
Ionic Liquids as Surfactants – Applications as Demulsifiers of Petroleum Emulsions

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1. Introduction

Emulsions are made by mixing two immiscible phases, preferentially in the presence of an emulsifying agent. Hence, crude oil production is invariably accompanied by water in mature oil reservoirs where the formation of stable water-in-oil (W/O) emulsions are frequently encountered [1]. The dispersion of water droplets in oil is facilitated by the presence of interfacial active agents in the crude oil such as asphaltenes, waxes, resins and naphthenic acids. The content of these natural emulsifiers is more abundant in heavy than in light crude oils, altogether with a specific density closer to water that difficult water separation that favor the formation of more stable emulsions in heavy crude oils [2].

The presence of water causes several operational problems like corrosion in equipments and pipelines, and generally increases the cost of oil production. Therefore, water must be separated from crude oil before refining process [3]. There are several physical methods (thermal, mechanical, electrical and chemical) to break water/oil emulsions. However, chemical demulsification by adding demulsifiers is still one of the most frequently applied industrial method to break crude oil emulsions [4]. The latter are generally combined with physical methods to accelerate the demulsification process [5].

Currently most of the recoverable crude oil around the world is heavy crude, i.e. specific density equal or lower than 20 API. Their composition complexity and high viscosity makes them difficult and expensive to produce and transport through pipeline because of their low mobility and flowability. Different strategies to facilitate the handling and transport of such crude oils are the dilution with condensates or lighter oils, the use of flow improvers and drag reducing additives, and the formation of oil in water emulsion (O/W), known as inverse emulsions, to increase the crude oil fluidity [6].

The formation of O/W emulsions is competitive when compared to conventional technology. However, this approach requires water separation and conditioning prior to crude oil processing and refining [7]. Thus, the demulsification process is important to break direct emulsions, more commonly W/O emulsions in order to avoid operational problems caused by the presence of water in the refining process. Secondly, demulsification is needed to break inverse O/W emulsions, that may also be formed naturally, but most commonly promoted as a method for fluidizing heavy crude before pipelining [8].

In this regard, ionic liquids (ILs) have been widely studied in the last two decades because of their unique properties, as an ecological alternative to solvents, cosolvents and catalysts in organic synthesis [9], and in the chemical industry [10]. Since they have a very low vapor pressure, thermal stability and non-flammability, they have been considered as "green, ecofriendly chemicals" [11]. ILs have found a variety of applications in the oil industry, such as pollutant removal, corrosion inhibitors and viscosity reducers [12-14]. ILs have found also wide applications as surfactants [15-16], and recently the application of ILs as demulsifiers for both W/O and O/W in petroleum industry have been described [17-19].

The purpose of this work is to share the qualitative perspective of ILs applications as surfactants and specially their applications as demulsifiers of petroleum emulsions. The chapter is then divided into two parts. The first part involves a review about generalities about surfactants, theories of emulsion and demulsification, variability of applied chemicals, emulsion's formation, type of emulsion, factors affecting the emulsion's stability, chemical demulsification, and proposed mechanisms for emulsion's breaking. In the second part, we discuss the ILs applications as surfactants with focus as demulsifiers of both O/W and W/O emulsions for oilfield applications. The effect of microwave irradiation on breaking crude oil emulsions in conjugation with ionic liquids is also discussed.

2. Theory about emulsions

2.1. Emulsion formation

An emulsion is generally defined as a system in which a liquid is distributed or dispersed relatively in the form of droplets in another substantially immiscible liquid. An emulsion is a lyophobic colloid, i.e. a sol that cannot be formed by spontaneous dispersion. The emulsions are thermodynamically unstable, but they may be kinetically stabilized by the presence of an emulsifying agent or surfactant. The latter forms a surface film on the existing interface between each droplet and the continuous medium, thereby reducing interfacial tension and preventing coalescence.

When a system containing enough surfactant, water and oil is subjected to mixing, one of the phase is preferentially dispersed as droplets into the other and resulting in an emulsion [20]. The mission of the surfactant is to facilitate the extension of the interface during the formation of the emulsion, and secondly, stabilizing the emulsion by retarding the coalescence of dispersed phase droplets. The surfactant possesses an amphipathic nature, which allows

locating at the interface between each droplet and the continuous medium and thereby reducing interfacial tension and preventing coagulation.

There are three minimal requirements to form an emulsion:

- Two immiscible liquids such as water and oil.
- Enough shear force provided by mixing to disperse one liquid into droplets in the other.
- An emulsifying agent to allow reduction of the free surface energy and stabilize the dispersed phase.

The nature of dispersion and continuous phases may be more complex as is the case of multiple emulsions. By instance, the dispersion of oil droplets into segregated water phases that in turn are dispersed in a continuous oil phase (oil/water/oil, O/W/O emulsion). The petroleum industry uses to classify direct emulsions (Figure 1), i.e. water-in-oil emulsions, as hard and soft. By definition a hard emulsion is very stable and difficult to break, mainly because the dispersed water droplets are very small. Moreover, a smooth emulsion or dispersion is unstable and easy to break. The inverse or oil-in-water emulsions are also present but more like a complex emulsion rather than it self. Emulsions are difficult to treat from the operational point of view and cause several problems, including difficulties to separate gas/oil phases, crude out of specification, generate high pressures in pipes and also because water contains many dissolved salts causing severe corrosion problems in pipelines, storage tanks and equipment.

