthesizing the green formulation which can contribute to mitigating the environmental impacts of oil spills and enhancing the efficiency of cleanup operations.



1. INTRODUCTION

Marine oil spills devastate aquatic life and the coastal communities that rely on healthy ecosystems. The primary response to an oil spill involves mitigating the damage to aquatic life, stopping oil from approaching the coastline via recovery, and increasing the decomposition of unrecovered oil. The environmental damage can be significantly minimized by quickly and efficiently extracting the spilled oil from the water. It is crucial to comprehend the various remediation approaches for oil spills, which encompass physical, thermal, chemical, and bioremediation techniques.[1] Among them, chemical dispersants are considered efficient due to their ability to quickly break down oil slicks, owing to the presence of surfactants and hydrocarbon-based solvents.[2,3] These surfactants reduce the oil−water interfacial tension, breaking the oil layer into smaller droplets.[4] Chemical dispersants have been employed in numerous oil spill incidents.[5] In all major accidental oil spills, Corexit was the most frequently used chemical dispersant when compared to other dispersants. There are apprehensions about the environmental impact of Corexit compounds, as they have been identified as toxic to marine life and potentially enhance the toxicity of oil when combined with it.[6] These concerns have prompted scrutiny from researchers and governments, regarding the use of chemical dispersants in oil spill responses, leading to a growing demand for environmentally friendly alternatives due to increasing global awareness of ocean protection.[7]

Nonionic surfactants exhibit notable self-assembly characteristics in various industries such as cosmetics, food, paint, and pharmaceuticals.[8] As a greener alternative to commercial dispersants, nonionic surfactants have been investigated for dispersing oil spills in water bodies owing to their lower toxicity.[9,10] Among the most well-known nonionic surfactants are Tween 80, Span 80, and Saponin, which have been utilized for oil spill remediation.[11] Nonionic surfactants alone are less effective in oil spill remediation as they cannot reduce the interfacial tension (IFT) to the ultralow levels required for effective dispersion.[10] A common practice involves combining nonionic surfactants with traditional surfactants like anionic, cationic, and zwitterionic types to improve the stability and performance of oil dispersion.[12] Jia et al. investigated the effect of cationic/anionic surfactant (1-dodecyl-3-methylimidazolium

Received: March 21, 2024
Revised: May 2, 2024
Accepted: June 27, 2024
Published: July 6, 2024

https://doi.org/10.1021/acsomega.4c02742

Table 1. Formulation of SAILs and Non-Ionic Surfactants at Various Compositions

	mass ratio (wt/wt %)					dispersion stability (h)			
formulations	[Bmim][Lausar]	[Cho][Mys]	Tween 80	Span 80	water	0.5	1	3	5
F1	5	5	5	5	80	+	+	−	−
F2	5	5	10	5	75	+	−	−	−
F3	10	10	5	5	70	−	−	−	−
F4	10	5	15	5	65	++	+	−	−
F5	10	10	20	15	45	+++	+++	++	+
F6	5	5	15	15	60	+++	++	+	−
F7	10	10	10	5	65	+++	++	−	−
F8	10	10	5	10	65	++	+	−	−
F9	10	10	15	10	55	+++	+++	+++	+++
F10	10	10	15	15	50	+++	++	+	+
F11	15	10	20	10	45	++	++	+	−
F12	10	10	20	20	40	++	++	−	−

chloride/sodium dodecyl sulfate) mixtures at the oil−water interface. The results revealed that IFT was reduced to the ultralow level ($<10^{-2}$ mN/m) compared to using pure surfactants.[13] Riehm and McCormick used a mixture of Span 80, Tween 80, and DOSS (dioctyl sodium sulfosuccinate), varying the proportions of these surfactants. Their findings demonstrated that modifying the composition of the dispersant mixture (including the proportions of DOSS, Span 80, and Tween 80) leads to a substantial improvement in emulsion stability and dispersion effectiveness, even with an increase in the toxicity of the formulation.[14] Nonionic surfactants generally exhibit improved performance when combined with traditional surfactants; but, the resulting mixture often proves more toxic in many cases.[6,10] There is a necessity to blend nonionic surfactants with other environmentally friendly surfactants that offer tunable properties.

The application of surface-active ionic liquids (SAILs) has been suggested as a viable alternative for effectively dispersing oil spills, primarily because of their low toxicity and strong surface activity.[15] Ionic liquids (ILs) have captured interest as new surfactants owing to their ability to lower interfacial tension among oil and water across different salinity levels and temperatures.[16] Numerous research investigations have demonstrated the effectiveness of SAILs and their formulations with other surfactants in the remediation of oil spills.[17,18] A series of SAILs with impressive results was developed in a recent study. These newly synthesized SAILs proved to be highly efficient in dispersing various types of crude oils while maintaining lower toxicity and high degradation rates.[19,20] Nazar et al. investigated the aggregation behavior and dispersion effectiveness for the binary mixture of 1-butyl-3-methylimidazolium lauroyl sarcosinate [Bmim][Lausar] and Tween 80. The findings demonstrated that the combination of these two components showed a synergistic effect, successfully dispersing Arabian crude oil with an impressive dispersion effectiveness of 83.45%.[17] The environmental factors (temperature, salinity, and stirring speed) were optimized for the binary mixture of [Bmim][Lausar] and Tween 80 to obtain the highest dispersion effectiveness at different environmental conditions.[21] Until now, there is less literature available on the optimization of dispersants formulation of nonionic and SAIL surfactants for oil spill remediation.

This study extends the concept of enhancing surfactant mixtures to achieve effective dispersion of crude oil by combining nonionic surfactants (Tween 80 and Span 80) with SAILs ([Cho][Mys] and [Bmim][Lausar]). The surfactants were combined at an optimized ratio to formulate a new green dispersant formulation, characterized by its high effectiveness in dispersing crude oil with low toxicity and high biodegradability. Various factors including crude oil type, dispersant-to-oil ratio (DOR), and salinity were optimized to achieve maximum dispersion effectiveness. To ensure safe usage, toxicity and biodegradability assessments of the formulated product were conducted. The chemical structures of Tween 80, Span 80, [Cho][Mys], and [Bmim][Lausar] are provided in Figure S1 in the Supplementary Data.

2. MATERIALS AND METHODS

The details of the material and methods used in this study are given below:

2.1. Materials. Tween 80 (polyoxyethylene sorbitan monooleate), Span 80 (Sorbitan monooleate), *N*-lauroyl sarcosine sodium salt, ethanol, dichloromethane (DCM), NaCl, $MgCl_2$, Na_2SO_4, and acetone were obtained from Merck (Hohengrunn, Germany). The IL BmimCl, myristic acid, and choline hydroxide used to synthesize ILs were purchased from Sigma-Aldrich. Table S1 depicts the basic properties of all chemicals used in this research. Three different types of crude oil, two medium crude oils (Arab, Ratawi) and one heavy crude oil (Doba) were used in this study. The procurement of the aforementioned crude oils was carried out through Malaysian Refining Company Sdn Bhd (PETRONAS). The physiochemical characteristics of crude oils are depicted in Table S5 in the Supplementary Data. A developed method was employed to prepare the stimulated seawater,[22] and Table S2 provides details of this procedure. The black zebrafish (*Danio rerio*) were acquired from a fish shop in Seri Iskandar, Malaysia.

