Evaluation of the efficiency of ionic liquids in the demulsification of oil-in-water emulsions

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ABSTRACT

The production of oil in water emulsions (O/W-EMUL) is prevalent in the petroleum sector due to the presence of several stabilizers; however, O/W-EMUL is an unwanted phenomenon. Given that, this study evaluates the efficiency of three ionic liquids (ILs), two halogenide ILs (HILs-1, HILs-2), and one is non-halogenide IL (Non-HIL) as demulsifiers for the recovery of oil from O/W-EMUL at a concentration of 500 mg/L. The percentage demulsification efficiency (D%) (i.e., the percentage of oil removed from the O/W-EMUL) was examined using tube and bottle tests. The results of the bottle tests demonstrated that the halogenide ionic liquids (HILs) could achieve a higher D% in comparison to the Non-HIL. The D% achieved within 20 min of treatment with HILs-1, HILs-2, and Non-HIL was found to be ∼97.7%, 88.2%, and 85.2%, respectively. Increasing the volume of ILs (V_{ILs}), which are normally recycled, can help overcome the surfactant's effect to achieve a D% > 95%. The demulsification mechanism is based on ion exchange between the anionic part of the ILs and the oil–surfactant interphase. Recycling the ILs can be enhanced by reestablishing the IL anion part using water-free inversed ion exchange mixed with salts. The results suggest that ILs can be an appropriate substitute for commercial demulsifiers. Though, further efforts are needed to produce non-toxic and cost-effective ILs with low viscosity. The efficiency of the demulsification process may be further enhanced when using ILs with other separation processes. The achieved results support upcoming research works that apply ILs for oil removal from O/W-EMUL.

1. Introduction

The techniques of enhanced oil recovery (EOR) are used for oil recovery after the initial and secondary methods of oil generation. In oil recovery procedures, polymers, surfactants, alkaline, and other integrations are added to raise the water viscosity and achieve a very low interfacial tension (IFT) for the O/W-EMUL (Hou et al., 2005; Bera et al., 2014). However, a portion of the formed oils are in the shape of steady emulsions, which require separation to obtain the proper concentration of oil (<200 mg/L) and water concentrations in the range of <0.3–0.5 vol% for oil movement in the pipeline to the refineries (Hirasaki et al., 2011; Salam et al., 2013). As such, chemical demulsification is an efficient technique to speed up the oil and water separation (Razi et al., 2011; Nikkhah et al., 2015). Several demulsifiers, including polymeric flocculants, ethoxylated phenolic resins, and alkylphenol formaldehyde resins, have been used for W/O-EMUL and O/W-EMUL separation from natural production processes steadied with crude oil resins and asphaltenes contents (i.e., natural surfactants). However, these materials are not operative for oil separation from generated O/W-EMUL, which vary from

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natural emulsions (oil field emulsions) (Nguyen et al., 2012). The presence of surfactants, alkali, and polymers are strongly attached to both the oil and water (Dalmazzone et al., 2012).

In our previous study, magnetite magnetic nanoparticles (Fe$_3$O$_4$-MNPs), (Fe$_3$O$_4$-SiO$_2$-MNPs), and Fe$_3$O$_4$-SiO$_2$-MNPs grafted with hyperbranched polyglycerol polymers (HPG) were applied as demulsifiers for the demulsification process of O/W-EMUL (Elmobarak and Almomani, 2021a,b,c). The results indicated that as-synthesized Fe$_3$O$_4$-MNP could achieve a D% $\geq$ 90% for oil concentrations in the range of 200–660 mg/L using a demulsifier volume of 10 mg/L (Elmobarak and Almomani, 2021b). Similarly, the functionalized MNPs (Fe$_3$O$_4$-SiO$_2$-MNPs) obtained a D% $\geq$ 98% with a demulsifier dose of 10 mg/L (Elmobarak and Almomani, 2021a,d,e). The application of MNPs-HPG demulsifiers also exhibited a significant oil recovery efficiency. For example, a demulsifier of 100 mg/L was sufficient to achieve a D% of 93% for a high oil concentration of 4000 mg/L (Elmobarak and Almomani, 2021c). The magnetic demulsifiers were recycled up to 15 times with a steady D% in the range of 89.1% to 88.6% for oil concentrations between 100–4000 mg/L (Elmobarak and Almomani, 2021a). Other research on oil recovery highlighted how anionic surfactants such as the mixture dodecyl alkyl sulfate are typically added as demulsifiers to the O/W-EMUL and achieve high separation rates (Arjmand and Roostaei, 2014; Ko et al., 2014). Cationic surfactants are also efficient for separating O/W-EMUL by decreasing the electrostatic repulsion between the droplets and decreasing the emulsion stability (Hirasaki et al., 2011; Nguyen et al., 2012). Given the contribution of anionic/cationic functional groups on separating oil from O/W-EMUL, it was proposed that ILs can be successfully used for O/W-EMUL or W/O-EMUL separation (Guzman-Lucero et al., 2010a; Guzmán-Lucero et al., 2010b; Silva et al., 2013). To explain, ILs can be modified to produce cationic surface-active composites via changing cation and anion integrations (Guzman-Lucero et al., 2010a; Guzmán-Lucero et al., 2010b; Silva et al., 2013).

Various HILs with ammonium or imidazolium cations and Non-HILs with fluorinated anions such as PF$_6$ and BF$_4$ have been applied for breaking W/O-EMUL (Guzman-Lucero et al., 2010a; Guzmán-Lucero et al., 2010b; Lemos et al., 2010; Flores et al., 2014). The aforementioned ILs have exhibited excellent behavior, specifically in combination with the microwave radiation method (MR) used to speed up heating and decrease viscosity. However, the fluorinated anions' higher cost and negative environmental impact make them undesirable for application in the demulsification process. Therefore, ammonium ILs with anions such as [HSO$_4$]$^-$, [Cl]$^-$ or [H$_2$PO$_4$]$^-$ were used to remove the water from W/O-EMUL, though the effectiveness of the demulsification process differs between these ILs (Flores et al., 2014). Further, octyl trimethylammonium bromide mixed with an industrial cationic surfactant exhibited an excellent removal efficiency (Hirasaki et al., 2011).

