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Development of nanoemulsions containing a polyoxide surfactant and asphaltenes dispersant

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ABSTRACT

This article reports the development of oil-in-water nanoemulsions containing additives capable of dispersing asphaltenes and evaluation of their use as a new alternative for breaking down oil emulsions. The nanoemulsions were prepared in the presence of a surfactant based on polyethylene oxide using a high pressure homogenizer with different processing conditions, which led to different droplet sizes. These sizes influenced the stability and demulsification efficiency. All nanoemulsions were efficient in phase separation of water-in-oil emulsions. The nanoemulsion containing the additive was the one that promoted fastest separation.

1. Introduction

Crude oil contains natural surfactants such as asphaltenes, resins, acids and organic bases, which are responsible for the stabilization of water-in-oil emulsions during production of crude oil [1]. These surfactants concentrate at the water–oil interface, creating a physical barrier (interfacial film) that prevents droplet flocculation and coalescence [2,3].

Water-in-oil emulsions are preferentially formed due to the dominant lipophilic character of these natural surfactants. Natural emulsifiers reduce the interfacial tension and promote droplet dispersion and emulsification [4].

The stability of the interfacial film formed by these natural surfactants, and thus the emulsions stability, depends on many factors, including the quantity of heavy material (asphaltenes, resins and paraffins) and solids, temperature, droplet size and size distribution, pH and composition of the crude oil and brine [5,6]. Studies suggest that asphaltene aggregates are the main species responsible for the stabilization of these emulsions [7,8] because they adsorb at the water–oil interface, causing the formation of a film with high rigidity and elasticity [5].

It is believed that asphaltene aggregates are dispersed in crude oil by the action of resins [9]. These aggregates are formed due to the overlapping of the π–π bonds between the aromatic rings, as well as the hydrogen bonds between the functional groups, among others. The size of the aggregates varies according to the polydispersion and structure of the asphaltene molecules. Smaller aggregates tend to stabilize the emulsions formed. However, there are other problems associated with asphaltenes, like their ability to form larger aggregates, resulting in solid deposits that obstruct wells and flow in pipes, clog safety valves and reduce the capacity of storage tanks, thus hampering the transport and processing of oil [2].

The chemical composition of the crude oil is also an important factor that influences the formation of asphaltene aggregates. According to Sjoblöm [10], the mixture of paraffinic oil with heavy crude rich in asphaltenes can diminish the solvation force of the resins in relation to asphaltenes alone. The presence of waxy components can cause desorption of the adsorbed resins at the surface of the asphaltenes. This can be associated with the higher affinity of the resins for other compounds.

Crude oil emulsions can be broken down by various methods, including chemical treatment, mechanical methods, thermal treatment (such as microwave radiation), separation by membranes and electrostatic treatment [11]. One of the most effective methods is the addition of chemical demulsifiers to the emulsion followed by heating [4,12,13]. These demulsifiers are normally formed by polymers, such as poly(ethylene oxide)-b-poly(propylene oxide) (PEO-PPO) block copolymers, ethoxylated phenols, alcohols, ethoxylated amines, ethoxylated resins, ethoxylated nonylphenols and sulfonic acid salts [14–16].

The mechanism by which crude oil emulsions are demulsified is still not fully understood. It has been proposed that demulsifiers,

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when added to the emulsion, migrate to the interface because of their superficial activity, rupturing or weakening the interfacial film that acts as a barrier and facilitating the coalescence of droplets in the dispersed phase. These demulsifiers act by displacing the components that contribute to the stability of the interfacial film that surrounds the dispersed droplets. They also alter the viscosity of the film, helping to destabilize it [14].

Factors affecting demulsification of crude oil emulsions such as demulsifier chemical structure, water content, partition coefficient (KP) and concentration were discussed by Al-Sabagh [17].

With the development of nanotechnology, nanoemulsions are being studied for a variety of uses. These systems are dispersions with droplet size between 1 and 100 nm [18–20]. However, these systems do not form spontaneously; they require an energy source, generally supplied by mechanical devices or the difference between the chemical potential of the components [19,21,22].

The most common mechanical method to prepare nanoemulsions is high-pressure homogenization (HPH). Studies have shown that increasing the processing pressure from 5000 to 17,500 psi and also the number of processing cycles leads to more stable systems, with nanometric-sized droplets and low size dispersion [23,24].

