EMULSION INVERSION OF CRUDE OIL BY SOLID PARTICLE AND SURFACTANT ADDITION

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ABSTRACT

Crude oil produced as water-in-oil (W/O) emulsion can show high viscosity, causing difficulties during pipeline transportation. The production of O/W emulsion by adding an aqueous phase containing solid particles and surfactant is an alternative to decrease oil viscosity. Thus, the objective of this work is to study the synergistic effect of a surfactant (Triton X-100) and a solid particle (sodium bentonite) addition on emulsion inversion. Emulsions were characterized in conductivity, rheology, kinetic stability, and droplet size analyses. W/O to O/W emulsions inversion occurred when aqueous solutions were between 30 and 40% (m/m), according to conductivity and rheology analyses. The increment of water content from 30 to 50 % (w/w) increased mean droplet size from 2.6 to 10.6 μm , increased phase separation from 9.5 to 68.0 (v/v), and decreased emulsion viscosity from 183 to 1.07 mPa.s. Aqueous solution containing solid particle and surfactant affected emulsions' properties, producing systems with lower viscosity than crude oil, making it easier for oil pumping and pipeline transportation.

KEYWORDS

petroleum; sodium bentonite; Triton-X-100; pipeline transportation; rheology

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1. INTRODUCTION

Petroleum is produced naturally as water-in-oil (W/O) emulsion, a system composed of water droplets dispersed in an oil continuous phase. Water and oil mixtures typically present in the reservoir pass over chokes and valves, and mechanical input leads to form water droplets. The emulsion is, then, stabilized by natural surfactants such as asphaltenes and resins (Hasan et al., 2010; Santana et al., 2017).

W/O emulsions can present higher viscosity than dehydrated oil. Emulsion viscosity depends on oil and water content, temperature, shear rate, droplet size distribution, and amount of solids in the crude oil (Kokal, 2005; Meriem-Benziane et al., 2012). Oil pumping operations occur at a typical shear rate of 500 s^{-1} (Santos et al., 2011), and the viscosity required for transport is limited to 0.25 and 0.40 Pa.s at 37.8°C (Muñoz et al., 2016). Oil emulsions with 0.40 mPa.s may be attained only with 25–30% w/w water content. Above 30% of water in emulsion, the viscosity may become too high (Martinez-Palou et al., 2011). Different methods are used to reduce oil viscosity for pipeline transportation, including dilution with light oils or alcohols, heating, use of emulsion viscosity reducers, and use of surfactants to stabilize oil-in-water (O/W) emulsions (Hasan et al., 2010; Santos et al., 2017).

Many authors suggest the use of surfactants for O/W emulsification (Pilehvari et al., 1988; Ashrafizadeh & Kamran, 2009; Hasan et al., 2010; Abdurahman et al., 2012; Plasencia et al., 2013). In this method, the oil phase becomes dispersed in the water phase and stable O/W emulsions are formed with the aid of suitable surfactants. O/W emulsions showed a significant reduction in system viscosity, with values in the range of approximately 0.05 and 0.2 Pa.s. Determining the viscosity is important for establishing the dimensions of pipeline and equipment (Salager et al., 2001; Abdurahman et al., 2012; Plasencia et al., 2013).

Surfactants are amphyphilic molecules that reduce the interfacial tension between crude oil and water, stabilizing droplets. O/W emulsions produced using surfactants should be stable during pipeline transportation. These O/W emulsions should be easily broken before oil refining in order to separate the water to be treated from water

discharge or recycling, requiring a minimal quantity of surfactant and other additives (Hasan et al., 2010; Martínez-Palou et al., 2011).

The main difficulties related to the use of this technology are the selection of surfactant and reduction of the costs associated with the selection (Hasan et al., 2010). Non-ionic surfactants are cheap and they are not affected by water salinity. Triton X-100 (polyethylene glycol octylphenyl ether) has a chemical formula of $\text{C}_{33}\text{H}_{60}\text{O}_{10}$. It is a non-ionic surfactant used in O/W emulsification of crude oil to reduce oil viscosity. Authors such as Abdurahman et al. (2012) and Hasan et al. (2010) have evaluated its use in the reduction of viscosity.

Solid particles can also be added in order to produce O/W emulsion, adjusting its viscosity and stability (Souza, 2012). Solid particles act in water-oil interface due to their mutual affinity to oil and water, which depends on both the contact angle of particle and the water cut (Luz et al., 2008; Kralova et al., 2011). Particle contact angles (θ measured through the aqueous phase) slightly below 90° result in O/W emulsions; when θ is slightly above 90° W/O emulsions are formed. Conditions giving extreme contact angles (close to 0° or 180°), no stable emulsions are formed. Its efficiency on stabilizing W/O or O/W emulsions depends on particle concentration, wettability, inter-particle interactions, particle shape, and size. A particle should be typically limited to a few micrometers in size, and it must be much smaller than the emulsion droplet size (Tambe & Sharma, 1993).

