



# CRUDE OIL-IN-WATER EMULSIFICATION USING SOLID PARTICLE FOR PIPELINE TRANSPORTATION

## EMULSIFICAÇÃO ÓLEO-EM-ÁGUA DE PETRÓLEO USANDO PARTICULA SÓLIDA PARA TRANSPORTE EM OLEODUTOS

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### RESUMO

Óleo cru pode apresentar elevada viscosidade devido à presença de uma estrutura do tipo emulsão A/O (água-em-óleo) e/ou à presença de altas concentrações de asfalteno (como em óleo pesado), levando a dificuldades durante o seu escoamento em oleodutos. A produção de emulsões O/A (óleo-em-água) a partir de partículas sólidas é uma alternativa para alcançar a redução da viscosidade do óleo de petróleo. Assim, o objetivo deste estudo é obter emulsões O/A através da adição de solução aquosa contendo partícula de bentonita. As emulsões foram caracterizadas em análises de condutividade, reologia, estabilidade cinética e tamanho de gotas. A transição de emulsões A/O para O/A ocorreu entre 30 e 40 % (m/m) de solução aquosa, segundo as análises de condutividade e reologia. O incremento de solução aquosa de 30 para 40 % (m/m) resultou no aumento do tamanho médio de gotas e da separação de fases, e na redução da viscosidade das emulsões. A adição de partículas sólidas afetou as propriedades das emulsões, produzindo sistemas de menor tamanho de gota e menor viscosidade que o óleo cru. Neste sentido, pode-se concluir que a bentonita sódica foi eficiente na inversão da emulsão e na produção de emulsões O/A de baixa viscosidade, facilitando o bombeamento e transporte do petróleo em dutos.

### ABSTRACT

Crude oil can show high viscosity due to the presence of W/O (water-in-oil) emulsion structure and/or the presence of a high concentration of asphaltenes (as in heavy oil), causing difficulties during pipeline transportation. The production of O/W emulsion by solid particles is an alternative to decrease oil viscosity. The objective of this study is to obtain O/W (oil-in-water) emulsions with low viscosity by the addition of an aqueous phase containing sodium bentonite. Emulsions were characterized in conductivity, rheology, kinetic stability and droplet size analyses. W/O to O/W emulsions transition occurred between 30 and 40% (m/m) of aqueous solution, according to the conductivity and rheology analyzes. The increment of water content from 30 to 50 % (w/w) increased mean droplet size and phase separation, and decreased emulsion viscosity. Solid particles addition affects emulsions properties, producing systems with smaller droplet size and lower viscosity than crude oil. In this way, it can be concluded that sodium bentonite was efficient to induce emulsion inversion and produce O/W emulsion with low viscosity, making easier oil pumping and pipeline transportation.

## 1. INTRODUCTION

Petroleum is the dominant source of energy of the world and heavy oils represent the majority of the recoverable oil resources. However, heavy oil presents high viscosity and complex composition, causing difficulties during pipeline transportation due to the low mobility and flowability of the crude and wax and asphaltene deposition on pipeline wall surfaces (MARTÍNEZ-PALOU et al., 2011).

Crude oil is another problem that occurs in the petroleum industry, since it is naturally produced as water-in-oil (W/O) emulsion. W/O emulsions are systems composed of water droplets dispersed in an oil continuous phase that presents higher viscosity than dehydrated oil (SANTANA et al., 2017). Water and oil mixtures pass over chokes and valves, and mechanical energy input leads to the formation of water droplets (HASAN et al., 2010) which are stabilized by natural surfactant (as asphaltenes, resins and solid particles) (SANTANA et al., 2017).

Several types of particles are present in the petroleum fluid such as reservoir particles (silica, clays), mineral scales ( $\text{CaCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{SrSO}_4$ ,  $\text{CaSO}_4$ ) and corrosion products ( $\text{FeS}$ , oxides) (KRALOVA et al., 2011). Inorganic particles may be modified by the adsorption of heavy crude oil components, like resins and asphaltenes, changing emulsion stability.

The required viscosity for transportation, typically around 400 cP, may be attained only with 25–30% w/w water content. Above 70% of oil in emulsion, the viscosity may become too high, causing problems related to corrosion and break in desalting and dehydrating (MARTÍNEZ-PALOU et al., 2011). Besides water and oil content, emulsion viscosity depends on temperature, droplet size distribution and amount of solids in the crude oil (KOKAL, 2005; MERIEM-BENZIANE et al., 2012). Different methods are used in order to reduce the viscosity of oil for pipeline transportation, as dilution with lighter crudes or alcohols, heating, and the use of surfactants to stabilize oil-in-water (O/W) emulsions (HASAN et al., 2010).