Other articles report the efficiency of oil-in-water nanoemulsions in breaking down crude oil emulsions (water-in-oil emulsions), with the results indicating that the nanoemulsions used in small volumes are more efficient in breaking down emulsions compared to other systems (aqueous surfactant solutions) [25,26]. Besides this, it has been observed that the concentration of the oil phase influences the speed of the demulsification process: the higher the concentration of oil phase, the faster the breakdown of the petroleum emulsion.

The objective of this study was to develop oil in water nanoemulsions containing an asphaltene dispersant additive in the oil phase and to analyze their efficiency to demulsify water-in-oil emulsions. In the specific case of this work, this development is aimed mainly at reducing of active material and replacement of solvents for water in the formulations prepared and used as demulsifiers, which is of environmental interest and cost savings for suppliers of chemical. Another problem encountered by the chemical industry is to obtain formulations with chemicals products of different solubility able to generate a stable final product thermally during 30 days. As the nanoemulsion is formed starting from two immiscible liquids, it is feasible to solubilization of these chemicals in the same formulation and thus obtain stable products. These nanoemulsions can have surfactant contents (active material) in the range of 12–20% of the mixture mass, and in addition, the masses of oil used in the nanoemulsions formation process are also low (5–10% m), the remainder consisting of water. Thus, these stable nanoemulsions can be applied in the oil field of the same ways that demulsifier additives.

2. Experimental

2.1. Materials

The oil-in-water (o/w) emulsions were composed of:

- Aqueous phase: commercial nonionic surfactant Ultramona®R400 (donated by Oxiteno, Brazil), called in this paper R400. This surfactant is a product of the reaction of castor oil with ethylene oxide (EO) and has 40 ethylene oxide units in its chain. The chemical structure is showed in Fig. 1. It was used at a concentration of 20 wt% in distilled and deionized water.
- Oil phase:

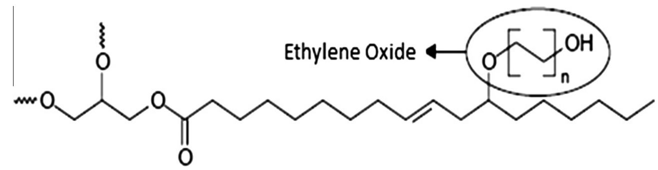

Fig. 1. Chemical structure of nonionic surfactant (R400).

Table 1
Composition of the oil/surfactant/water dispersions.

System	Surfactant (%wt)	Oil phase (%wt)			Water (%wt)
		Solbrax (%wt)	Butanol (%wt)	LBS (%wt)	
1S	20	5.00	–	–	75
2S		4.95	–	1	
3S		4.75	–	5	
3SB		4.25	10	5	
4S		4.50	–	10	
4SB		4.00	10	10	
		Oil phase (%wt)			
		Xylene (%wt)		LBS (%wt)	
1X	20	5.00		–	75
2X		4.95		1	
3X		4.75		5	
4X		4.50		10	

(a) Xylene, acquired form Vetec Química Fina. A previous study reported that this organic solvent can be used as a co-additive to improve the diffusion of the surfactant in the emulsion [27].

(b) Solbrax Eco, which is produced and sold exclusively by Petrobras Distribuidora, Brazil. SolbraxEco 175/225 is mainly composed of aliphatic and naphthenic hydrocarbons, with a distillation range between 175 and 225 °C. The low aromatics content is obtained by catalytic hydrogenation, which converts the aromatics into naphthenic compounds, reducing the sulfur content, saturating the olefins and eliminating polar impurities [28]. The solvent was also characterized by ^{13}C-NMR, confirming that the main constituents were hydrocarbons with linear or branched chains. The presence of other compounds, such as alkenes or heteroatoms, was not observed [29]. These solvents were used at a concentration of 5 wt% to prepare the o/w emulsions.

Also in this oil phase we used dodecylbenzene sulfonic acid (LBS) as an asphaltene dispersant. This additive was dissolved in the oil phase (xylene or Solbrax) at concentrations of 1 wt%, 5 wt% and 10 wt%. In some formulations (Solbrax oil phase) the solvent butanol was used as a co-surfactant, at a concentration of 10 wt% in the oil phase. The composition of the dispersions used to prepare the nanoemulsions is shown in Table 1.

The crude oils (designated P1 and P2) used to prepare the synthetic W/O emulsions were donated and characterized by the Petrobras Research Center (CENPES). The characteristics of these samples P1 and P2, respectively, are: water content of 0.090 and 0.058 wt/wt% and °API density of 22 and 30.

3. Methods

3.1. Preparation and characterization of the o/w emulsions

The oil-in-water emulsions were prepared in an Emulsiflex C5 high-pressure homogenizer using pressure of 15,000 psi and four