In such research, the D% of the ILs is associated with the IL structure. Flores highlighted how additional hydrophilic anions on the surface of the ILs could slightly improve the D% (Flores et al., 2014). In contrast, hydrophobic anions on the surface of ILs significantly improve the D% (Silva et al., 2013). Moreover, Flores determined that the cations with longer alkyl chains help achieve a better D% than shorter chains. Though, the reverse was presented by Guzman-Lucero et al. (2010a) and Guzmán-Lucero et al. (2010b). Abdullah et al. (2017) exemplified how Trihexyltetradecylphosphonium chloride-based ILs (HIL-1) can enhance oil recovery up to 85% and help with asphaltene. The experiments conducted by Yousefi et al. (2017) indicated that HIL-1 achieves a high D% up to 90% and can decrease the IFT at a high salinity and elevated temperatures. Painter et al. (2010a,b) examined the efficiency of trihexyltetradecyl phosphonium dicyanamide (Non-HIL) to recover aromatic oil in a sand-pack column model. The findings demonstrated that a flooding method used for 4 pore volumes (with the pore volume identified as the model empty volume) might remove up to 65.7% of oil, which is approximately twice the recovery in the brine solution (NaCl [2 wt%]) (Painter et al., 2010a,b). Nabipour et al. (2017) studied trihexyltetradecyl phosphonium bromide (HIL-2), which was efficient and appropriate for tertiary oil recovery and increased the total oil recovery rate by 6.3%. Further, the study demonstrated that raising the inserted pore volume of trihexyltetradecyl phosphonium bromide (HIL-2) to 1 improved the oil recovery efficiency by 8.0% (Nabipour et al., 2017).

Although the literature review suggests promising results for EOR, several other considerations that can impact the efficiency of the separation were not studied. For example, the oil properties such as water content, density, viscosity, and the conditions of the demulsification process (e.g., temperature, demulsifier concentration, mixing time, and surfactant concentration) were not investigated. As such, it is crucial to study the mechanism of the demulsification process using the ILs and to explore the procedure(s) and method(s) for the regeneration of ILs. Given the high cost of ILs, they should be regenerated and reused in the process. It was proposed that the regeneration of ILs is possible if the ion exchange mechanism is removed (Janssen et al., 2013). Thus, the present study aims to guide the choices and strategies of ILs for the demulsification process and to strengthen knowledge about the role of ILs in demulsification methods. Three types of ILs with differing hydrophobicity, sequence of phosphonium, and lengths of hydrocarbon chains were examined for oil recovery from O/W-EMUL. In addition, the D% of the ILs for oil recovery from O/W-EMUL with an oil concentration of 500 mg/L were investigated at room temperature using tube and bottle tests. Further, the mechanism of the demulsification process for all the studied ILs was determined and correlated to the change in zeta potential and Gibbs energy. In the present study, the findings showed promising results for the application of ILs in the EOR process.

2. Material and methods

2.1. Materials

Gasoline oil (95%) and polysorbate surfactant (Tween-80, technical grade) were purchased from Sigma Aldrich. The ionic liquids were provided by Power2 Group LL Qatar with a purity of >95% and were used as delivered. Their names and short forms are outlined in Table 1.

Table 1

The names, short forms, and abbreviations of studied ionic liquids (ILs).

Name of ILs	Forms	Abbreviation
Trihexyltetradecylphosphonium chloride	$P_{666,14}Cl$	HIL-1
Trihexyltetradecylphosphonium bromide	$P_{666,14}Br$	HIL-2
Trihexyltetradecylphosphonium dicyanamide	$P_{666,14}[N(CN)_2]$	Non-HIL

2.2. Synthesis of O/W-EMUL

In this study, gasoline was used as an oil, and a Tween-80 surfactant was applied as an emulsifier to formulate the O/W-EMUL. First, 0.05 g/L of Tween-80 surfactant and water solutions (50 mL) were added to the gasoline oil (2 mL) in a 5L glass bottle using a shear emulsifying homogenizer (model BRH1-100, USA). The solution was initially mixed for 2 min at a rate of 600 rpm. After that, it was mixed for an additional 10 min at 1800 rpm to obtain stable and homogenous emulsions. No phase separation was noted after 24 h.

2.3. Emulsion characterization

An optical microscope with $10\times$ magnification (Olympus BH-2) was used to verify the nature of the O/W-EMUL. The tests were performed by taking one drop from the O/W-EMUL and placing it onto a clean and smooth microscopic slide. The drop was allowed to seep out onto the plate with no external control. No cover glass was positioned on the emulsion sample, which helps to prevent movement of the emulsion. Images were taken for the boundary zones of oil–water droplets and were examined with specified software. A Lasentec® S400 A focused beam reflectance measurement (FBRM) supplied with a PI 14/206 probe (Mettler Toledo, 8 mm) was used to measure oil's actual droplet size distributions in oil the O/W-EMUL. The FBRM measurements were carried out at a temperature of 20 °C and an angle of 45°. The probe tip was placed under the emulsion surface in bottles mixed at the rate of 800 rpm to reduce the possibility of particles sticking on the probe. The FBRM uses a rotating laser beam that is reflected by the drops. The reflection times are converted into chord size distributions which are altered to actual droplet size distributions using a modification factor.

2.4. Demulsification experiments

The bottle experiments were consistent with the approach outlined by Guzman-Lucero et al. (2010a), Guzmán-Lucero et al. (2010b) and Flores et al. (2014). First, 50 ml of synthesized O/W-EMUL was added to graduated glass bottles. Second, 10 mg/L of each IL was added. All the bottles were mixed at a rate of 800 rpm and room temperature using a four-blade impeller for 1 min. Then, the bottles were permitted to stabilize and settle while registering the removed amounts of gasoline versus the time immediately after stopping the impeller. To examine the D%, the 50 mL of the synthesized emulsion was initially moved to the tubes. Thereafter, 10 mg/L of the IL was added without stirring. The ratio of IL to surfactant (Tween-80) was set at 10 mg/L_{ILs}:0.05 g/L_{sur}. A tube including 50 mL emulsion and no ILs were used as a blank sample. The D% versus time was verified immediately after the addition of the ILs. The D% was calculated using Eq. (1) (see Section 2.5). All tests were carried out in triplicate, and the average value and standard deviation (St.Dev.) at a 95% confidence level were used in reporting the data.