When water droplets of large diameter are present (> 100 microns), they are often easily removed by gravitational force that favor coalescence and formation of a water continuous phase. The water that is separated in less than five minutes is usually called free water. The amount of water that remains emulsified may vary widely from 1 to 60% by volume. In case of medium and light crude oils (> 20 ° API), emulsions typically contain 5 to 20% by volume of water, while 10 to 35% water may still be present in heavy and extra heavy oil (<20 ° API).

Emulsions can also be classified according to their dispersed phase:

- Between 0 and 5% of dispersed phase, the emulsions present droplets that have no direct interactions with each other..
- Between 5 to 30% of dispersed phase, droplets have some interactions with each other but emulsion properties are mainly ruled by the continuous phase.
- Between 30 and 74% of dispersed phase, emulsions are considered as medium dispersed phase, and their properties show remarkable deviations from Newtonian behavior and rely heavily on their formulation and emulsification protocol.
- More than 74% of dispersed phase results on an emulsion of high dispersed phase, in which contact between the droplets is very large, and the emulsion properties are ruled by the dispersed phase.

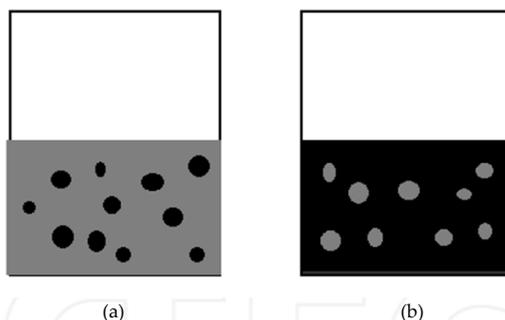


Figure 1. Representative scheme of two type of emulsions, oil-in-water (a) and water-in-oil (b) (oil in black, water in grey).

2.2. Emulsion stability

Some emulsions are easily broken down into water and oil phases after formation, while others can persist for days, months or even years. Stability is a consequence of the small droplet size, the oil/water ratio, the presence of surfactants and factors as temperature, salt content, pH of water, etc. The processes concerning emulsion breaking may be considered as:

- **Creaming:** Creaming is the opposite to the sedimentation phenomenon and is the result of different densities between the two liquid phases which creates a concentration gradient that moves the light dispersed phase to the top, and virtually no coalescence is present because the attractive forces are not strong enough to cause aggregation and coalescence.
- **Sedimentation:** Droplets go to the bottom due to their larger density when compared to the continuous phase but they retain their integrity and no coalescence is present.
- **Coalescence:** it occurs when droplets are near enough to others for a certain time and the attractive forces acting among them cause droplets to merge and form larger drops until a separated phase occurs (Figure 2).

When the interfacial film between droplets has thinned below a critical thickness, it is broken and the difference in capillary pressure causes the emulsion to break. So the properties of the thin film are extremely important for separation. All emulsions except perhaps microemulsions are thermodynamically unstable, but may be relatively stable in the kinetic sense. An emulsion may be kinetically stable against coalescence but unstable with respect to aggregation. The emulsions may be characterized as stable, unstable or mesoestable emulsions.

2.3. Factors affecting the stability of emulsions in petroleum

Some of the most important factors affecting the stability of emulsions are:

- **Heavy fraction of crude:** Emulsions are stabilized by the presence of emulsifiers that locate at the water/oil interface and form an interfacial film. Some organic molecules as asphaltenes

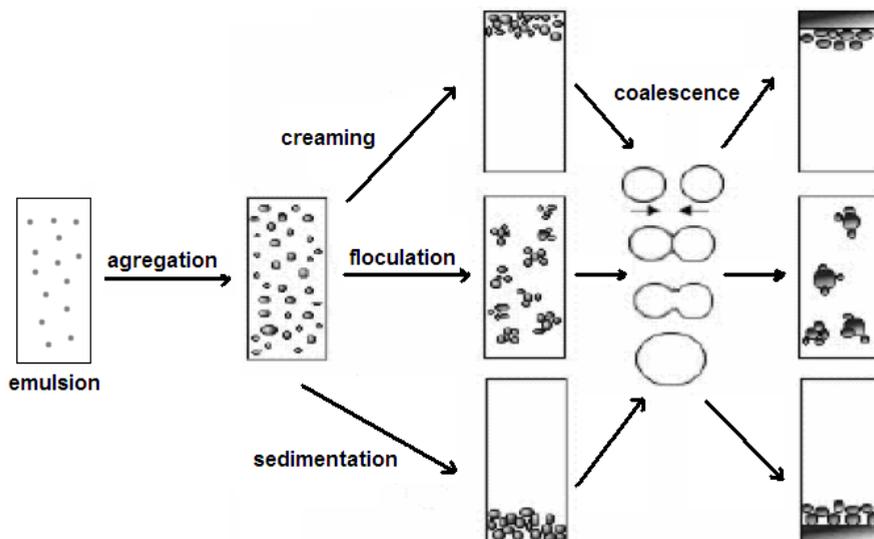


Figure 2. Scheme of emulsion breaking adapted from [4].

and resins present in the crude can act as natural emulsifiers. These polar compounds tend to migrate to the oily surface, reduce the interfacial tension and promote the dispersion and emulsification of water (Figure 3).

