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Chapter

Chemical Enhanced Oil Recovery Using Ionic Liquid-Based Surfactants

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Abstract

Critical challenges have forced the oil industry to improve chemical enhanced oil recovery (CEOR) processes using more effective materials. In this regard, ionic liquid-based surfactants (IL-based surfactants) with noteworthy features such as good interfacial activity, recyclability, environmentally friendliness, and stability at high temperatures and salinity can be considered as a significant option. While IL-based surfactants have been of interest in various fields, their applications in CEOR have not been systematically reviewed. In this frame, this chapter overviews the performance of IL-based surfactants in different portions of oil production. For this purpose, a brief explanation of the characteristics of the IL-based surfactants and their applicability in CEOR is first provided. Then, the performance of the IL-based surfactants in surfactant flooding, micellar flooding, and wettability alteration are surveyed in detail. Also, the activity of IL-based surfactants in all three regions has been monitored with the effect of the chemical structure, as well as comparing the performance of different types of IL-based surfactants. Relevantly, a comparison with conventional surfactants is also included. The crucial challenges and possible directions for the use of IL-based surfactants and the conclusions are summarized in the final section.

Keywords: ionic liquid-based surfactants, surfactant flooding, micellar flooding, wettability alteration, chemical enhanced oil recovery

1. Introduction

With existing many challenges facing the oil industry, including dwindling crude oil reserves and the limited possibility of finding new oil fields, and more importantly, only one-third of the original oil in place (OOIP) can be recovered through primary and secondary oil recovery, the oil industry needs to pursue chemical enhanced oil recovery (CEOR) techniques [1]. Among the various methods, the use of surfactants, which focuses on reducing interfacial tension (IFT) and microemulsion formation as well as wettability modification has attracted much attention [2]. However, the low resistance and poor performance of conventional surfactants at high temperatures and salinity conditions have convinced researchers to use more effective and economical materials in this field [3].

Ionic liquid-based surfactants (IL-based surfactants) can be considered a significant alternative in CEOR. Most IL-based surfactants exhibit powerful interfacial activity compared to conventional surfactants with the same molecular structure [4, 5]. IL-based surfactants by adsorbing at the oil-water interface can reduce IFT and form microemulsion, and by changing the properties of reservoir rock surfaces alter wettability, which completely rises the mobility of crude oil in the reservoirs, and as a result of oil production increases [3, 5]. Relevantly, the unique properties of IL-based surfactants, such as stability at high temperatures and salinity as well as their environmentally friendly nature, make them suitable for CEOR [6, 7]. As another effect, high molecular weight IL-based surfactants can increase the viscosity of the injected fluid and provide sweeping efficiency [8]. Additionally, IL-based surfactant molecules are adjustable and by inserting the appropriate cation/anion into their structures, task-specific IL-based surfactants can be employed in CEOR [4]. Accordingly, various types of IL-based surfactants, including Cationic, Anionic, Multicationic, Catanionic, and Zwitterionic, have been synthesized and their remarkable properties have been investigated [3].

Despite IL-based surfactants indicating favorable results in the oil industry, screening their performance in different aspects of oil recovery is a necessary step before using them for large-scale CEOR. In spite of many efforts, no comprehensive report has been provided in this field. Thus, this chapter first provides a brief description of the IL-based surfactant characteristics and their applicability in the oil industry. In the next step, the performance of the IL-based surfactant in the important regions of CEOR is surveyed. These regions include the following:

- Surfactant flooding
- Micellar flooding
- Wettability alteration

Relevantly, the effect of the chemical structure of the IL-based surfactant and the characteristics and outstanding performance of the new types of IL-based surfactant are considered to highlight the advantages of the respective materials [3, 4, 7, 9]. To select the most suitable surfactants and display higher interfacial activity, a brief comparison between the IL-based surfactant and conventional surfactants is presented subsequently. In the final step, the important challenges as well as possible directions and conclusions of this chapter are summarized in the last section. Overall, this chapter aims is to provide in-depth information on the use of IL-based surfactants in the oil industry and to pave the way for the development of better IL-based surfactants that may meet the requirements of the CEOR processes.

2. Characteristics of ionic liquids

2.1 Ionic liquids and their properties

Ionic liquids (ILs) are composed of organic cations and inorganic/organic anions [4]. The steric asymmetry between the size and morphology of the ions causes mismatches and the formation of unstable crystal lattices, which lowers the melting point [10]. ILs have melting points below 100°C, and room temperature ionic liquids

(RTILs) specifically refer to salts that form electrolytes that are liquid in the room temperature range or even below [3]. For a better explanation, a comparison between the structure of the IL and common salt is presented in **Figure 1**.

The remarkable properties of IL, such as high chemical and thermal stability even under harsh conditions, low vapor pressure, recyclability, non-flammability, and an environmentally friendly manner, confirm a large number of applications of these materials [11, 12]. Furthermore, the properties of IL can be upgraded by modifying/altering various parts of their molecular structure, usually by simple strategies, making them “designer” materials [13, 14]. In this regard, many organic cations can be coupled to various inorganic or organic anions, ranging from simple inorganic ions to more complex organic species. For better illustration, some commonly used cations and anions are presented in **Figure 2**. As well, some general ILs specifications are listed in **Table 1**.

2.2 Ionic liquid-based surfactant

IL-based surfactants are a class of ILs that have both hydrophilic (lipophobic, water liking, or oil disliking) and hydrophobic (lipophilic, oil liking, or water

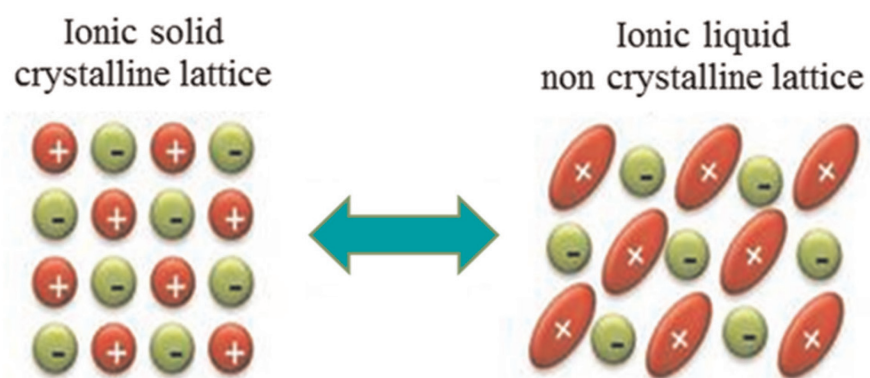


Figure 1.
Comparison between the structure of the IL and common salt.

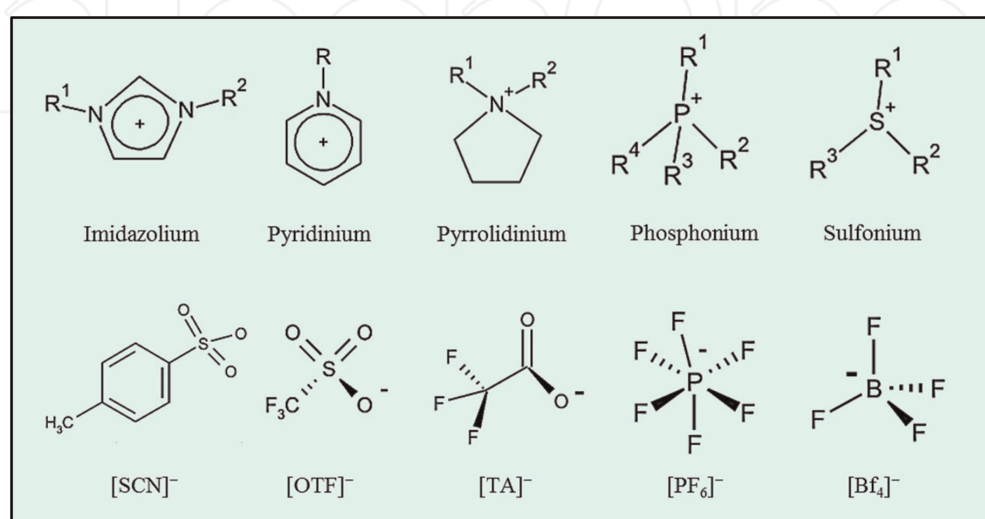


Figure 2.
Some conventional IL cations and anions.

Melting point	Below 100°C
Liquidus range	Often more than 200°C
Thermal stability	High
Chemical stability	High
Viscosity	Normally less than 100 cPo
Polarity	Moderate
Specific conductivity	Less than 10 mS.cm ⁻¹
Solvent or catalyst	Good for a lot of reactions
Vapor pressure	Negligible

Table 1.
General ILs specifications [3].

disliking) groups that are “amphiphilic” in nature [3, 4]. To better illustrate, the three major parts of the chemical structure of $[C_6mim][Br]$, as a common Cationic IL-based surfactant, include the hydrophobic side chains and the hydrophilic head group, which form the cationic portion, as well as the counter anion are shown in **Figure 3**.

The ionic or polar hydrophilic group gives water solubility to IL-based surfactants; however, the organic hydrophobic group gives them oil solubility. After the dissolving of IL-based surfactants in the aqueous or oil phase, like conventional surfactants, their molecules are adsorbed at the oil-water interface in the way that the hydrophilic portions are adjacent to the water phase and the hydrophobic portions are adjacent to the oil phase. This structure provides different interfacial activities for the IL-based surfactant such as IFT reduction and emulsion formation. On the other hand, partial adsorption of IL-based surfactant on the solid surface of rocks changes the surface properties, and depending on the interface orientation the surface wettability can be changed [5]. These points will be discussed in detail in the following sections.

