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Crude Oil Desalting Process

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Abstract

Desalting is a water-washing operation performed initially at the production field and thereafter at the refinery site for additional crude oil cleanup. Salt and water content specifications are even more rigid because of their negative effect in downstream processes due to corrosion, and catalyst deactivation. An optimum formulation concept is presented to describe emulsion breaking in desalting process. In the stabilization mechanism is accepted that water droplets are stabilized by the formation of a mechanically strong and viscoelastic film at the interface composed of asphaltenes. In the case of water-in-crude-oil emulsions, a balanced optimum formulation is attained by adding to the lipophilic natural surfactants contained in the crude oil, demulsifiers which are hydrophilic. The aim is to relate the nature and concentration of the added demulsifier products to the amphiphilic mixture at the interface. All formulation parameters, such as solvent, alcohols, kind and concentration of demulsifier, amoung others, can be explained for proportional and saturation regimens.

Keywords: Desalting, asphaltenes, demulsifier, , emulsions, physicochemical formulation

1. Introduction

Petroleum recovered from reservoir is mixed with a variety of substances such as gases, water, chloride salts, and dirt, which contain other minerals. Thus, petroleum processing actually commences shortly after the production of fluids from reservoir, where pretreatment opera-

tions are applied to the crude oil prior to transportation. Any crude oil to be shipped by pipeline, or by any other form of transportation, must meet strict regulations in regard to water and salt content.

Desalting is a water-washing operation performed initially at the production field and thereafter at the refinery site for additional crude oil cleanup, where the salt and water content specifications are even more rigid because of their negative effect in the downstream processes due to scale formation, corrosion, and catalyst deactivation. Desalting involves mixing heated crude oil with washing water, using a mixing valve or static mixers to ensure a proper contact between the crude oil and the water, and then passing it to a separating vessel, where a proper separation between the aqueous and organic phases is achieved.

Since emulsions can be formed in this process, there is a risk of water carryover in the organic phase. In order to overcome this problem chemical demulsifiers are added to promote the emulsion breaking. When this operation is performed at a refinery, an electric field across the settling vessel is applied to coalesce the polar salty water droplets, and, therefore, a decreasing in water and salt content is achieved.

The understanding of the different variables that affect the desalting process, especially the effect of the amount of chemical demulsifiers used, is imperative in order to optimize operating costs. According to data published by Vafajoo [1], the demulsifier concentration used for desalting could reach up to 100 ppm. Considering a demulsifier cost about 1.5 $/lb [2] for a medium capacity refinery (200 MBPD), the operating cost related to chemical demulsifiers would be in the order of 2 MM$/year. Thus, any reduction in demulsifier concentration in crude oil desalting would generate savings in the order of many thousand dollars. In the current work, a technical description of desalting crude oil and a wide description of stability emulsion phenomena are carried out. Finally, this work aims mainly at understanding the demulsifiers role from the viewpoint of physicochemical formulation.

2. Process description

Salts in crude oil are mainly in the form of magnesium, calcium, and sodium chlorides, sodium chloride being the most abundant. These salts can be found in two forms: dissolved in emulsified water droplets in the crude oil, as a water-in-oil emulsion, or crystallized and suspended solids.

The negative effect of these salts in downstream processes can be summarized as follows: salt deposit formation as scales where water-to-steam phase change takes place and corrosion by hydrochloric acid formation. Hydrochloric acid is formed by magnesium and calcium chlorides' decomposition at high temperatures (about 350 °C) as follows [3]:

$$CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl$$

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$
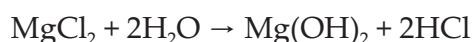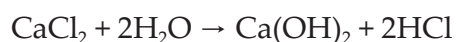
In addition, other metals in inorganic compounds present in reservoir dirt and sand produce catalyst poisoning in downstream processes such as hydrotreaters and cat crackers because of they are chemically adsorbed on the catalyst surface.

The objective of desalting process is to remove chloride salts and other minerals from the crude oil by water-washing. Depending on the desired salt content in the desalted crude oil, a one- or two-step process could be applied. For refining purposes, a salt concentration of maximum 1, 5 PTB (pound of salt measured as NaCl per thousand barrels) is desired. By desalting, a considerable percentage of suspended solids (sand, clay, or soil particles, or even particles product from corrosion of pipelines and other upstream equipments) are removed. Figure 1 shows a general process flow diagram for one- and two-step desalting process.
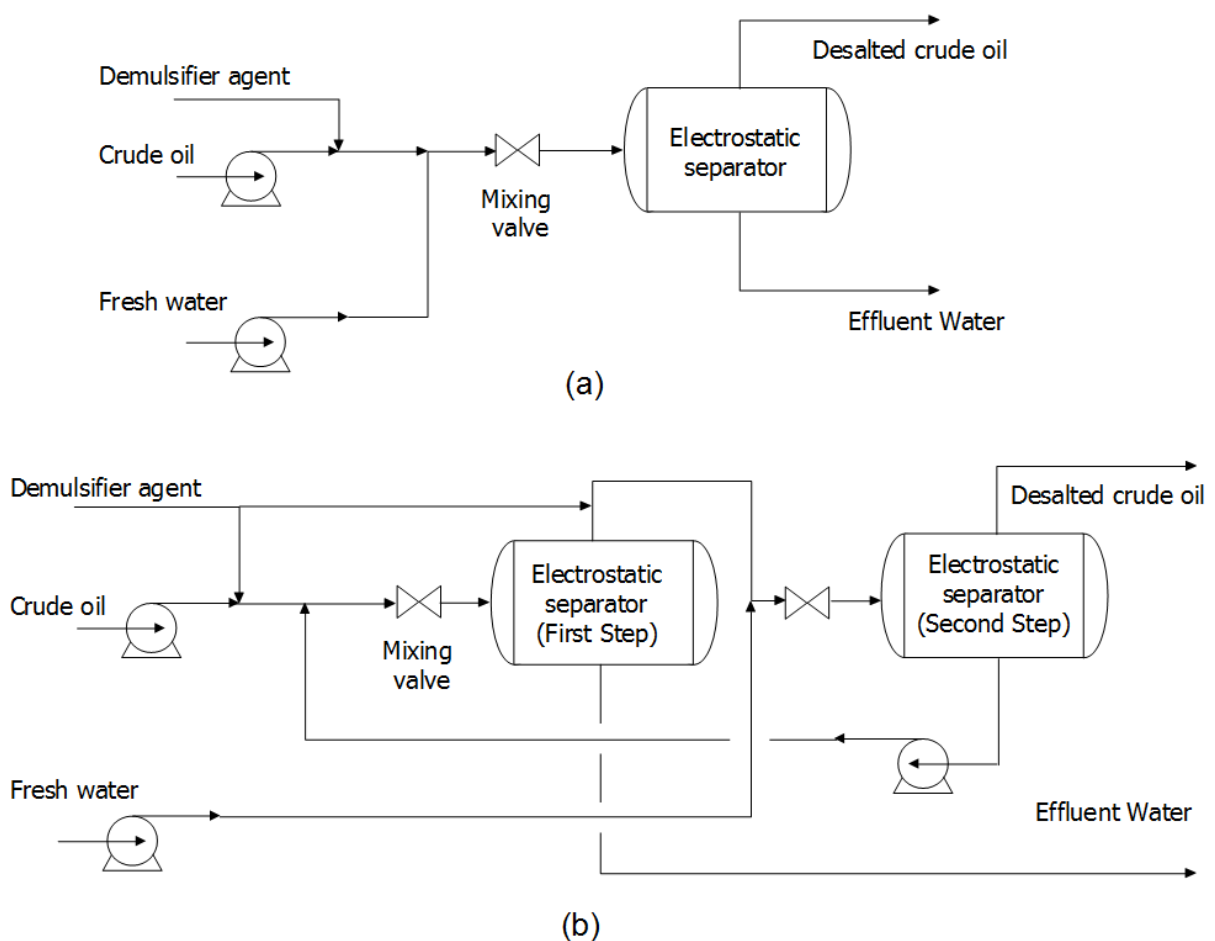