Solid particle can also be added to crude oil in order to prevent the formation of W/O emulsions, benefiting the transportation of oil. The W/O emulsion inversion into O/W emulsion may occur via catastrophic inversion, when the disperse phase volume expands above critical values. The use of solid particle, such as surfactants, in emulsion inversion is a recent technique, with scarce studies applied to petroleum emulsions (SOUZA, et al., 2012). Unlike surfactants, solid particles do not reduce oil-water surface tension (HUNTER et al., 2008).

Solids particle acts at water-oil interface due to its mutual affinity to oil and water which depends on both the contact angle of particle and the water cut (KRALOVA et al., 2011; LUZ et al., 2008). Particle contact angles ( $\theta$  measured based on the aqueous phase) slightly below  $90^\circ$  resulted in O/W emulsions, and for conditions giving  $\theta$  slightly above  $90^\circ$ , W/O emulsions were formed. Interestingly, conditions giving extreme contact angles (close to  $0^\circ$  or  $180^\circ$ ) no stable emulsions were formed (HUNTER et al., 2008). Solid particle efficiency on stabilize W/O or O/W emulsions depends on particle concentration, wettability, inter-particle interactions, particle shape and size. O/W emulsion stabilized by solids should be completely coverage with at least a particle monolayer, similar to the critical

micellar concentration at which the interface is completely saturated.

Sodium bentonite, silica and kaolinite nanoparticles are solid particles recently used on catastrophic phase inversion for emulsions (GU et al., 2003; KRALOVA et al., 2011; SOUZA et al., 2012). Bentonite is a hydrophilic material widely used in the industrial sector. It is formed mainly of clay-minerals from montmorillonite group with adsorbed cation sodium (SOUZA et al., 2012).

The proposed study evaluated the effect of sodium bentonite addition on crude oil-in-water emulsification in order to produce low viscous emulsions. Conductivity, kinetic stability, rheology and droplet size of W/O and O/W emulsions at different water solution concentration (30, 40 and 50 % w/w) containing of bentonite particle (0, 0.5 and 1.5% w/w) were evaluated.

## 2. MATERIAL AND METHODS

### 2.1. Material

Crude oil samples were obtained from Brazilian fields (north of Espírito Santo). Sodium bentonite with particle size smaller than  $44 \mu\text{m}$  (Proquímicos, Brazil) were used to produce emulsions. Magnetic stirrer (IKA, Germany) and Ultra-Turrax T25 (IKA, Germany), were used to solution and emulsion preparation.

### 2.2. Emulsion Preparation

W/O and O/W emulsions composed of crude oil (10 - 90 % w/w) and aqueous solution (90 - 10 % w/w) were produced in an Ultra-Turrax, at 15,000 rpm/2 min. Aqueous solution was composed of 0, 0.5 or 1.5% (w/w) of sodium bentonite, and the corresponding emulsions were named as P0, P05 and P15, respectively.

Initially, an aqueous phase composed of distilled water and sodium bentonite (0, 0.5 and 1.5 % w/w) was magnetically stirred during 2 minutes before emulsion preparation at rotor-stator device. The aqueous phases was added into the crude oil and the mixing was conducted to form emulsions. Afterwards, the emulsion was taken for the conductivity, stability and optical microscopy measurements. All preparations and measurements were realized at room temperature ( $25^\circ\text{C}$ ) in duplicate.

### 2.3. Emulsion Characterization

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

**Kinetic stability:** The prepared emulsions were tested for their stability by transferring the emulsion into a 50 mL capacity glass cone-shaped tubes graduated in 0.1 mL graduations. The separated aqueous phase water volume was registered for 7 days at room temperature.

**Optical microscopy and droplet size distribution:** The microstructure of the emulsions was immediately observed 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 analyzed using the public domain software Image J v1.36b (<http://rsb.info.nih.gov/ij/>). Micrographs of the

emulsions were analyzed by measuring the diameter of at least 300 droplets (one by one). After conversion of the pixel-scale into microns by a scaling factor, droplet diameters data was used to plot a histogram of droplet frequency (number percentage) versus droplet size category. Considering spherical droplets, the surface mean diameters ( $d_{32}$ ) 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  $d_i$ .

