

EFFECT OF WATER CONTENT, TEMPERATURE AND AVERAGE DROPLET SIZE ON THE SETTLING VELOCITY OF WATER-IN-OIL EMULSIONS

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Abstract - Water-in-oil (W/O) emulsions are complex mixtures generally found in crude oil production in reservoirs and processing equipment. Sedimentation studies of water-oil emulsions enable the analysis of the fluid dynamic behavior concerning separation of this system composed of two immiscible liquids. Gravitational settling was evaluated in this article for a model emulsion system consisting of water and a Brazilian crude oil diluted in a clear mineral oil as organic phase. The effects of water content and temperature were considered in the study of sedimentation velocity of water-oil emulsions. Water contents between 10% and 50 % and temperatures of 25, 40 and 60 °C were evaluated, and a Richardson-Zaki type correlation was obtained to calculate settling velocities as a function of the process variables investigated. Water contents and average droplet sizes were monitored at different levels in the settling equipment, thus enabling identification of the effect of these variables on the phenomena of sedimentation and coalescence of the emulsions studied. The results showed that the emulsion stability during sedimentation was governed by the emulsion water content, which yielded high settling velocities at low water contents, even when very small droplets were present. A quantitative analysis of the combined effects of drop size and droplet concentration supports the conclusion that a stronger effect is produced by the higher concentration of particles, compared with the relatively smaller effect of increasing the size of the droplets.

Keywords: Water-in-oil emulsions; Stability; Settling velocity; Water-oil separators.

INTRODUCTION

Crude oil is a mixture of hydrocarbons with a wide range of sizes and functionalities. These species contribute to the formation and stability of emulsions. Asphaltenes and resins are two solubility classes of crude oil identified as other important factors for the enhanced stability of water-in-crude

oil emulsions. The interplay between the asphaltenes and resins forms strong and elastic films at the oil-water interface (Opedal *et al.*, 2011). In the offshore production of petroleum, emulsions are present at different stages of the production and transportation processes. Many operations must be considered in a platform design for emulsion destabilization, including equipments such as coalescers and separators (Urdahl

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et al., 2001). Santos *et al.* (2014) provided an extensive revision of the methods involved on recovery and transportation methods of heavy oil.

Separation of two-phase systems, including dispersed and continuous liquids, is a challenge in advanced separation technology. Liquid-liquid separations require the use of special equipment when the drop sizes are small, typically in the range of 1-50 μm in size (Orciuch *et al.*, 2012). In the extraction processes, the "crude oil" is a complex mixture consisting of oil, gas, water and solid particulates. As the first step, this mixture is transferred to primary gravity separators, which typically are cylindrical vessels designed to slow down the flow of the mixture, allowing a sufficient residence time for gravity driven settling/separation to produce well defined layers of gas, oil and water.

Clearly, the accurate detection of interface positions (when they have formed) and the phase content measurement (when heterogeneous mixtures persist) are critical from the operation efficiency point of view. This procedure enhances the separation equipment design and helps prevent environmental hazards such as the accidental discharge of oily process water into the sea (Jaworski and Meng, 2009). This ill-defined thick material is known as a rag layer and is comprised of emulsified water and/or oil, asphaltenes, clays, and solids. Rag layers are undesirable because they reduce separation efficiency and can upset the process. The growth of a rag layer depends on the settling/creaming and coalescence rates of the emulsified droplets, which are a function of droplet size, phase densities, viscosity and interfacial properties (Khatri *et al.*, 2011).

Emulsions are thermodynamically unstable systems and will, as a function of time, separate to minimize the interfacial area between the oil and water phases. If a density gradient between the dispersed and continuous phases is present, dispersed droplets experience a vertical force in a gravitational field. The gravitational force is opposed by the fractional drag force, and by the buoyancy force. The resulting settling rate V_{STOKES} of a single droplet is given by Eq. (1), named Stokes' law (Stokes, 1851):

$$V_{STOKES} = \frac{(\rho_d - \rho_c)gd^2}{18\mu_c} \quad (1)$$

where V_{STOKES} is the sedimentation velocity (m/s); ρ_d and ρ_c are the densities of the dispersed and continuous phases, respectively (kg/m^3); g is the gravitational constant (m/s^2); d is the particle diameter (m); and μ_c is the dynamic viscosity of the con-

tinuous phase (Pa.s). Stokes law has several limitations and is strictly applicable only for noninteracting spherical droplets at low concentration with a monodisperse droplet size distribution. Predictions or calculation of settling/creaming rates in concentrated emulsions, where other than hydrodynamic factors come to account, are therefore complicated (Gundersen and Sjöblom, 2001; Frising *et al.*, 2006).

Stokes' law is an analytical solution of the Navier-Stokes equation for the simplified flow case of solid particles and creeping flow. In the case of fluid particles and in the absence of surface-active components, internal circulation inside the particle will reduce the drag force. The viscosity correction term for this case is given by Eq. (2) {called the Hadamard-Rybczynski equation, Hadamard (1911), Rybczynski (1911)}. This equation was obtained through the analytical solution of the momentum transfer equations for the velocity fields inside and outside during the settling of an isolated drop (Levich, 1962). The viscosity correction term for this case is given in Eq. (2).

$$V_{HR} = \frac{(\rho_d - \rho_c)gd^2}{18\mu_c} \frac{\mu_c + \mu_d}{\frac{2}{3}\mu_c + \mu_d} \quad (2)$$

From this equation it can be seen that, for large viscosity differences between the dispersed and continuous phases, the settling will approach the Stokes velocity or 3/2 of the value predict by Stokes' law velocity. Viscous liquid drops in a gas approach Stokes' law (negligible circulation), while gas bubbles in viscous liquids approach 3/2 of the value predict by Stokes' law due to formation of a velocity field for gas bubbles in viscous liquids with a high degree of circulation (Arntzen and Andresen, 2001).