Figure 1. Simplified desalting process flow diagrams for different configurations: (a) one-step and (b) two-step.

The process starts by mixing the raw crude oil with an appropriate amount of washing water also known as dilution water. The washing water as a volume percent of the crude oil processed could oscillate between 3 and 10%, depending on the API gravity of the crude oil – the heavier the crude oil, the more the water required [2]. Demulsifiers are added to the crude oil in this process step.

In order to promote the effective mixing between the organic and aqueous phases, and ensure the proper dilution of the salts and minerals in the aqueous phase, a mixing valve is used. This is a common globe valvewhich causes a pressure drop and, as a result, a shear stress over the droplets that promotes an intimate water and oil mixture. The main aspect that needs to be considered is the pressure drop, whose value it is about 10-50 psi and varies according to the flux through the valve (automatic differential pressure controllers could be used). In addition to the mixing valve, upstream premixing device could be used, such as spray nozzles at the point of water injection or static mixers, between the water injection point and the mixing valve [4]. High delta pressure in the mixing valve promotes smaller droplets, which is positive because it improves the contact among the phases; however, very small droplets could yield a more stable emulsion, which could cause problems in the separating vessel. Therefore, it is very important to balance both effects in the selection of the operation pressure drop.

Then this mixture goes to the desalter, a horizontal cylindrical tank that provides long enough residence time to separate the water and oil mixture in two phases. Some water droplets diameters are so small that they could not be separated by gravity; so, an electrostatic field between two electrodes installed into the desalter is used to promote coalescence. Due to the dipolar nature of the water molecule, this electric field promotes an attraction with the other water molecules in the neighbor droplets promoting coalescence. According to Gary et Al. [2], either AC or DC fields may be used and potentials from 12, 000 to 35, 000 volts. The attraction force (F) between the water droplets is given by:

$$F = \frac{K_s \cdot \varepsilon^2 \cdot d^6}{s^4} \tag{1}$$

where ε is voltage gradient, d is droplet diameter, s is the distance between drops centers and K_s is a constant for the system [4].

Finally, after coalescence, water droplets settle according to the well-known Stock's law given by:

$$Settling\ rate = \frac{k \cdot (\rho_{water} - \rho_{oil}) \cdot d^2}{\mu_{oil}} \tag{2}$$

where k is a constant, d is the droplet diameter, ρ is density, and μ is viscosity.

In a one-step configuration, shown in Figure 1(a), 90% of salt removal can be achieved. For higher salt removal percentages, a two-step configuration, shown in Figure 1(b), should be required. As far as the last process configuration is concerned two demulsifier injection points are used, both before the mixing valve in the first and second step. In addition, freshwater is fed to the second stage, and effluent water from this stage is recycled to the first one. With this configuration, a 99% salt removal could be achieved.

3. Crude oil emulsions

Emulsions are present in the main operations of the petroleum industry. The more well-known emulsions in the petroleum industry are those when the crude oil is the external phase (W/O). Water-in-oil emulsions are robustly stabilized by natural surfactants from crude oil, where a "special film" takes place and it is the responsible for emulsion stability. Film at the oil–water interface is highly viscous and is formed by asphaltenes, resins, waxes, and small solid particles [5, 6].

A main feature for interfacial film is the irreversible adsorption of asphaltenes at the oil–water interface in combination with other natural surfactants [7-10].

In the study of water-in-oil emulsions, it is important to know the structure and properties of the crude oil components, their tendency to associate and accumulate at the interface, as well as solubility and sensitivity to pressure and temperature changes.

3.1. Formation of water-in-oil emulsions

In secondary oil recovery processes, the oil is contacted with formation water or water injected to produce the oil drain water. Water is used as a piston to push the oil from the well during the production process and then remove to the refinery [11]. In the reservoir, the fluid velocity is very slow (1 ft/day) to produce the emulsion, and emulsion is not formed during the two phase flow in porous media but later in equipment where oil is processed. Hence, the shear is responsible of making emulsion by pumping through valves, pipes, elbows, and others [7].

Damage to environment may occurs when petroleum or its products are spilled into the sea or the river, due to which water–oil emulsions are also formed. These emulsions (called "chocolate mousse") has special properties and characteristics [12-13]. Changes in the emulsions properties, such as viscosity and stability, are notable due to internal phase increasing [13].

The formation of water/oil emulsions is generally caused by the presence of resins and asphaltenes present in the oil, which play the role of natural emulsifiers [9]. These emulsifiers have a mutual attraction resulting in the formation of an elastic membrane around the droplets, preventing water droplets from uniting and decanting by gravity. This membrane is thick and could be easily visible using an optical microscope [14].