2.5. Characterization analysis

The ILs are formed from two parts cations and anions. The surfactant and ionic liquids present in the mixture after demulsification were analyzed using an Agilent 1200 High-Pressure Liquid Chromatography (HPLC) operated at 40 °C and equipped with a ZORBAX Eclipse XDBC18 column and detector. The detection wavelength was set at 220 nm (UV accurateness <0.2%) with a mobile phase mixture comprised of 35 vol% Na_2HPO_4 aqueous solutions and 65 vol% acetonitrile was supplied at a flow rate of 0.2 mL/min. The calibrated Tween-80 and IL anions samples were formed from HILs-1, HILs-2, Non-HIL, and Tween-80 surfactant. The presence of the anions ($N(CN)_2$, Cl^-, and Br^-) in the water phase, after demulsification, was examined by applying ion chromatography (IC-850 Professional I, Metrohm®), using anion and cation columns as well as a conductivity detector by calibrating Tween-80 and IL anions ($N(CN)_2$ Cl^-, and Br^-). The cation column eluent is an acidic mixture (1.7 mM 2,6-Pyridinedicarboxylic acid and 1.7 mM nitric acid) with a 1.25 mL/min flow rate. In contrast, the anion column eluent is a basic solution (7.5 mM Na_2CO_3 and 0.75 mM KOH) with a 1.0 mL/min flow rate.

Additionally, the aggregation performance of the ILs in the O/W-EMUL was assessed using an electrophoretic light scattering instrument (DLS; Zetasizer Nano ZS, Malvern Instrument Ltd., Malvern, UK). The performance of the ILs was also determined through the polydispersity index (PDI), hydrodynamic diameter (nm), and zeta potential at a concentration of 0.001 M KCl aqueous solution at 25 °C. The tests were conducted with samples diluted $100\times$ in deionized water at room temperature. The device was designed to replicate the process a minimum of five times. Moreover, the demulsification efficiency of the ILs using bottle and tube tests was assessed by determining the oil content by applying ultraviolet–visible

spectroscopy (UV–Vis, 400–800 nm). UV–Vis spectroscopy is used to determine the oil concentration in the O/W-EMUL systems. The absorption of UV radiation at 254 nm was linearly correlated to the total organic carbon (TOC) content in the mixture following Beer's law. Quality assurance and the detection limit of the absorption method were supported by presenting numerous solvent extraction measurements. This method includes choosing random samples and extracting the oil from water into carbon tetrachloride to verify the oil content using an NDIR analyzer (Elmobarak and Almomani, 2021a,b,c).

2.6. Definition of the demulsification efficiency using ILs

The percentage demulsification efficiency (D%) was calculated using Eq. (1). The D% is defined as the amount of oil removed from the emulsion, divided by the initial dissolved oil.

$$\text{demulsification efficiency (D\%)} = \frac{V_{t0,oil} - V_{t,oil}}{V_{t0,oil}} x100\% \tag{1}$$

$V_{t,oil}$ is the initial volume of oil introduced in the emulsion at t = 0, and $V_{t,oil}$ is the removed amount of gasoline at t = t. All the experiments were duplicated, and the error bars are shown in the corresponding figures.

2.7. Statistical analysis

The statistical analysis and t-test were conducted using the Prism GraphPad statistics software package. All the assessments were performed in triplicate, and the outcomes were presented as mean ± standard deviation (St.Dev.). The oil recovery findings were evaluated based on the St.Dev. and one-way analysis of variance (ANOVA). The ANOVA was conducted to confirm statistical variations in the reported oil recovery rates at a significance level of 5%. The one-way analysis of variance was implemented to compare the data. A value of $p < 0.05$ was noted as statistically significant.

3. Results and discussion

3.1. Emulsion analysis

The stability of the emulsion is associated with the type of emulsion, droplet size distribution, and the ratio between the two-phase volumes. Before examining the demulsification of the O/W-EMUL using the ILs, the synthesized emulsion samples were analyzed. The microscopy images of the O/W-EMUL (Fig. 2) indicate that oil particles fill most of the area, suggesting that the solution disperses the oil phase. As per the synthesis process, the volume of water added is greater than the gasoline oil. Thus, it may be concluded that the O/W-EMUL were generated. This was substantiated during the analysis as a pink color was observed in the water (i.e., continuous phase) produced by the potassium permanganate (KMNO$_4$). The KMNO$_4$ is an indicator used to identify the volume of the water phase during the microscopic analysis.

The Tween-80 surfactant is soluble in water, in congruence with Bancroft's principle, which states that the continuous phase occurs when the surfactant (i.e., emulsifying agent) is highly soluble (Bancroft, 2002). The emulsion droplet size distribution was evaluated at 800 rpm in a stirred vessel mixed using an FBRM device. After the addition of the surfactant, the electrostatic forces among the oil droplets are negligible. Consequently, the size distribution becomes smaller. Moreover, due to the coalescence of larger oil drops, the size distribution is altered to a lesser size over time because tiny droplets will remain in the emulsion. Similarly, reducing the numeric concentration of oil drops produces a secondary O/W mixture (formation of O/W-EMUL) (Benito et al., 2004).

Fig. 1 highlights how the droplet's diameter was generally <100 μm, with the most frequently observed particles between 1 to 15 μm. The microscopic analysis in Fig. 2 supports this. Additionally, the reported droplet size range is compatible with the values reported by other demulsification research (Lemos et al., 2010; Silva et al., 2013). The peak near 250 μm is assumed to be produced by air bubbles, and the noise is due to the formation of microbubbles as a result of high mixing speed. These microbubbles contribute to the separation of O/W by creating an airlifting or stripping action of oil droplets. Thereafter, the isolated air droplets are attached to the IL and removed from the emulsion. Excluding the air bubble effect, the adjusted droplets' mean diameter is 130 μm, which was consistent with research by Schuur et al. (2012).

