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Development of microemulsions to reduce the viscocity of crude oil emulsions

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ABSTRACT

The formation of water-in-oil (W/O) emulsions during extraction of petroleum is a major problem, because these emulsions increase the oil's viscosity and thus significantly lower the production rates. In these situations, chemical products called emulsion viscosity reducers (EVRs) can be injected during crude oil production. The development of EVRs consisting of oil-in-water (O/W) microemulsions can attract a good deal of attention due to the possibility of reducing costs and increasing environmental friendliness (they are mostly composed of water instead of large volumes of organic solvents). This article describes the preparation of O/W microemulsions, using the solvents kerosene, Solbrax or xylene as components of the oil phase and three commercial nonionic polymer surfactants based on poly(ethylene oxide) as the aqueous phase. For this purpose, first ternary phase diagrams (water/oil/surfactant) were constructed to determine the optimal concentrations of these components to prepare the O/W microemulsions, selecting 16 wt% surfactant, 4 wt% oil phase and 80 wt% aqueous phase as the common composition of all the systems studied. The efficiency of the microemulsion systems was investigated by rheological tests in synthetic water/oil emulsions prepared from a heavy crude oil (°API 20). The microemulsion systems were tested regarding their interfacial activity by analyzing the interfacial tension and the average size of the water droplets dispersed in the crude oil, before and after adding the systems developed. The results showed that the performance of the O/W microemulsions did not depend on the type of oil phase, but that the insertion of an oil phase (i.e., the formation of an O/W microemulsion) improved the performance of the surfactant in the medium compared to the efficiency of the aqueous surfactant solutions.

1. Introduction

The formation of water-in-oil (W/O) emulsions during extraction of petroleum can cause a substantial reduction in the production rates. This happens due to the high viscosity of these emulsions, which rises with increase in the quantity of water until reaching the phase inversion point (PIP). Knowledge of both the viscosity and PIP of the emulsion is important to establish the size of lines and equipment as well as to determine the production strategy [1–3].

During the production of crude oil, there are various processes during which mechanical energy is transmitted to the production fluids and an emulsion can form. One of them is the elevation process, when the oil flow is subject to shear forces and pressures generated by the mechanical forces of a submersible electric pump or by application of the gas lift technique (injection of gas in wells to push the fluids upward to the production platform) [3].

Pure hydrocarbons are unable to form stable emulsions with fresh or brine. However, due to the presence of natural surfactants (asphaltenes, resins and naphthenic acids) in crude oil and the high water cut that occurs during the extraction process, there is a tendency for W/O emulsions to form [2]. These emulsions cause a considerable increase in the apparent viscosity and the rheological (pseudoplastic) behavior of the crude oil, meaning the viscosity declines as the shear rate increases [4]. Some factors can contribute to increase the viscosity of these systems: viscosity of the oil, viscosity of the water, temperature, droplet size distribution, quantity of solids in the oil and shear rate [5].

At low water cuts (low water concentrations), when the emulsions formed are diluted, the hydrodynamic forces during the collision of the droplets govern the rheological behavior. As the water cut increases, meaning a more concentrated W/O emulsion, flow resistance can be induced by the deformation and rearrangement of the structures of the thin liquid films formed between the droplets [5]. This flow resistance increases as wells become depleted and the quantity of water extracted along with the oil rises (to as much as 90% of total production). This high water percentage comes from both the water naturally contained in the formation and water that is injected in oil reservoirs to increase

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the pressure and enhance oil recovery [6].

To counteract the problems caused by the presence of W/O emulsions during production of crude oil, chemical products called emulsion viscosity reducers (EVRs) can be applied to decrease the fluid's apparent viscosity, making the elevation process more efficient. These products have a dual chemical structure, one hydrophilic, which interacts preferably with the water molecules, and the other lipophilic, having greater affinity with the oil phase [7].

Many different methods have been studied to reduce the viscosity of crude oil, but research is relatively scant regarding the development of emulsion viscosity reducers. Much still remains to be learned, mainly about specific conditions, due to the complex composition of crude oil, and consequently of the emulsions produced [1].

With the development of nanotechnology, new discoveries are being made about nanoemulsions and microemulsions for various applications. In recent years, various studies have examined the formation, characterization and application of these systems, essentially because of their multiple potential applications in many branches of science and technology. Specifically in the case of the oil industry, the most common applications studied are for enhanced oil recovery [8] and demulsification of W/O emulsions [9–13].

A microemulsion can be defined as a thermodynamically stable dispersion that is macroscopically monophasic, fluid and transparent. Microemulsions can consist of isotropic mixtures of oil, water and a surfactant, often in combination with a cosurfactant, stabilized by an interfacial film composed of the surfactant, forming droplets with diameters ranging from 5 to 100 nm [1,14]. They are formed spontaneously when the aqueous phase, oil and surfactant come into contact [15,16] and have the ability to combine large quantities of two immiscible liquids in a single homogeneous phase [17]. Nanoemulsions have small droplets in the dispersed phase, as do microemulsions. However, unlike microemulsions, they are only kinetically stable and do not need the presence of a cosurfactant. Their formation depends on the preparation method, in which it is necessary to apply energy [18].