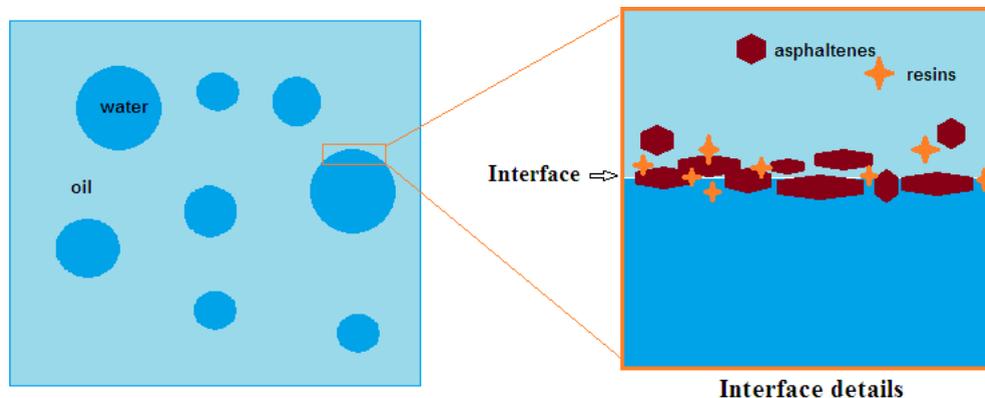


Figure 3. a) W/O emulsion. b) Details of the interface of a drop of water forming a stabilized emulsion.

The asphaltenes are complex structures formed by a variety of polyaromatic and polycyclic compounds. These compounds are attracted by electrostatic forces, mainly π bonds and

hydrogen bonds, that allow an arrangement and packaging that generate clusters with high stability and with paraffins are mainly responsible for the high viscosity and stability of the heavy oil emulsions. In the other side, resins are complex molecules with high molecular weight and soluble in *n*-heptane but very low soluble in ethyl acetate. The role of these compounds is not well defined, but some theories consider that associated with asphaltenes may form micelles that favor emulsion stability. The asphaltene/resin ratio appears to play an important role in the type of film that forms and consequently are associated with the stability of emulsions. Other important macromolecules present in the crude oil and especially in some heavy crude oils are paraffins. Paraffinic compounds with high molecular weight hydrocarbons, known also as waxes, which crystallize when the crude oil is cooled down its cloud point. It has been found that the addition of a specific amount of asphaltene to a waxy oil promotes the formation of stable emulsions. Indeed, paraffins may act synergistically with asphaltenes to produce stable emulsions.

The main factors that can affect the stability of the emulsions are [2]:

- Solids: The presence of finely divided solids in the oily phase favors the stability of emulsions. The effectiveness of the stability of these solids depends on factors such as particle size, interaction between the particles and wettability of the solid particles. Solid particles stabilize the emulsion by spreading across the interface.
- Temperature: The temperature can significantly affect the stability of the emulsion. Temperature affects the physical properties of oil-water interfacial film and the solubility of surfactants, all of which influence the stability of the emulsion. Probably the most important effect is related to the viscosity of the phases in the emulsion since it decreases with increasing temperature. The increase in temperature also causes an increase in the thermal energy of the droplets and therefore the actual number of collisions between them, which in turn reduces the interfacial tension and favor the coalescence of the drops. It has been shown that the increase in temperature causes a gradual destabilization of the oil/water interface. Compressibility of the interface is also affected by changing the surfactants's solubility in the oily or aqueous bulk.
- Drop size: The dispersed droplets into a typical emulsion are found commonly between 1 to 50 microns. Bigger droplets tend to coalesce and resolve into a separated phase. The smaller the droplets are, the emulsion is more stable and its viscosity increases since the free volume between droplets diminished.
- pH: The pH of the aqueous phase strongly influences the stability of the emulsion. The addition of acids or inorganic bases cause ionization of the interfacial film and drastically changes the physical properties of the film. Acid pHs favor the formation of W/O emulsions, while basic pHs favor the formation of O/W emulsions.
- Interfacial tension. A substantial reduction of interfacial tension is not sufficient to increase the stability of the emulsion. It is need also a stabilizing agent that prevent aggregation, sedimentation, creaming and coalescence.

- **Viscosity.** A high viscosity of the continuous phase decreases the diffusion coefficient and the collision frequency of the droplets, favoring the stability of the emulsion. A high concentration of droplets also increases the apparent viscosity of the continuous phase and stabilizes the emulsion. This effect can be minimized by heating the emulsion.
- **Phase volume ratio.** Increasing the volume of the dispersed phase, droplet number and/or droplet size favor the probability of collision of droplets and reduce the stability of the emulsion.
- **Interface aging.** As the emulsion aged, the interface surfactant adsorption is completed and due to the lateral interaction between molecules, the rigidity of the interfacial film reaches a stable value in about 3 to 4 hours. This film or skin around the droplets becomes thicker, stronger and tougher. Furthermore, the amount of emulsifying agents is increased by oxidation, photolysis, evaporation or by the action of bacteria.
- **Salinity.** The brine concentration is an important factor in forming stable emulsions. Fresh water or brine with low salt promotes emulsion stability. Conversely, high salt concentrations tend to reduce it.
- **Nature of oily phase.** An oily phase rich in paraffins does not form stable emulsions, whereas the presence of polar compounds as naphthenic acid and favor stable emulsions. The presence of waxes, resins, asphaltenes and solids can influence the stability of the emulsion.
- **Density.** The net force of gravity acting on a drop is directly proportional to the difference in densities between the droplet and the continuous phase. The increase in density gap by increasing the temperature, accelerates the rate of sedimentation or creaming of the droplets and therefore coalescence.
- **The presence of metal ions.** Divalent cations such as calcium and magnesium tend to produce a compactation of the adsorbed film, probably as a result of electrostatic screening on both sides, provoking the precipitation of insoluble salts in the interface.
- **Interfacial rheological properties.** Generally, chemical gradients are generated when an interface with adsorbed surfactant molecules stretches or expands due to external factors and consequently, the interface presents certain elasticity.