During the formulation and optimization of these dispersants, including Tween 80, Span 80, [Bmim][Lausar], and [Cho][Mys], the compatibility and synergy between the nonionic surfactants and surface-active ionic liquids was the big issue. This was addressed through systematic experimentation to find the optimal combinations and ratios that could enhance the dispersant effectiveness.

2.2. Synthesis of the SAILs. The synthesis of [Bmim][Lausar], denoting the 1-butyl-3-methylimidazolium lauroyl sarcosinate, was conducted using the metathesis reaction approach established by Mustahil et al.[20] and the detailed procedure is explained in the Supplementary Data. The choline myristate-based SAIL was synthesized by the method developed by Petkovic et al.[23] In brief, myristic acid and

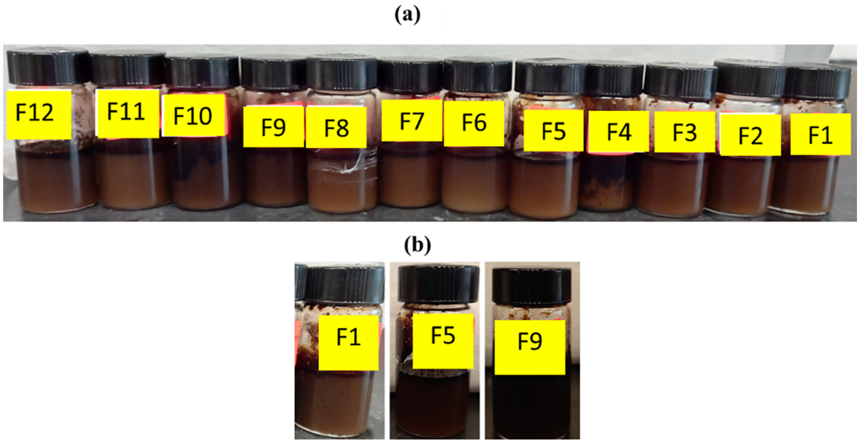


Figure 1. (a) Emulsion stability of the 12 formulations, (b) emulsion formulation of F1, F5, and F9. In all formulations, Arab crude oil was used.

choline hydroxide solution were mixed in a 1:1 molar ratio at room temperature (25 °C). The solution was refluxed for 24 h at 80 °C with constant stirring. For the removal of any remaining water from the resulting IL surfactant, the product underwent vaporization using a rotary evaporator at 80 °C and 272 mbar for 5 h, followed by a freeze-drying process lasting 48 h. The synthesized SAILs were confirmed by ^{1}H NMR spectroscopy (Figure S2).

2.3. Determination of the Best Formulation by Optimizing the Surfactants. Overall, 12 formulations were developed by combining the nonionic surfactants (Tween 80, Span 80) and SAILs ([Bmim][Lausar], [Cho][Mys]) at specific ratios. All formulation compositions were made to 100% using distilled water, as shown in Table 1. After that, each formulation was vortexed at the speed of 2500 rpm for 3 min and left to stand for 5 h. The appearance and phase segregation of the resulting formulations were observed physically. The formulations were examined after 72 h and found to be stable and homogeneous, indicating their stability and consistency. The centrifugation technique was used to ensure the homogeneity of the formulations.

2.4. Measuring the Surface Tension and Critical Micelle Concentration. The surface tension of the formulation, which consisted of nonionic surfactants and SAILs, was determined at room temperature by dynamic contact angle tensiometer (Data Physics DCAT 15, Germany). Before each measurement, the plate was rinsed with distilled water and dried using a blue Bunsen flame. The experiment was performed three times under similar conditions with an uncertainty not exceeding 0.03 mN m^{-1}. Before the experiment was initiated, the accuracy of the instrument was validated by assessing the surface tension of double-distilled water, resulting in a value of 71.99 mN m^{-1}. This finding aligns with the values reported in the literature.

2.5. Evaluation of Interfacial Tension. The interfacial tension (IFT) between Arabian crude oil and simulated seawater was measured by applying the spinning drop approach with the use of a Data Physics SVT 20 apparatus. Simulated seawater was injected into a fast exchange syringe, specifically the Data Physics FEC 622/400-HT, while the oil and dispersant solution were introduced at the central point of the bulk phase. IFT measurements were taken over a range of rotational velocities from 5500 to 8000 rpm. The IFT of the formulated mixture was assessed for Arabian crude oil at varying dispersant-to-oil (DOR) ratios and different salinity levels. IFT values were determined at various temperatures.

2.6. Determination of Dispersion Effectiveness. The dispersion efficiency was evaluated through the approved baffled flask test (BFT) methodology sanctioned by the U.S. Environmental Protection Agency (EPA).[15] The baffled flask was filled with 120 mL of simulated seawater (SSW), and subsequently, 100 μL of crude oil was applied onto the surface of the SSW. Application of 4 μL of dispersant directly onto the crude oil layer led to a dispersant-to-oil ratio (DOR) of approximately 1:25. In cases where DOR deviated from 1:25, the volume of applied dispersant was adjusted while maintaining a constant volume of crude oil. The Baffled flask comprising this solution was shaken for 10 min at 200 rpm at 25 °C in an incubator shaker. Following that, dichloromethane (DCM) was employed to extract crude oil from 30 mL of diluted water solution containing dispersed crude oil. The absorption of specimens was determined by using a spectrophotometer to determine how much each sample absorbs oil at 340, 370, and 400 nm. Dispersion effectiveness is defined as the ratio of dispersed oil in simulated seawater to the total oil introduced into the system. Equation 1 was used to determine the dispersion effectiveness.[3]

$$\text{Effectiveness}(\%) = \frac{\text{Total oil dispersed}}{\rho_{\text{oil}} V_{\text{oil}}} \tag{1}$$

ρ_{oil} = density of crude oil in (g/L); V_{oil} = Volume of crude oil (100 μL = 10^{-4} L).

2.7. Determination of Fish Toxicity of the Formulation. The formulation's acute toxicity was examined on zebrafish (*Danio rerio*) following an established methodology outlined in Guideline No. 203 by the Organization for Economic Co-operation and Development (OECD).[24] The detailed procedure for the determination of toxicity is explained in the Supplementary Data.