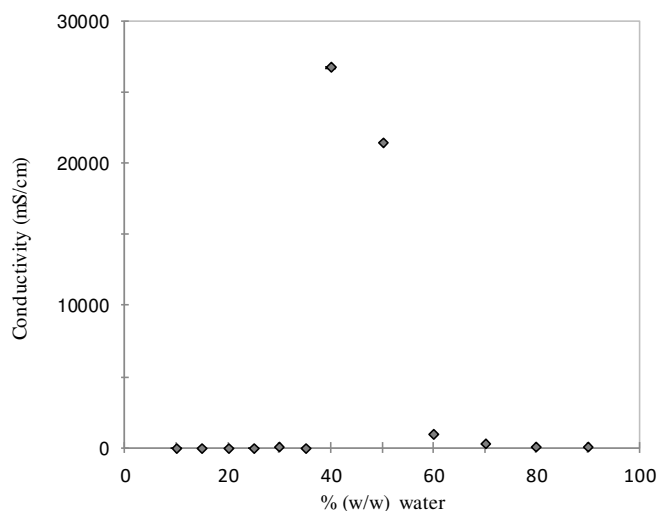
**Rheology:** Rheological measurements of the emulsions were carried out using a viscosimeter OFITE model 900 (United States). The samples were analyzed immediately after homogenization process. Steady shear measurements were made in triplicate at 25 °C. Flow curves were obtained by an up-down-up steps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

### 3. RESULTS AND DISCUSSION

#### 3.1. Conductivity

Electric conductivity is affected by water content and by dispersed phase size (SCHRAMM, 1992). In this way, conductivity measurements can be used to identify emulsion structure (W/O or O/W). W/O show low conductivity values, since the continuous phase (oil) presents low conductivity, while O/W emulsions show high conductivity values.

Figure 1 shows conductivity values of emulsions composed by a large range of water content, between 0.5 and 90 % (w/w), without solid particle. Emulsions with aqueous solution content lower than 40% (w/w) showed low conductivity values, and an abrupt increase of emulsion conductivity occurred at 40 % (w/w) of aqueous solution, suggesting emulsion inversion



**Figure 1. Conductivity values for emulsions containing 10 - 90 % (w/w) of aqueous solution without solid particle.**

Table 1 shows conductivity values of emulsions containing 30, 40 and 50 % (w/w) of aqueous solution with different solid particles concentrations (0, 0.5 and 1.5 % w/w). Conductivity increased when the water content increased from 30 to 40 % (w/w) of water in the majority of the conditions evaluated, suggesting emulsion inversion (W/O to O/W emulsion) between 30 e 40 % (w/w) of water. These results will be confirmed by the other analysis, as viscosity, since conductivity is a qualitative measurement of emulsion inversion.

**Table 1 – Conductivity values ( $\mu\text{S}\cdot\text{cm}^{-1}$ ) of emulsions with different water concentration (30, 40 and 50% w/w) and solid particle concentration (0, 0.5 and 1.5 % w/w).**

Solid particle concentration (w/w)	% aqueous phase		
	30	40	50
0 %	12.7	26,800	21,430
0.5 %	32.1	19,340	16,230
1.5 %	5.01	25,350	22,000

#### 3.2. Kinetic stability

Kinetic stability is traditionally measured by the macroscopic observation of emulsion phase separation along time (MORAN, 2007). All the emulsions showed phase separation, producing an inferior aqueous phase and an upper phase rich in oil. Table 2 shows the percentage (% v/v) of phase separation after 1 hour, 1 day and 1 week. The major phase separation occurred in the first hour. Emulsion instability increased with water content in all emulsions produced, as observed by Abdurahman et al. (2012). Probably, it occurred due the decrease of the more viscous component (oil), increasing destabilization phenomena, as sedimentation. The higher stability of the majority of the emulsions with 30 % (w/w) of aqueous phase can be also associated with their W/O structure, as suggested in conductivity measurements. Solid particle addition in the emulsions leads to a decrease in stability of emulsions with 30% of water. At higher water contents (40 and 50 % w/w), no tendency was observed with solid particle addition.