2.4. Demulsification

The demulsification is the breaking of an emulsion and resolution of the phases. This process has gained importance in the petroleum industry because many crudes from offshore reservoirs contain emulsified water that must be separated before processing of the crude oil.

The demulsification process can be carried out by four main methods: mechanical, thermal, electrical, chemical and their combinations. The pH adjustment, voltage application, filtration and membrane separation are comprised among the available methods. Thermal demulsification may be reached by the use of microwaves [21]. The radiation favors temperature elevation process by a non-conventional heating mechanism known as dielectric heating. Many works of demulsification have been focused on the effect of microwave irradiation to break emulsions [22-27].

Now, the most common technologies employed in petroleum industry are the combined use of heat and chemicals designed to neutralize and eliminate the effects of the emulsifying agents. The selection of a suitable chemical is crucial to the demulsification process. However, this process is rather an art than a science, because many factors play a role in this very complex phenomenon. A chemical formulation can exhibit excellent performance for demulsification of a crude oil and become completely ineffective when there are changes in the composition of the oil. An emulsifier is usually a formulation of one or more chemicals dissolved in a suitable solvent. The demulsifiers are commonly polymer chains with ethylene oxide alcohols, ethoxylated phenols, ethoxylated alcohols and amines, ethoxylated nonylphenol, polyhydric alcohols and sulfonic acid salts. The more common procedure for selecting a demulsifier is through bottle tests in the laboratory. These tests allow the selection of right chemicals, evaluate a suitable formulation and define the conditions of concentration, residence time and process temperature. Due to the wide variety of components present in the crude oil, it is not surprising that the performance of demulsifiers is largely dependent on the type of oil and composition, whereby the performance of a formulation can vary drastically from one oil to another.

2.5. Possible chemical mechanisms for demulsification

The emulsification with the use of chemicals is a very complex phenomenon. Different theories have been proposed to explain the mechanisms of demulsifier's action. It is known that demulsifiers establish an opposite type emulsion that those formed by the natural emulsifiers (emulsion stabilizers), thereby displacing the emulsifiers of the drop interface, which favors the coalescence of water or oil droplets. Therefore, the efficiency of demulsifier depends on their adsorption capacity at the interphase in competition with other surface active species present in the emulsion.

In 1949, Griffin introduced the concept of Hydrophilic-Lipophilic Balance (HLB) as an empirical scale to weight the effect of the structural aspect of surfactant molecule and it is related to the chemical groups that are similar or antagonistic to water [28]. The HLB for polyethoxylated surfactants defined as 20 times the weight of the part consisting of polyoxyethylene. For example, for 5 sets of nonylphenol with ethylene oxide, the HLB is 10 and because this molecule is exactly the same weight of the hydrophilic and lipophilic moiety, a rule has been established that an $HLB \leq 8$ (or $HLB \geq 12$) indicate that this is a lipophilic surfactant (or hydrophilic and this results in a W/O (or O/W emulsion) according to the Bancroft rule. The HBL has the drawback that it does not take into account parameters such as temperature, salinity, or the nature of the hydrophilic group so they cannot be used as a parameter for comparison between different families of surfactants. So it was developed an equivalent taking into account all these effects through a mathematical equation known as hydrophilic-lipophilic deviation (HLD). The HLD can take positive or negative values related to the type of O/W or W/O emulsion. The minimum emulsion stability occurs when the HLD equals zero. The HLD is the dimensionless version of the SAD (surfactant affinity difference) and developed by Salager and coworkers [29-32].

When a surfactant or mixture of surfactants have a high hydrophilic or lipophilic affinity, they generally give non-stable emulsions, as the surfactant is preferably immersed in the medium

bulk by having high affinity and preferably not at the interface stabilizing the emulsion. Moreover, when a surfactant has exactly the same affinity for both phases, also they generate very unstable emulsions. The emulsion stability is high when the surfactant has a moderate lipophilicity (for the case of a W/O emulsion) or moderately hydrophilic (in the case of O/W), which is associated with a HLD of +3 or +4 for the case of a W / O emulsion or -3 to -4 for the case of an O/W. The affinity of the surfactant by either phase can be manipulated through variations in the formulation, i.e. by varying the nature of the components and their interaction with the interface as variation in salinity (salt addition, the electrolyte type and concentration), oil type (number of carbon atoms of the alkane or equivalent), size of the head and tail of the surfactant, alcohol type and concentration, temperature and/or pressure.