2.8. Biodegradability Evaluation of the Formulation. The experiment to determine biodegradability was carried out using the 301D Closed Bottle Test (CBT) technique developed by the OECD guidelines 1992.[25] The biodegradation percentage was derived by directly measuring the dissolved oxygen content in each bottle. The oxygen demand of the blank sample was used to correct these results for the theoretical oxygen demand (TheOD). The OD for the measured compounds was assessed by using eq 2, and % of degradation was computed using eq 4 as mentioned below.

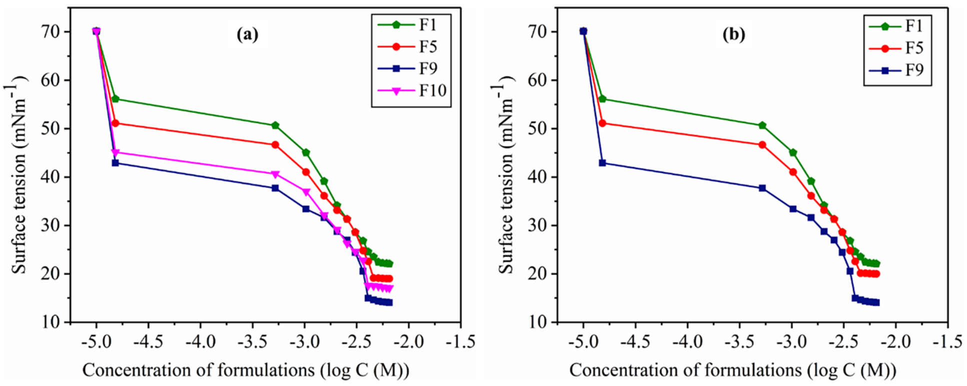


Figure 2. Surface tension at CMC for the different formulations (a) F1, F5, F9, and F10 and (b) F1, F5, and F9.

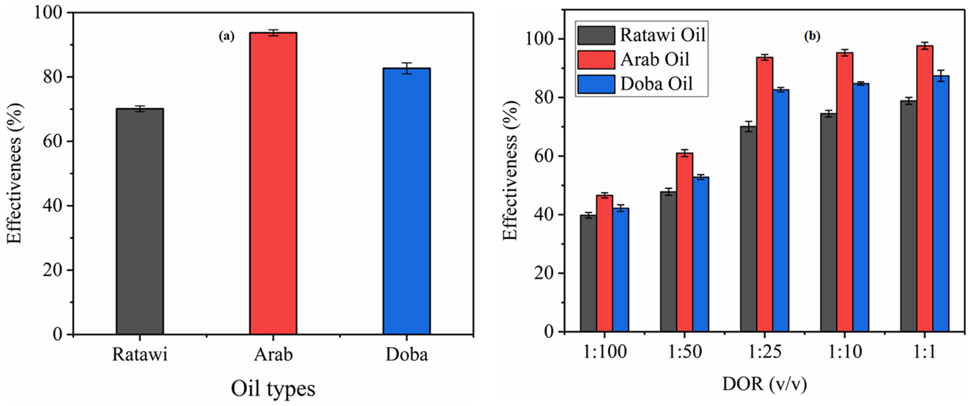


Figure 3. (a) Dispersion effectiveness of the formulation (F9) for various crude oils and (b) dispersion effectiveness of various crude oils at different DOR at 25 °C.

$$\mathrm{TheOD} = \frac{16\left[2\mathrm{C} + \frac{1}{2}(\mathrm{H} - \mathrm{Cl} - 3\mathrm{N}) + 3\mathrm{S} + \frac{5}{2}\mathrm{P} + \frac{1}{2}\mathrm{Na} - \mathrm{O}\right]\mathrm{mg/mg}}{\mathrm{MW}} \quad (2)$$

$$\mathrm{BOD} = \frac{\mathrm{O_2\ uptake\ by\ test\ substance\ in\ mg/L} - \mathrm{O_2\ uptake\ by\ blank\ in\ mg/L}}{\mathrm{Test\ substance\ in\ bottle\ mg/L}} \quad (3)$$

$$\%\mathrm{degradation} = \frac{\mathrm{BOD(mgO_2/mg\ test\ substance)}}{\mathrm{ThOD(mgO_2/mg\ test\ substance)}} \times 100 \quad (4)$$

3. RESULTS AND DISCUSSION

The nonionic surfactant and SAILs were optimized accordingly:

3.1. Optimization of Nonionic and SAILs Dispersant Formulation.

It is a well-known fact that surfactant concentration significantly influences dispersant effectiveness.[22] The nonionic and SAIL dispersants were formulated in the current study by mixing all surfactants at specific concentrations. Tween 80 and Span 80 were nonionic surfactants selected due to their lower CMC value and green nature. [Bmim][Lausar] and [Cho][Mys] SAILs also have excellent surface-active properties and are environmentally friendly. Unlike conventional dispersants, the developed formulation was entirely water-based and did not include any hazardous or toxic volatile organic solvents.[17,19]

To optimize nonionic-based and SAIL formulations, a total of 12 samples with various concentrations were studied, and their dispersion stability was examined as shown in Figure 1a. The dispersion stability of all individual nonionic surfactants, SAILs, and developed formulations was evaluated for 5 h using Arab crude oil (Table 1 and supplementary data Table S4). The dispersion stability of the individual surfactants in water was shown to be relatively low. Formulations 9 and 10, with surfactant concentrations ranging from 45 and 50%, were determined to be the most stable of the 12 formulations even after 5 h. Nevertheless, a higher concentration of surfactants decreases the oil−water emulsion stability, as indicated for formulations 11 and 12. These results indicate that concentrations of surfactants beyond a specific limit have an adverse effect on the stability of the oil−water emulsion. The emulsion stability results demonstrated a high oil−water emulsion stability for F9 that remained nearly stable for 24 h, as seen in Figure 1b. These findings are corroborated by the previous literature[26] in which it was revealed that the surfactants enhanced the stability and thickness of the oil−water interface by adsorbing onto it.

The four formulations, designated as Formulation 1 (F1), Formulation 5 (F5), Formulation 9 (F9), and Formulation 10 (F10), were chosen, and a comprehensive examination of their stability was conducted based on the surface tension of each surfactant formulation (Figure 2a). It is noteworthy that the three formulations mentioned earlier were specifically chosen to cover a range of stabilities, including the lowest stability (F1), maximum stability (F9), and intermediate stability (F5), as depicted in Figure 2b.

The electrostatic, hydrophobic, and van der Waals interactions are responsible for the formation of micelles, which contributes to the spontaneous micellization process. Head groups of cationic surfactants with the same charge produce electrostatic repulsion which acts as the main contributor to increase the free energy of micelle formation. Thus, if a surfactant with oppositely charged or no charged headgroup is incorporated, the micelle aggregation number is expected to increase. Due to this strong interaction of molecules, CMC is also expected to reduce to lower values. When nonionic and cationic surfactants were mixed, it enhanced the formation of micelles because Tween 80 or Span 80 reduces the surface potential via charge neutralization and increases the ionic strength by virtue of released counterions.

