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Study of the stability and homogeneity of water in oil emulsions of heavy oil

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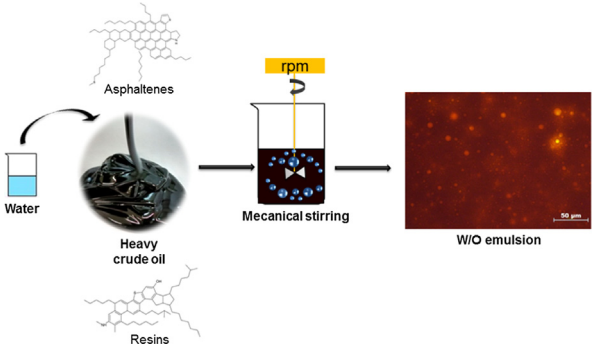
GRAPHICAL ABSTRACT



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ABSTRACT

Water-in-oil (W/O) emulsions are present in applications from well drilling to refining and cause diverse problems. The present paper details the results of a study of the stability and homogeneity of W/O emulsions of a heavy oil using the optical microscopy technique. The W/O emulsions used previously dehydrated heavy oil with the addition of increasing volumes of 10, 20, 30, 35 and 40% w/v of deionized water and formation water, under mechanical stirring at 2500, 5000, 10,000 and 15,000 rpm. Moreover, a saturated sodium chloride solution was added to the oil in the contents at 10, 20 and 30% w/v under stirring at 5000 rpm, in order to verify the influence of the electrolyte type on the stability of the emulsions. The W/O emulsions were subjected to a gravitational separation test to verify stability and photomicrographs of the emulsions were analyzed to evaluate the homogeneity and the droplet size distribution (DSD). The results showed that the prepared emulsions were stable and homogeneous even after aging for 30 days and after being subjected to heating. This stability may be related to the high content of resins and asphaltenes in the studied oil. The emulsions prepared with formation water showed higher DSD values than those prepared with saturated NaCl solution and deionized water. This distinction of droplet sizes can be related to the presence of ions of different charges in the formation water.

1. Introduction

During oil extraction, water may be associated with oil as a result of the reservoir conditions (formation water) or by its injection into wells in secondary and tertiary recovery operations. Steam injection is a commonly used procedure to reduce the oil viscosity and to maintain

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the pressure in the reservoir, thus facilitating the flow, especially for heavy oils [1]. The turbulent flow due to the shear action created in pumps and valves, associated with the presence of natural emulsifiers, favors the formation of stable emulsions. Asphaltenes, resins [2–4], phenols, organic acids [5], metal salts [4,6,7], sediments, clays and waxes [8–11] are the main natural emulsifying agents present in petroleum.

The most common type of oil emulsion is the water-in-oil (W/O) emulsion because of the hydrophobic nature of the emulsifying agents present therein. Stable W/O emulsions are defined as those that persist without phase separation for five days or more [12]. Factors such as temperature, droplet size, agitation, time and type of emulsifying agent are the main stabilizers of an emulsion [13–15]. Increase in temperature leads to reduction in viscosity and consequently allows faster coalescence (rupture of the droplet film) [16,4]. The formed droplets vary in size, generating a droplet size distribution (DSD) and W/O emulsions with droplet sizes between 1 and 10 μm are classified as stable [17]. The intensity of the mechanical stirring and its application time tend to cause a reduction of droplet size due to the higher shear [15]. Kokal (2002) highlights that emulsifying agents have an effective action in the stabilization of the emulsion because they concentrate at the oil-water interface, forming a rigid film, providing interfacial tension reduction, contributing to droplet dispersion and emulsion stabilization [4].

Asphaltenes and resins have a strong tendency to bind together into micelles [18]. The polar part of resins interacts with the polar centers of the asphaltene molecules and these interact with other similar molecules, forming aggregates of solvated asphaltenes with resins in the oil. These aggregates are adsorbed at the interface of the water droplets and form a rigid structure enveloped by the droplets, favoring stability of the emulsions [11]. Thus, high levels of resins and asphaltenes in heavy oils, coupled with the presence of water in production steps and the shear induced during production, favor the formation of W/O emulsions that present high stability, which causes difficulty in oil dehydration during primary processing. In addition, the salts present in petroleum can be found at the oil-water interfaces as a result of ionic interactions with the asphaltenes and resins, further increasing the stability of these emulsions [9,6].