Solid particles, as sodium bentonite, silica, and kaolinite nanoparticles have been used on catastrophic phase inversion for emulsions. This means that W/O to O/W emulsion transition happens with the addition of a water solution (Kralova et al., 2011; Souza et al., 2012). Bentonite is a hydrophilic material used widely in the industrial sector. It is formed mainly of clay minerals from the montmorillonite group with adsorbed cation sodium (Souza, et al. 2012).

Surfactant and solid particle can show a synergistic effect when added to petroleum emulsions. Wang et al. (2004) reported that kaolinite particles are attracted by opposite charges of surfactants (anionic palmitic acid and cationic dodecyl amine) and they are adsorbed onto oil-water interface. In addition, surfactant addition to O/W emulsions stabilized by kaolinite cause an

interfacial surface tension decrease. On oil-brine emulsions composed of solid particles (barium sulphate, calcium carbonate, and silica), the synergistic effect was attributed to the increase of particle contact angle on adsorption when surfactant stearic acid is added. However, high surfactant concentration can compete for active sites on the oil-water interface, inhibiting particle adsorption and decreasing emulsion stability (Tambe & Sharma, 1993, 1994a, 1994b; Hunter et al., 2008). Similar results were observed on the work of Gosa and Uricanu (2002) analyzing systems composed of silica and PEO-PPO-PEO block copolymers. Instability phenomena increased due to flocculation of silica with surfactant adsorption.

The proposed study evaluates the synergistic effect of surfactant and solid particle on crude oil-in-water emulsification in the production of low viscous emulsions. This study evaluates the conductivity, kinetic stability, rheology, and droplet size of W/O and O/W emulsions at different water solution concentrations (30, 40, and 50 % w/w) containing bentonite particle (0.5 % w/w) and Triton-X-100 (1.0 % w/w).

2. MATERIALS AND METHODS

2.1 Materials

Crude oil sample was obtained from a field located in Brazil. It was used without previous treatment in the production of petroleum emulsions. Crude oil shows 75.7 mPa.s at 100 s⁻¹ (Pena et al., 2018). Triton-X-100 (Neon, Brazil) and sodium bentonite with particle size smaller than 44 µm (Proquímicos, Brazil) were used to produce emulsions.

2.2 Emulsion preparation

Emulsions composed of crude oil (70, 60, and 50 % w/w) and aqueous solution (30, 40, and 50% w/w) were produced in an Ultra-Turrax T25 (IKA, Germany), at 15000 rpm/ 2 min.

Initially, an aqueous phase was prepared using distilled water. Surfactant Triton-x-100 (1% w/w) and sodium bentonite (0.5 % w/w) were weighted and the aqueous solution was magnetically stirred for 2 minutes prior to the emulsion preparation at

rotor-stator device. Solid particle concentration was previously defined according to a study conducted by Pena et al. (2018). The required amount of the crude oil was added gradually into the aqueous phase, and the mixing formed the emulsion. Afterwards, the emulsion was taken for conductivity, stability, and optical microscopy measurements. All preparations and measurements were conducted at room temperature (25°C) and in triplicate.

2.3 Emulsion characterization

2.3.1 Conductivity

Electric conductivity of emulsions was evaluated immediately after homogenization process in a conductimeter W12D (BEL Engineering, Italy).

2.3.2 Kinetic stability

The emulsions prepared were tested for stability by transferring the emulsions into 50 mL capacity graduated cone-shaped glass tubes, with 0.1 mL graduations. The phase separation was registered for 7 days at room temperature.

2.3.3 Optical microscopy and droplet size distribution

The microstructure of the emulsions was studied immediately after homogenization process using an optical microscopy (Leica, Germany). The samples were poured onto microscope slides, covered with glass cover slips, and observed at a magnification of 40x. At least 10 images were taken for each sample, and the best 5 sharp pictures were analyzed using the public domain software Image J 1.50i (ImageJ, 2017). Micrographs of the emulsions were analyzed by measuring the diameter of at least 500 droplets (one by one) (Santana et al., 2011). After conversion of the pixel-scale into microns by a scaling factor, droplet diameter data were used to plot a histogram of droplet frequency (number percentage) versus droplet size category. Considering spherical droplets, the surface mean diameter (d_{32}) of the emulsions were calculated as $d_{32} = \Sigma(n_i d_i^3) / \Sigma(n_i d_i^2)$, where n_i is the number of particles with diameter d_i .

Table 1. Kinetic stability of emulsions with 30, 40, and 50% (w/w) water at different periods (1 hour, 1 day, and 7 days).

% (w/w) water	Volume (ml) of aqueous phase separation		
	1 hour	1 day	7 days
30%	8.50	9.50	9.50
40%	26.3	41.3	42.3
50%	56.0	67.3	68.0

2.3.4 Rheology

Rheological measurements of the emulsions were carried out using a viscosimeter OFITE model 900 (United States). The samples were analyzed immediately after homogenization process. Steady shear measurements were made in triplicate at 25 °C. Flow curves were obtained using an up-down-up step program using a shear rate range between 0 and 300 s⁻¹.

3. RESULTS AND DISCUSSIONS

3.1 Conductivity

Electric conductivity is affected by water content and by dispersed phase size. Emulsion inversion from W/O or O/W type can be identified by conductivity measurements, since W/O emulsions show low conductivity values, while O/W emulsions show high conductivity values (Schramm, 1992).