As shown in Figure 2a, F9 has higher surface activity with a CMC value of 3.52 mM compared to F10, F1, and F5, whose CMC values were 4.08, 5.09, and 4.72 mM, respectively. Similar results were found in the previous research, indicating that the micellar mechanism and dispersion efficacy were improved by the synergistic impact of various surfactant agents (such as cationic, nonionic, anionic, and ionic liquids-based surfactants).[27] The published research also confirmed this; developed dispersants with reduced CMC produced more extraordinary oil spill dispersant performance.[3,15]

3.2. Dispersion Effectiveness of the Selected Formulation. Dispersion effectiveness is crucial for oil spill remediation, as it enhances the breakdown of oil, facilitating faster and more environmentally safe cleanup. The dispersion effectiveness was evaluated for the best formulation (F9) at room temperature with a DOR of 1:25 against three different crude oils: Arab, Ratawi, and Doba. This dispersant formulation efficiently dispersed different kinds of crude oils from medium to heavy, as illustrated in Figure 3a. Arab crude oil has the maximum dispersion effectiveness of 93.72% among all crude oils. Despite being classified as a medium crude oil, Ratawi crude oil demonstrated the lowest dispersion effectiveness among all of the tested crude oils, with only 70.12% dispersion. The oil characteristics, including viscosity and composition of the crude oil, considerably impact the dispersant efficiency. It was predicted that the efficiency of the dispersants would be reduced due to the high resin content in Ratawi crude oil.[28] Oils mainly composed of these compounds disperse inefficiently when dispersants were used for dispersion. The same findings were reported by Zhu et al.[4] and Nawavimarn et al.,[29] indicating that the micellar mechanism and dispersion efficacy were improved by the synergistic impact of various surfactant agents (such as chemical and biological surfactants, and ionic liquids). It is considered that light oil is the ideal medium for dispersants to work best.[30]

The dispersant formulation (F9) effectiveness was evaluated at various DORs of 1:1, 1:10, 1:25, 1:50, and 1:100. Based on the results, dispersant formulation F9 exhibited remarkable effectiveness across the entire DOR range from 1:1 to 1:25 for all examined crude oils, including both medium and heavy types. These findings align with those reported in other studies, such as Riehm et al. and Dos Santos et al.[22,31] With a substantial decrease in DOR, a larger amount of dispersant became accessible for the same volume of oil, leading to a reduction in the IFT within the oil-dispersant mixture. This decrease in IFT contributes to achieving a high level of dispersion effectiveness.[32] As a result, the dispersant demonstrated a maximum effectiveness of 97.68% for Arab crude oil at a DOR of 1:1. In contrast, for Ratawi and Doba crude oils, the effectiveness ranged between 39.8 and 42.22% at a DOR of 1:100, as depicted in Figure 3b.

3.3. Determination of Dispersion Effectiveness of the Formulation at Different Salinities. The efficacy of the formulation in dispersion was evaluated using saline water having concentrations ranging from 1.0 to 4.5%, while freshwater (0% salinity) served as a reference to analyze the effect of salinity on the effectiveness of the dispersant. The findings revealed that the developed formulation (F9) showed high dispersion effectiveness of 93.72% at a salinity level of 3.4 wt % for Arab crude oil (Figure 4). The predicted high effectiveness of the developed formulation (F9) was attributed to the collective ionic strength of the four surfactant components responsible for stabilizing the surfactant-oil droplet. Because of their desalting function, anionic surfactants often degrade when salts (NaCl) are added.[33] This phenomenon illustrates the benefit of catanionic surfactants, where salinity does not affect surface activity but enhances stability. the effectiveness was reduced. These findings were consistent with earlier research, suggesting that effective dispersion occurs within the 3.0 to 4.0 wt % salinity range.[26,34]

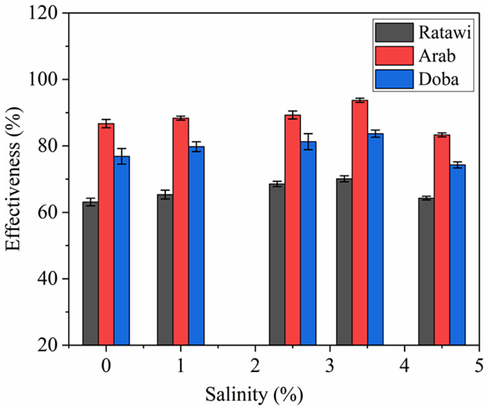


Figure 4. Effect of the Salinity on the effectiveness of the developed formulation (F9) for different crude oil.

Some studies have indicated a decline in the dispersant efficiency as system salinity decreases, particularly in pure water-based systems. Nevertheless, the newly formulated dispersant demonstrated enhanced efficiency even at low salinity (freshwater), achieving an efficiency of approximately 86% with Arab crude oil. In conclusion, it was established that the effectiveness of the developed dispersant formulation is minimally affected by salinity. This suggests that salinity enhances ionic strength as well as stabilizes dispersion formation up to 3.0 wt % salinity. The dispersion effectiveness is notably influenced by the nature of the crude oil, as depicted in Figure 4.

3.4. Interfacial Tension of the Formulation at Different DORs and Temperatures. Interfacial tension (IFT) was identified as the principal resistance to droplet breakdown. Lower IFT produces more efficient droplet breakdown and smaller particles. The decrease in IFT results in a reduced degree of coalescence and improved ability to incorporate oil particles into the water column, with varying levels of mixing energy.[35] The interfacial tension (IFT) of formulation (F9) was determined because it was the most stable formulation.

Arab crude oil at 200 rpm with 3.4% salinity was used to measure the IFT. The crude oil−water IFT increased slightly with rising temperature when no dispersant was applied. The IFT for Arab crude oil decreased from 16.120 to 1.030 mN m^{-1} at 25 °C, under conditions of 3.4% salinity and 1:100 DOR. At 50 °C, a comparable drop was seen, but at 80 °C, a slightly lower reduction was recorded (Figure 5). The dispersant formulation lowered the IFT between oil and water, a direct reflection of the dispersant's efficacy, as demonstrated by the dramatic decrease in the IFT value at a ratio of 1:100 DOR. At a higher DOR (1:1), the IFT values were extremely low, ranging from 0.625 to 2.172 mN m^{-1} at 25 and 80 °C, correspondingly. The identical results were reported in the earlier research in which authors found high dispersion effectiveness at lower IFT.[36]

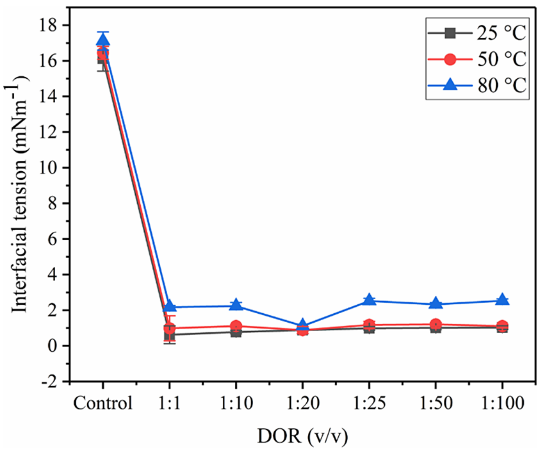


Figure 5. IFT values of Arab crude oil at various temperatures and DOR for formulation F9.