3.2. The efficiency of ILs as demulsifiers

Fig. 3 illustrates the D% achieved by HIL-1, HIL-2, and the Non-HIL for the bottle test at different separation times between 0–100 min, conducted at an IL ratio to surfactant of mg/L$_{ILs}$ to 0.05 g/L$_{sur}$. The D% for the two halogenide ILs (HILs-1, HILs-2) after 20 min were 97.7%, 88.1%, respectively, which is significantly higher and faster than the D% reported for the Non-HILs. Conversely, the D% achieved by the Non-HIL after 20 min was 85.2% and 89.5%, respectively. As highlighted by previous research, the nature of the cation (i.e., molecular weight and length of side chains) and anion (i.e., size and water solubility) ILs significantly impacts the interfacial activity of the emulsion (Guzman-Lucero et al., 2010a; Lemos et al., 2010). Given that, the larger molecular weight of the HILs-1 and HILs-2 is a significant parameter for understanding
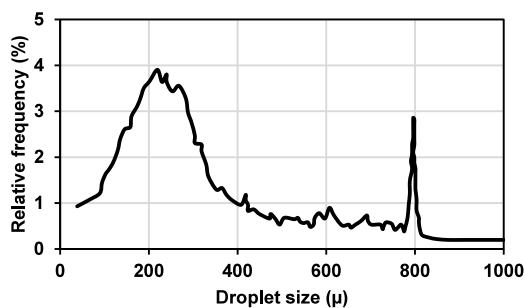
Fig. 1. The droplet size distribution of the synthesized gasoline O/W-EMULs (oil phase = gasoline oil; emulsifier agent = Tween-80 surfactant).
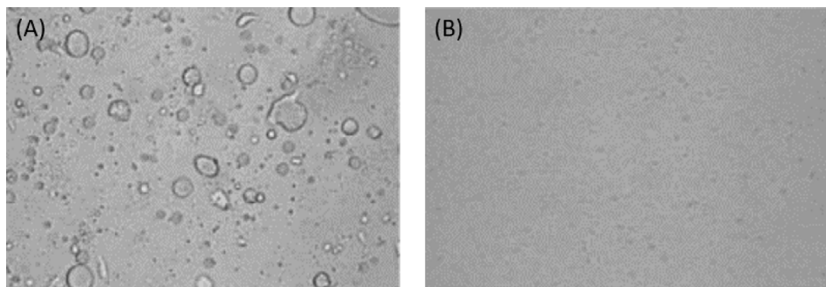

Fig. 2. (a) Microscopy image of the prepared emulsions (b) Microscopy image ($\times 10$ magnification). . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

its higher demulsification efficiency. It is thought that a larger molecular weight plays an integral role in increasing the capability of the HILs to behave as a flocculant to assemble the oil droplets. Further, the greater hydrophobic nature of the HIL cations may indicate their superior demulsification efficiency, as proposed by Silva et al. (2013). In comparison to the Non-HIL, the high content alkyl chains in the HILs contribute to a high demulsification efficiency.

As suggested by Li et al. (2016), to evaluate the D% using ILs and correlate the trends to IL characteristics (hydrophilic and hydrophobic), the conductor-like screening model for real solvents (COSMO-RS) technique was used to determine the partition coefficient (C_p) denoted as $\log_{10}(P_o/w)$.

An emulsion with C_p values in the range -8.3 to -10.7 is considered hydrophilic, producing significant separation efficiency by the hydrophobic HIL. It was assumed that the reported efficiency achieved in the present study was directly connected to this parameter. The higher and faster D% achieved by the HILs is dependent on the halogenide anions ratio, which is 100 times greater than the Non-HIL. It is likely that halogen anion's hydration acts as an essential component of the demulsification process and contributes to the higher D%. However, this supposition is inconsistent with the results reported by Li (2017). The researchers observed a lower D% efficiency for the HILs compared to the Non-HIL (Li, 2017). As such, further investigative research is needed to establish this correlation.

The low ionic charge on the HIL and the higher cationic portion generates hydrophobic properties with a high attachment to oil. Li et al. (2016) suggested that the integration between the anion and cation on the ILs is important for determining the hydrophobicity and hydrophilicity of the interfacial surface. Further, Li et al. (2016) exemplified how high surface activity was detected because of the integration of the hydrophobic cation ($P_{666,14}$) and the hydrophilic anionic portion [$N(CN)_2$]. This consequently lowers the D% for the Non-HIL. Further, Li et al. (2016) found that Non-HIL has no impact on the demulsification process as the total influence of anions with hydrophilic properties is small due to high hydrophilicity.

3.3. The efficiency of the demulsification process in tube tests

As the demulsification rate of the HILs is fast, it was difficult to examine the impact of the cation alkyl chain length on the reported D% using the bottle test. Given that, the demulsification tests were repeated using tube tests without mixing. This step was taken to control the D% at a measurable scale and carefully observe the amount of oil removed. The tube tests were conducted using the HIL-1, HIL-2, and the Non-HIL at a fixed IL to surfactant ratio. The concentration of ILs was twice-diluted using isopropanol (C_3H_8O) to reduce the viscosity (for greater control). Finally, the blank tests were performed by adding an equivalent volume of C_3H_8O to the emulsion.

The findings indicated that the handled emulsions achieved high stability after 24 h. It was also determined that the impact of the C_3H_8O on the demulsification process was insignificant. The D% of the three ILs is outlined in Fig. 4. Among
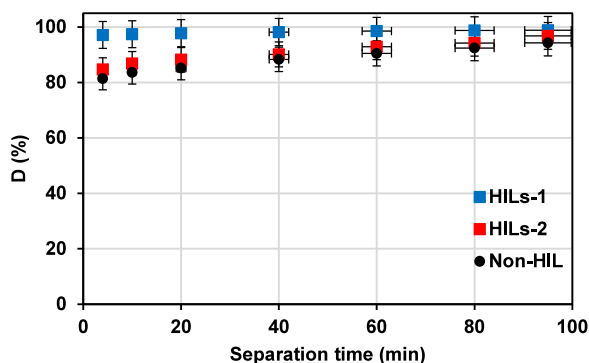
Fig. 3. D% of HIL-1, HIL-2, and the Non-HIL in bottle test at different separation times between 0–100 min with surfactant volume (V_{sur}) = 0.05 g/L and ILs volume (V_{ILs}) = 10 mg/L.
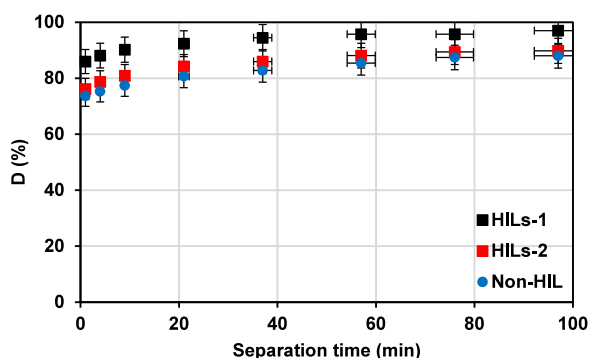

Fig. 4. D% of the three types of ILs in tube tests without mixing; surfactant volume (V_{sur}) = 0.05 g/L, ILs volume = (V_{ILs}) 10 mg/L.

all the examined ILs, the HIL-1 exhibited the greatest D%, followed by HIL-2 and then Non-HIL. The cation portion ($P_{666,14}$) in the Non-HIL exhibited shorter cation and better diffusivity. However, the surface action was reduced, which negatively affected the dispersity and D%.