The objective of this study was to develop oil-in-water (O/W) microemulsions and to analyze their efficiency in reducing the viscosity of crude oil emulsions. In particular, we aimed to replace solvents with water in the formulations prepared and used as EVRs, to produce less expensive and more environmentally friendly formulations.

2. Experimental

2.1. Materials

The oil-in-water (O/W) microemulsions were prepared using the commercial ethoxylated nonionic surfactants Ultrol®L70 and Ultrol®L90, which are produced through the reaction of lauryl ether with ethylene oxide, respectively containing 7 and 9 ethylene oxide units, and Ultranex®NP80, produced by reacting nonylphenol with ethylene oxide, containing 8 ethylene oxide units. All these surfactants were purchased from Oxiteno (São Paulo, Brazil).

The following solvents were used as the oil phase:

- Xylene: an organic solvent, widely used in the bases of demulsifiers. A previous study [19] showed that xylene can act as a co-additive, improving the diffusion of the surfactant in the emulsion [20].
- Solbrax Eco 175/225: a solvent composed mainly of aliphatic hydrocarbons with different sizes, in the range of 9–13 carbon atoms, also containing traces of aromatic compounds, olefins and sulfur, giving it lower toxicity and odor [21,22]. This 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 [22].
- Kerosene: a mixture of solvents, formed by aliphatic, naphthenic and aromatic hydrocarbons, with distillation range between 150 and 300 °C [23].

Table 1
Results of HLB determination tests of the oil phases.

Emulsion	HLB mixture	Emulsion kerosene/water	Emulsion solbrax/water	Emulsion xylene/water
1	6.0	Phase separation	Phase separation	Phase separation
2	7.0	Phase separation	Phase separation	Phase separation
3	7.5	Phase separation	Phase separation	Phase separation
4	8.0	Phase separation	Phase separation	Phase separation
5	8.5	Phase separation	Phase separation	Phase separation
6	9.0	Relative Homogeneity	Phase separation	Phase separation
7	9.5	Phase separation	Relative Homogeneity	Phase separation
8	10.0	Phase separation	Phase separation	Phase separation
9	10.5	Phase separation	Phase separation	Phase separation
10	11.0	Phase separation	Phase separation	Relative Homogeneity

As the aqueous phase the distilled and deionized water was used. The crude oil sample used to prepare the O/W emulsions was from a Brazilian offshore oil field, donated by the Petrobras Research Center (CENPES-PETROBRAS, Rio de Janeiro-Brazil).

2.2. Methods

2.2.1. Characterization of the oil phases

The oil phases (the solvents xylene, kerosene and Solbrax) were characterized by determining the hydrophilic-lipophilic balance (HLB), as described by [24]. The method consists of obtaining emulsions from mixtures of surfactants in varied proportions, to obtain defined HLB values. The emulsions were prepared under stirring and were then left at rest, at room temperature (25 °C).

Dispersion samples weighing 50 g were prepared, formed by the aqueous solutions of mixtures of the nonionic surfactants polyethylene glycol sorbitan monolaurate (Tween 80) and sorbitan monooleate (Span 80), both acquired from Sigma Aldrich (USA), with respective HLB values of 15 and 4.3. The concentration of the surfactant mixture was set at 5 wt% and the oil content at 10 wt%, both in relation to total weight of the three components (water, surfactant and oil phase). The weights of the surfactants in the mixture were calculated based on the relations presented in Eq. (1), to obtain emulsions with HLB values of the known mixture, in the range of 4–15.

$$Surfactant\ Concentration\ (\%)\ \alpha = \frac{(HLB* - HLB\ b)}{HLB\ \alpha - HLB\ b} \times 100 \quad (1)$$

where

α – Surfactant a
b – Surfactant b
HLB* – desired HLB value
HLB a – HLB value of surfactant a
HLB b – HLB value of surfactant b

The emulsions were prepared by adding the surfactants in the aqueous phase, and then mixing in the oil phase, under constant magnetic stirring for 15 min. The emulsions were then left standing for 24 h at room temperature 25 °C.

After this, the emulsions were evaluated visual to note those with greatest stability. The HLB value of the crude oil corresponded to the HLB of the mixture of surfactants used in the dispersion that presented the greatest stability, i.e., the one that did not present a lumpy appearance or separation of phases.

2.2.2. Obtaining the ternary phase diagrams

To select the best water/oil/surfactant mixture to prepare the O/W microemulsions, ternary phase diagrams were plotted. For this, it was