2.3 Impact of the structure of ionic liquid-based surfactant

There is a strong relationship between the chemical structures of IL-based surfactant and their properties. In general, IL-based surfactant has three major parts in its

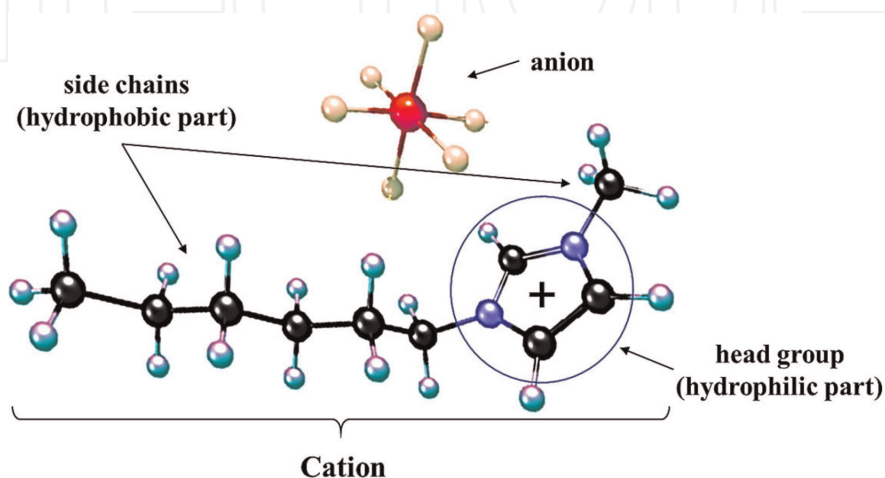


Figure 3.
The three major parts of the chemical structure of $[C_6mim][Br]$.

molecule: alkyl chain, head group, and counter anion. By changing the structure of these parts, the characteristics of the IL-based surfactant can be modified for specific applications [15, 16]. For example, the hydrophobicity, interfacial activity, miscibility, and thermal stability of IL-based surfactant can be improved by altering the structure of the counter anions, while the hydrophobicity, interfacial activity, adsorption tendency, aggregate formation, viscosity, and density are significantly changed with head groups and/or the alkyl chains structure [3]. In this regard, an overview of the characteristics of IL-based surfactants concerning to different parts of their structure is described here.

2.3.1 Alkyl chain

The length of alkyl chains and the number of involved branches are two important factors for IL-based surfactant characteristics that affect the hydrophobicity, solubility, interfacial activity, and adsorption tendency of IL-based surfactants. A longer alkyl chain provides more adsorption tendency, hydrophobicity, and interfacial activity for IL-based surfactant, however, the solubility in the water phase is reduced. The longer hydrophobic chain also causes more van der Waals attraction between the IL-based surfactants molecules and the crude oil phase, leading to highly stable adsorption at the interface. The same behavior has been observed for the second alkyl chain in the IL-based surfactant structure, if present [17, 18].

2.3.2 Head group

The structure of the head group can affect the hydrophilicity character of the IL-based surfactant. The size of the head groups, the presence of the π -electron ring, and their polarity have distinct effects on the hydrophilicity and interfacial activity of IL-based surfactants. Generally, due to their greater hydrophobicity, poor hydration, and low electrostatic repulsion forces, bulky heterocyclic head groups with π -electron rings cause better IFT reductions compared to those with simple groups. These head groups facilitate migration and lead to greater adsorption at the interface. In this respect, the widely studied IL-based surfactant for IFT reduction includes bulky and asymmetric organic cations such as imidazolium, pyridinium, ammonium, sulfonium, phosphonium, pyrrolidinium, pyrazolium, thiazolium, and guanidinium [19, 20].

2.3.3 Counter anion

The nature of the counter anions affects the miscibility of IL-based surfactants in polar/non-polar solvents and their interfacial activity, although to a lesser extent compared to the alkyl chain and the head group. The molecular dynamics simulations studies confirm that bulkier and more polarizable counter anions increase the interfacial activity of IL-based surfactants. This is because large counter anions are less prone to effective hydration, making them easier to adsorb at the interface, which reduces the electrostatic repulsion between the head groups and facilitates IFT reduction. Also, cations can easily penetrate the electron cloud of the bulky and polarizable counter anions, which facilitates interfacial adsorption. Some common inorganic and organic anions in IL-based surfactants are hexafluorophosphate $[\text{PF}_6]^-$, tetrafluoroborate $[\text{BF}_4]^-$, acetate, $[\text{Ac}]^-$, alkyl sulfate $[\text{AS}]^-$, bis(trifluoromethylsulfonyl)imide $[\text{NTf}_2]^-$, trifluoromethanesulfonate, $[\text{OTf}]^-$, and halides [13, 21].

In some IL-based surfactants, the counter anions have an alkyl chain that affects the activity of IL-based surfactant. In these cases, by increasing alkyl chain length, more hydrophobicity and less hydration are expected, leading to higher IL-based surfactants adsorption even at low concentrations, which provides the higher interfacial activity [22].

2.4 New types of IL-based surfactants

Various types of IL-based surfactants with specific properties and different structures have been used in the oil industry, which is schematically shown in **Figure 4**. In general, IL-based surfactants can be classified as follows based on the nature of the surface active moiety and the number of head groups [3, 4, 23].

The “Cationic” type, in which surface active parts have a positive charge and are the most usual IL-based surfactant.

The “Anionic” type, consists of long alkyl chain anions, with or without branches, coupled to rather large heterocyclic cations. As an important advantage, Anionic IL-based surfactants have lower toxicity compared to other types of IL-based surfactants.

The “Catanionic” type, in which both cationic and anionic parts have a surface active character. This structure provides the higher interfacial activity. The asymmetry in the cation and anion parts, as well as linear or branched alkyl chains, are the factors affecting their activity.

The “Multicationic” type, in which more than one hydrophilic head group, each attached to hydrophobic alkyl chains, is connected with a spacer giving them high interfacial activity. This structure provides good hydrophobicity, high IFT reduction, desired micellization, and low toxicity. Here, the length and structure of the spacer play an important role in the hydrophobicity and molecular orientation at the interface.

The “Zwitterionic” type, in which the cationic and anionic parts are linked together by a covalent bond. With this structure, the electrostatic repulsion of charged groups is neutralized giving ordered and intense molecular orientations at the interface.

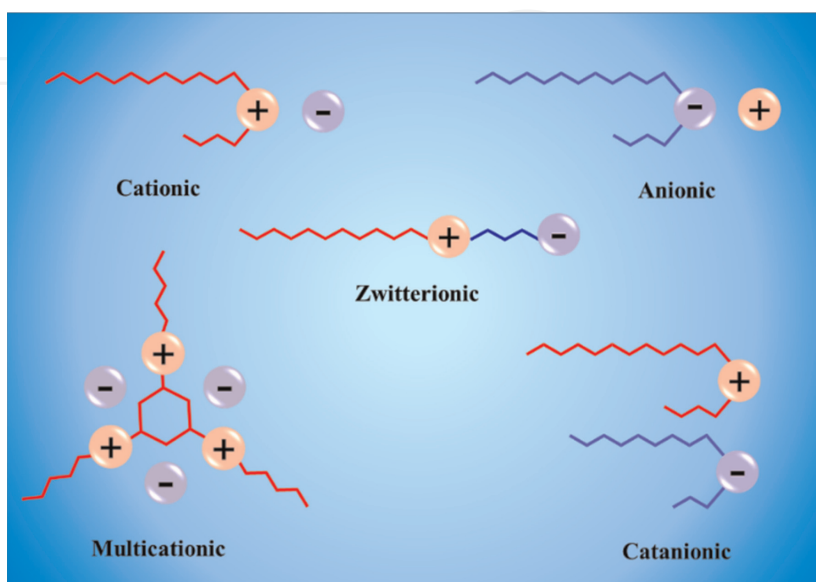


Figure 4. Schematic of the different types of IL-based surfactants.

It is worth noting that novel nanostructured IL-based surfactants have recently been successfully designed, synthesized, and tested under various conditions [24–26]. This new type of IL-based surfactant shows good interfacial activity and exhibits some nanoparticle properties that make it significant material in various aspects of the oil industry. However, their investigation is in the early stages and more research is needed in this area.

3. Chemical enhanced oil recovery and ionic liquid-based surfactants

3.1 Enhanced oil recovery

Crude oil is a natural source of petroleum that consists of carbon, nitrogen, oxygen, and sulfur elements as well as traces of metals. Crude oil naturally forms in the earth's porous rock deposits, "oil reservoirs". Such a complex mixture of crude oil is divided into four components: Saturates (S), Aromatics (A), Resins (R), and Asphaltenes (A), which are abbreviated as SARA [27]. Different crude oils are classified based on their composition, i.e. SARA percentage and API degree.

Although the energy consumption is growing worldwide and is estimated to quadruple by the year 2100 [28], dwindling crude oil reserves, the low probability of discovering new oil fields, and meeting demand for crude oil pose a serious challenge to the oil industry. Furthermore, the use of primary and secondary recovery techniques could only extract one-third of the original oil in place (OOIP) [2]. To solve these problems, most of the mature oil fields in the world require enhanced oil recovery (EOR) techniques to maintain their production levels. EOR is the process of injecting gases, chemicals, and/or using thermal energy to recover excess crude oil [1]. The main subdivisions of the EOR methods are shown in **Figure 5**. Among them, chemical enhanced oil recovery (CEOR) is notable due to its efficiency and low cost handling. In this method, selected chemicals such as surfactants, alkalis, polymers, and organic solvents are used. To facilitate a more comprehensive comparison, the advantages and disadvantages of different EOR methods are summarized in **Table 2**.

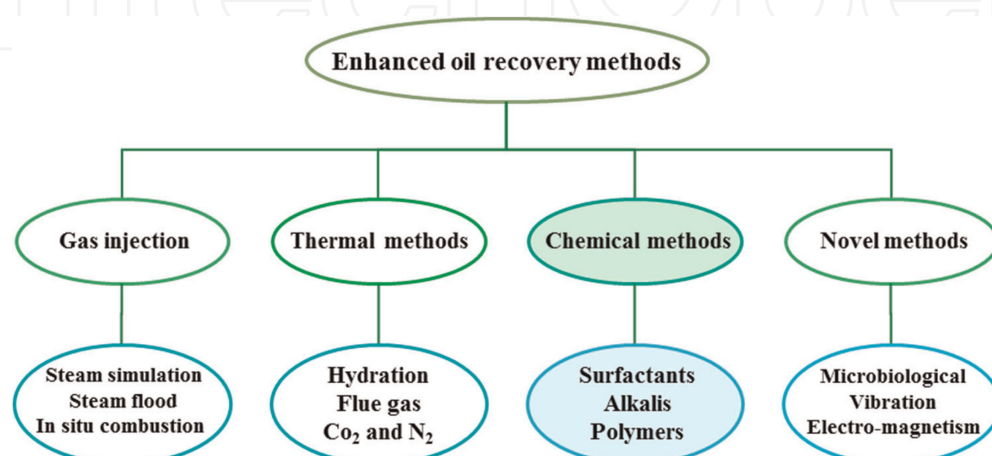


Figure 5.
The classification of EOR methods.

EOE methods	Advantages	Disadvantages
Gas injection	High efficiency Inexpensive	Gas corrosion Asphaltene problems
Thermal methods	Improved recovery factor Can be used for heavy crude oils	High cost Heat lost
Chemical methods	High efficiency No damage to reservoir rock	Sensitive to salinity and heat High cost
Novel methods	Environmental benefits Inexpensive in some cases	Low recovery in some case Sensitive to reservoirs condition

Table 2.
EOE methods: Advantages and disadvantages [1, 2].