In contrast, the significant removal rate by the HIL-1 and HIL-2 in a short time indicates that the overall amount of alkyl carbon in the cation plays an essential role in the removal process. (Though, the amount of alkyl carbon in every chain associated with phosphorus does not significantly affect the removal process.) Additionally, although the HIL-1 and HIL-2 have the same cation, the D% using HIL-1 is slightly faster than HIL-2. This difference occurred because of the small size of the Cl^- that slightly reduces Gibbs energy of hydration to -340 kJ/mol, which is lower than Gibbs energy of hydration for Br^- (-315 kJ/mol).

The observed trends suggest that the IL diffusion controls the D% in the tube tests rather than the emulsion near the interface between the bulk phase and particles. To explain the interaction between the surfactant and the ILs, the oil removal process in tubes was conducted with V_{ILs} of 10 mg/L from HILs-1 and HILs-2 and varying volumes of surfactant ranging between 0.05–0.5 g/L. As observed in Fig. 5, the highest D% was achieved after 50–90 min. The final D% corresponds to the volume of added ILs. All the tests with higher ILs and low surfactant concentrations achieved D% >95%. The oil recovery findings were evaluated depending on the St.Dev. and ANOVA. The statistical analysis relied on the factors that have statistical consequences on the oil separation efficiency. The ANOVA manipulation was consistent with the model terms with a P-value $\leq$ of 0.05, while the values more than 0.05 were judged as insignificant.

Table 2 presents a comparison between the demulsification process efficiency of both tube and bottle tests using the three IL types. As highlighted in Table 2, the highest demulsification efficiency was achieved using the two HIL in both bottle and tube tests. In addition, the D% for HIL-1 is marginally higher than HIL-2 and the Non-HIL. These results were observed because of the normal size of the Cl^- that slightly decreased Gibbs energy of Cl^-, which is lower than Gibbs energy of hydration for the two anions Br^- and $N(CN)_2$.

3.4. Zeta potential measurements

The oil droplets' zeta potential (ξ) was examined with varying IL concentrations of (C_{IL}) 10 mg/L, 30 mg/L, and 50 mg/L. The oil droplets ξ became less negative as the C_{IL} increased, indicating that IL cations and surfactants could be adsorbed at the O/W interface. Further, the surfactant present on the oil droplets surface can be replaced because of the anion exchange
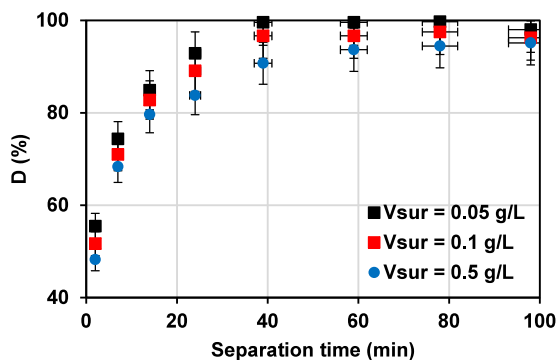
Fig. 5. Demulsification efficiency of HIL-1 in tube tests with surfactant volumes (V_{sur}) ranging from 0.05 g/L to 0.5 g/L and an IL volume (V_{ILs}) of 10 mg/L.

Table 2
A comparison between the efficiency of the demulsification process of tube and bottle tests using the three IL types.

Type of ionic liquid (ILs)	%D time (min)		
	20	50	90
Bottle test			
HILs-1	97.7%	>98%	>98.7%
HILs-2	88.1%	>90%	>94.2%
Non-HIL	85.2%	>88%	>92.4%
Tube tests			
HILs-1	92.3%	>94.4%	>85.7%
HILs-2	84.2%	>85.9%	>89.3%
Non-HIL	80.67%	>82.7%	>87.4%

mechanism. The ξ achieved a high value of ~-49 mV without adding ILs. However, after adding 10 mg/L of HILs-1, HILs-2, and Non-HIL, the ξ value decreased to -23 mV, -25.2 mV, and -29.3 mV, respectively. The reduction in the ξ of the oil droplets suggests a decrease in the electrostatic repulsion forces, subsequently encouraging their coalescence. The ILs and the emulsion surfactants are adsorbable on the oil particle's surface, altering the zeta potential. Although ILs contain both ionic and cationic parts, the adsorption increases the negative electric charge density on the surface of the oil particles. Thus, the stabilization of oil droplets occurs through the mechanism of electrostatic stabilization.

Additionally, the ILs lowered the charge on the surface of the oil particles, reduced the film's elasticity, and decreased the interfacial tension reduction rate, which led to faster phase separation. Therefore, depending on the zeta potential measurements during different phases, the presence of ILs can have a powerful impact on the value of the zeta potential on the O/W-EMUL system. Moreover, in this study, the addition of the ILs effectively reduced the value of the zeta potential. Similarly, the efficiency of the ILs in reducing the zeta potential values was evident in all IL-O/W systems, as reported by Ezzat et al. (2020). Thus, the ILs can "neutralize" the charge of the studied O/W-EMUL systems, which can cause wettability alteration and improve the oil recovery rates (Pillai et al., 2018).

3.5. Mechanism of the demulsification process using ILs

During the continuous and rapid separation of the oil and water phases through the HILs, some obscurity in both (oil and water) phases was noted. The lack of clarity is due to the precipitation of some solids in the samples (IL cations and the surfactant anions) rather than partial oil removal (i.e., demulsification). Though, lack of clarity as partial oil removal was shown with the remaining amount of water in the gasoline phase. The water concentrations, estimated with Karl-Fisher titration, were 2.89%, 10.3%, and 11.99% for HILs-1, HILs-2, and the Non-HIL, respectively, suggesting an effective demulsification. The flocculated compounds (resulting from the IL cation and the surfactant anion) indicated that the ion exchange between the surfactant and the ILs occurred. A further indication of the ion exchange mechanism was achieved with the analysis of the water phase using ion chromatography (IC) after the oil recovery process and the addition of the ILs. The IC findings exemplify how all Na^+ remained in the water phase, with $> 86\%$ of Cl^- or Br^- anions. A faster demulsification process occurred with the use of HILs-1, HILs-2, and Non-HIL. Because of the densities, the ILs allowed us to see three phases: the oil phase on top, the water phase on the bottom, and the IL droplets as the mid-phase.