3.2. Asphaltenes

Asphaltene is the petroleum most complex fraction which is insoluble in normal alkanes such as n-pentane, n-hexane, or n-heptane, but soluble in benzene or toluene. Asphaltenes are composed by high molecular weight molecules and the most polar components in crude oil [15].

Usually, asphaltene structure comprises fused polyaromatic rings substituted by short aliphatic chains (1-3 carbons atoms) and cycloalkanes. Aromatic rings containing some polar functional group than content heteroatom such as sulfur, nitrogen and oxygen and some

metals like nickel, vanadium and iron, which confer polarity and amphiphilic characteristics to these macromolecules [16]. Asphaltenes can generate a wide distribution of molecular structures that can vary greatly from one crude to another [17].

Asphaltenes are composed of several polynuclear aromatic sheets surrounded by hydrocarbon tails, and form particles whose molar masses are between 500 and 20.000 g. They contain many functional groups, including some acids and bases [18].

The specific structure of asphaltenes is unknown; however, molecular weight averages about 750 and there is a planar aromatic structure surrounded by alkane groups, some with heteroatoms, sulfur (S), nitrogen (N), and oxygen (O) [19]. Deposition of asphaltenes often causes some changes in the flow behavior of the oil fields through processing facilities, and difficulties in oil recovery. The problems caused by asphaltenes are closely related to its stability. Due to pressure variations, oil composition, and temperature, asphaltenes tend to form aggregates [14].

Experimental evidence from a combination of spectroscopy techniques and elemental analysis suggest that resins contains several fused five-and-six carbons rings in addition to alkyl chains.

Crude oil can be defined as a dispersed system where asphaltenes are colloids. Asphaltene molecules are in the center of the structure of the liquid oil, the other components are organized around the layer of asphaltenes decreasing polarity (resins, saturated and aromatic hydrocarbons). This simple model allows reconciling the compatibility presence within the same fluid and asphaltenes.

3.3. Mechanism of asphaltene aggregation: Colloidal behavior

Asphaltenes can be considered as a complex polydisperse system of molecules in which subcomponents with significantly different characteristics can be distinguished as the result of solubility differences [17, 20].

From the colloidal point of view, it has been stated that asphaltenes in general are a blend of two main fractions. Acevedo et al. [21] proposed a model for asphaltene colloids in toluene which consists of two subfractions with different solubilities, called A1 and A2. The subfraction A1 (90 mg/L in toluene), which is insoluble in aromatic solvents such as toluene, cumene, and others, is found in greater proportion than a second subfraction A2 (57 g/L in toluene), which is soluble in these solvents and acts as a promotor in the dispersion of A1. The solubility of the latter is similar to the total mixture. Asphaltene aggregation phenomena is well understanding under the vision of colloidal nature of both fractions. [22]. Furthermore, this colloidal model has been found very useful in accounting for other phenomena such as trapping of compounds, flocculation, aggregation promoted by A1, asphaltene aggregation at very low concentration, and metal distribution [17].

In the vapor pressure osmometry (VPO) technique for molecular weight measures, the polarity of solvent is a critical parameter. Using o-dichlorobenzene, a 1000 g mol^{-1} value was reported for A2 solutions at 120 °C. On the other side, A1 afforded higher values (around 2600 g mol^{-1}), emphasizing the strong aggregation tendency of this fraction [23].

Asphaltenes can form different types of aggregates depending on the environment: oil, solvent, interface, and others. Mullins et al. [24] proposed a scheme to explain the aggregation of asphaltenes in toluene. At low concentration, asphaltene is a group of individual molecules that evolve into nanoclusters and are associated in particles until reaching a system susceptible to flocculate. Floccules are unstable aggregates that eventually precipitate. In certain cases, stable aggregates that give the crude viscoelastic properties are formed.

Due to the presence of polar groups, asphaltenes can behave as surfactants, exhibiting the phenomena of adsorption and aggregation. However, it is wrong to attribute a critical micelle concentration (CMC) for asphaltenes and other macromolecules from crude oil. CMC is a parameter exclusive for surfactants, such as sodium dodecyl sulfate ($8.3 * 10^{-3}$ M in water). Parameters such as aggregation number, shape and size of the micelle, electrolyte effect on the micellization and other additives are well known for surfactants. For petroleum asphaltenes this knowledge does not exist, mainly because the structure of an asphaltenes molecule is unknown. Aggregates phenomena best describes asphaltenes behavior. Asphaltene in toluene begins to form aggregates at 50 ppm concentration [25].

In summary, the use of CMC term for asphaltenes and other natural surfactants contained in the crude oil should be avoided. The emulsions in crude oil are produced for a mechanism starting with asphaltenes migrate into the oil–water interface, a process which is regulated by the diffusion of the soluble asphaltenes [19]. Adsorption of asphaltenes at the interfaces is a very slow process. The initial diffusion step toward the interface is rapid and it is followed by a long reorganization and the progressive building of multilayers. Asphaltenes diffuse from the bulk of crude oil to oil–water interface and are then adsorbed, decreasing the interfacial tension [26]. Asphaltenes can also form multilayers on solid surfaces such as silica. It has been found that increasing the concentration of asphaltenes in solution tends to increase its state of aggregation, which decreases the rate of adsorption on the surface [22].

3.4. Stability of water-in-crude-oil emulsions

In terms of time, the stability of the emulsion has a range from few minutes to years and it varies by the characteristics of the crude oil and water [27]. The stability mechanism is, of course, related to the composition of crude oil, such as type and the concentration of natural surfactants, the physical properties of oil, and the interfacial rheology of the interface around water droplet, which provides information about elasticity and viscosity and, for instance, the presence of a film (called skin) for the specific case of petroleum crude oil at this interface [10, 28].