The HLD expression for a system containing ethoxylated surfactants can be expressed as following:

$$\text{HLD} = \beta - k\text{EACN} + bS - \varphi(A) + c_T\Delta T$$

Where β is a characteristic parameter of the surfactant or surfactant mixture which increases insofar as this is more lipophilic, *EACN* is the carbon number of the alkane or oil equivalent if this is not an alkane, *S* is salinity and expressed in % by weight of salt in the aqueous phase, $\varphi(A)$ is a function of alcohol (type and concentration) which is commonly used as a cosurfactant and ΔT is the difference in temperature of the surfactant relative to room temperature (25 °C) and *k* and *c_T* are constants. Thus, if the experiment was carried out using distilled water in the absence of alcohol and at room temperature, the last three terms in the equation would be zero and hence the HLD depend only on the characteristics of the surfactant and the concentration of solvent.

When any of these variables change monotonically (i.e. salt concentration or temperature), keeping all other variables constant can be studied very promptly the effect of these on the emulsion stability. Another equation is set to non-ionic surfactants of ethoxylated type, which can be expressed as follows:

$$\text{HLD} = \alpha - \text{EON} + b \times S - k \times \text{ACN} + t(T - 25) + a \times A$$

Where α , *k* and *t* are surfactant parameters, *EON* is the degree of ethoxylation of surfactant, *ACN* is the carbon number of the alkane, *S* and *A* are the concentration of salt and alcohol, and *T* the temperature. The above equation may be described as follows:

$$\text{HLD} = k \times \beta + b \times S - k \times \text{ACN} + t(T - 25) + a \times A$$

Where the parameter β can be defined as:

$$\beta = (\alpha - \text{EON}) / k,$$

W/O emulsions naturally occur to the lipophilic nature of the natural surfactants, which have a HLD value greater than 0, so demulsification essentially involve adding a second surfactant to displace HLD value to 0. Accordingly, the surfactant to be added should be hydrophilic in nature and must be added to such a concentration that the mixture to generate a natural surfactant HLD=0, indicating that has the same affinity for the water than oil.

2.6. Chemical products for demulsification

Usually commercial demulsifiers are mixtures of several components having different chemical structures and polymeric materials with a broad molecular weight distribution. Demulsifiers are formed by a 30 to 50% of active material (surfactant) plus the addition of suitable solvents such as alcohols and aromatic naphtha. Many kind of demulsifiers have been employed since 1920 as soaps, naphthenic acids and salts, aromatics and alkylaromatic, sulfonated compounds, sulfonated and castor oils, esters, organic acids, epoxides, block copolymers of ethylene and propylene oxide, alkylphenol-formaldehyde resins, polyamines, fatty alcohols, polyesteramines and oxyalkylated amines and mixtures thereof [33]. Figure 4 shows some structures of commercial chemicals used in the demulsifier formulations in the last decades. Commercial demulsifiers usually contain one or more of these active ingredients in a suitable solvent. For polymers, molecular weight and chain distribution plays also an important role in the demulsifier effects.

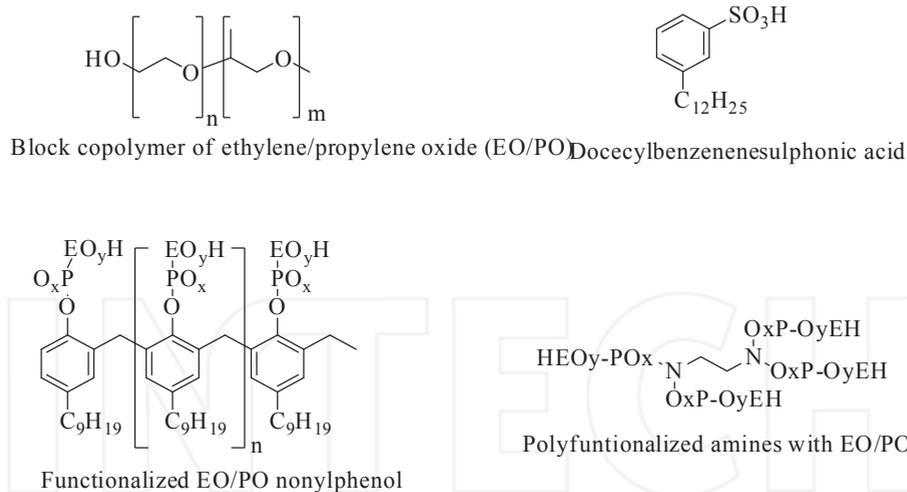


Figure 4. Structures of some commercial chemicals used as demulsifiers in Petroleum Industry.

2.7. Ionic liquids as surfactants

As described throughout this book, ILs present exceptional properties such as high solvent abilities, negligible vapor pressures, extremely high electrical conductivities, chemical and

thermal stability [34-35] that have been exploited in applications as diverse as in organic synthesis [36-37], catalysis [38-39], biocatalysis [40-41], separations [42], extraction [43], dissolution [44], polymerization reactions [45] and electrochemistry [46]. In petroleum industry, ILs have found wide applications as corrosion inhibitors [14, 47], as inhibitors of asphaltene precipitation [48] and for removing pollutants from refineries feedstocks [13].

Moreover, ILs with long-chain hydrocarbon residues exhibit surfactant properties in water [49-53] and in other ILs as solvents [54]. ILs have also been widely explored as potential ionic surfactants with different areas and applications such as extraction of organic compounds, metal ions and radioactive isotopes [55-56], as template to produce micro/mesoporous materials [57-58], in microemulsion [59-61]. The surfactant properties of ILs are easily understood if we consider that these compounds generally have a well-defined structure with hydrophilic character and another with hydrophobic character, i.e. they are amphipatic. Moreover, these compounds may be or anionic or cationic nature depending that in which section of their structure the amphiphilic character is present. Switterion type ILs have also well studied (Figure 5).