To identify the demulsification process mechanism using HILs-1, HILs-2, and Non-HIL, the volume of surfactant and the three ILs in the water phase (after the oil removal process) were examined using an HPLC device. The analysis exemplified
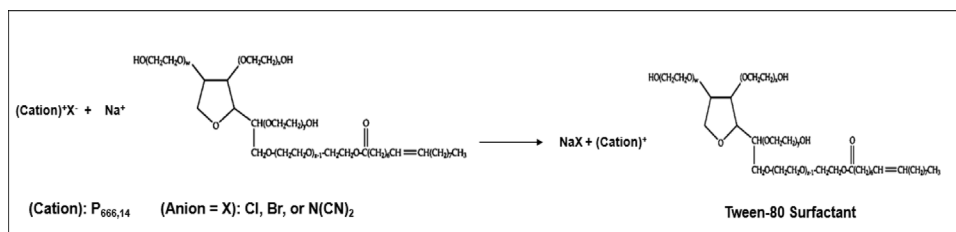
Fig. 6. Anion exchange reaction between Tween-80 surfactant and the three IL types (HILs-1, HILs-2, and the Non-HIL).

oil removal percentages of 89.3%, 88.5%, and 87% for three ILs, respectively, in the water phase. The IC findings also demonstrated that all the Na^+ remained in the water phase. This exemplifies how the demulsification mechanism with the three IL types was an anion exchange. Fig. 6 highlights that during the demulsification process, a chemical reaction based on an ion exchange occurs between ions and the hydrophilic part of the ILs. This reaction exhibited excellent driving force and rapid demulsification when HILs was confirmed by a high value of Gibbs energy for Cl^- and Br^- hydration compared with sodium. The ion hydration Gibbs energy values at $298.15°K$ were -315 kJ/mol, -340 kJ/mol, and -365 kJ/mol for the bromide (Br^-), chloride (Cl^-), and sodium (Na^+), respectively. It was observed that the interaction between cations from ILs and the surfactant created an additional phase that provided an extra driving force for higher demulsification efficiency. The cation-surfactant integrations were determined to be hydrophobic with high dispersion in water, the conditions that improve the separation efficiency. As such, the ionic strength of ILs contributes to the dispersion of phases and the overall efficiency.

The demulsification mechanism of the O/W-EMUL using ionic liquids contains two essential stages: diffusion and adsorption. The diffusion method disperses the IL particles in the continuous phase before reaching the O/W interface. On the other hand, the adsorption method suggests that the dispersed IL molecules move across the continuous phase (water) to the O/W interface (Hezave et al., 2013; Hassanshahi et al., 2020). Then, the IL particles replace the natural emulsifying agents (i.e., surfactants) at the interface and alter the viscoelastic properties of the interfacial films. This results in a separation of the strong film over the O/W drop and improves the coalescence of the distributed drops (Martínez-Palou and Aburto, 2015; Grenoble and Trabelsi, 2018).

The oil particles present in the emulsion are steadied using the surfactant, which remains at the O/W interface with the hydrophilic polyoxyethylene *group* (marked in red in Fig. 7) (Shi and Guo, 2010; Zolghadr et al., 2014). This group faces the water and hydrophobic chains that connect with the oil (Shi and Guo, 2010; Zolghadr et al., 2014). The sodium cations (marked in green in Fig. 7 are distributed in water and produce an electric dual-layer, preventing droplet interaction and increasing the droplets. After adding efficient IL demulsifiers (cations marked in black including Cl^-, Br^-, $N(CN)_2$, and anions in blue) to the emulsions, the interface is damaged because of the IL and surfactant ion exchange. The damage decreases the oil droplets electrostatic repulsion and affects the stability of the emulsion. Thereafter, the oil is removed from the water phase (Fig. 7a). The recently produced flocculate substances accumulate to create the third phase, as exemplified in Fig. 7b. This substantiates the high efficiency of the ILs as demulsifiers for O/W-EMULs applying an ion exchange mechanism. Because of the ion exchange mechanism in the demulsification process, the anions escape into the water phase and the cations integrate with the surfactant. For the IL and surfactant regeneration, an inversed ion exchange procedure is required. However, such a procedure may restrict the industrial ability of the ILs as demulsifiers for the treatment of O/W-EMUL. As such, future research is required on the regeneration of ILs that apply ion exchange methods. Further, to make the IL demulsification process more economic, appropriate recycling methods should be used.

The IL properties and characteristics play a significant role in the demulsification process. (Patel and Lee, 2012). Most researchers favor creating and producing room temperature ionic liquids (RTIL). The RTIL can be obtained by producing nitrogen or phosphorous organic cations with various organic anions, inorganic anions, dicyanamide, chloride, bromide, acetate, trifluoromethyl sulfate, or hexafluorophosphate (Berthod et al., 2008). ILs are an appealing O/W interface because of their amphiphilic nature. Further, they interact with the polar parts of crude oil because of their dielectric properties (Guzman-Lucero et al., 2010a; Guzmán-Lucero et al., 2010b; Lemos et al., 2010). ILs also have an amphiphilic structure, which attracts them to the oil and water phases, as they prefer the movement of the surfactants, consequently leading to an effective removal (Martínez-Palou and Aburto, 2015; Shehzad et al., 2018). The amphiphilic character may be in the cation or anion portion of the IL structure. Recent research has shown that hydrophobic surface-active ILs can be effectively used to demulsify O/W-EMUL in the oil and gas industries (Forsyth et al., 2004; Atta et al., 2016). The study conducted by Hazrati et al. (2018) noted that hydrophobic ILs (e.g., HIL-1 and HIL-2) are better than hydrophilic ILs for the demulsification process (e.g., Non-HIL). Moreover, Hazrati et al. (2018) obtained a total petroleum hydrocarbon recovery of 95%.