The use of surfactants is mainly for surfactant flooding as well as micellar flooding [29]. These are the two major CEOR techniques that focus on reducing IFT and creating emulsions/microemulsions to increase the oil mobilization through porous rocks and direct residual oil flows toward the production well [5, 8]. The wettability alteration is another important mechanism by which surfactants can change the wettability of the reservoir rocks from oil-wet to water-wet [30]. With the change in wettability, the movement of crude oil in reservoirs smooths, and oil production increases [31]. Briefly, these three methods are the main applications of surfactants in CEOR.

3.2 Ionic liquid-based surfactants applicability in CEOR

Different types of conventional surfactants have been investigated for CEOR purposes. But almost all of them lose their effectiveness under harsh conditions of salinity and temperature [6]. For instance, The C-S-O bonds in sulfate-based surfactants are hydrolyzed at 60°C, and this causes the loss of performance of this group of surfactants above this temperature [32]. In this respect, IL-based surfactants can be considered a significant alternative. The stability of IL-based surfactants at high temperatures and salinities, as well as their notable amphiphilic nature, make them good candidates for CEOR. Based on this, IL-based surfactants reduce IFT and form emulsions by adsorbing and directing to the oil-water interfaces and by changing the properties of the rock surface to facilitate the wettability alteration.

Meanwhile, IL-based surfactants with high molecular weight increase the mobility of the crude oil by increasing the viscosity of the injected fluid, giving it a high sweeping effect. Due to their high thermal stability, IL-based surfactants are also suitable for thermal oil recovery and can enhance oil production by this method, particularly for heavy crude oils. Likewise, the aromaticity of some IL-based surfactants can assist oil production. As an additional benefit, IL-based surfactants may reduce water consumption during oil extraction, which in turn helps to separate sand and clay from crude oil and reduce corrosion problems.

Despite the high potential of IL-based surfactants for use in the CEOR process, the entire injected fluid system and reservoir conditions such as the nature of crude oil, rock type, and structure of IL-based surfactants must be considered for the operation. Consequently, the screening of the IL-based surfactants is a necessary step before using them for the CEOR process to correctly predict their behavior.

4. Surfactant flooding

High IFT values between crude oil and water are the main reason for the low mobility of residual crude oils in the reservoirs. IFT represents the extent of molecular cohesive forces at the interface of immiscible liquids, which arise from the unbalanced forces that molecules feel from adjacent molecules [33]. **Figure 6** shows a schematic diagram of the involved forces at the liquid-liquid interface. IFT plays a vital role in sketching and operating with immiscible fluids as well as the hydrodynamic and contact of the phases. Therefore, it is important to find a way to reduce IFT for higher oil production.

In the surfactant flooding method, IL-based surfactant molecules are adsorbed at the interface of crude oil-water. The adsorption of IL-based surfactant at the interface reduces the intermolecular forces between the phases and thus provides the IFT reduction. As the IFT decreases to an ultralow value, the capillary number (representing the relative effect of viscous drag forces versus IFT forces acting across an interface between crude oil-water in the reservoirs) increases [4]. As a result, the capillary forces that are the major cause of oil trapping in the pores are weakened and the production of crude oil from the reservoirs is significantly enhanced. The oil recovery mechanism based on IFT reduction is schematically presented in **Figure 7**.

Investigations show that using imidazolium IL-based surfactants, about 90% of the extra-heavy crude can be recovered from Utah and Canadian tar sands and IL-based surfactants could be recycled up to 5 times without significant performance loss even at high salinity levels [34].

4.1 Effect of ionic liquid-based surfactants structure

Because the decrease in IFT is attributed to the ability of IL-based surfactants to adsorb at the crude oil-water interface, slight changes in the structure of IL-based surfactants such as alkyl chain, head group, and counter anion, significantly alter the surfactant flooding process.

Accordingly, the longer the hydrophobic alkyl chain, the greater the ability of IL-based surfactants to reduce IFT. This can be attributed to the higher adsorption at the interface as well as the stronger van der Waals attraction between the alkyl chain of

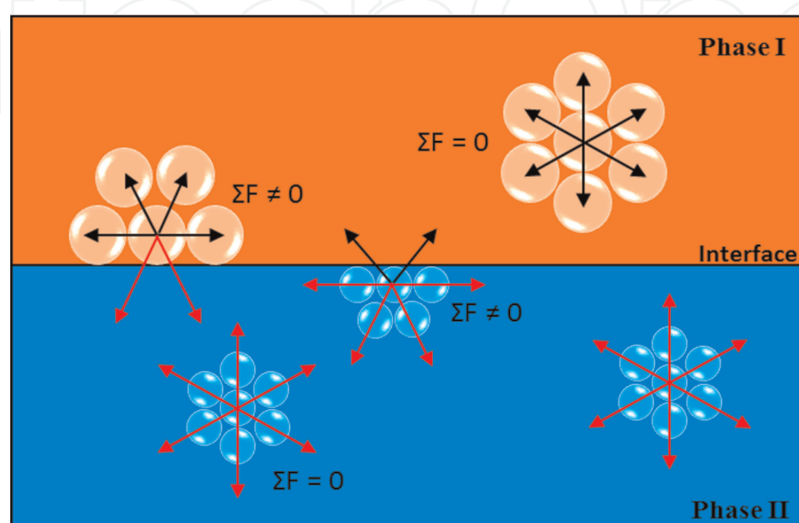


Figure 6.
Schematic of the involved forces at the liquid-liquid interface.

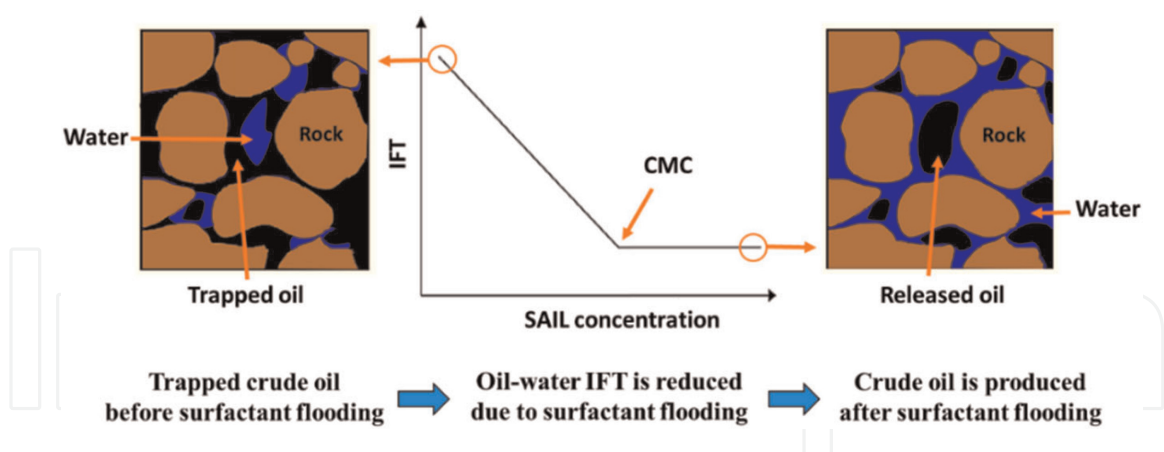


Figure 7.
Mechanism of crude oil recovery with the IFT reduction [5].

the IL-based surfactants and the hydrophobic part of the crude oil. Besides, branched alkyl chains meaningfully decrease the crude oil-water IFT. One advantage is that due to high performance, small amounts of long chain IL-based surfactants are required to achieve a certain IFT value that is economically and environmentally beneficial [3]. In this respect, comparing the effect of $[C_8mim][Cl]$, $[C_{12}mim][Cl]$, $[C_8py][Cl]$, and $[C_{12}py][Cl]$, indicates stronger performances with longer alkyl chain IL-based surfactants [18, 35, 36]. For more illustration, the change of IFT with the alkyl chain length of $[C_nim-C_4-imC_n][Br_2]$ $n = 4, 8,$ and 12 at different concentrations has been investigated in various researches [26, 37, 38]. The results of these studies are shown in **Figure 8**.

By investigating the effect of head groups, it was found that IL-based surfactants with bulky heterocyclic head groups as well as nonlocal charge rings such as imidazolium or thiazolium show higher interfacial activity and are greater effective in the IFT reduction. This phenomenon is due to the superior hydrophobicity of IL-based surfactants with heterocyclic head groups as well as the strong interaction of aromatic

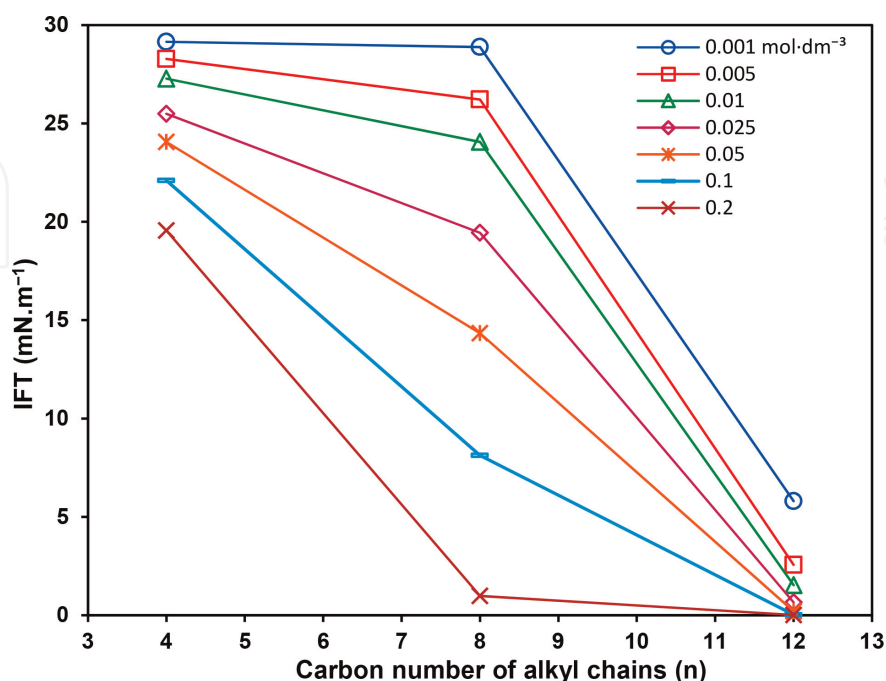


Figure 8.
IFT variation as a function of alkyl chain length for $[C_nim-C_4-imC_n][Br_2]$ [26, 37, 38].

compounds of the crude oil with the aromatic head group of the IL-based surfactant. Likewise, the reduction of IFT by $[\text{C}_4\text{mim}][\text{H}_2\text{PO}_4]$ and $[\text{C}_6\text{mim}][\text{HSO}_4]$ with bulky heterocyclic imidazolium head groups was 37.8 and 42.4%; but for $[\text{Et}_2\text{NH}_2][\text{H}_2\text{PO}_4]$ and $[\text{Et}_3\text{NH}][\text{HSO}_4]$ with the quaternary ammonium head group is only 32.6 and 37.7%, respectively [39].