**Table 2 - Kinetic stability of emulsions (30, 40 and 50 % w/w of aqueous solution with 0, 0.5 and 1.5% w/w of solid particle) at different periods (1 hour, 1 day and 7 days).**

Solid particle concentration (w/w)	Storage time	Water content (% w/w)		
		30	40	50
0 %	1 hour	15.0	35.1	39.7
	1 day	15.5	35.6	40.0
	7 days	15.7	35.6	40.0
0.5 %	1 hour	23.5	20.0	34.0
	1 day	25.0	24.5	37.0
	7 days	25.0	24.5	37.5
1.5 %	1 hour	29.8	29.8	39.5
	1 day	37.5	30.8	40.5
	7 days	37.5	36.3	42.5

#### 3.3 Viscosity

Crude oil viscosity decreased with shear rate (Figure 2), showing 75.7 mPa.s at 100 s<sup>-1</sup>. Non-Newtonian behavior was also observed in crude oil evaluated by Hasan et al. (2010).

The viscosity between 0 and 300 s<sup>-1</sup> of W/O and O/W emulsions are showed in Figure 3, while viscosity at 100 s<sup>-1</sup> was showed at Table 3, a typical shear rate of pipe flow (STEEFE, 1992). Emulsions viscosity decreased significantly with water content increment. The decrease of emulsion viscosity with water addition was also observed by Hasan et al. (2010) and Zaki (1997). The high viscosity of emulsions with 30% (w/w) of aqueous phase indicated that these systems are W/O emulsion. 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 (ASHRAFIZADEH and KAMRAN, 2009), with lower values than crude oil (Figure

2). In addition, emulsion viscosity decreased with the increment of solid particle concentration. Thus, solid particle was efficient in produce emulsion with low viscous property.

### 3.4. Droplet size

Mean droplet size ( $d_{32}$ ) of the emulsions and droplet size distribution of the emulsions are shown in Figure 3. Mean droplet size tended to increase with water increment, varying between 4.56 and 9.20  $\mu\text{m}$ . In addition, emulsion with higher water content showed a higher frequency of bigger droplets, including droplets larger than 5 $\mu\text{m}$ , increasing emulsion polydispersity. Water content addition led to larger droplet size, higher phase separation and lower viscosity. Coalescence may result in an increase in droplet size which is usually followed by a reduction in the viscosity of the emulsion when flocculation is not present (TADROS, 2009).