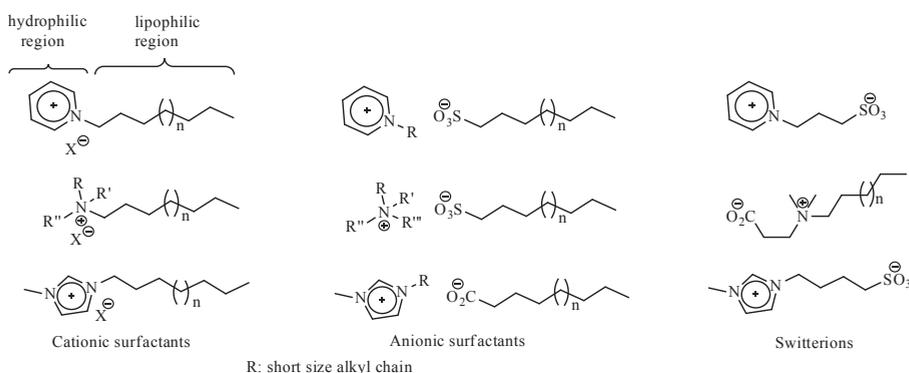


Figure 5. Some examples of surfactants ILs.

There is an interesting study about the influence of ionic and non-ionic amphiphiles, i.e., Cetyltrimethylammonium bromide (CTAB) and 1-(2-aminoethyl)2-heptadecyl-2-imidazoline (1), on the pore hierarchy and morphology of siliceous particles synthesized with. The amphiphile (1) leads to the formation of spherical silica particles of about 250 nm diameter, while the ionic surfactant CTAB led to porous silica spheres of about 750 nm diameter. A single-particle analysis using High Resolution Electron Microscopy and Optical Density Transforms show the inner pore structure of the particles synthesized with CTAB and low molecular weight alcohols co-surfactants (ethanol and propanol) is oriented along the sphere radius, while silica particles synthesized with (1) have a random-like pore structure. Both systems were used as supports for adsorption of a photosensitive spirocyanine (i.e., Spiro-6) type compound (1',3',3'-trimethyl-6-nitrospiro-(2H-1-benzopyran-2,2'-indoline)) and their interaction with the silica surface was characterized by IR spectroscopy, showing a weak interaction

with respect to other silicates (lamellar clays). These effects are potentially interesting for applications on biomarkers, stable photosensitive materials, solid-phase organic synthesis and dyes [62].

In petroleum industry, surfactant ILs have been explored as efficient chemicals for Enhanced Oil Recovery (EOR) that is a generic term for techniques that increase the amount of crude oil that can be extracted from a reservoir. It is estimated that two-thirds of crude oil remains in oil reservoirs after primary and secondary (water flooding) recovery stage and with the decrease in world oil reserves and a higher demand for petroleum and its derived products, the effective exploitation of oil reservoirs has become increasingly important.

EOR-assisted by surfactants is an effective method for recovering the oil from reservoirs that have lost their drive after the application of primary and secondary recovery methods. In this sense, ILs have showed good potential as surfactant with this purpose [63-64], thus Lago et al. showed the suitability of several ILs as effective replacements for conventional surfactants in EOR [65-66]. The reservoir fluid has been modelled as a ternary system of water (pure water or aqueous solution of NaCl) plus the IL: trihexyl(tetradecyl)phosphonium chloride plus dodecane. Determination of its liquid-liquid phase equilibrium indicates the formation of a Winsor type III system, with a triphasic region and adjacent biphasic regions. The interfacial tensions in the system corroborate the ability of the IL to act as a surface active agent, as desirable for its use in an EOR process. A relevant transport property such as viscosity, in addition to density, has been experimentally measured for the equilibrium phases [65]. The same research group showed in 2013 that the three-phase system generated when adding trihexamethyl(tetradecyl)phosphonium chloride to the water-oil mixture remain stable in the wide range of temperature and in the presence of salt, in contrast with other system, no co-surfact is required. When the temperature increases, an important decrease of the microemulsion-water/brine interfacial tension was observed [66].

Recently, the application results of ILs was reported, for the first time, at laboratory scale using a sand-pack column model for EOR. A 2 wt% aqueous solution of 1-ethyl-3-methylimidazolium tosylate ($[\text{C}_2\text{MIM}][\text{OTs}]$) was used to recover an aromatic oil. The results show that a flooding processes using only 4 pore volumes (PV) could recover 65.7% (± 1.0) of the oil in place, almost the double of what was recovered with a brine solution (NaCl, 2 wt%). These preliminary results, requiring further optimization of the IL characteristics and concentration, and other process parameters, suggest that water-flooding with aqueous solutions of ILs can contribute to EOR in mature reservoirs [67].

2.8. Ionic liquids as demulsifiers of emulsions in petroleum industry

ILs have also found application as surfactants in demulsification process for oil field application. As discussed above, crude oil is invariably accompanied by water and formations of stable W/O emulsions are frequently encountered in the oil industry. These emulsions contain significant quantities of contaminants, salts and other corrosive compounds and their stability is increased for heavy and ultra-heavy crude oils due to the content of these natural emulsifiers that is more abundant than in light crude oils [33].