Similarly, Saha et al.[37] evaluated the IFT of several surfactant formulations at different temperatures, composed of sodium dodecyl sulfate (SDS), Span 80, sodium dodecylbenzene sulfonate surfactant (SDBS), Tween 80, Brij 30, and Triton-X 100. The lowest IFT recorded was 3.7 × 10^{-2} mN m^{-1} at 30 °C, and it rose up to 2.14 × 10^{-1} mN m^{-1} at 80 °C. At lower temperatures, surfactant monomers show slower diffusion in both oil and water, forming a stable film at the interface. This film effectively decreases the interfacial tension. On the other hand, higher temperatures cause the interface film to destabilize, thereby raising IFT values. Due to the exothermic nature of adsorption, higher system temperatures impede the diffusion of surfactant molecules at the interface, resulting in the destabilization of the film and an increase in IFT values.

3.5. Interfacial Tension of the Formulation at Different Salinities and Temperatures. IFT measurements for the dispersant formulation (F9) were conducted with Arab crude oil at different temperatures. The results indicated a consistent decrease in IFT values as the temperature increased, as illustrated in Figure 6. These results indicated that at 3.4% salinity, the IFT values were reduced even at ambient temperature; however, at 90 °C, the IFT values were almost constant for each salinity range. As a result, it was determined that the dispersant formulation (F9) was stable at high temperatures and had the most significant IFT decrease at 3.4% salinity at all temperatures investigated.

Similarly, Pillai et al.[38] evaluated the IFT of ionic liquids at various salinities. They found that the IFT values decreased more by adding NaCl until ideal salinity was attained. The positive charge of the cationic component in ionic liquids forms an electrical attraction with the salt's negative ion, a phenomenon arising from the presence of oppositely charged salt ions in the aqueous solution. These opposite ions decreased the electrical repulsion between the positive head of ILs and, as a result, increased IL molecule adsorption at the interface. The salt ions in a water solution may compete with the cations and anions of ILs for water molecules, reducing the ionic liquid solubility. As a result, the IL is less ionized and firmly adsorbed at the crude oil/water contact, resulting in a drop in the IFT. IFT reduces with increasing salt content until it reaches a minimal value; after that, it increases. The salt concentration corresponding to the lowest IFT was referred to as optimal salinity. This study demonstrates the application of dispersant formulation for efficient oil spill removal, which can improve oil removal under challenging circumstances such as high salinity and temperatures.

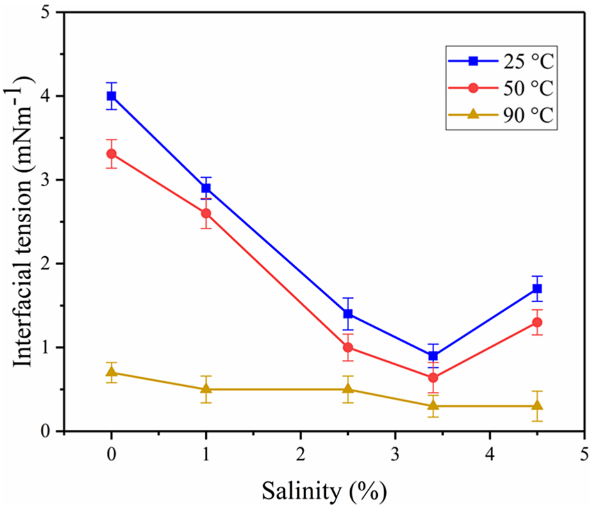


Figure 6. IFT values of the developed dispersant formulation (F9) at various salinities and temperature.

3.6. Particle Size Analysis of the Formulation at Different DOR. A particle size analyzer (PSA) was used to measure the dispersed crude oil particle size for the developed dispersant formulation (F9). As previously stated, the efficiency and stability of emulsions produced with smaller oil particles were notably higher than those formed by big oil droplets.[17] Increasing the DOR led to a gradual decrease in the size of the dispersed oil particles. The formulation (F9) underwent size calculations for dispersed oil droplets at various DORs, including 1:1, 1:25, 1:50, and 1:100, as depicted in Figure 7.

At the DOR 1:1, a smaller size oil droplet (280 nm) was produced, and the size of the droplet increased continuously from 972, 1480, and 1920 nm for DOR of 1:25, 1:50, and 1:100, respectively. The results of this study indicated that an increase in the dispersant concentration led to a reduction in the size of oil droplets. The developed dispersant formulation produced the most stable emulsion, with the smallest dispersed oil droplets.

3.7. Acute Toxicity of the Developed Formulation. The acute toxicity of a formulation is significant in oil spill remediation, as it determines the environmental safety and potential impact on marine life. The acute fish toxicity for the dispersant formulation (F9) against zebrafish was investigated.

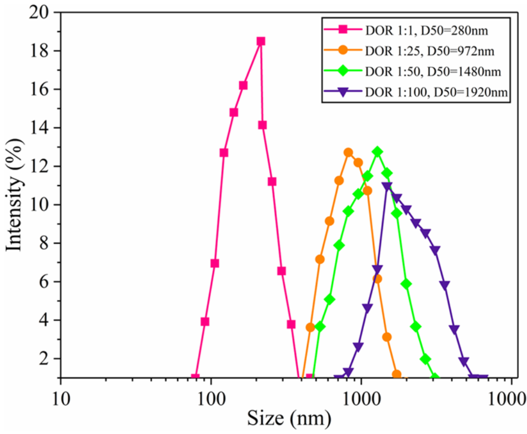


Figure 7. PSA of dispersed oil droplets at various DORs for the developed formulation (F9).