Gao et al. [29] quantitatively studied the formation of interfacial film by the asphaltenes on the oil–water interface. They propose to measure the appearance of crumpling in the interfacial film, using imaging drop following compression by extraction volume, by the following relationship:

$$CR = \frac{A_f}{A_i} = \frac{\pi R_{f^2}}{\pi R_{i^2}} = \frac{R_{f^2}}{R_{i^2}} \tag{3}$$

where CR is crumpling ratio; A_i is the projected drop initial area; A_f is the projected area of the drop observed just before crumpling; R_i is the projected drop initial radio; and R_f is the radio of the drop observed just before crumpling. Figure 2 shows a schema of the contraction of a drop of oil in water. In Figure 2 (a), crumpling phenomenon does not occur; drop reduces its volume to be sucked into the syringe. In Figure 2 (b), volume drop is contracted when the drop crumpling phenomenon occurs in the interfacial film. The scheme shows its building. CR parameter is related to the irreversible adsorption of asphaltenes at the water–crude interface; an increasing of CR means an increasing in emulsion stability.
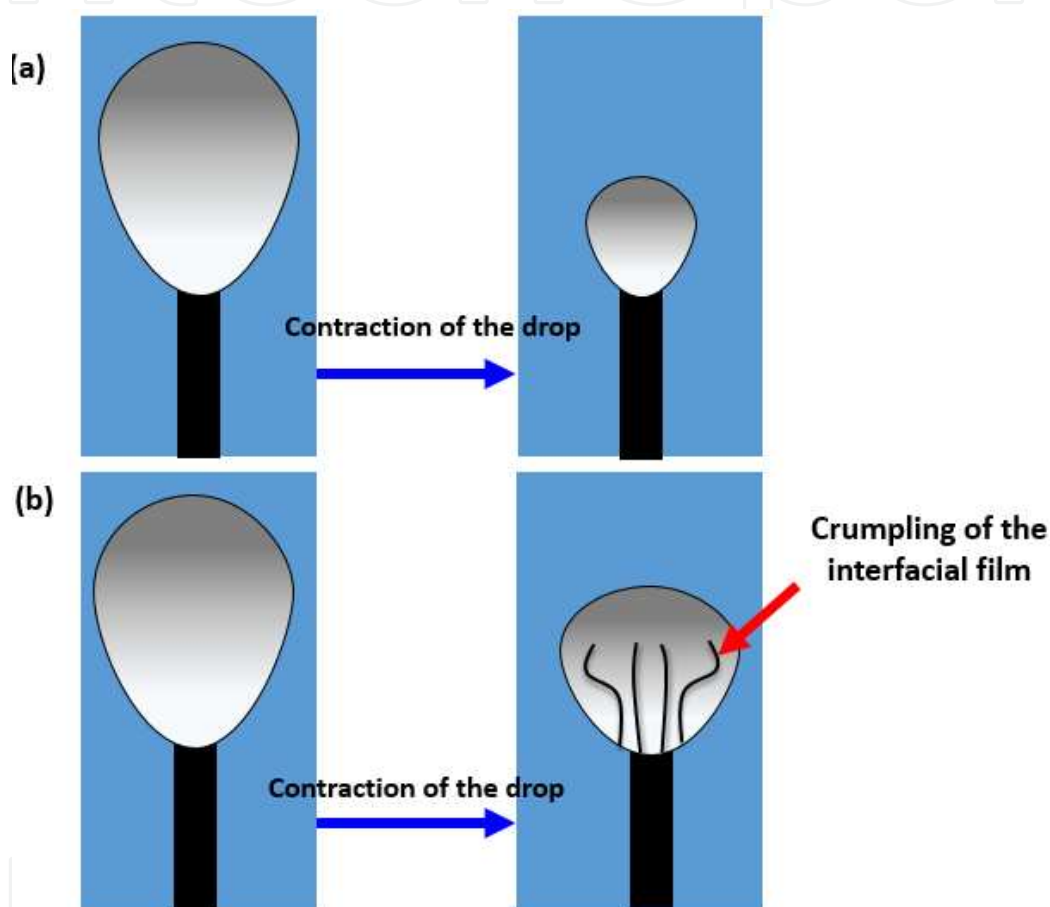

Figure 2. Volume contraction scheme of a drop of oil in water system: (a) absence of crumpling phenomenon and (b) presence of crumpling phenomenon occurs.

As part of the stabilization mechanism, it is accepted that the water droplets are stabilized by the formation of a mechanically strong and viscoelastic film at the interface, composed of asphaltenes [30].

Subsequently, several workers reviewed emulsions and concluded that asphaltene content is the most important factor in the formation of emulsions [7-10]. Asphaltene fraction is mainly responsible for the high emulsion stability of water-in-crude-oil; thus, they were found to be capable of forming rigid, cross-linked, and elastic films [19].

Asphaltenes stabilize water-in-oil emulsions if they are near or above the point of incipient flocculation, i.e., solid particles which can be. Other investigators have also suggested that asphaltene colloids are responsible for stable emulsions. Asphaltenes may be at the interface as fine solid particles or resin-asphaltene colloids. However, Yarranton et al. [31] reported that, at low asphaltene concentrations (<0.2 wt %), molecular state of asphaltenes predominant onto the colloidal form. It is also necessary to consider the effect of resins as they may influence asphaltene aggregation, adsorption on the interface, and emulsion stability [32].

One of the most used methods for studying emulsion stability is the bottle test. Figure 3 shows the bottle test sample for evaluating the stability of water-in-oil emulsion. It was observed that in the tubes on the left side there are stable emulsions, while in the tubes in the center and on the right side, there is a good separation of the two phases.

Figure 3. Stability bottle test of water-in-crude-oil emulsion (Silva, 2012).

Langmuir technique has been widely used for the characterization of the interfacial film formed by natural surfactants from crude oil [33-37]. Isotherms provide surface-pressure-area information on the compressibility of the film formed by the asphaltenes and other natural surfactants. The interfacial film can be collected with the Langmuir-Blodgett technique. Extensive morphological characterization of the interfacial film has been performed, including properties such as contact angle, thickness, and aggregate size, among other. Images obtained using Atomic Force Microscopy have contributed to the understanding of the mechanisms of interfacial adsorption, swelling, aggregation of colloidal interactions, and asphaltene [38, 39].

Aromaticity, length of the alkyl side chains, and branch reduction in the aliphatic chains of resins and asphaltenes are associated with the formation of stable emulsions. Another important parameter is the pH of the aqueous phase. Asphaltenes and resins are composed of polar functional groups; these groups can be ionized at alkaline pH. Surface charge density increases due to ionization of polar groups, generating internal repulsive forces destroying the mechanical properties preventing droplet coalescence [14].

4. Chemical demulsification: physicochemical formulation

When emulsion formation and stabilization take place, demulsifiers (generally a surfactant) must be used. A surfactant is a specie that, when present at low concentration in a medium, has the property of adsorbing onto the surfaces or interfaces of the system, altering the surface or interfacial free energies of those surfaces (or interfaces) [40].