Destabilization of emulsions is an important step to obtain water-and salt-free oils, being the chemical demulsification and desalting the most frequently applied industrial methods to break crude oil emulsions. This process can be very difficult and non-efficient to demulsify and desalt water-in-oil emulsions of heavy viscous crude oils, being also time consuming [68]. A study about W/O demulsification for three types of Mexican crude oils was reported using several surface-active ILs analogues. The efficiency of these ILs was studied using emulsions of medium, heavy and ultra-heavy crude oils under conventional heating. Some of these surfactants were able to break water in oil emulsion in heavy and ultra-heavy crude oils. The effect of microwave irradiation as non-conventional energy source to accelerate and increase the efficiency of demulsification for heavy crude oil was also demonstrated [69]. Brazilian researchers have also studied ILs and microwave effect on demulsification of crude oil emulsions [17]. In their more recent work, they investigated the effect of five ILs, [BMIM][NTf₂], [OMIM][NTf₂], [C₁₂MIM][NTf₂], [BPy][NTf₂] and [OMIM][OTf] and a set of operation parameters on the demulsification process, including the heating type (conventional and microwave), IL concentration (0.6 to 6.2 g/dm³), effect of alkyl chain length, and effect of cation and anion type on demulsification efficiency. The results indicated that the demulsification was favored when more hydrophobic ILs and longer cation alkyl chains were employed, such as [C₁₂MIM][NTf₂], reaching values close to 92% of water removal. Also microwaves in conjunction with IL showed the highest demulsification efficiency [70]. Flores et al. studied the anion and cation effect as ammonium type ILs as dehydrating agent of ultra-heavy crude oil from the experimental and theoretical point of view using series of trioctylammonium (TOA) ILs containing the anions: Cl⁻, HSO₄⁻ and H₂PO₄⁻, and other new ammonium salts (OCD) with HSO₄⁻, MeSO₃⁻ and MePhSO₃⁻. According with this study, the ranking of water removal efficiency for the TOA series at 1000 ppm was Cl⁻ > HSO₄⁻ > H₂PO₄⁻, while for ODC series, the rankings for efficiency at 360 min were HSO₄⁻ > MeSO₃⁻. Theoretical studies by means of density functional theory (DFT) suggested that an increase in the softness and electrophilicity of the cations correlated with lesser effectiveness as demulsifiers. Finally, the partition coefficient of the cations showed that if the viscosity of the crude oil is low, it is possible to use ILs with a low partition coefficient (log P), but if the viscosity is high, the log P of IL should be near to the [TOA][Cl] value [71].

Ammonium-type IL anionic surfactants have also shown good efficiency as demulsifiers of W/O emulsions. Four amphiphilic cholinium carboxylates were synthesized by ionic exchange from choline chloride (Vitamin B₄) and fatty acid salts under microwave irradiation (Fig. 6). These environmentally friendly anionic surfactants were evaluated as demulsifiers to break water in crude oil emulsions using short intervals of microwave dielectric heating to follow the kinetics of the demulsification and the results of the evaluations were validated and confirmed by the classical “bottle test” procedure. Choline palmitate showed the best performance as demulsifier of the heavy Mexican crude oil emulsion [72].

Another application of ILs is on the demulsification of O/W emulsions, or inverse emulsions. Unlike the W/O emulsion which tend to increase the viscosity, the inverse emulsion are less common. The continuous phase of such emulsions is water, which substantially reduces the viscosity of high viscous oils like heavy, extra heavy and bituminous oils and represents an

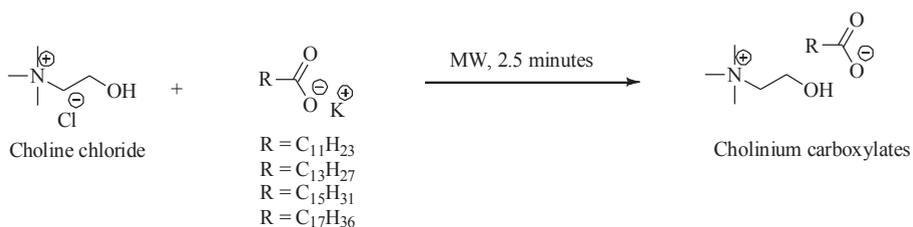


Figure 6. Microwave-assisted anion exchange to obtain choline carboxylates.

interesting alternative for their transportation through pipelines. Nevertheless, crude oils must be conditioned by removal of water and salts before further refining. Hence, the potential of aminoacid based ILs as demulsifiers of O/W emulsions was probed to break an emulsion from heavy crude oil [73]. The aforementioned O/W emulsions were prepared using alkyl-O-glucoside and-cellobioside biosurfactants [74]. The effect of the addition of the ILs surfactant GlyC12 (1000 ppm) on the water separation of an O/W emulsion was evaluated using oil bath or microwave heating at 50 W (Fig. 7). As was observed, microwave heating is more effective than oil bath heating in terms of rate of demulsification. Indeed, MW heating during two minutes allowed water separation of 77% and only 37% under oil bath heating. The emulsion in the presence and in the absence of GlyC12 reaches a water separation of 87% and 89% respectively after 10 minutes of treatment.