4. Conclusion and future prospective

- Halogenide ionic liquids with hydrophobic cations and non-halogenide ionic liquids efficiently separated oil from O/W-EMUL. An excellent demulsification efficiency was also demonstrated when similar volumes of ILs and surfactant were used (D% >95%).
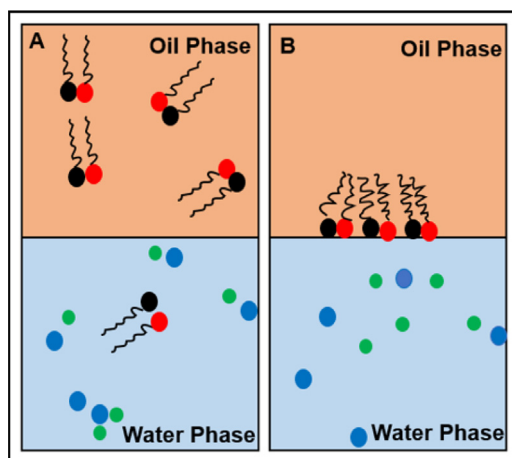
Fig. 7. Demulsification mechanism of O/W-EMULs using ILs. (a) Formation of ILs as flocculates after the addition of IL cations in both phases, and the formation of two liquid phases (gasoline oil and water) after the demulsification process (b) The produced IL precipitation and formation of a third phase between the oil and water phases (the place relied on the three phases densities). . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

- Bottle tests showed that the demulsification process using HILs has a higher oil removal rate than Non-HIL (D% of 97.7%, 88.2%, and 85.3% for HIL-1, HIL-2, and Non-HIL, respectively).
- The mechanism of the demulsification process is an ion exchange between the surfactant and the anions of the ILs, which is controlled by the discharge of sodium salt into the water phase. Moving forward, inversed ion-exchange methods are required to regenerate these ILs, which will likely reduce their industrial application as demulsifiers.
- The demulsification efficiency can be improved by choosing appropriate ILs, IL amounts for certain emulsion types and determining the optimum treatment conditions.
- ILs are green solvents, making them suitable for several potentially dangerous and volatile organic solvents currently used for oil removal.
- Although there are many advantages of ILs, their disadvantages need further investigation to determine their appropriateness for widespread usage. Further research should focus on the recycling and regeneration of ILs. A greater examination is also required to enhance the application of ILs, including verifying the best-operating conditions to reduce the necessary concentration of ILs to achieve the required D%.

Nomenclature

ILs	Ionic liquids
O/W-EMULs	Oil in Water emulsions
W/O-EMULs	Water in Oil emulsions
HILs	Halogenide ionic liquids
Non-HILs	Non-halogenide ionic liquids
D%	Demulsification efficiency
IFT	Interfacial tension
V_{sur}	Surfactant volume
V_{IL}	Ionic liquid volume
EOR	Enhanced oil recovery
g/L	gram/liter
mg/L	milligram/liter
mL/min	milliliter/minute
min	minute
vol%	volume%
h	hour

CRediT authorship contribution statement

Wamda Faisal Elmobarak: Conceptualization, Methodology, Modeling, Figures preparation, Software, Pre-writing, Validation, Tables preparation, Writing – review & editing, Writing – original draft, Data curation, Discussion. **Fares Almomani:** Conceptualization, Methodology, Modeling, Figures preparation, Software, Pre-writing, Validation, Tables preparation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abdullah, M.M., AlQuraishi, A.A., Allohedan, H.A., AlMansour, A.O., Atta, A.M., 2017. Synthesis of novel water-soluble poly (ionic liquids) based on quaternary ammonium acrylamidomethyl propane sulfonate for enhanced oil recovery. J. Molecular Liquids 233, 508–516.

Arjmand, O., Roostaei, A., 2014. Experimental investigation of viscous surfactant-based enhanced oil recovery. Pet. Sci. Technol. 32 (13), 1607–1616.

Atta, A.M., Al-Lohedan, H.A., Abdullah, M.M., ElSaeed, S.M., 2016. Application of new amphiphilic ionic liquid based on ethoxylated octadecyl ammonium tosylate as demulsifier and petroleum crude oil spill dispersant. J. Ind. Eng. Chem. 33, 122–130.

Bancroft, W.D., 2002. The theory of emulsification, V. J. Phys. Chem. 17 (6), 501–519.

Benito, J.M., Ríos, G., Pazos, C., Coca, J., 2004. Droplet Size Distribution of Oil-Water Emulsions By Confocal Laser Scanning Microscopy. ACS Publications.

Bera, A., Mandal, A., Guha, B., 2014. Synergistic effect of surfactant and salt mixture on interfacial tension reduction between crude oil and water in enhanced oil recovery. J. Chem. Eng. Data 59 (1), 89–96.

Berthod, A., Ruiz-Angel, M., Carda-Broch, S., 2008. Ionic liquids in separation techniques. J. Chromatogr. A 1184 (1–2), 6–18.

Dalmazzone, C., Noïk, C., Argillier, J.-F.o., 2012. Impact of chemical enhanced oil recovery on the separation of diluted heavy oil emulsions. Energy Fuels 26 (6), 3462–3469.

Elmobarak, W.F., Almomani, F., 2021a. Application of Fe3O4 magnetite nanoparticles grafted in silica (SiO2) for oil recovery from oil in water emulsions. Chemosphere 265, 129054.

Elmobarak, W.F., Almomani, F., 2021b. Application of magnetic nanoparticles for the removal of oil from oil-in-water emulsion: Regeneration/reuse of spent particles. J. Pet. Sci. Eng. 203, 108591.

Elmobarak, W.F., Almomani, F., 2021c. Enhanced oil recovery using hyperbranched polyglycerol polymer-coated silica nanoparticles. Chemosphere 131295.

Elmobarak, W.F., Almomani, F., 2021d. A new insight into the separation of oil from oil/water emulsion by Fe3O4–SiO2 nanoparticles. Environ Res 202, 111645. http://dx.doi.org/10.1016/j.envres.2021.111645.

Elmobarak, W.F., Almomani, F., 2021e. Functionalization of silica-coated magnetic nanoparticles as powerful demulsifier to recover oil from oil-in-water emulsion. Chemosphere 279, 130360. http://dx.doi.org/10.1016/j.chemosphere.2021.130360.

Ezzat, A.O., Atta, A.M., Al-Lohedan, H.A., Aldalbahi, A., 2020. New amphiphilic pyridinium ionic liquids for demulsification of water Arabic heavy crude oil emulsions. J. Molecular Liquids 312, 113407.

Flores, C.A., Flores, E.A., Hernández, E., Castro, L.V., García, A., Alvarez, F., Vázquez, F.S., 2014. Anion and cation effects of ionic liquids and ammonium salts evaluated as dehydrating agents for super-heavy crude oil: Experimental and theoretical points of view. J. Molecular Liquids 196, 249–257.

Forsyth, S.A., Pringle, J.M., MacFarlane, D.R., 2004. Ionic liquids—an overview. Aust. J. Chem. 57 (2), 113–119.

Grenoble, Z., Trabelsi, S., 2018. Mechanisms, performance optimization and new developments in demulsification processes for oil and gas applications. Adv. Colloid Interface Sci. 260, 32–45.