Balsamo et al. [41] showed that effective demulsifiers formed complexes with natural anionic surfactants present in the oil phase, weakening the irreversible film; this is well correlated with low emulsion stability. When emulsion breaker was added to the system, a synergistic effect was observed between natural surfactant and demulsifier with further lowering of the interfacial tension (IFT).

It is known that an unstable emulsion occurs when amphiphilic formulation at the interface corresponds to an exact affinity balance of the surfactant mixture for the oil and water phase [7, 42-44]. From a physicochemical viewpoint, the optimum formulation is achieved when the standard potentials (μ^*) of a surfactant (or mixture) in oil (μ_o^*) and water (μ_w^*) are equal, i.e., when (μ_w^*)=(μ_o^*). Physicochemical phenomena have been qualitatively related to the emulsion breaking occurrence. In the case of water/crude emulsions, the balanced optimum formulation is attained by adding hydrophilic demulsifiers to the lipophilic natural surfactants contained in the crude oil. From our point of view the aim is relate to the nature and concentration of the added demulsifier products to the amphiphilic mixture at the interface.

A new methodology has been presented by several authors [7, 42-44]. It is essentially a formulation scan study carried out by adding a hydrophilic demulsifier at different concentrations, until a minimum emulsion stability is reached. At this optimum formulation point, the lipophilic natural surfactants (i.e., asphaltenes, resins, naphthenic acids, and other crude oil amphiphiles at the interface) referred to as asphaltenes (A) are balanced by the added hydrophilic demulsifiers (D). The hydrophilic–lipophilic contributions of both types in the interfacial mixture are dependent on their adsorbed concentration and on the strength of their effects. Consequently, the hydrophilic contribution of the demulsifier may be varied by changing its hydrophilicity or its concentration [44]. In general, it has been shown that the more hydrophilic the nature of the demulsifier, the lower is the concentration required to reach the minimum emulsion stability when they join asphaltenes [44], mixing rule is approximately linear, i.e., that the demulsifier is not too hydrophilic (because it would go essentially to water) or not too close to matching hydrophobicity (because it would not compensate the asphaltene hydrophobic effect). However, there are others factors to be considered such as the viscoelastic properties of the asphaltene interfacial layer than improve the understanding of demulsifier action.

Pensini et al. [45] measured the viscoelastic properties of the interface as a function of aging time as the asphaltenes diffused toward the interface and adsorbed on the water–toluene interface. With gradual accumulation of asphaltenes on the toluene–water interface, the interface changes from a viscous to an elastic-dominant microstructure. Focusing on the effect of demulsifier addition, at 6000 s of interfacial aging are not shown. Once the condition G'

(elastic component) = G″ (viscous component) was reached, the demulsifier was added at 2.3 ppm (optimum dosage from the bottle tests). When the elastic contribution is predominant, asphaltenes are intimately linked, forming a cohesive interfacial network. To assess the demulsifier performance, in penetrating and breaking the cohesive network of asphaltenes, the shear viscoelastic moduli was measured. Upon addition of 2.3 ppm demulsifier in toluene, both viscous and elastic shear modulus of the interfacial film decreased.

The problem when handling formulation issues in a crude oil system is that only a small part of the asphaltenes is present at the interface. This implies that the total asphaltenes' concentration in the crude oil does not participate with the demulsifier at the interfacial mixture. As a consequence, the optimum concentration of the demulsifier is not dependent on its mixture with all the asphaltenes in the system. Only a fraction of asphaltenes is adsorbed, and the rest forms aggregates, flocculates, or precipitates, an important amount of it being segregated close to the interface, but not at the interface (see Figure 4). This asphaltene excess is responsible for the characteristic skin at the water–crude oil interface [7, 9, 10].
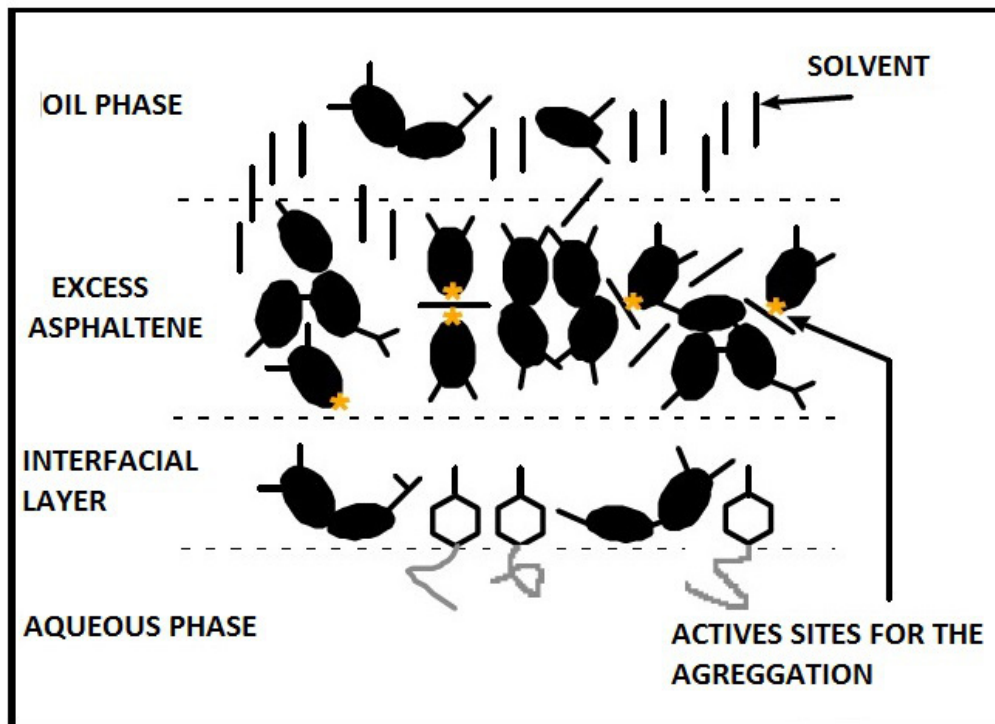

Figure 4. Asphaltene excess than there are out of interface. This situation corresponds to Ca> 1, 000 ppm. Solvent can to penetrate in this layer asphaltene and interact with them for limit its aggregation due solvation effects (Pereira, 2009).