Emulsions conductivity values (Figure 1) increased when the water content increased from 30 to 40 % (w/w) of water, suggesting an emulsion inversion (W/O to O/W emulsion) in water concentration range. Phase inversions between 30 and 40% (w/w) of water were also observed by [Pena et al. \(2018\)](#) in emulsions composed by the same crude oil and solid particle (without surfactant addition), and by [Bento et al. \(2015\)](#) in emulsions composed by Tween 80, a hydrophilic non-ionic surfactant as Triton-X-100. The same authors also observed phase inversion at higher water contents (60 and 90 % w/w, depending on oil phase and temperature) when a Span 60 was used. The hydrophobic surfactant tends to form W/O emulsion in a larger range of water compositions.

3.2 Kinetic Stability

The percentages of aqueous phase separated from the emulsions after 1 hour, 1 day, and 7 days of storage are shown in Table 1. The phase separation was faster in the first hour, and it continued increasing up to 7 days of storage. The

Figure 1. Conductivity (μS/cm) (●) of emulsions with 30, 40, and 50 % (w/w) of water.

Figure 2. Flow curves of emulsions with 30 (◆), 40 (■), and 50 % (w/w) (▲) of water.

Figure 3. Viscosity of emulsions with 30 (◆), 40 (■), and 50 % (w/w) (▲) of water.

emulsion with 30 % (w/w) of water showed high kinetic stability, with only 9.50 % (v/v) of separation. This behavior can be explained by the emulsion type (W/O) identified on conductivity measurements. Moreover, this emulsion had lower water content if compared to other emulsions. The increment of water to 40 and 50 % (w/w) increased emulsion instability to 42 and 68 % (v/v) of phase separation, respectively.

3.3 Rheology

Flow curves and viscosities results for the studied emulsions are shown in Figures 2 and 3. Emulsions with 30 and 50 % (w/w) water showed a

Newtonian behavior, while emulsion with 40 % (w/w) showed a non-Newtonian behavior. Emulsion viscosities decreased significantly with water content increment. Emulsions with 30 % (w/w) of aqueous phase showed a higher viscosity (183 mPa.s at 100 s^{-1}) if compared to crude oil (75.7 mPa.s, at 100 s^{-1}) (Pena et al., 2018), indicating that this system is a W/O emulsion, in agreement with conductivity results. Emulsion inversion occurred between 30 and 40 % (w/w) of water, since emulsions with 40 and 50% (w/w) of aqueous phase showed reduced viscosity (6.33 mPa.s and 1.07 mPa.s, respectively) (Ashrafizadeh & Kamran, 2009), with lower values than emulsions composed by the same crude oil and solid particle, in absence of surfactant (Pena et al., 2018). Abdurahman et

Figure 4. Optical microscopy of emulsion with 30 (A), 40 (B), and 50 % (w/w) (C) of water.

Figure 5. Droplet size distribution of emulsions with 30 % (A), 40 % (B), and 50 % (C) (w/w) of aqueous solution.

al. (2012) showed that the use of Triton-X-100 changed the properties of 72% v/v crude oil emulsions, prepared at 1700 rpm/15 min, in absence of solid particles, at 30°C. Emulsions with a slight increase in the viscosity and a significant increase in stability were produced with the increment of Triton concentration from 0.0125 to 1.5 % (w/w).

3.4 Microstructure and mean droplet size

Figure 4 shows an emulsion microstructure, while Table 2 and Figure 5 present mean droplet size (d_{32}) and droplet size distribution, respectively.

Mean droplet size increased with water increment, varying between 2.8 and 10.6 μm . In addition, the increment of water content produced emulsions with a higher polydispersity, and a higher frequency of droplets bigger 2.5 μm . One can also note that the emulsions with bigger droplet size showed lower viscosity and worst kinetic stability. These are desired properties to pipeline transportation and posterior water separation at the end of this process. Bigger droplet size and higher kinetic instability of emulsion with 40 and 50 % (w/w) will turn easy emulsion destabilization during primary treatment.

Table 2. Mean droplet size ($d_{32}/\mu\text{m}$) of emulsions with different water concentration.

% (w/w) of water	d_{32} (μm)
30	2.80 ± 0.870
40	6.29 ± 1.59
50	10.6 ± 1.29

4. CONCLUSIONS

Emulsion inversion was confirmed by the evaluation of all emulsion properties. W/O to O/W emulsion occurred between 30 and 40 % (w/w) of aqueous phase. The emulsion with 30% (w/w) water showed low conductivity and high viscosity. High viscosity is associated with continuous phase composed by oil. Moreover, the emulsion with 30% (w/w) water showed small droplet size and, consequently, high kinetic stability. On the other hand, emulsions with 40 and 50 % (w/w) water showed high conductivity, low viscosity, bigger droplet size, and lower kinetic stability. Solid particle and surfactant addition affect emulsion properties, inducing emulsion inversion and producing O/W emulsion with lower viscosity than crude oil, attaining adequate conditions to pipeline transportation of petroleum emulsions when using 40 or 50% (w/w) water.

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