For counter anion, with increasing polarizability, more interface activity is obtained. This is attributed to the greater interaction of polarizable counter anions with the IL-based surfactant cations that reduce the repulsion between the cationic head groups at the interface and provide more reduction of IFT [40]. For example, using $[\text{C}_4\text{mim}][\text{X}]$ variants, the effectiveness was shown to be in the order $[\text{H}_2\text{PO}_4]^- > [\text{PF}_6]^- > [\text{BF}_4]^- > [\text{HSO}_4]^-$ [39]. The positive effect of the alkyl chains in counter anions is also attractive. For instance, for the applied cations of $[\text{CP}]^+$, $[\text{BT}]^+$, $[\text{PA}]^+$, and $[\text{3-HPA}]^+$, the IFT reduction was effective in the order $[\text{C}_6\text{H}_{13}\text{COO}]^- > [\text{CH}_3\text{COO}]^- > [\text{HCOO}]^-$ [22]. This is due to the interaction of alkyl chains and crude oil, which enhances the adsorption of IL-based surfactants at the interface.

4.2 New types of ionic liquid-based surfactants

New types of IL-based surfactants indicate better interfacial activity compared to conventional Cationic IL-based surfactants. In this regard, ultra-low IFT values can be obtained with Catanionic, Zwitterionic, and Multicationic IL-based surfactants. Notably, it is common to use co-surfactants to achieve ultra-low IFTs, but no co-surfactants have been used for these types [3]. These advantages reflect the stronger amphiphilic nature of the mentioned IL-based surfactants, which is the result of less electrostatic repulsion of charged moieties and closer molecular orientation at the interface, as well as multiple alkyl chains in their structure. Accordingly, the use of $[\text{P144,4}][\text{DS}]$, as a Catanionic IL-based surfactant, has resulted in a reduction of the crude oil-water IFT to $0.1 \text{ mN}\cdot\text{m}^{-1}$, which is much lower than about $10 \text{ mN}\cdot\text{m}^{-1}$ that can be achieved by $[\text{C}_{12}\text{py}][\text{Cl}]$, $[\text{C}_8\text{mim}][\text{Cl}]$, and $[\text{C}_{12}\text{mim}][\text{Cl}]$, with the same concentrations [41].

In the case of the Zwitterionic IL-based surfactants, the covalent bonding between the cationic and anionic groups of the molecules neutralizes the electrostatic repulsion of the charged moieties and makes intense molecular arrangements at the interface. Correspondingly, comparing the interfacial activity of $[\text{C}_{16}\text{IPS}]$ and $[\text{C}_{16}\text{IPS-Nsa}]$ Zwitterionic IL-based surfactants with the same alkyl chains Cationic IL-based surfactants of $[\text{C}_{16}\text{mpyr}][\text{Br}]$ and $[\text{C}_{16}\text{mim}][\text{Br}]$, displays that $[\text{C}_{16}\text{IPS}]$ and $[\text{C}_{16}\text{IPS-Nsa}]$ can reduce the IFT from 20 to 1 and $0.1 \text{ mN}\cdot\text{m}^{-1}$, respectively. However, the decrease was 5.8 and $3.7 \text{ mN}\cdot\text{m}^{-1}$ for $[\text{C}_{16}\text{mpyr}][\text{Br}]$ and $[\text{C}_{16}\text{mim}][\text{Br}]$ respectively, under same concentrations [42].

As an important feature, ultra-low IFTs can be obtained using Multicationic IL-based surfactants. In this regard, Gemini IL-based surfactants, as a type of Multicationic IL-based surfactants, show that can significantly reduce IFT, even at low concentrations. A comparison between the performance of $[\text{C}_{12}\text{im-C}_4\text{-imC}_{12}][\text{Br}_2]$ and $[\text{C}_8\text{im-C}_4\text{-imC}_8][\text{Br}_2]$ Gemini IL-based surfactants with $[\text{C}_{12}\text{mim}][\text{Cl}]$ and $[\text{C}_8\text{mim}][\text{Cl}]$ as an analog Cationic IL-based surfactants demonstrate the better performance of Gemini IL-based surfactants [26, 37, 38]. Also, the effect of Gemini IL-based surfactants increases with extending the alkyl chain length. For instance, the long alkyl chain $[\text{C}_{12}\text{im-C}_4\text{-imC}_{12}][\text{Br}_2]$ was able to decrease the crude oil-water IFT from 32 to about $10^{-3} \text{ mN}\cdot\text{m}^{-1}$ [38].

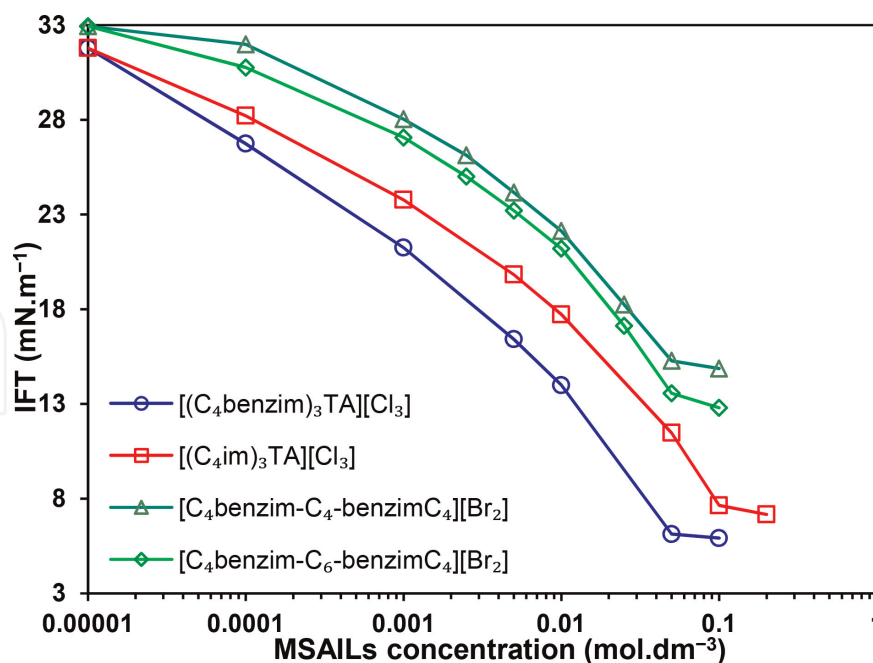


Figure 9. Comparing IFT variation of a Tripodal IL-based surfactants and analog Gemini IL-based surfactants in crude oil-water system [43].

Tripodal IL-based surfactants, as the newest synthesized Multicationic IL-based surfactants, exhibit a noteworthy capability. For a better explanation, the performance of the benzimidazolium and imidazolium Tripodal IL-based surfactants with short chain lengths, namely [(C₄benzim)₃TA][Cl₃] and [(C₄im)₃TA][Cl₃], were compared with two structurally analog benzimidazolium Gemini IL-based surfactants [C₄benzim-C_n-benzimC₄][Br₂] n = 4 and 6 [24, 25, 43]. The results are presented in **Figure 9**. As can be seen, the Tripodal IL-based surfactants produce a significant reduction in IFT even at lower concentrations that are economically important in CEOR. These results are due to greater hydrophobicity and the higher tendency to migrate toward the interface. Also, in comparison between the Tripodal IL-based surfactants, the benzimidazolium outperformed the imidazolium with 7.5% higher IFT reduction because of the better spread electrostatic repulsion between the positively charged head groups [43].

According to these results, new types of IL-based surfactants can provide the next generation of surfactants with distinct properties, especially in obtaining ultra-low IFT values.

5. Micellar flooding

In addition to “surfactant flooding”, IL-based surfactants can solubilize crude oils in the core of micelles and form emulsion or microemulsion in a process called “micellar flooding” [8]. The emulsion is the dispersion of one phase in another immiscible phase in the form of small droplets. However, microemulsions are practically more effective in CEOR. Danielsson and Lindman [44], defined a microemulsion as “a system of water, oil, and an amphiphilic compound that has a single optically isotropic and thermodynamically stable liquid solution”. The droplet size of microemulsions is smaller than conventional emulsions but bigger than micelles. Based on the Winsor

organization, four types of microemulsions are predictable. Type I is an oil-in-water (O/W) microemulsion in which the oil is dissolved as micelles in a continuous aqueous water phase with an additional oil phase (Winsor I). Type II is a water-in-oil (W/O) microemulsion in which water is dissolved as reverse micelles in an oil phase with an additional water phase (Winsor II). Type III is a three-phase system where the intermediate phase microemulsion is balanced with additional oil and water phases (Winsor III). Type IV is a single-phase microemulsion in which oil and water phases are combined in one phase (Winsor IV) [8]. For a better explanation, four types of Winsor microemulsion structures are shown schematically in **Figure 10**.

For droplet formation and dissolution of O/W or W/O microemulsions, the interface must be divided into new small parts with more total interface areas, which requires a reduction in IFT. Therefore, to perform CEOR by micellar flooding, IL-based surfactants should decrease the crude oil-water IFT to about 10^{-3} mN.m⁻¹ and it is essential that the IL-based surfactant concentration was higher than the corresponding CMC [3]. Therefore, the use of IL-based surfactants with low inherent CMC is more suitable [8]. To form O/W emulsions, the polar part of IL-based surfactants remains in the aqueous phase and the non-polar part extends into the oil phase. While for W/O emulsion, this arrangement is reversed. For better illustration, the formation of O/W and W/O emulsions with IL-based surfactants is presented in **Figure 11**.