The surfactant mixtures were evaluated at concentrations of 100 mg L^{-1}, revealing that the 96 h LC_{50} value of the surfactant (i.e., the concentration at which a chemical kills half of the population) was higher than 100 mg L^{-1}. As discussed in Section 2.7 (according to the OECD guidelines), the dispersant formulation did not classify as 'toxic' to fish. The complete acute toxicity can be omitted from the research. Nonetheless, to validate these findings, a complete test was conducted on zebrafish (*Danio rerio*) to assess the surfactant mixture's toxicity precisely. Experiments were then performed to evaluate the actual toxicity of formulation (F9). Eight dispersant concentrations, such as 100, 200, 300, 350, 400, 450, 500, and 550 mg L^{-1}, were selected and introduced into different tanks; each tank contained 10 fish. At intervals of 24 h over a span of 4 days, the behavior of the fish was visually examined to determine the % mortality. The dead fish was removed immediately from the tank. The essential fish survival factors like water temperature, dissolved oxygen concentration (DO), and pH were also measured daily. The results showed the average of triplicate experiments. The formulation LC_{50}, or the concentration at which 50% of the population died, was found to be 450 mg L^{-1} (Table 2) and classified as 'practically nontoxic'. Following the classification proposed by Passino and Smith,[39] materials with an LC_{50} falling between 100 and 1000 mg L^{-1} are considered 'practically nontoxic,' as mentioned in Supplementary Table S3.

In recent research, an investigation was conducted on the toxicity of various SAILs, particularly focusing on [Bmim]-[Lausar] on zebrafish (*Danio rerio*) and grouper fish (*Epinephelinae*). The findings revealed that [Bmim][Lausar] demonstrated nearly nontoxic characteristics, with an LC_{50} of 173.78 mg L^{-1}.[19] The toxicity of the newly formulated dispersant was compared with that of traditional dispersants. For example, when Finasol OSR 52 was investigated for toxicity toward various aquatic organisms, it demonstrated an average LC_{50} of 43.27 mg L^{-1}.[40] Similarly, Pie and Mitchelmore investigated the toxicities of different commercial surfactants. They reported that Corexit 9500, Petro-Clean, Ocra, and Dispersit SPC 1000 had LC_{50} values of 55, 52, 76.5, and 10.1 mg L^{-1} respectively, indicating that all surfactants are toxic to living organisms.[41] Compared to commercial and developed dispersants, the dispersant exhibits lower toxicity.

3.8. Biodegradability of the Developed Formulation.

Biodegradability research is essential because it is beneficial for evaluating the removal of persistent substances from the environment.[42] Biodegradation is the process of breaking down organic matter through the action of microorganisms such as fungi and bacteria under aerobic circumstances, resulting in the production of CO_2 and water. The biodegradation process led to a notable decrease in both the number of carbon atoms in the chemical formula and the molecular weight.[19] The biodegradability of the formulation, pure [Cho][Mys], [Bmim][Lausar], Tween 80, and pure Span 80 were also investigated. The assessment of biodegradability for both the pure surfactants and the formulation (F9) was conducted through closed-bottle tests. In accordance with OECD guidelines, a surfactant qualifies as 'readily biodegradable' if at least 60% of its initial quantity degrades within 28 days under an aerobic environment. The findings from the present study, as presented in Table 3, indicate that the degradation value for [Cho] [Mys] was 65.82%, [Bmim][Lausar], Tween 80 degraded at rates of 60.82 and 70.98%, accordingly, and pure Span 80 82.78%. On the other hand, the biodegradability of the dispersant formulation was determined, and it can be seen from the results that the dispersant formulation biodegradability value is 73.26%, as presented in Table 3.

The findings of the current research were compared to those of prior studies. For example, Brakstad et al. investigated the biodegradation of DOSS in seawater. According to their findings, after 54 days, DOSS degraded 16%.[43] Corexit 9500A biodegradability was studied by Cai et al.,[44] and they found that it had poor biodegradability (10−20%) after 30 days. According to the OECD recommendations, the mixture was readily biodegradable.

Table 2. Acute Toxicity Assessment for the Developed Formulation (F9)

	test fish number			number of dead fish					
concentration (mg L^{-1})	R1	R2	R3	R1	R2	R3	mortality (%)	SD	probit variable
100	10	10	10	0	0	0	0	0.00	0.00
200	10	10	10	0	0	0	0	0.00	0.00
300	10	10	10	0	0	0	0	0.00	0.00
350	10	10	10	2	2	2	20	0.00	4.16
400	10	10	10	5	4	5	46	0.58	4.92
450	10	10	10	5	5	5	50	0.00	5.00
500	10	10	10	9	9	8	87	0.58	6.13
550	10	10	10	10	9	10	97	0.58	6.75
positive control	10	10	10	10	10	10	100	0.00	8.72
negative control	10	10	10	0	0	0	0	0.00	0.00

Table 3. Biodegradability Analysis of Developed Formulation and Pure Surfactants

test material	R1	R2	R3	biodegradation[a] % ± SD	biodegradation[b] %
formulation	74.90	70.14	72.20	72.41 ± 2.38	73.26
[Cho][Mys]	66.85	65.76	64.77	65.78 ± 1.10	65.82
[Bmim][Lausar]	61.02	60.76	60.59	60.85 ± 1.02	60.82
Tween 80	70.61	71.08	71.20	70.99 ± 1.03	70.98
Span 80	85.71	83.12	81.19	82.77 ± 2.30	82.78
reference[c]	93.12	94.97	95.78	94.63 ± 1.36	93.98

[a] The mean biodegradation of three replicates [b] calculated using the formulas in eqs 2, 3, and 4. [c] Sodium acetate serving as reference material.

4. CONCLUSIONS

The present research aimed to evaluate the feasibility of combining nonionic surfactants with ILs-based surfactants to formulate an environmentally benign dispersant to remove oil spills. Nonionic surfactants (Tween 80, Span 80) and SAILs ([Bmim][Lausar], and [Cho] [Mys]) were blended to develop 12 dispersant formulations. The formulation F9 with the highest dispersion stability was selected and then further optimized to examine its efficacy under various environmental parameters. The highest dispersant efficiency, reaching 93.73%, was obtained with the F9 formulation on Arab crude oil. The F9 formulation was demonstrated to be efficient in dispersing crude oil under various salinity and DOR ratio conditions. The acute toxicity of the formulation was assessed using zebrafish, and the results revealed an LC_{50} exceeding 100 mg L^{-1} after 96 h of experiment, indicating its practical nontoxicity. The biodegradability tests indicated that the formulation was readily biodegradable, achieving a value of 73.26%. Based on the findings, the dispersant formulation with improved dispersion effectiveness, reduced toxicity, and easy-to-biodegrade characteristics present significant potential for its utilization in oil spill remediation. Besides, further research is required to evaluate their performance across different environmental conditions, long-term impacts on marine ecosystems, and techno-economic analysis for large-scale deployment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c02742.

> Synthesis of the SAILs, determination of fish toxicity of the formulation, chemical structures of surfactants, NMR spectra, physical characteristics of the chemicals preparation of simulated seawater, acute toxicity, dispersion stability, and crude oil properties (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Syed Muhammad Shakil Hussain − *Center for Integrative Petroleum Research (CIPR), College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia;* orcid.org/0000-0002-6806-2326; Email: smshakil@kfupm.edu.sa

Muhammad Moniruzzaman − *Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Perak 32610, Malaysia;* orcid.org/0000-0002-2523-4159; Email: m.moniruzzaman@utp.edu.my

Authors

Masooma Nazar − *Center for Integrative Petroleum Research (CIPR), College of Petroleum Engineering and Geosciences, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

Aqeel Ahmad − *Interdisciplinary Research Center for Refining and Advanced Chemicals, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.4c02742

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge the support of the College of Petroleum Engineering and Geosciences (CPG) at KFUPM and Centre of Research in Ionic Liquids, from Universiti Teknologi PETRONAS, Malaysia.