An experimental method has been recently proposed to estimate the asphaltene–demulsifier adsorbed mixture composition, so that interfacial formulation may be estimated [7]. It consists in diluting the crude oil so that the asphaltenes' concentration in the oil phase is reduced. At some point, asphaltenes' concentration is low enough so there is no excess of aggregates or flocculates in the oil phase. In this situation, asphaltenes and demulsifiers species may be

considered as two types of surfactants adsorbed at the interface, according to the physico-chemical conditions in the bulk phases at equilibrium. It has been found that below a concentration of asphaltenes 500–1000 ppm, the concentration of demulsifier required to attain optimum formulation varies proportionally to the concentration of asphaltenes (see Figure 5). In this so-called proportional regime [7], a quantitative formulation effect at the interface can be estimated without taking into account physical effects such as viscosity, convection, and diffusion through bulk oil (these are not formulation issues). This method allows evaluating the demulsification performance as a function of different formulation variables (demulsifier hydrophilicity, salinity, and crude oil characteristics) [7, 42-44], which represents a significant practical progress in designing commercial products.
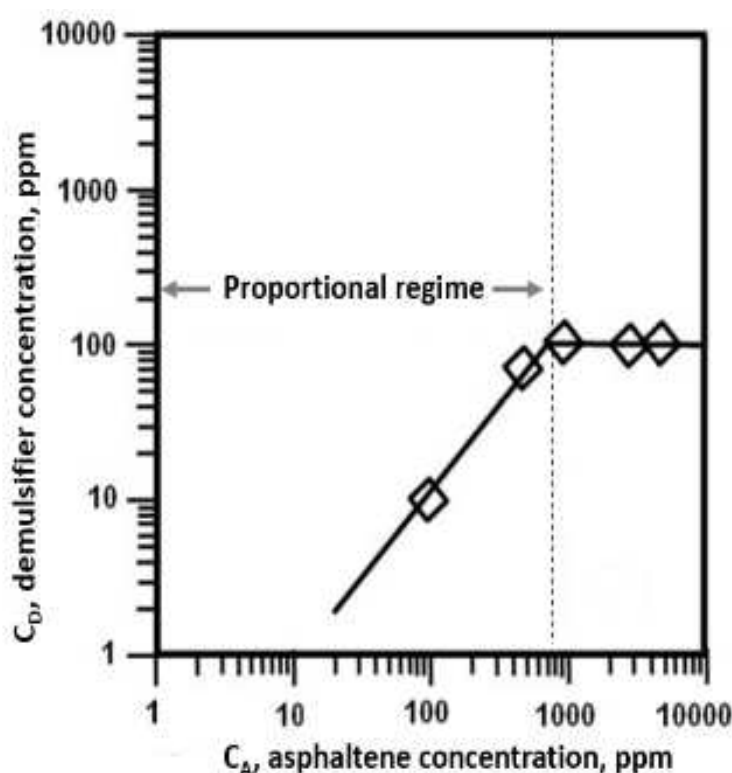

Figure 5. Demulsifier concentration as a function of the asphaltene concentration to reach optimum formulation (Pereira, 2009).

HLB method (hydrophile–lipophile balance) is often used. In this method, a number (0–40), indicative of emulsification behavior and related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule, has been assigned to many commercial surfactants [42].

Using HLB concept, the proportional regime can be estimated, as follows, [7, 42-44]:

$$HLB_{optMixt} = X_A HLB_A + X_D HLB_D \qquad (4)$$

where X_A and X_D are the fractions of A and D at the interface ($X_D = 1 - X_A$) and $HLB_{OptMixt}$ is a characteristic value (close to 10 correspond to the affinity) for the system. This can be calculated from the experimental correlation (bottle test) when the crude, brine, and temperature are fixed. The effect of any additive can be easily qualified as favorable or not when decreasing the fraction of demulsifier required (X_D) to attain the optimum formulation for the lowest stability. Since the experiments are much easier and more accurate in the proportional regime, this is the zone where the tests of the additive effects are mostly carried out. Silva et al. [8] used this methodology to estimate, in a semiquantitative manner, the effects of organic acid and amine additives on the formulation of the components at the interface. The results indicate that water-soluble additives (acetic acid and ethylamine) have no significant effect on the required demulsifier concentration C_D^*. Even if they considerably alter the pH aqueous phase, additives do not reach a value to ionize asphaltenes species. The additives of lipophilic nature (hexanoic acid and hexylamine) both interact on the other side of the interface (i.e., asphaltenes in the oil phase). The hexanoic acid is found to marginally increase the emulsion stability, probably because it could lead to a slightly more hydrophobic co-surfactant effect. In contrast, the hexylamine, which is likely to interact with the asphaltenes through an acid–base mechanism, produces the delocalization of charges (ionization), resulting in an increase of hydrophilicity, and reducing the hydrophilic demulsifier requirement to attain optimum formulation.

Commercial demulsifiers are chemical cocktails or complex mixtures of surfactants (active substance), polymers, polar additives (alcohols, amines, ketones, and others), and solvents. Alcohols are useful substances to promote changes on the interfacial properties of surfactant–oil–water systems [46, 47]. Pei et al. [48] reported correlation between the interfacial tension and solubility in water of alcohols. Interfacial concentration of the surfactant is dependent on the less water-soluble alcohol additives will provide higher alcohol concentrations at the oil–water interface. Generally, the formulation of such products is protected by patents. The mechanisms and modes of action remain undisclosed in open literature. Therefore, the methodology explained constitutes a useful tool for the petroleum industry.

Solvents are used as carriers of the active molecules, and they play a critical role in the performance of a commercial demulsifier. Polar aromatic hydrocarbons are soluble in water, and are frequently used as dissolvent in the formulation of commercial products. Careful consideration is necessary of the solvent is surfactant dispersions then its addition in crude oil is most effective. An inadequate choice of solvent may result in a delay in the rate of breaking of emulsion and therefore other variables of the process physical o chemical are needed in order to improve crude oil desalter operations. Pereira shows that the solvent role can be understood using the criteria of proportional regime with solvents mixtures [7]. The position of optimum concentration of demulsifier (C_D^*) is influenced by the nature of the solvent.

5. Conclusions

Here it was explained the approach from the optimum formulation concept to assist emulsion breaking in desalting process. As part of the stabilization mechanism is accepted that the water

droplets are stabilized by the formation of a mechanically strong and viscoelastic film at the interface composed of asphaltenes.