Guzman-Lucero, D., Flores, P., Rojo, T., Martínez-Palou, R., 2010a. Ionic liquids as demulsifiers of water-in-crude oil emulsions: study of the microwave effect. Energy Fuels 24 (6), 3610–3615.

Guzmán-Lucero, D., Flores, P., Rojo, T., Martínez-Palou, R., 2010b. Ionic liquids as demulsifiers of water-in-crude oil emulsions: study of the microwave effect. Energy Fuels 24 (6), 3610–3615.

Hassanshahi, N., Hu, G., Li, J., 2020. Application of ionic liquids for chemical demulsification: A review. Molecules 25 (21), 4915.

Hazrati, N., Beigi, A.A.M., Abdouss, M., 2018. Demulsification of water in crude oil emulsion using long-chain imidazolium ionic liquids and optimization of parameters. Fuel 229, 126–134.

Hezave, A.Z., Dorostkar, S., Ayatollahi, S., Nabipour, M., Hemmateenejad, B., 2013. Investigating the effect of ionic liquid (1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl]) on the water/oil interfacial tension as a novel surfactant. Colloids Surf. A 421, 63–71.

Hirasaki, G.J., Miller, C.A., Raney, O.G., Poindexter, M.K., Nguyen, D.T., Hera, J., 2011. Separation of produced emulsions from surfactant enhanced oil recovery processes. Energy Fuels 25 (2), 555–561.

Hou, J., Liu, Z., Zhang, S., Yang, J., 2005. The role of viscoelasticity of alkali/surfactant/polymer solutions in enhanced oil recovery. J. Pet. Sci. Eng. 47 (3–4), 219–235.

Janssen, C.H., Sánchez, A., Witkamp, G.J., Kobrak, M.N., 2013. A novel mechanism for the extraction of metals from water to ionic liquids. ChemPhysChem 14 (16), 3806–3813.

Ko, K.M., Chon, B.H., Jang, S.B., Jang, H.Y., 2014. Surfactant flooding characteristics of dodecyl alkyl sulfate for enhanced oil recovery. J. Ind. Eng. Chem. 20 (1), 228–233.

Lemos, R.C., da Silva, E.B., dos Santos, A., Guimaraes, R.C., Ferreira, B.M., Guarnieri, R.A., Dariva, C., Franceschi, E., Santos, A.F., Fortuny, M., 2010. Demulsification of water-in-crude oil emulsions using ionic liquids and microwave irradiation. Energy Fuels 24 (8), 4439–4444.

Li, X., 2017. Ionic liquids in separations: applications for pyrolysis oil and emulsion systems.

Li, X., Kersten, S.R., Schuur, B., 2016. Efficiency and mechanism of demulsification of oil-in-water emulsions using ionic liquids. Energy Fuels 30 (9), 7622–7628.

Martínez-Palou, R., Aburto, J., 2015. Ionic liquids as surfactants–applications as demulsifiers of petroleum emulsions. The ionic liquid current state of the art. pp. 305–326.

Nabipour, M., Ayatollahi, S., Keshavarz, P., 2017. Application of different novel and newly designed commercial ionic liquids and surfactants for more oil recovery from an Iranian oil field. J. Molecular Liquids 230, 579–588.

Nguyen, D., Sadeghi, N., Houston, C., 2012. Chemical interactions and demulsifier characteristics for enhanced oil recovery applications. Energy Fuels 26 (5), 2742–2750.

Nikkhah, M., Tohidian, T., Rahimpour, M.R., Jahanmiri, A., 2015. Efficient demulsification of water-in-oil emulsion by a novel nano-titania modified chemical demulsifier. Chem. Eng. Res. Des. 94, 164–172.

Painter, P., Williams, P., Lupinsky, A., 2010b. Recovery of bitumen from Utah tar sands using ionic liquids. Energy Fuels 24 (9), 5081–5088.

Painter, P., Williams, P., Mannebach, E., 2010a. Recovery of bitumen from oil or tar sands using ionic liquids. Energy Fuels 24 (2), 1094–1098.

Patel, D.D., Lee, J.M., 2012. Applications of ionic liquids. Chem. Rec. 12 (3), 329–355.

Pillai, P., Kumar, A., Mandal, A., 2018. Mechanistic studies of enhanced oil recovery by imidazolium-based ionic liquids as novel surfactants. J. Ind. Eng. Chem. 63, 262–274.

Razi, M., Rahimpour, M.R., Jahanmiri, A., Azad, F., 2011. Effect of a different formulation of demulsifiers on the efficiency of chemical demulsification of heavy crude oil. J. Chem. Eng. Data 56 (6), 2936–2945.

Salam, K., Alade, A., Arinkoola, A., Opawale, A., 2013. Improving the demulsification process of heavy crude oil emulsion through blending with diluent. J. Pet. Eng..

Schuur, B., Kraai, G.N., Winkelman, J.G., Heeres, H.J., 2012. Hydrodynamic features of centrifugal contactor separators: Experimental studies on liquid hold-up, residence time distribution, phase behavior and drop size distributions. Chem. Eng. Process.: Process Intensif. 55, 8–19.

Shehzad, F., Hussein, I.A., Kamal, M.S., Ahmad, W., Sultan, A.S., Nasser, M.S., 2018. Polymeric surfactants and emerging alternatives used in the demulsification of produced water: A review. Polym. Rev. 58 (1), 63–101.

Shi, W.-X., Guo, H.-X., 2010. Structure, interfacial properties, and dynamics of the sodium alkyl sulfate type surfactant monolayer at the water/trichloroethylene interface: A molecular dynamics simulation study. J. Phys. Chem. B 114 (19), 6365–6376.

Silva, E.B., Santos, D., Alves, D.R., Barbosa, M.S., Guimaraes, R.C., Ferreira, B.M., Guarnieri, R.A., Franceschi, E., Dariva, C., Santos, A.F., 2013. Demulsification of heavy crude oil emulsions using ionic liquids. Energy Fuels 27 (10), 6311–6315.

Yousefi, M., Naseri, A., Abdouss, M., Beigi, A.M., 2017. Synthesis and characterization of eight hydrophilic imidazolium-based ionic liquids and their application on enhanced oil recovery. J. Molecular Liquids 248, 370–377.

Zolghadr, A.R., Ghatee, M.H., Zolghadr, A., 2014. Adsorption and orientation of ionic liquids and ionic surfactants at heptane/water interface. J. Phys. Chem. C 118 (34), 19889–19903.