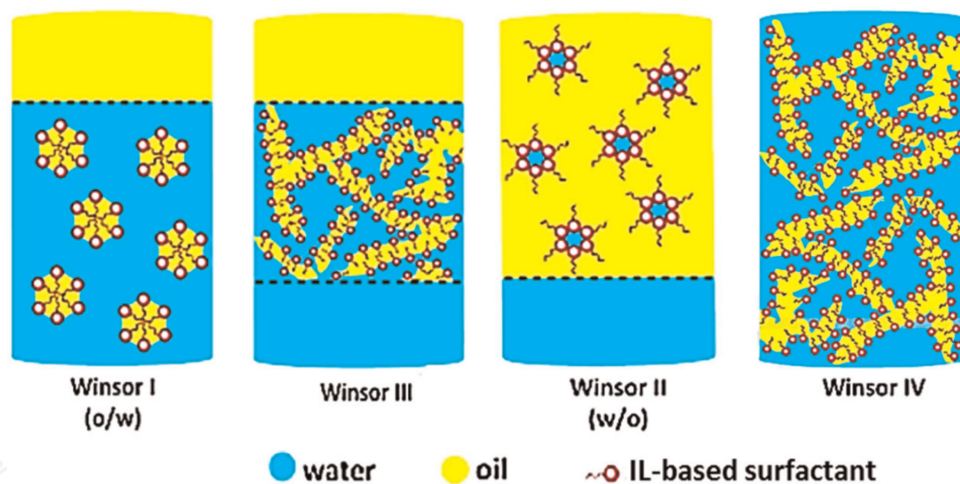


Figure 10.
Four types of Winsor microemulsion structures [8].

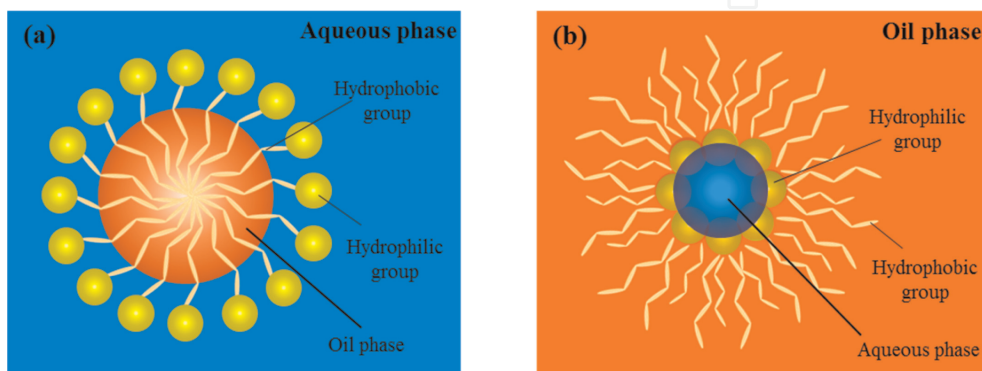


Figure 11.
Formation of oil-in-water (a) and water-in-oil (b) emulsions with IL-based surfactants.

After creating microemulsions, IL-based surfactants prevent droplet coalescence by forming protective layers with electrostatic and steric stabilization capabilities. In this regard, by covering the surface of the droplets with IL-based surfactants, their surface becomes electrically charged, so the positive or negative charges of the droplets separate them electrostatically and keep them stable. Also, the bulky and large IL-based surfactant head group sterically prevents the coalescence of droplets effectively. It is important to note that IL-based surfactants, due to their strong cohesive forces, could form stable microemulsions without co-surfactant, which are volatile and pose environmental hazards [8].

Research has shown that micellar flooding is an important CEOR process for depleted reservoirs. Microemulsions in reservoirs generally contain a transparent mixture of crude oil, an aqueous phase, and surfactants (sometimes with co-surfactants) in which oil, water, or both are dispersed [7]. In this regard, the study of various imidazolium IL-based surfactant microemulsions confirms their remarkable suitability to help to solubilize crude oils and create stable microemulsions to increase displacement and sweep efficiency [8]. Similarly, $[C_8mim][BF_4]$, $[C_{10}mim][BF_4]$, and $[C_{12}mim][BF_4]$ can form Winsor III type microemulsion [45]. This feature is so appropriate because core flooding experiments confirm that the aqueous and oil phases coexisted in the intermediate phase of Winsor III microemulsions have the ultralow IFT value (less than $10^{-3} \text{ mN}\cdot\text{m}^{-1}$), which leads to noteworthy CEOR in micellar flooding [7].

5.1 Effect of ionic liquid-based surfactants structure

The molecular structure of IL-based surfactants influences the morphology and droplet size of the microemulsions. In terms of the alkyl chain length, interface disruption happens more easily with longer chain IL-based surfactants, resulting in producing small droplets. For instance, emulsion experiments with $[C_nmim][BF_4]$ ($n = 8, 10, \text{ and } 12$), confirmed that longer alkyl chains lead to more stable microemulsions [45]. In another work, it has been confirmed that $[C_{16}mim][Cl]$, as a long chain imidazolium IL-based surfactant, can produce highly stable microemulsions [46]. In the same manner, longer alkyl chains in the anionic portions, by improving the amphiphilic nature, contribute to microemulsion formation. Accordingly, by studying the formation of microemulsions with $[C_2mim][AS]$ ($n = 2, 4, 6, \text{ and } 8$), it was shown that longer alkyl chain anions create more stable microemulsions [47].

The head group of IL-based surfactants plays a major role in determining whether microemulsions are formed in a polar or non-polar phase. In this regard, investigations on three Catanionic IL-based surfactants show that $[C_4mim][AOT]$ creates stable microemulsions in both the aqueous and oil phases; though, $[CTA][AOT]$ and $[BHD][AOT]$ with hydrophobic head groups can only produce vesicles in the aqueous phase and microemulsions in the oil phase [48].

By changing the polarity of the counter anions, the effectiveness of IL-based surfactants on microemulsion formation changes. The bulkiness counter anions with greater polarizability provide better and more stable microemulsions. In this regard, the results show that the imidazolium IL-based surfactants work in the order $[C_4mim][NTf_2] > [C_4mim][PF_6] > [C_4mim][BF_4]$ [49]. The counter anions, depending on their nature, can also affect the phase in which the microemulsions are formed, i.e. in the polar or non-polar phase.

5.2 New types of ionic liquid-based surfactants

Micellar flooding also strongly depends on the type of IL-based surfactants. Predictably, the formation and stability of microemulsions have been significantly enhanced with the newly introduced types of IL-based surfactants. In this regard, the study of the interfacial activity of the [P666,14][Cl], indicated that it provided stable microemulsions with no co-surfactant even at high temperatures [50, 51]. In another work, using the novel Anionic IL-based surfactant of [HOPro][DBS] reduced the IFT to an ultra-low value of $3 \times 10^{-3} \text{ mN.m}^{-1}$, resulting in a highly stable microemulsion [52]. The results of microemulsions with Catanionic IL-based surfactant of $[\text{C}_{12}\text{mim}][(\text{i-C}_8)_2\text{PO}_2]$ confirm their excellent performance even at low concentrations [53].

Tripodal and Gemini IL-based surfactants as a type of Multicationic, create stable microemulsions of crude oil in aqueous solutions. In this respect the effect of two benzimidazolium Gemini IL-based surfactants $[\text{C}_4\text{benzim-C}_n\text{-benzimC}_4][\text{Br}_2]$, $n = 4$ and 6 are shown in **Figure 12**. As it is possible to see, stable microemulsions were obtained by them after one day and one week [25]. Similar results were achieved for imidazolium Gemini IL-based surfactants, which also improved with alkyl chain length [54, 55].

In another study, the performance of imidazolium Tripodal IL-based surfactant $[(\text{C}_4\text{im})_3\text{TA}][\text{Cl}_3]$ was compared with three imidazolium Gemini IL-based surfactants of $[\text{C}_4\text{im-C}_n\text{-imC}_4][\text{Br}_2]$ $n = 2, 4$ and 6 . The results are shown in **Figure 13**. As it is possible to see, the Tripodal IL-based surfactant also presents a greater emulsification performance even at an order of magnitudes lower concentration, which is due to superior hydrophobicity that provides easier interface disrupting and, consequently, the easier formation of smaller droplets [24].

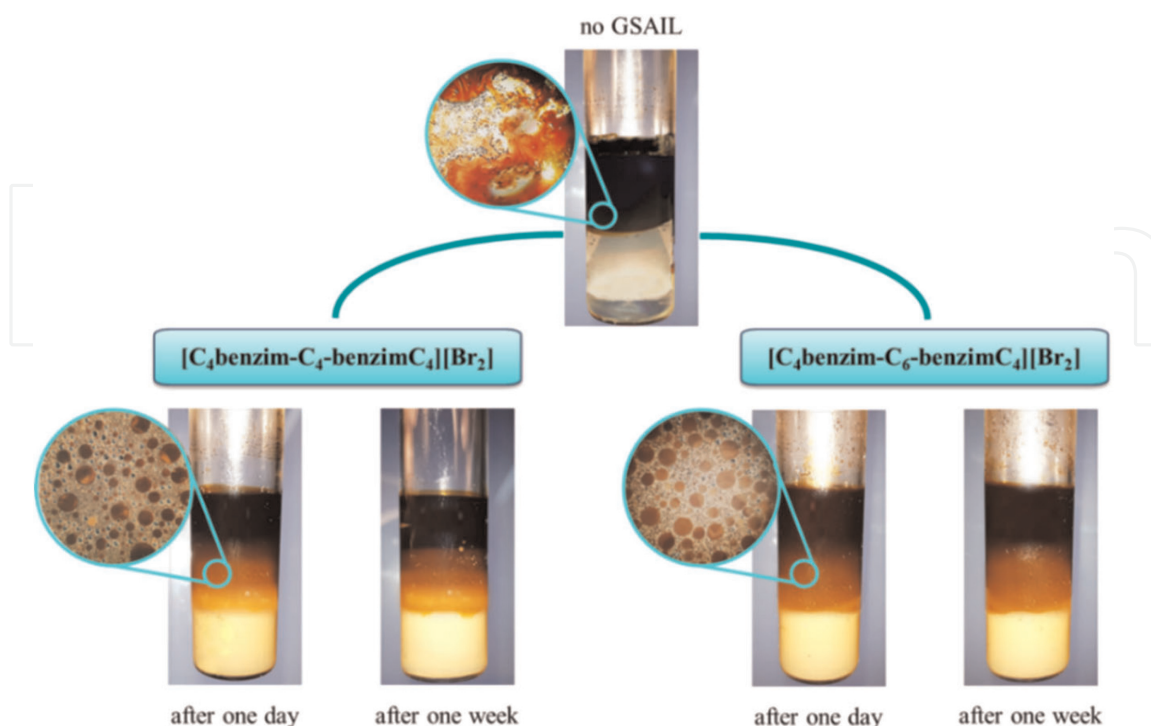


Figure 12. The crude oil-water emulsions and the microscopic images ($45 \times$ magnification) with no Gemini IL-based surfactants and with 0.01 mol.dm^{-3} of them after one day and after one week [25].