It is known in the literature that the stability of petroleum emulsions is favored by the presence of natural emulsifiers, in particular resins and asphaltenes. In a recent study, Zhang et al. (2016) [19] prepared model W/O and O/W emulsions with the aqueous phase composed of simulated water formation and with the addition of asphaltenes, resins and waxes, in order to evaluate the influence of these surfactants on the interfacial properties. For W/O emulsions, those that were prepared with asphaltenes were more stable than the others. The effects of salts on the stability of W/O emulsions still require elucidation and many studies are being carried out to obtain a good understanding of this subject. Ghannan (2005) [20] evaluated the effect of NaCl addition on W/O emulsions and observed that increasing the concentration of salt increased the emulsion stability. The effect of cations and salinity on the formation of W/O emulsions was studied by Perles et al. (2012) [21]. Munhoz and Solling (2017) [22] studied the effect of cation nature on the stability of W/O emulsions with the addition of KCl and NaCl solutions at different concentrations and the results showed that the salinity of the aqueous phase had an effect on the droplet size.

The stability of a W/O emulsion is usually evaluated by a gravitational thermal test, with or without a demulsifier [23], as well as by investigation of the rheology [24–28] and with the use of microscopy (optical, electron transmission and electron scanning) [29]. Other techniques, such as laser diffraction [30], low field nuclear magnetic resonance (NMR) [31,32] and medium infrared spectroscopy [33,34] also can be used for DSD determination. Optical microscopy is a visual technique used for direct measurement of the sample through image analysis [29]. In addition to size measurements, it is also possible to perform measurements of particle shape, which provide more information compared to other conventional techniques [35].

Due to their high salinity, W/O emulsions can cause problems, such as corrosion, formation of hydrates and incrustation in installations [36,37]. In addition, the increased viscosity, caused by the presence of dispersed water in oil, causes an increase in energy cost and instability in the process control [38]. The water present in oil is considered to be a non-economic load and when transported with oil, it overloads the pumping system and pipelines, burdening the transportation cost. Thus, oil needs to be dehydrated during primary processing in order to proceed to the next steps.

The evaluation in real emulsions of the combined effect of petroleum chemical composition, in terms of asphaltenes and resins, with the salts in the aqueous phase is needed in order to gain a greater understanding of this issue. In this sense, this work had the objective of studying the stability and homogeneity of W/O emulsions of heavy oil using the optical microscopy technique.

2. Methodology

This study used a previously dehydrated heavy oil from which W/O emulsions were prepared by adding a varying aqueous phase at concentrations of 10, 20, 30, 35 and 40% w/v. Stability of the emulsions was evaluated by gravitational separation tests at room temperature (25 °C) and with heating (30–80 °C) for 30 days. To study the electrolytes' influence on the emulsion stability, deionized water, formation water and saturated NaCl solution were evaluated as aqueous phases. Homogeneity and stability of the W/O emulsions were evaluated from the DSD obtained by optical microscopy.

2.1. Oil sample treatment

A heavy oil sample from an onshore field of the Espírito Santo (Brazil) Sedimentary Basin was used in the study. The procedure for collecting the crude oil sample was carried out following the ASTM D5854 standard [39]. Prior to the characterization step, free water was separated from the sample by decanting over an one-hour period [40] and it was then dehydrated by adding 250 μL of commercial demulsifier (containing isoprene and propylene glycol oligomeric species surfactants) and centrifuged at 2000 rpm for 20 min at 60 °C [41]. After this procedure had taken place, the water content in the oil was quantified by a standardized method [42], which confirmed that the water content was lower than 1% (v/v). The dehydrated oil was characterized according to the following physicochemical properties: water content (ASTM D4377) [42], density at 20 °C (ASTM D5002) [43], API gravity (ASTM D1250 and ISO 12185) [44,45], total acid number (TAN) (ASTM D664) [46], total sulfur content (ASTM D4294) [47], dynamic viscosity at 50 °C (ASTM D4402) [48], saturated, aromatic, resin and asphaltene contents (SARA) (ASTM D6560 and ASTM D2549) [49,50].

2.2. Oil characterization

2.2.1. Water content

The water content determination was performed by potentiometric titration using the Karl Fischer (KF) reagent without pyridine, according to ASTM D4377 [42].

2.2.2. API gravity

Oil density was determined according to ASTM D5002 [43] using an Anton Paar digital viscometer (Stabinger SVM 3000 model) with a detection limit of 0.0002 $g \cdot cm^{-3}$ at 20 °C. Approximately 5 mL of the sample, previously heated to the same test temperature, was injected into the measuring cell of the viscometer. Analysis was performed in duplicate at 40 and 50 °C. Then, the API gravity was calculated according to ASTM D1250 [44] and ISO 12185 [45]. The density measured at 40 and 50 °C was converted to its equivalent value at 20 °C for the API gravity calculation [51].