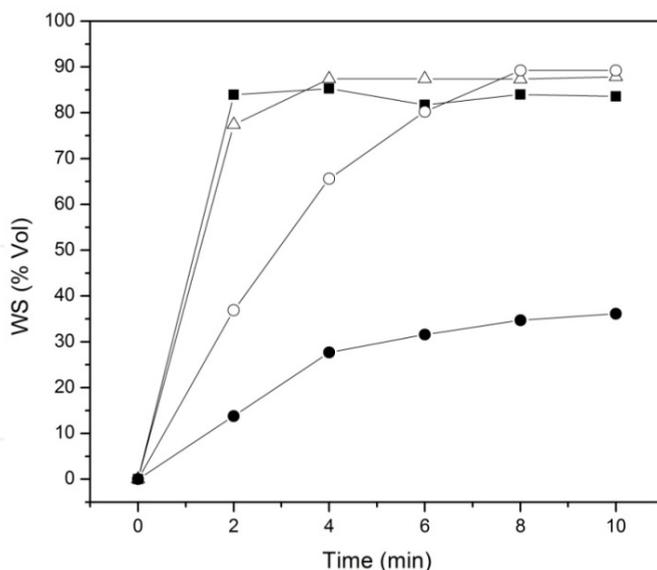


Figure 7. Kinetics of the separated water (WS) from the initial O/W emulsion treated under oil bath (●) and MW heating (■); and in the presence of a demulsifier (GlyC12, 1000 ppm) under oil bath (○) and MW heating (△).

The addition of the demulsifier increased the water separation efficiency for oil bath heating, the separated water increased from 30% to 80% after 6 minutes of contact. It is clear that both demulsifying approaches reached a high percentage of separated water after 10 minutes of heating when the demulsifier was used. MW heating appears to be a good demulsifying process for O/W emulsions since water separation occurs rapidly within the first minutes of heating (Fig. 8) [18].



Figure 8. Photographs showing separated water (WS) from the initial O/W emulsion containing GlyC₁₂ (1000 ppm) at 50 W, 60°C. Initial O/W emulsion before MW irradiation (A), emulsion after MW irradiation during 2 (B), 4 (C), 8 (D), 10 minutes (E).

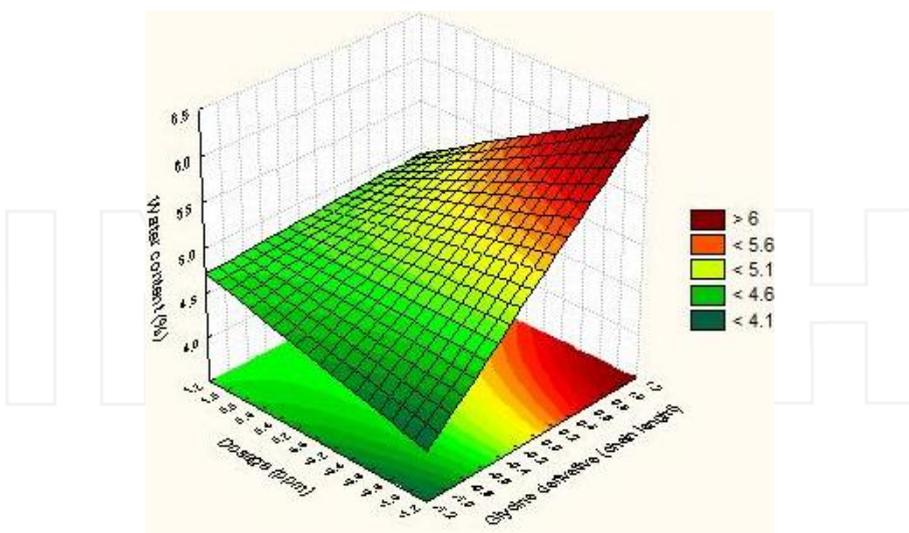


Figure 9. Surface response of the water content respect to the dosage and chain length of Glycine-based demulsifiers at 60°C.

We undertook recently a screening of commercial and synthesized emulsifiers and demulsifiers to develop a comprehensive and environmentally friendly methodology for transporting ultra-heavy crude oil. For the screening of demulsifiers, a factorial 2^k design was employed and demulsification parameters as temperature, demulsifier concentration and pH were studied (Fig. 9). A “green” ionic demulsifiers synthesized from glycine have satisfactory dewatering ability for ultra-heavy crude oil emulsion. When GlyC14 was employed at 900 ppm, the dewatering efficiency reach 89.5% at pH 3. Considering low toxicity surfactants as emulsifier and demulsifier, an environmentally friendly and technically feasible technology was develop for transporting EHCO [75].

3. Conclusions

Complex emulsions are present during production and transporting of crude oil affecting operations in a daily basis and further petroleum refining. It is important to understand the emulsion phenomena: formation, stability and rupture; and all the alternatives that exist to resolve and diminish this problem, including well-known technologies as well as innovatives ones as the use of ionic liquids as demulsifiers of such complex emulsions. Specially for heavy, extra heavy and non conventional crude oils as shale oil, bitumen, etc. Then, ionic liquids present very interesting properties to break out such complex emulsions and resolve in separate aqueous and oily phases. We presented then some current research on the field but strongly believe that ionic liquid research may go further to develop greener chemicals, like amino acid-or sugar-based liquid ionics; instead of conventional pyridinium or imidazolium-based ones.

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