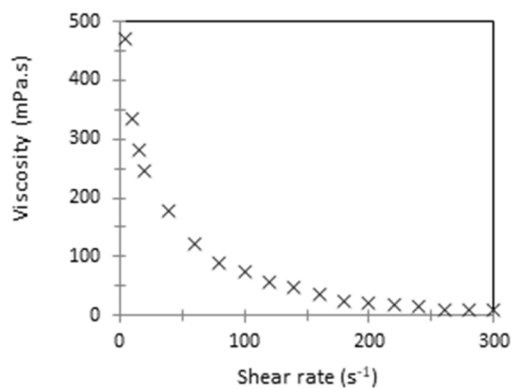


Figure 2. Viscosity of crude oil

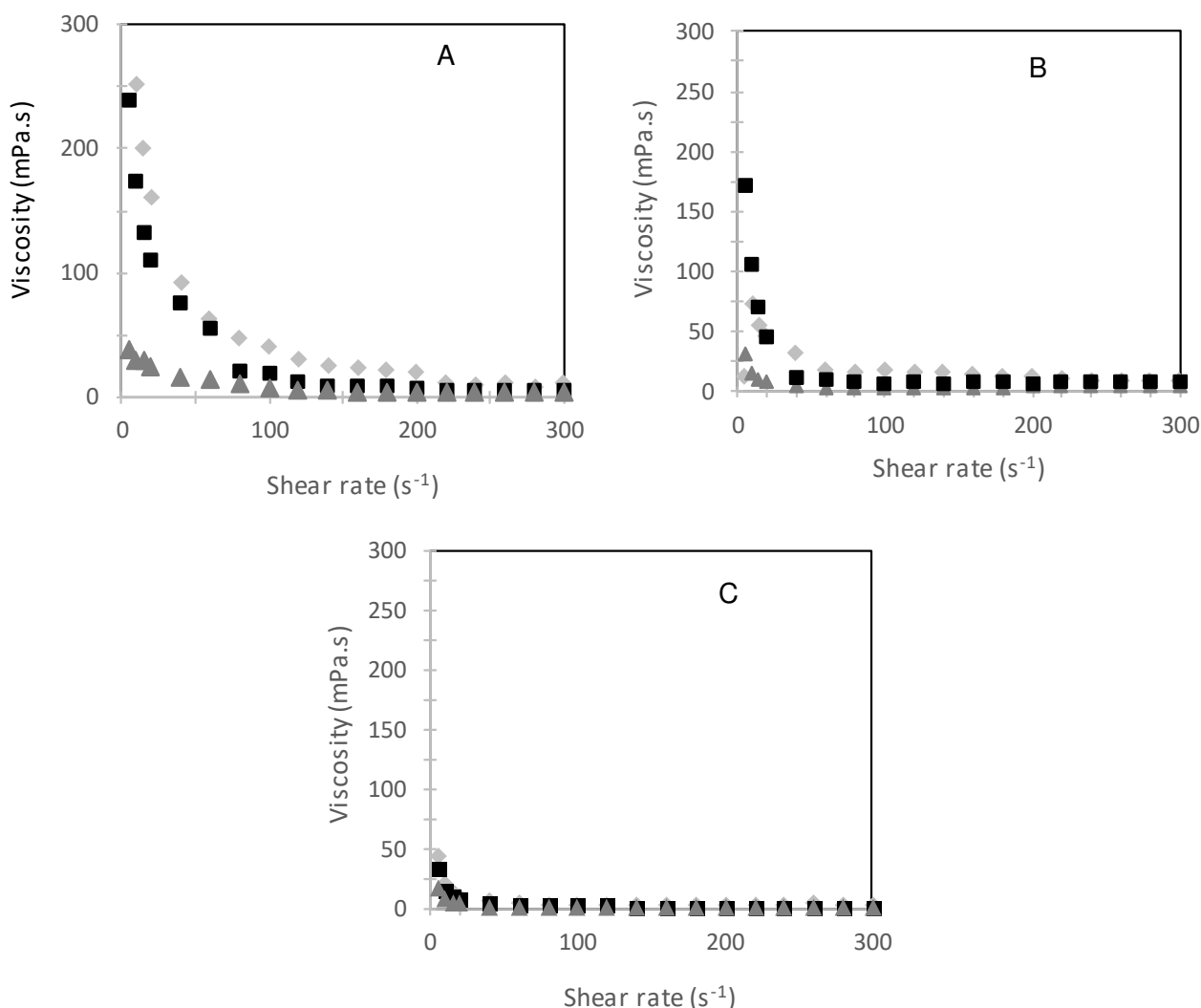
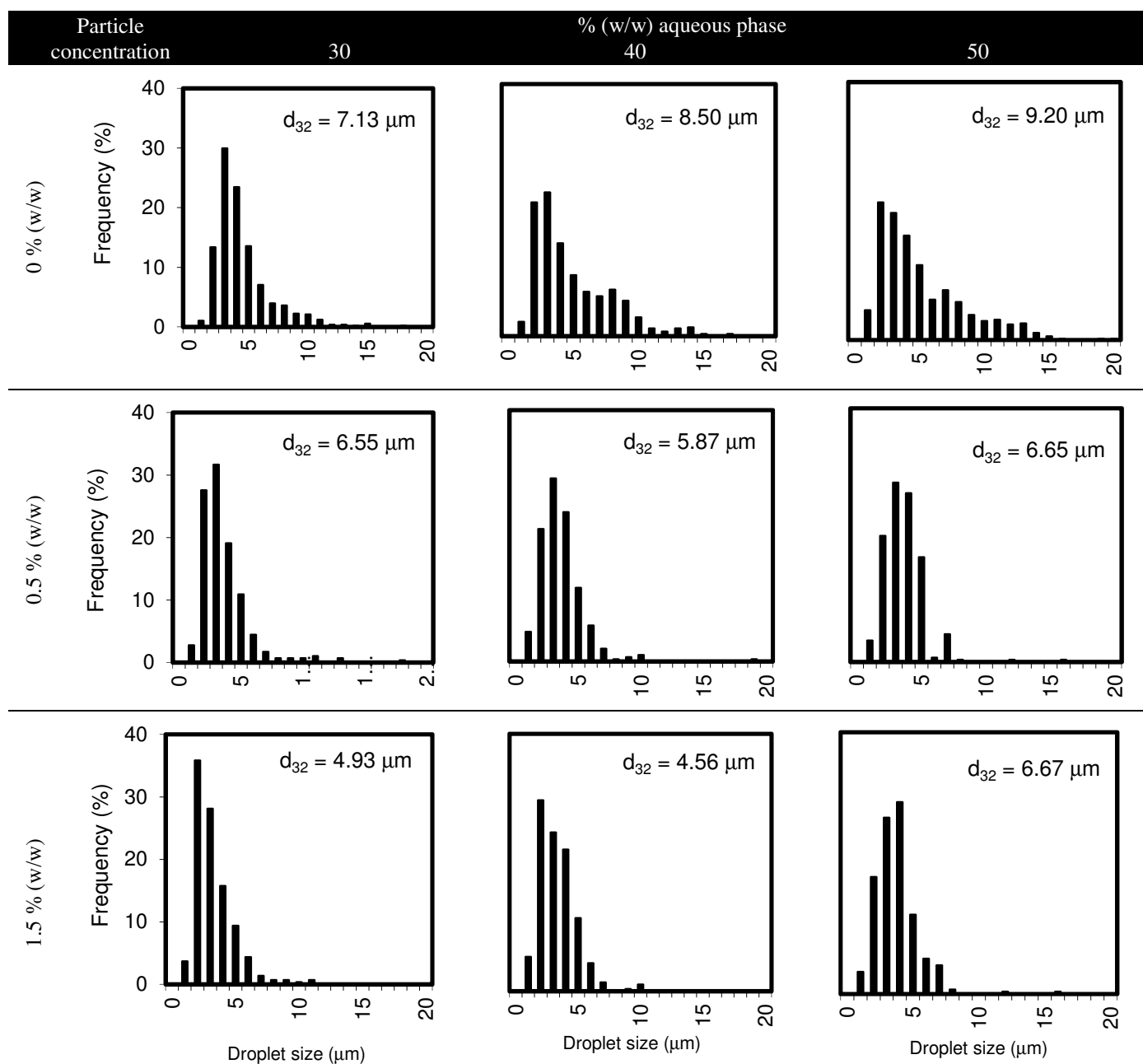