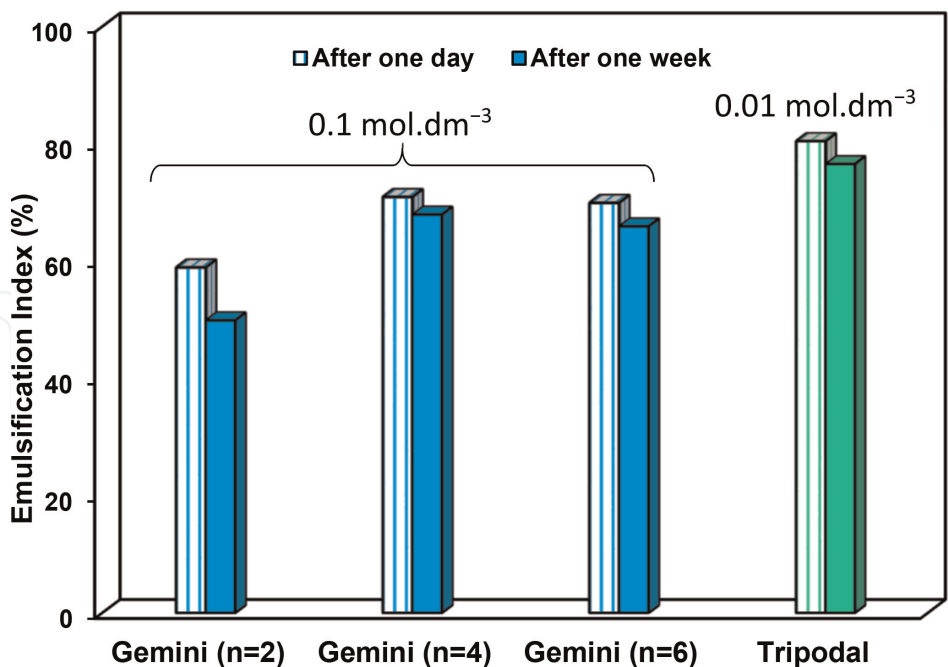


Figure 13. The emulsification indices for 0.01 mol·dm⁻³ of the Tripodal and 0.1 mol·dm⁻³ of the Gemini IL-based surfactants after one day and one week [24].

6. Wettability alteration

Wettability, as determined by the interaction between rock surfaces and reservoir fluids (crude oil or brine), is recognized as one of the key parameters controlling the remaining original oil in place (OOIP). The wettability alteration in CEOR, which is related to the process of converting the reservoir rock from oil-wet to water-wet, remarkably increases the final oil recovery from the reservoirs. Likewise, wettability can be evaluated from the contact angle between the solid surfaces and the fluids as well as the three involved IFTs in the phase boundaries. The relationship between the contact angle and the involved three IFTs is determined using the well-known Young equation, which is presented for the solid-water-air (Eq. 1) and solid-water-oil (Eq. 2) systems as [56]:

$$\gamma_{s/a} - \gamma_{s/w} = \gamma_{w/a} \cos\theta \quad (1)$$

$$\gamma_{s/o} - \gamma_{s/w} = \gamma_{w/o} \cos\theta \quad (2)$$

In these Equations, θ is the contact angle and the various subscripts of s, o, w, and a, indicate the solid, oil, water, and air phases, respectively.

Solids with a contact angle less than 90° are hydrophilic surface (water-wet), solids with a contact angle of 90° have moderate behavior (intermediate-wet), and solids with a contact angle greater than 90° are hydrophobic (oil-wet). The contact angle for different wettability conditions of the solid-water-oil system is shown schematically in **Figure 14**. It is worth mentioning that for the oil droplets formed in the aqueous phase and in contact with the solid surface, the external contact angle with respect to the aqueous phase is considered.

In the wettability alteration, the adsorption of the IL-based surfactants on the surface of reservoirs makes the oil-wet rocks partially or completely water-wet.

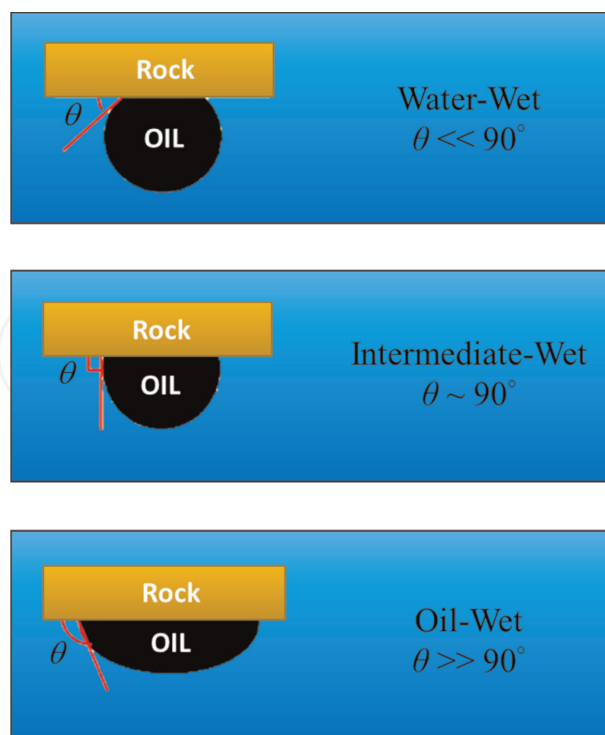


Figure 14.
Schematics of contact angle for different wettability conditions of the solid-water-oil system.

The mechanism by which IL-based surfactants alter the wettability of conventional rock pores is termed a cleaning mechanism, whereby IL-based surfactants desorb crude oil from the rock surface, so more oil can be extracted. The charge density, structure, and concentration of the IL-based surfactants as well as the surface charge of the rocks and the nature of the crude oil affect this procedure.

In carbonate reservoirs, negatively charged organic components of crude oil are adsorbed on the mineral surface by positively charged rock pores. When Cationic IL-based surfactants are added, ion-pair creation happens between the IL-based surfactants and the adsorbed anionic components of the crude oil (mainly carboxylate). This phenomenon repels crude oil from the rock surface by neutralizing the electrical charge of the adsorbed material (**Figure 15a**). Then, water imbibition takes place and the wettability of the rock becomes water-wet. In contrast, Anionic IL-based surfactants are unable to remove the crude oil carboxylates from the rock surface due to similar surface charges. As an alternative, as presented in **Figure 15b**, the hydrophobic interaction between the tail of the IL-based surfactants and the adsorbed crude oil on the surface of the reservoir rocks, such that the polar parts of the IL-based surfactants are directed toward the solution, this configuration hydrophilizes the rock surface. Though these configurations displace the crude oil from the rock surface, the interaction is not as efficient as the ion-pair interaction and only alterations the rock surface from oil-wet to intermediate-wet [57]. Generally, the Cationic IL-based surfactants are more effective than other types of wetting agents in carbonate reservoirs.

The proposed mechanism of wettability modification by the IL-based surfactants on the carbonate surfaces could be used to clarify the wettability alteration of the oil-wet sandstone rock (with negatively charged), albeit in reverse. So, Anionic IL-based surfactants are more effectual for sandstone reservoirs.

Regarding the concentration effect, a study on the wettability alteration of crude oil-water-quartz system in the presence of imidazolium IL-based surfactants shows

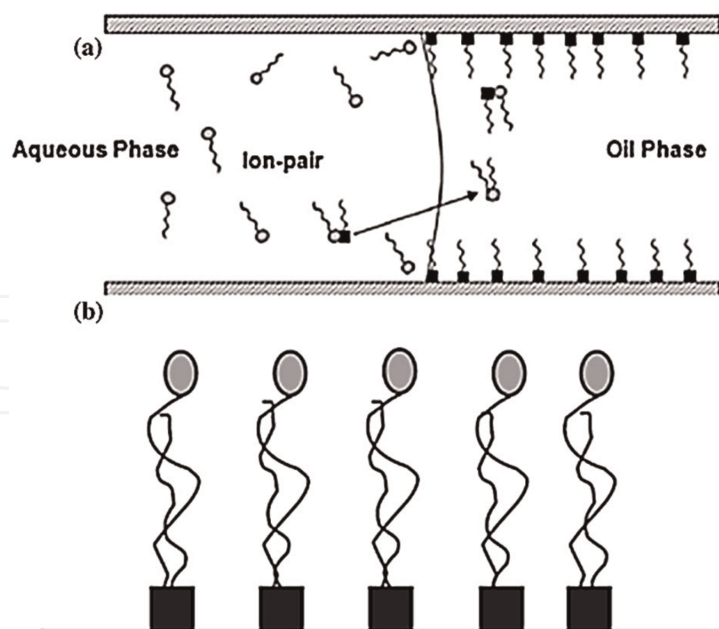


Figure 15. Wettability alteration by cationic (a) and anionic IL-based surfactants (b) in carbonate reservoirs [57].

that with increasing IL-based surfactant concentration, the contact angle decreases rapidly in direction of changing wettability from oil-wet to water-wet [58].

6.1 Effect of ionic liquid-based surfactants structure

The change in the structure of IL-based surfactants meaningfully affects the wettability alteration. In this regard, the length of the alkyl chain appears to have a greater impact. Based on this, investigations on the effect of different imidazolium IL-based surfactants of $[C_n\text{mim}][X]$ with $n = 4, 6, \text{ and } 8$, and $X = [\text{Cl}]^-$, $[\text{Br}]^-$ and $[\text{HSO}_4]^-$, on the wettability of quartz surface in contact with model oil (including pentane, hexane, heptane, octane, decane, and dodecane) were carried out. The results revealed that IL-based surfactants with longer hydrocarbon chains switch wettability from oil-wet to water-wet better than shorter ones and provide lower contact angles [59]. Furthermore, the change of wettability in the presence of $[C_n\text{mim}][\text{BF}_4]$ with $n = 8, 10, \text{ and } 12$, indicated that as the chain length of IL-based surfactant increases, the contact angle decreases and leads to more favorable oil extraction [45].

The ability of the IL-based surfactant head groups to change carbonate surface wettability has also been investigated by measuring the contact angle of the oil droplets in the presence of two long alkyl chain IL-based surfactants of $[C_{18}\text{Py}][\text{Cl}]$ and $[C_{18}\text{mim}][\text{Cl}]$. The results show that imidazolium IL-based surfactants are better than pyridinium ones in changing wettability to water-wet [30].