In the case of water-in-crude emulsions, a balanced optimum formulation is attained by adding demulsifiers which are hydrophilic to the lipophilic natural surfactants contained in the crude oil. This study aimed to determine an optimal and to relate the nature and concentration of demulsifier products added to the amphiphilic mixture at the interface. Proportional and saturation regimens can explain the impact of formulation parameters, such as solvent, alcohols, kind and concentration of demulsifier, amoung others as useful tool by the formulating personal of petroleum industry.

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References

[1] Vafajoo L, Ganjian K, Fattahi M. Influence of key parameters on crude oil desalting: An experimental and theoretical study. *J Petrol Sci Engin*. 2012;90-91:107-111. DOI: 10.1016/j.petrol.2012.04.022

[2] Gary J, Handwerck G (eds.). *Petroleum Refining: Technology and Economics*. 4th edn. Marcel Dekker, Inc. New York. USA; 2001. p. 49. ISBN: 0-8247-0482-7

[3] Fahim M, Alsahhaf T, Elkilani A. Crude Distillation. In: Fahim M, Alsahhaf T, Elkilani A, *Fundamentals of Petroleum Refining*. 1st edn. Elsevier B.V. Oxford. UK; 2010. p. 77. DOI: 10.1016/B978-0-444-52785-1.00004-8

[4] Arnold K, Stewart M. Choosing a Process. In: Surface Production Operations. Volume 1. *Design of Oil Handling Systems and Facilities*. 1st edn. Elsevier. B.V. Massachusetts. USA; 2007. p.30. DOI: 10.1016/B978-088415821-9/50011-7

[5] Kang W, Xu B, Wang Y, Li Y, Shan X, An F, Liu J. Stability mechanism of w/o crude oil emulsion stabilized by polymer and surfactant. *Colloids Surfaces A*: *Physicochem Engin Asp*. 2011;384:555-560. DOI:10.1016/j.colsurfa.2011.05.017

[6] Ramalho J, Lechuga FC, Lucas EF, Effect of the structure of commercial poly(ethylene oxide-bpropylene oxide) demulsifier bases on the demulsification of water-in-crude oil emulsions: elucidation of the demulsification mechanism. *Quím Nova*. 2010;33:1664-1670. DOI: 10.1590/S0100-40422010000800009

[7] Pereira JC, Phenomena of Rupture and Inversion Emulsions: Physicochemical and Kinetic Aspects [Thesis]. Mérida: University of Los Andes; 2009: 11-12, 33, 11, 25-26, 46-47, 64, 46-47, 61-63, 46-47, 77-81.

[8] Silva I, Borges B, Blanco R, Rondón M, Salager J.L, Pereira JC. Breaking of water-in-crude oil emulsions. 5. Effect of acid-alkaline additives on the performance of chemical demulsifiers. *Energy Fuels*. 2014;28:3587-3593. DOI: 10.1021/ef5006918

[9] Kilpatrick P. Water-in-crude oil emulsion stabilization: review and unanswered questions. *Energy Fuels*. 2012;26:4017-4026. DOI: 10.1021/ef3003262

[10] Kralova I, Sjöblom J, Øye G, Simon S, Grimes B, Paso K. Heavy crude oils/particle stabilized emulsions. *Adv Colloid Interf Sci*. 2011;169:106-127. DOI: 10.1016/j.cis. 2011.09.001

[11] Daaou M, Bendedouch D. Water pH and surfactant addition effects on the stability of an Algerian crude oil emulsion. *J Saudi Chem Soc*. 2012;16:333-337. DOI: 10.1016/j.jscs. 2011.05.015

[12] Fingas M, Fieldhouse B. Studies of the formation process of water-in-oil emulsions. *Marine Poll Bull*. 2003;47:369-396. DOI: 10.1016/S0025-326X(03)00212-1

[13] Fingas M, Fieldhouse B. Studies on water-in-oil products from crude oils and petroleum products. *Marine Poll Bull*. 2012;64:272-283.DOI: 10.1016/j.marpolbul.2011.11.019

[14] Delgado J. Study of Properties of Asphaltene from Boscan Crude Oil [Thesis]. Mérida: University of Los Andes. 2005: 30-32, 12, 30.

[15] Shirani B, Nikazar M, Naseri A, Mousavi-Dehghani S. Modeling of asphaltene precipitation utilizing Association Equation of State. *Fuel*. 2012;93:59-66. DOI: 10.1016/j.fuel.2011.07.007

[16] Batista J, Lechuga F, Lucas E. Effect of the structure of commercial poly(ethylene ox-ide-b-propylene oxide) demulsifier bases on the demulsification of water-in-crude oil emulsions. *Quim Nova*. 2010;33:1664-1670. DOI: 10.1590/S0100-40422010000800009

[17] Acevedo S, García L.A, Rodríguez P. Changes of diameter distribution with tempera-ture measured for asphaltenes and their fractions A1 and A2. Impact of these meas-urements in colloidal and solubility issues of asphaltenes. *Energy Fuels*. 2012;26:1814-1819.DOI: 10.1021/ef201947h

[18] Dicharry C, Arla D, Sinquin A, Graciaa A, Bouriat P. Stability of water/crude oil emulsions based on interfacial dilatational rheology. *J Colloid Interf Sci*. 2006; 297:785-791.DOI: 10.1016/j.jcis.2005.10.069

[19] Fingas M, Fieldhouse B. Studies on crude oil and petroleum product emulsions: wa-ter resolution and rheology. *Colloids Surfaces A: Physicochem Engin Asp*. 2009;333:67–81.DOI: 10.1016/j.colsurfa.2008.09.029

[20] Pacheco-Sanchez JH, Alvarez-Ramirez F, Martinez-Magadan JM. Morphology of ag-gregated asphaltene structural models. *Energy Fuels*. 2004;18:1676-1686. DOI: 10.1021/ef049911a

[21] Acevedo S, Castro A, Vasquez E, Marcano F, Ranaudo M.A. Investigation of physical chemistry properties of asphaltenes using solubility parameters of asphaltenes and their fractions A1 and A2. *Energy Fuels*. 2010; 24:5921-5933.DOI: 10.1021/ef1005786

[22] Acevedo S, Ranaudo M.A, García C, Castillo J, Fernández A. Adsorption of asphal-tenes at the toluene-silica interface: a kinetic study. *Energy Fuels*. 2003;17:257-261.DOI: 10.1021/ef020104q

[23] Acevedo S, Caetano M, Ranaudo M, Jaimes B. Simulation of asphaltene aggregation and related properties using an equilibrium-based mathematical model. *Energy Fuels*. 2011; 25:3544-3551.DOI: 10.1021/ef200107k