Figure 3. Viscosity of emulsions containing 30 % (♦), 40 % (■) and 50 % w/w (▲) of aqueous solution containing 0 (A), 0.5 (B) and 1.5 (C) % w/w of solid particle.

Table 3: Viscosity at 100 s<sup>-1</sup> (mPa.s) of emulsions with different water content (30, 40 and 50 % w/w) and solid particle concentration (0, 0.5 and 1.5 % w/w).

Solid particle concentration (% w/w)	% (w/w) aqueous phase		
	30	40	50
0 %	38.9	18.6	5.15
0.5 %	16.8	6.4	3.15
1.5 %	3.6	2.3	2.00



**Figure 3. Mean droplet size ( $d_{32}/\mu\text{m}$ ) and droplet size distribution of emulsions with 30, 40 and 50 % (w/w) of aqueous phase containing 0, 0.5 and 1.5 % (w/w) of solid particle.**

Solid particle addition decreased emulsion mean droplet size. Systems without solid particle showed mean droplet size between 7.13-9.20  $\mu\text{m}$ , while emulsions with 0.5 % (w/w) of solid particle showed mean droplet size between 5.87 and 6.65  $\mu\text{m}$ . In addition, the increment of solid particle concentration to 1.5 % (w/w) generally reduced emulsion mean droplet size. Polydispersity of droplet size also decreased with solid particle increment. Particle size distribution affects emulsion properties, as stability phenomena and viscosity (SCHRAMM, 1992).

A relationship between lower droplet size, higher phase separation and higher viscosity with solid particle addition can be explained by flocculation phenomena which results in an increase in the viscosity (TADROS, 2009).

#### 4. CONCLUSION

Emulsion inversion was observed between 30 and 40 % (w/w) of aqueous phase according to conductivity and viscosity measurements. Emulsions with lower water content (W/O emulsions with 30% w/w of aqueous solution) showed low conductivity, higher kinetic stability and viscosity and smaller droplet size. Solid particle addition affects emulsions properties, producing systems with smaller mean droplet size and lower viscosity than crude oil. In this way, it can be concluded that sodium bentonite was efficient to induce emulsion inversion and produce O/W emulsion with low viscosity, attaining adequate conditions to pipeline transportation of petroleum emulsions.

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