6.2 New types of ionic liquid-based surfactants

It is reasonably expected that new types of IL-based surfactants will have a fundamental effect on the wettability alteration. But unfortunately, little work has been done to investigate the performance of these new types in this field. In general, IL-based surfactants with different charges have different attractions and repulsions with the rock surfaces. Therefore, Cationic IL-based surfactants are preferred for use in carbonate reservoirs, while Anionic IL-based surfactants are suitable for sandstone

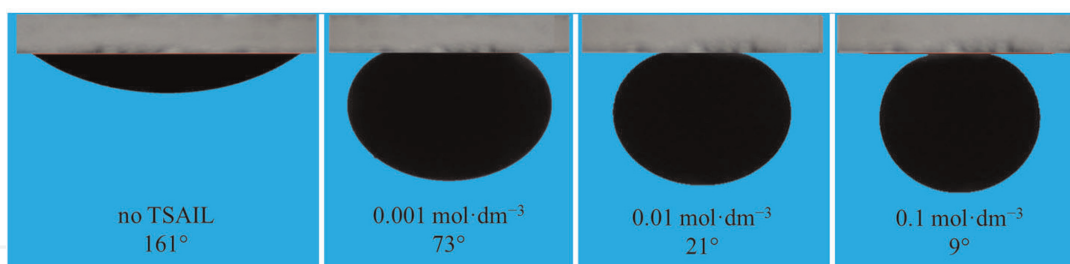


Figure 16.

The shapes of the crude oil drops on the quartz surface surrounded with different aqueous solutions of $[(C_4\text{benzim})_3\text{TA}][\text{Cl}_3]$ [43].

reservoirs. So, appropriate IL-based surfactants should be selected based on the characterization of the reservoir's rock structure.

Investigations indicated better performance of Catanionic as well as Multicationic IL-based surfactants than other types of IL-based surfactants. In this regard, Gemini and Tripodal IL-based surfactants, as a type of Multicationic, significantly reduce the contact angle of crude oil in quartz surfaces so that even complete oil displacement with long chain Gemini IL-based surfactant $[\text{C}_{12}\text{im}-\text{C}_4-\text{imC}_{12}][\text{Br}_2]$ has been observed [38, 60]. For a better explanation, the change of contact angles of crude oil droplets on the quartz surface surrounded by different concentrations of $[(C_4\text{benzim})_3\text{TA}][\text{Cl}_3]$ as a Tripodal IL-based surfactant is presented in **Figure 16**.

As another comparison, the performance of the benzimidazolium and imidazolium Tripodal IL-based surfactants of $[(C_4\text{benzim})_3\text{TA}][\text{Cl}_3]$ and $[(C_4\text{im})_3\text{TA}][\text{Cl}_3]$ as well as benzimidazolium Gemini IL-based surfactants $[\text{C}_4\text{benzim}-\text{C}_4-\text{benzimC}_4][\text{Br}_2]$ and $[\text{C}_4\text{benzim}-\text{C}_6-\text{benzimC}_4][\text{Br}_2]$ are shown in **Figure 17**. The results demonstrated that the benzimidazolium IL-based surfactants (specifically Tripodal) can greatly change the surface wettability, which confirms the higher hydrophobicity of the benzimidazolium rings [43].

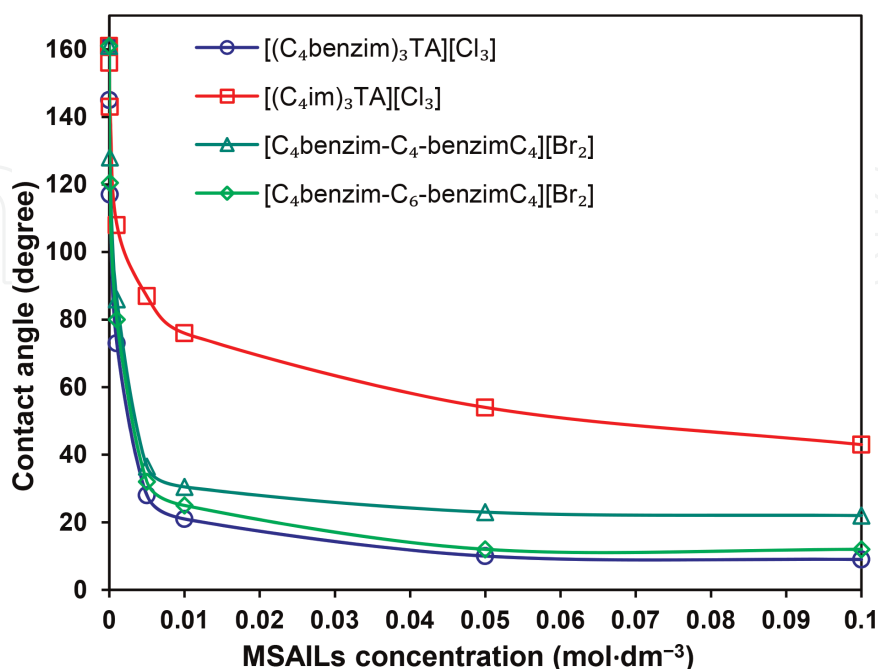


Figure 17.

The contact angles of crude oil drops on the quartz surface surrounded with multicationic IL-based surfactants solutions [43].

7. Ionic liquid-based surfactants versus conventional surfactants

In almost all cases, IL-based surfactants are more efficient in reducing the IFT of the crude oil-water system than conventional surfactants with similar alkyl chain lengths and counter anions. This is attributed to the bulkier head group or heteroatom ring, which gives IL-based surfactants greater hydrophobicity and easier transport to the interface; i.e. more interfacial activity. For better comparison, the molecules of a typical IL-based surfactant as well as a typical cationic surfactant are illustrated in **Figure 18**.

From a practical point of view, this is useful in CEOR processes as it allows the use of low amounts of IL-based surfactants. Correspondingly, the efficiency of IL-based surfactants can be enhanced by choosing suitable alkyl chains or anions as well as larger head group, preferably nitrogen-containing heterocyclic rings with delocalized charges. For comparison, the effects of 11 IL-based surfactants from three different families (lactam, ammonium, and hydroxylammonium) show that they could reduce the IFT better than Tergitol 15-S-5, Tergitol 15-S-7, and Tergitol 15-S-9 as conventional non-ionic surfactants [22, 56]. Also, the maximum reduction of crude oil-water IFT with $[C_{16}mim][Br]$ and $[C_{12}mim][Cl]$ was about 72%, which is higher than CTAB and DTMAC surfactants with similar structures but different head groups, whose reduce the IFT to about 68% [23].

It has to mention that some conventional surfactants may have a greater impact on IFT reduction even to very low levels. The performance of Cationic IL-based surfactants in IFT reduction can reach 10^{-2} mN.m⁻¹ orders; however, some conventional surfactants can reduce IFT to about 10^{-3} (sometimes to 10^{-4}) mN.m⁻¹. To solve this problem, ultra-low IFT values can be achieved by developing the structure of IL-based surfactants as well as using Zwitterionic, Catanionic, Multicationic, or Anionic IL-based surfactants. For instance, the Catanionic IL-based surfactant of $[P666,14][(i-C_8)_2PO_2]$ has shown a greater IFT reduction for the water-model oil system than conventional surfactants [61]. Moreover, the Anionic IL-based

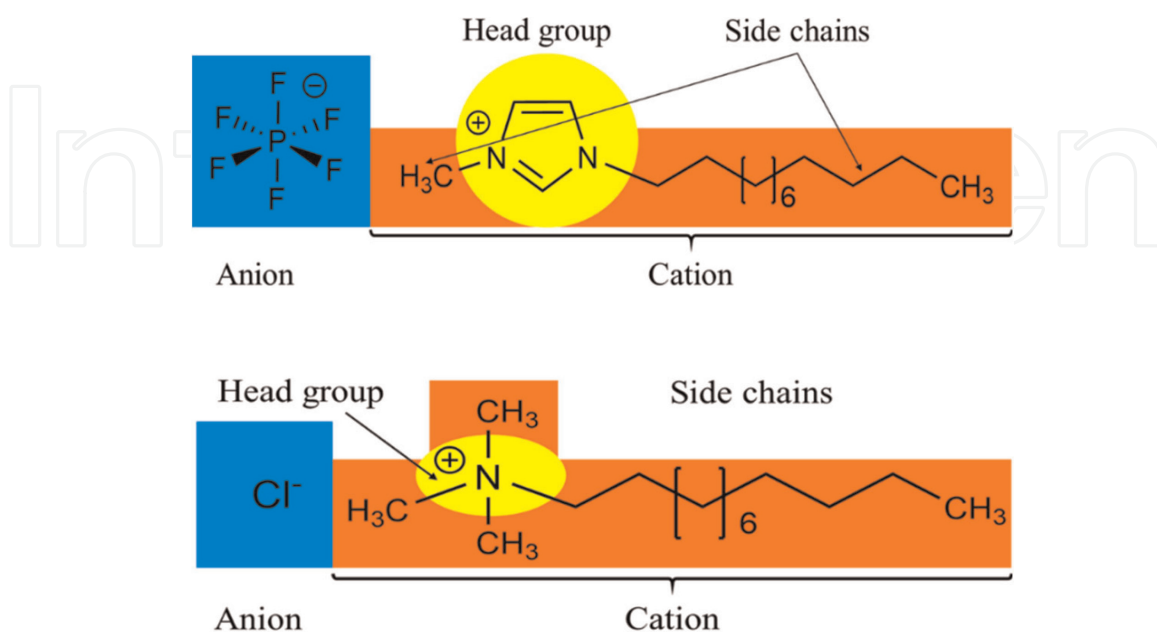


Figure 18. Molecular structures of an imidazolium IL-based surfactant, $[C_{12}mim][PF_6]$, and a conventional cationic surfactant, [DTMAC].

surfactant of [C₄mim][DS] effectively reduced the IFT of the water-benzene system to 0.9 mN.m⁻¹; whereas, by using SDBS and SDS as two conventional Anionic surfactants, this value was, respectively, about 5 and 8.5 mN.m⁻¹, respectively [62, 63]. In addition, the long chain Multicationic IL-based surfactants of [C₁₂im-C₄-imC₁₂][Br₂] can reduce the IFT of the crude oil-water system from 32 to about 10⁻³ mN.m⁻¹ [38]. According to these results, newly introduced types of IL-based surfactants can be the next generation of surfactants with distinct properties, particularly in achieving ultra-low IFT values.