■ REFERENCES

(1) Haider, F. U.; Ejaz, M.; Cheema, S. A.; Khan, M. I.; Zhao, B.; Liqun, C.; Salim, M. A.; Naveed, M.; Khan, N.; Nunez-Delgado, A. J. Phytotoxicity of petroleum hydrocarbons: Sources, impacts and remediation strategies. *Environ. Res.* **2021**, *197*, No. 111031.

(2) Lewis, A.; Prince, R. C. Integrating dispersants in oil spill response in Arctic and other icy environments. *Environ. Sci. Technol.* **2018**, *52* (11), 6098−6112.

(3) Wang, P. S.; Ahmad, A.; Nazar, M.; Rahmah, A. U.; Moniruzzaman, M. Biocompatible and Biodegradable Surfactants from Orange Peel for Oil Spill Remediation. *Molecules* **2023**, *28*, 5794.

(4) Zhu, T.; Kang, W.; Yang, H.; Li, Z.; Zhou, B.; He, Y.; Wang, J.; Aidarova, S.; Sarsenbekuly, B. J. Advances of microemulsion and its applications for improved oil recovery. *Adv. Colloid Interface Sci.* **2022**, *299*, No. 102527.

(5) Brakstad, O. G.; Lewis, A.; Beegle-Krause, C. A critical review of marine snow in the context of oil spills and oil spill dispersant treatment with focus on the Deepwater Horizon oil spill. *Mar. Pollut. Bull.* **2018**, *135*, 346−356.

(6) Jin, J.; Wang, H.; Jing, Y.; Liu, M.; Wang, D.; Li, Y.; Bao, M. An efficient and environmental-friendly dispersant based on the synergy of amphiphilic surfactants for oil spill remediation. *Chemosphere* **2019**, *215*, 241−247.

(7) Song, X.; Zhang, B.; Cao, Y.; Liu, B.; Chen, B. J. Shrimp-waste based dispersant as oil spill treating agent: Biodegradation of dispersant and dispersed oil. *J. Hazard. Mater.* **2022**, *439*, No. 129617.

(8) Corcoran, L. G.; Saldana Almaraz, B. A.; Amen, K. Y.; Bothun, G. D.; Raghavan, S. R.; John, V. T.; McCormick, A. V.; Penn, R. L. Using Microemulsion Phase Behavior as a Predictive Model for Lecithin-Tween 80 Marine Oil Dispersant Effectiveness. *Langmuir* **2021**, *37*, 8115−8128.

(9) Rocchio, J.; Neilsen, J.; Everett, K.; Bothun, G. D. A solvent-free lecithin-Tween 80 system for oil dispersion. *Colloids Surf. A: Physicochem. Eng. Asp.* **2017**, *533*, 218−223.

(10) Riehm, D. A.; Rokke, D. J.; Paul, P. G.; Lee, H. S.; Vizanko, B. S.; McCormick, A. V. Dispersion of oil into water using lecithin-Tween 80 blends: The role of spontaneous emulsification. *J. Colloid Interface Sci.* **2017**, *487*, 52−59.

(11) Nyankson, E.; Agyei-Tuffour, B.; Efavi, J. K.; Yaya, A.; Onwona-Agyeman, B.; Konadu, D. S.; Amedalor, R.; Frimpong, B. K.; Bensah, Y. D. Potential Application of Dioctyl Sodium Sulfosuccinate Salt (DOSS)-Saponin Binary Dispersant in Oil Spill Remediation: Synergistic Interaction Between DOSS and Saponin. *Water Air Soil Pollut.* **2020**, *231*, 1−13.

(12) Lv, G.; Wang, F.; Cai, W.; Zhang, X. Characterization of the addition of lipophilic Span 80 to the hydrophilic Tween 80-stabilized emulsions. *Colloids Surf. A: Physicochem. Eng. Asp.* **2014**, *447*, 8−13.

(13) Jia, H.; Lian, P.; Leng, X.; Han, Y.; Wang, Q.; Jia, K.; Niu, X.; Guo, M.; Yan, H.; Lv, K. F. Mechanism studies on the application of the mixed cationic/anionic surfactant systems to enhance oil recovery. *Fuel* **2019**, *258*, No. 116156.

(14) Riehm, D. A.; McCormick, A. V. The role of dispersants' dynamic interfacial tension in effective crude oil spill dispersion. *Mar. Pollut. Bull.* **2014**, *84*, 155−163.

(15) Nazar, M.; Shah, M. U. H.; Ahmad, A.; Goto, M.; Yahya, W. Z. N.; Moniruzzaman, M. Aggregation, toxicity, and biodegradability study of an ionic liquid-based formulation for effective oil spill remediation. *Chemosphere* **2023**, *344*, No. 140412.

(16) Al-Asadi, A.; Arce, A.; Rodil, E.; Soto, A. J. Enhanced oil recovery with nanofluids based on aluminum oxide and 1-dodecyl-3-methylimidazolium chloride ionic liquid. *J. Mol. Liq.* **2022**, *363*, No. 119798.

(17) Nazar, M.; Shah, M. U. H.; Yahya, W. Z. N.; Goto, M.; Moniruzzaman, M. Surface active ionic liquid and Tween-80 blend as an effective dispersant for crude oil spill remediation. *Environ. Technol. Innov.* **2021**, *24*, No. 101868.

(18) Nazar, M.; Goto, M.; Yahya, W. Z. N.; Moniruzzaman, M. Synthesis and determination of Surface tension of 1-butyl-3-methylimidazolium lauroyl sarcosinate IL and Tween 80. *J. Phys.: Conf. Ser.* **2021**, *1793*, No. 012045.

(19) Baharuddin, S. H.; Mustahil, N. A.; Reddy, A. V. B.; Abdullah, A. A.; Mutalib, M. I. A.; Moniruzzaman, M. Development, formulation and optimization of a novel biocompatible ionic liquids dispersant for the effective oil spill remediation. *Chemosphere* **2020**, *249*, No. 126125.

(20) Mustahil, N. A.; Baharuddin, S. H.; Abdullah, A. A.; Reddy, A. V. B.; Mutalib, M. I. A.; Moniruzzaman, M. Synthesis, characterization, ecotoxicity and biodegradability evaluations of novel biocompatible surface active lauroyl sarcosinate ionic liquids. *Chemosphere* **2019**, *229*, 349−357.