[24] Mullins O, Sheu E, Marshall A (eds.). *Asphaltenes, Heavy Oil and Petroleomic*. Springer. 2007. p. 668. DOI: 10.1007/0-387-68903-6

[25] Acevedo S, Ranaudo MA, Pereira JC, Castillo J, Fernández A, Pérez P, Caetano M. Termo-optical studies of asphaltene solutions: Evidence for solvent-solute aggregate formation. *Fuel*. 1999;78:997-1003. DOI: 10.1016/S0016-2361(99)00027-7

[26] Jeribi M, Almir-Assad B, Langevin D, Hénaut I, Argillier JF. Adsorption kinetics of asphaltenes at liquid interfaces. *J Colloid Interf Sci*. 2002;256:268-272. DOI: 10.1006/jcis. 2002.8660

[27] Roodbari H, Badieia A, Soleimani E, Khaniani Y. Tweens demulsification effects on heavy crude oil/water emulsion. *Arabian J Chem*. 2011:1-6. DOI: 10.1016/j.arabjc. 2011.08.009

[28] Nenningsland A, Gao B, Simon S, Sjöblom J. Comparative study of stabilizing agents for water-in-oil emulsions. *Energy Fuels*. 2011;25:5746-5754. DOI: 10.1021/ef2014265

[29] Gao S, Moran K, Xu Z, Masliyah J. Role of naphthenic acids in stabilizing water-in-diluted model oil emulsions. *J Physic Chem B*. 2010; 114: 7710-7718. DOI: 10.1021/jp910855q

[30] Sullivan P, Zaki N, Sjöblom J, Kilpatrick P. The stability of water-in-crude and model oil emulsions. *Canadian J Chem Engin*. 2007; 85: 793-807. DOI: 10.1002/cjce.5450850601

[31] Yarranton H, Hussein H, Masliyah JH. Water in-hydrocarbon emulsions stabilized by asphaltenes at low concentrations. *J Colloid Interf Sci*. 2000; 228:52-63. DOI: 10.1006/jcis.2000.6938

[32] Gafonova O, Yarranton H. The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. *J Colloid Interf Sci*. 2001;241:469-478. DOI: 10.1006/jcis.2001.7731

[33] Silva I. Breaking of Water-in-Crude Oil Emulsions: Effect of Acid-Alkaline Additives on the Performance of No Ionic Demulsifiers. [Thesis]. Caracas: University Simón Bolívar. 2012:24.

[34] Zhang L, Breen P, Xu Z, Masliyah JH. Asphaltene films at a toluene/water interface. *Energy Fuels*. 2007;21:274-285. DOI: 10.1021/ef0603129

[35] Delgado-Linares J, Pereira JC, Rangel A, Salazar F, Guevara M, Forgiarini A, Bullón J. Effect of addition of amphiphilic molecules on asphaltene film properties at air-water interface. *Revista de la Facultad de Ingeniería de la UC*. 2012;19:16-24. ISSN 1316-6832

[36] Solovyev A, Zhang L, Xu Z, Masliyah LY. Langmuir films of bitumen at oil/water interfaces. *Energy Fuels*. 2006;20:1572-1578. DOI: 10.1021/ef050409f

[37] Chandra M, Xu Z, Masliyah JH. Interfacial films adsorbed from bitumen in toluene solution at a toluene–water interface: a Langmuir and Langmuir–Blodgett film approach. *Energy Fuels*. 2008;22:1784-1791. DOI: 10.1021/ef700786u

[38] Zhang LY, Lawrence S, Xu Z, Masliyah JH. Studies of Athabasca asphaltene Langmuir films at air–water interface. *J Colloid Interf Sci*. 2003; 264:128-140. DOI: 10.1016/S0021-9797(03)00355-2

[39] Zhang L.Y, Xu Z, Masliyah JH. Characterization of adsorbed Athabasca asphaltene films at solvent-water interfaces using a Langmuir interfacial trough. *Indust Engin Chem Res*. 2005;44:1160-1174. DOI: 10.1021/ie049913i

[40] Rosen MJ (ed.). *Surfactants and Interfacial Phenomena*. 3rd edn. Wiley-Interscience, 2004; p. 455. ISBN 0-471-47818-0

[41] Balsamo V, Phan J, Nguyen D. Interfacial films of diluted heavy oil–aqueous systems at elevated temperatures and pressures: effect of reverse emulsion breakers. *Energy Fuels*. 2015;29:2823-2832. DOI: 10.1021/ef502072f

[42] Rondón M, Bouriat P, Lachaise J, Salager JL. Breaking of water-in-crude oil emulsions. 1. Physicochemical phenomenology of demulsifier action. *Energy Fuels*. 2006;20:1600-1604. DOI: 10.1021/ef060017o

[43] Rondón M, Pereira JC, Bouriat P, Graciaa A, Lachaise J, Salager JL. Breaking of water-in-crude-oil emulsions. 2. Influence of asphaltene concentration and diluent nature on demulsifier action. *Energy Fuels*. 2008;22:702-707. DOI: 10.1021/ef7003877

[44] Pereira JC, Delgado-Linares J, Scorzza C, Rondón M, Rodríguez S, Salager JL. Breaking of water-in-crude oil emulsions. 4. Estimation of the demulsifier surfactant performance to destabilize the asphaltenes effect. *Energy Fuels*. 2011;25:1045-1050. DOI: 10.1021/ef100979y

[45] Pensini E, Harbottle D, Yang F, Tchoukov P, Li Z, Kailey I, Behles J, Masliyah JH, Xu Z. Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric ethylene oxide–propylene oxide demulsifier. *Energy Fuels*. 2014;28:6760-6771. DOI : 10.1021/ef501387k

[46] Baviere M, Schechter R, Wade W. The influence of alcohols on microemulsion composition. *J Colloid Interface Sci*. 1981;81:266-279. DOI: 10.1016/0021-9797(81)90322-2

[47] Pereira JC. State of the art on the effect of alcohols on the interfacial properties of surfactants. *Revista Ingeniería* UC. 2012; 19:76-85. ISSN 1316-6832

[48] Pei H, Zhang G., Ge J, Zhang L, Mingchao MA. Effect of the addition of low molecular weight alcohols on heavy oil recovery during alkaline flooding. Ind Eng Chem Res. 2014; 53:1301-1307. DOI: 10.1021/ie4028318