Regarding micellar flooding, conventional surfactants are difficult to use in micellar flooding CEOR because they not only tolerate high temperature and salinity conditions but also form Winsor II type microemulsions even at low salinity. Notably, investigations have confirmed that the IL-based surfactants can maintain their emulsifier performance under harsh reservoir conditions and can also form Winsor III type microemulsions, which is an interesting phenomenon in CEOR processes. As another advantage, IL-based surfactants have lower CMC compared to conventional analog surfactants, which is a significant point in micellar flooding. This is attributed to the bulkiness of heterocyclic head groups that give IL-based surfactants more hydrophobicity and greater aggregation tendency. These properties are economically significant. For example, imidazolium IL-based surfactants exhibit lower CMCs than the alkyltrimethylammonium bromides (C_nTAB) with the same chain length and anionic portion, but CMC of this type of IL-based surfactants are comparable to the Anionic surfactants, such as sodium alkyl sulfates (SAS) [13]. Likewise, the CMCs of [C₁₆mim][Br] and [C₁₂mim][Cl] have been 81 and 63% of those of DTMAC and CTAB, respectively [23]. Consistently, the Catanionic IL-based surfactants exhibit a lower CMC compared to conventional surfactants. Another important feature of IL-based surfactants is that the creation of stable microemulsions based on the use of conventional surfactants often requires co-surfactants, the most common of which are volatile and environmentally hazardous medium chain alcohols. However, IL-based surfactants, due to their strong cohesive forces, can form stable microemulsions without the need for co-surfactant requirements.

Moreover, IL-based surfactants are more efficient in wettability alteration from oil-wet to water-wet. In this regard, comparing the performance of imidazolium IL-based surfactant [C₁₂mim][Cl] with some conventional surfactants of AN-120, NX-610, NX-1510, NX-2760, and TR-880, by contact angle measurements, showing that IL-based surfactants are superior in changing the wettability from oil-wet to water-wet [64]. Therefore, it can be concluded that apart from surfactant flooding and micellar flooding, wettability alteration also play an important role in improving oil recovery with IL-based surfactants in CEOR processes.

The presented results clearly indicate that the IL-based surfactant is more effective than the conventional surfactants in the recovery of residual oil under reservoir conditions. Based on these results, IL-based surfactants can be considered effective alternative surfactants for CEOR processes.

8. Conclusions and future perspective

The present chapter provides an overview of the properties of IL-based surfactants and highlights their effectiveness in the oil industry. The results clearly show that the IL-based surfactants can be considered noteworthy candidates in the CEOR processes

due to their high level performances in surfactant flooding and micellar flooding as well as wettability alteration that enhances crude oil production.

Surfactant flooding indicates that the IL-based surfactants have high interfacial activity and could reduce the IFT to a low value even under reservoir conditions. In view of the IL-based surfactant structure, increasing the length of the alkyl chain of cation and/or anion and the larger heterocyclic head group with π -electron ring, as well as bulkiness counter anion with higher polarizability, provides the more interfacial activity. Moreover, the new types of Catanionic, Multicationic, and Zwitterionic usually show higher interface activity compared to single analogs Cationic IL-based surfactants.

Furthermore, the study of IL-based surfactant microemulsions confirms their remarkable suitability to help solubilize crude oils and create stable microemulsions to enhance crude oil displacement and mobility. The molecular structure of IL-based surfactants influences the morphology and droplet size of the microemulsions. With longer chain IL-based surfactants, interface disruption occurs more easily, resulting in smaller droplets as well as more stable microemulsions. However, the head group plays the main role in determining the phase polarity of microemulsions formation, i.e. in the polar or non-polar phase. By increasing the polarity of the counter anion, the effectiveness of IL-based surfactants on microemulsion formation increases. The formation and stability of microemulsions are significantly enhanced by new types of IL-based surfactants, especially with Catanionic and Multicationic IL based-surfactants.

In the wettability alteration, adsorption of IL-based surfactants on the reservoir surfaces converts oil-wet rocks to water-wet. In general, Cationic IL-based surfactants are more efficient in carbonate reservoirs, while Anionic IL-based surfactants are better in sandstone reservoirs. The structure and concentration of IL-based surfactants affect this procedure, so IL-based surfactants with longer hydrocarbon chains and bulkier sizes have greater performance. As expected, new types of IL-based surfactants show better performance in changing wettability.

Comparison of IL-based surfactants with conventional surfactants demonstrates that due to larger cations or heteroatom rings, most of the IL-based surfactants show better interfacial activity in all three regions of surfactant flooding, micellar flooding, and wettability alteration than conventional surfactants with similar structures. Indeed, in all investigated cases, Zwitterionic, Catanionic, Multicationic or Anionic IL-based surfactants are more efficient.

The content of this chapter indicates that the advantages of IL-based surfactants make them a suitable candidates for use in the oil industry. In consequence, it is reasonably anticipated that IL-based surfactants can solve various problems in the oil industry. However, before large scale application, additional data such as crude oil nature, rock type, the interaction of IL-based surfactants with the surface of reservoir rocks, and solubility of IL-based surfactants in brine must be generated to provide real insight into their performance and economics. Thus, the screening of the IL-based surfactants is a necessary step before using them for the CEOR process to correctly predict the behavior of the IL-based surfactants.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

List of abbreviations and nomenclature

CEOR	Chemical enhanced oil recovery
CMC	Critical micelle concentration
EOR	Enhanced oil recovery
IFT	Interfacial tension
IL	Ionic liquid
OOIP	original oil in place
O/W	Oil-in-water
RTIL	Room temperature ionic liquid
SARA	Saturates, aromatics, resins and asphaltenes
Surfactant	Surface-active agent
W/O	Water-in-oil
θ	Contact angle
Cation part of IL-based surfactants	
[BHD]	Benzyl-n-hexadecyldimethylammonium
[BT]	Butyrolactam
[C _n mim]	1-Alkyl-3-methylimidazolium
[C ₂ mim]	1-Ethyl-3-methylimidazolium
[C ₄ mim]	1-Butyl-3-methylimidazolium
[C ₆ mim]	1-Hexyl-3-methylimidazolium
[C ₈ mim]	1-Octyl-3-methylimidazolium
[C ₁₀ mim]	1-Decyl-3-methylimidazolium
[C ₁₂ mim]	1-Dodecyl-3-methylimidazolium
[C ₁₆ mim]	1-Hexadecyl-3-methylimidazolium
[C ₁₈ mim]	1-Octadecyl-3-methylimidazolium
[C ₄ im-C _n -imC ₄]	3,3'-(Alkane-1,4-diyl)bis(1-butyl-1 <i>H</i> -imidazol-3-ium)
[C ₈ im-C ₄ -imC ₈]	3,3'-(Butane-1,4-diyl)bis(1-octyl-1 <i>H</i> -imidazol-3-ium)
[C ₁₂ im-C ₄ -imC ₁₂]	3,3'-(Butane-1,4-diyl)bis(1-dodecyl-1 <i>H</i> -imidazol-3-ium)
[C ₄ benzim-C _n -benzimC ₄]	3,3'-(Alkane-1,4-diyl)bis(1-butyl-1 <i>H</i> -benzo [<i>d</i>]imidazol-3-ium)
[C ₄ benzim-C ₄ -benzimC ₄]	3,3'-(Butane-1,4-diyl)bis(1-butyl-1 <i>H</i> -benzo [<i>d</i>]imidazol-3-ium)
[C ₄ benzim-C ₄ -benzimC ₄]	3,3'-(Hexane-1,6-diyl)bis(1-butyl-1 <i>H</i> -benzo [<i>d</i>]imidazol-3-ium)
[(C ₄ im) ₃ TA]	3,3',3''-(1,3,5-Triazine-2,4,6-triyl)tris (1-butyl-1 <i>H</i> -imidazol-3-ium)
[(C ₄ benzim) ₃ TA]	3,3',3''-(1,3,5-Triazine-2,4,6-triyl)tris (1-butyl-1 <i>H</i> -benzo [<i>d</i>]imidazol-3-ium)
[C ₁₆ mpyr]	1-Hexadecyl-1-methylpyrrolidinium
[C ₈ py]	1-Octylpyridinium
[C ₁₂ py]	1-Dodecylpyridinium

[C ₁₈ py]	1-Octadecylpyridinium
[Et ₂ NH ₂]	Diethylammonium
[Et ₃ NH]	Triethylammonium
[CP]	Caprolactam
[CTA]	Cetyltrimethylammonium
[HOPro]	Prolinolum
[PA]	Propylammonium
[P144,4]	Tributyl-methylphosphonium
[P666,14]	Trihexyl-tetradecylphosphonium
[3-HPA]	3-Hydroxypropylammonium
Anion part of IL-based surfactants	
[Ac]	Acetate
[AOT]	1,4-Bis(2-ethylhexyl) sulfosuccinate
[AS]	Alkyl sulfate
[BF ₄]	Tetrafluoroborate
[CH ₃ COO]	Acetate
[C ₆ H ₁₃ COO]	Hexanoate
[DBS]	Dodecylbenzenesulfonate
[DS]	Dodecylsulfonate
[HCOO]	Formate
[HSO ₄]	Hydrogen sulfate
[H ₂ PO ₄]	Dihydrogen phosphate
[(<i>i</i> -C ₈) ₂ PO ₂]	Bis(2,4,4-trimethylpentyl) phosphinate
[NTf ₂]	Bis(trifluoromethylsulfonyl)imide
[OTF]	Trifluoromethanesulfonate,
[PF ₆]	Hexafluorophosphate
[SCN]	Thiocyanate
[TA]	Trifluoroacetate,
IL-based surfactants	
[C ₁₆ IPS]	3-(1-hexadecyl-3-imidazolio) propanesulfonate
[C ₁₆ IPS-Nsa]	3-(1-hexadecyl-3-imidazolio) propanesulfonateβ-naphthalene sulfonate
Conventional surfactants	
AN-120	Dodecyl benzene sulfonic acid + Nonylpheno- lethoxylate
CTAB	Cetyltrimethylammonium bromide
C _n TAB	Alkyltrimethylammonium bromides
DTMAC	Dodecyltrimethylammonium chloride
NX-610	Dodecyl dimethyl amine betaine
NX-1510	Dodecyl dimethyl amine betaine + Octadecyl amine ethoxylate
NX-2760	Dodecyl dimethyl amine betaine + Octadecyl amine ethoxylated betaine
SDBS	Sodium dodecylbenzenesulfonate
SDS	Sodium dodecyl sulfate
SAS	Sodium alkyl sulfates
Tergitol 15-S-5	Ethoxylated C11 ~ 14 secondary alcohol
Tergitol 15-S-7	Ethoxylated C11 ~ 14 secondary alcohol
Tergitol 15-S-9	Ethoxylated C11 ~ 14 secondary alcohol

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