(21) Nazar, M.; Shah, M. U. H.; Ahmad, A.; Yahya, W. Z. N.; Goto, M.; Moniruzzaman, M. Ionic Liquid and Tween-80 Mixture as an Effective Dispersant for Oil Spills: Toxicity, Biodegradability, and Optimization. *ACS Omega.* **2022**, *7* (18), 15751−15759.

(22) Riehm, D. A.; Neilsen, J. E.; Bothun, G. D.; John, V. T.; Raghavan, S. R.; McCormick, A. V. Efficient dispersion of crude oil by blends of food-grade surfactants: Toward greener oil-spill treatments. *Mar. Pollut. Bull.* **2015**, *101*, 92−97.

(23) Petkovic, M.; Ferguson, J. L.; Gunaratne, H. N.; Ferreira, R.; Leitao, M. C.; Seddon, K. R.; Rebelo, L. P. N.; Pereira, C. S. Novel biocompatible cholinium-based ionic liquids-toxicity and biodegradability. *Green Chem.* **2010**, *12*, 643−649.

(24) No, O. T., 1992. 203: Fish, acute toxicity test. OECD. OECD guidelines for the testing of chemicals, section.

(25) OECD, O. Guideline for Testing of Chemicals: Ready Biodegradability. *Google Scholar*, 1992, 301.

(26) Zhang, J.; Ge, D.; Wang, X.; Wang, W.; Cui, D.; Yuan, G.; Wang, K.; Zhang, W. J. A. Influence of surfactant and weak-alkali concentrations on the stability of O/W emulsion in an alkali-surfactant−polymer compound system. *ACS Omega.* **2021**, *6* (7), 5001−5008.

(27) Shah, M. U. H.; Reddy, A. V. B.; Yusup, S.; Goto, M.; Moniruzzaman, M. Ionic liquid-biosurfactant blends as effective dispersants for oil spills: Effect of carbon chain length and degree of saturation. *Environ. Pollut.* **2021**, *284*, No. 117119.

(28) King, T.; Robinson, B.; Ryan, S.; Lee, K.; Boufadel, M.; Clyburne, J. Estimating the usefulness of chemical dispersant to treat surface spills of oil sands products. *J. Mar. Sci. Eng.* **2018**, *6*, 128.

(29) Nawavimarn, P.; Rongsayamanont, W.; Subsanguan, T.; Luepromchai, E. J. Bio-based dispersants for fuel oil spill remediation based on the Hydrophilic-Lipophilic Deviation (HLD) concept and Box-Behnken design. *Environ. Pollut.* **2021**, *285*, No. 117378.

(30) Grote, M.; van Bernem, C.; Böhme, B.; Callies, U.; Calvez, I.; Christie, B.; Colcomb, K.; Damian, H.-P.; Farke, H.; Gräbsch, C. J. The potential for dispersant use as a maritime oil spill response measure in German waters. *Mar. Pollut. Bull.* **2018**, *129*, 623−632.

(31) Dos Santos, A. V.; Simonelli, G.; Dos Santos, L. C. Review of the application of surfactants in microemulsion systems for remediation of petroleum contaminated soil and sediments. *Environ. Sci. Pollut. Res.* **2023**, *30*, 32168−32183.

(32) Liu, Z.; Callies, U. J. Implications of using chemical dispersants to combat oil spills in the German Bight-Depiction by means of a Bayesian network. *Environ. Pollut.* **2019**, *248*, 609−620.

(33) Qazi, M. J.; Liefferink, R. W.; Schlegel, S. J.; Backus, E. H.; Bonn, D.; Shahidzadeh, N. J. L. Influence of surfactants on sodium chloride crystallization in confinement. *Langmuir* **2017**, *33* (17), 4260−4268.

(34) Schrandt, M.; Powers, S.; Rikard, F. S.; Thongda, W.; Peatman, E. Short-term low salinity mitigates effects of oil and dispersant on juvenile eastern oysters: A laboratory experiment with implications for oil spill response activities. *PloS one* **2018**, *13*, No. e0203485.

(35) Zhao, L.; Torlapati, J.; Boufadel, M. C.; King, T.; Robinson, B.; Lee, K. J. VDROP: A comprehensive model for droplet formation of oils and gases in liquids-Incorporation of the interfacial tension and droplet viscosity. *J. Chem. Eng.* **2014**, *253*, 93−106.

(36) Owoseni, O.; Zhang, Y.; Omarova, M.; Li, X.; Lal, J.; McPherson, G. L.; Raghavan, S. R.; Bose, A.; John, V. T. Microstructural characteristics of surfactant assembly into a gel-like mesophase for application as an oil spill dispersant. *J. Colloid Interface Sci.* **2018**, *524*, 279−288.

(37) Saha, R.; Uppaluri, R. V.; Tiwari, P. J. C. Effects of interfacial tension, oil layer break time, emulsification and wettability alteration on oil recovery for carbonate reservoirs. *Colloids Surf. A: Physicochem. Eng. Asp.* **2018**, *559*, 92−103.

(38) Pillai, P.; Mandal, A. A comprehensive micro scale study of poly-ionic liquid for application in enhanced oil recovery: Synthesis, characterization and evaluation of physicochemical properties. *J. Mol. Liq.* **2020**, *302*, No. 112553.

(39) Passino, D. R. M.; Smith, S. B. Acute bioassays and hazard evaluation of representative contaminants detected in Great Lakes fish. *Environ. Toxicol. & Chem.* **1987**, *6* (11), 901−907.

(40) DeLorenzo, M.; Key, P.; Chung, K.; Pisarski, E.; Shaddrix, B.; Wirth, E.; Pennington, P.; Wade, J.; Franco, M.; Fulton, M. Comparative toxicity of two chemical dispersants and dispersed oil in estuarine organisms. *Arch. Environ. Contam. Toxicol.* **2018**, *74*, 414−430.

(41) Pie, H. V.; Mitchelmore, C. L. Acute toxicity of current and alternative oil spill chemical dispersants to early life stage blue crabs (Callinectes sapidus). *Chemosphere* **2015**, *128*, 14−20.

(42) Jordan, A.; Gathergood, N. Biodegradation of ionic liquids−a critical review. *Chem. Soc. Rev.* **2015**, *44*, 8200−8237.

(43) Brakstad, O. G.; Størseth, T. R.; Brunsvik, A.; Bonaunet, K.; Faksness, L. G. Biodegradation of oil spill dispersant surfactants in cold seawater. *Chemosphere* **2018**, *204*, 290−293.

(44) Cai, Q.; Zhu, Z.; Chen, B.; Lee, K.; Nedwed, T. J.; Greer, C.; Zhang, B. A Cross-comparison of Biosurfactants as Marine Oil Spill Dispersants: Governing Factors, Synergetic Effects and Fates. *J. Hazard. Mater.* **2021**, *416*, No. 126122.