Aiming to include the effect of phase concentration on the settling velocities of complex mixtures, Richardson and Zaki (1954) proposed an empirical correlation (Eqs (3) and (4)):

$$V_{RZ} = V_{STOKES} (1 - \phi)^n \quad (3)$$

or

$$V_{RZ} = V_{STOKES} (1 - 0.01 WC)^n \quad (4)$$

where ϕ is the volume fraction of the dispersed phase and n is an experimentally determined constant between 2.3 and 5 (Richardson and Zaki, 1954). Equations (1) to (4) constitute the theoretical basis for the study of droplet settling, but these fundamentals are not enough to explain the additional complex interfacial phenomena such as surfactant adsorption and

asphaltene/resin interactions involved in real emulsions systems. In the technical literature of the oil industry it is usual to replace ϕ by the water content (WC), expressed in percentage by volume of water in the mixture, so that $\phi = 0.01 WC$.

Research on emulsion layers in liquid-liquid dispersions without solids has progressed further and various models based on the sedimentation and coalescence of emulsified droplets have been proposed for these systems (Jeelani and Hartland, 1986a, 1986b, 1988, 1990, 1993, 2005a, 2005b; Cunha *et al.*, 2008; Noik *et al.*, 2013). In this work we studied the mechanism of phase separation due to gravity effects. The sedimentation velocity of droplets in a complex system composed of water-in-crude oil emulsion were investigated in a laboratory scale unit, monitoring the water droplet size distribution as a function of time and interface position.

MATERIALS AND METHODS

A model emulsion was used in the study. The organic phase was a Brazilian crude oil diluted in a mineral oil. The dynamic viscosity and density at 25 °C of the organic phase were 2.64 mPa.s and 0.83 g/cm³, respectively. The aqueous phase was distilled water. The crude oil is classified as a light crude oil with the following SARA characterization composition: saturates (47.2% wt), aromatics (26.9% wt), resins (23.1% wt), and asphaltenes (2.77% wt).

The emulsions were homogenized for 5 minutes at 17500 rpm in an Ultra-Turrax T-25 homogenizer fitted with a S24-25G dispersing tool (IKA). The total volume of each prepared emulsion sample was 1.6 liters. The sample was then rapidly transferred to a cylindrical settling vessel with internal dimensions of 110 x 30 x 380 mm. As shown in Figure 1, this vessel is jacketed and connected to a thermostatic bath for temperature control. Also, the vessel is equipped with 6 holes for emulsion sampling. For the sedimentation tests carried out in this work, emulsion samples were collected regularly from three sampling points (the second, fourth and sixth points), and analyzed for water content and droplet size distribution.

Visual measurements of the oil/emulsion and emulsion/water interface positions were taken each 5 minutes at the beginning of the experiments (up to 30 minutes), and then spacing the interval of the samplings once the evolution of the system slowed down. For the sedimentation experiments, initial

water contents (i.e., the volumetric water fraction in the system expressed in percent) of 10, 20, 30, 40, and 50% and temperatures of 25, 40, and 60 °C was investigated. For the sedimentation experiments, samples were taken each 20 minutes during 2 hours for the water content and drop size distribution determinations.

Digital pictures were taken of each sample using an Axiovert 40 MAT inverted optical microscope with a Charge Coupled Device camera. Axio Vison 4.7.2 software was used to determine the droplet size distribution. Several images were collected for each sample. In this work, around 800 droplets were analyzed for batch and decay experiments. The set of droplets diameters of each image was used for the $d_{4,3}$ diameter calculation using an algorithm implemented in Fortran language. The $d_{4,3}$ is the mean volumetric diameter that corresponds to the diameter of the sphere that has the same average volume of the particle system.

The organic phase viscosity at different temperatures was determined in a rheometer (Physical Rheolab MCR 301, from Anton Paar). The density of the organic phase as a function of temperature was assessed in an automatic DMA 4500M density meter (Anton Paar). The water content (WC) was determined by titration via the Karl Fischer (KF) method, using a mixture of dry methanol and chloroform (20% v/v). A Metrohm KF titrator (model 836 Titrando) equipped with a double platinum electrode was employed during the water content determinations.

RESULTS AND DISCUSSION

Effect of Temperature and Water Content on the Settling Velocity

The separation of model emulsions was followed for different water-cuts and temperatures. The water content and average droplet size profiles as a function of temperature are presented in Table 1. The results indicate that the increase in the average droplet size and the decrease of settling velocity are influenced by the WC , which is associated with the effect of droplet population. In this table, for each WC analyzed, the initial (0 min) and final (120 min) values of $d_{4,3}$ are significantly different, indicating a reduction in this property at the top with time, as a consequence of the sedimentation of bigger droplets from the top to the bottom of the vessel.

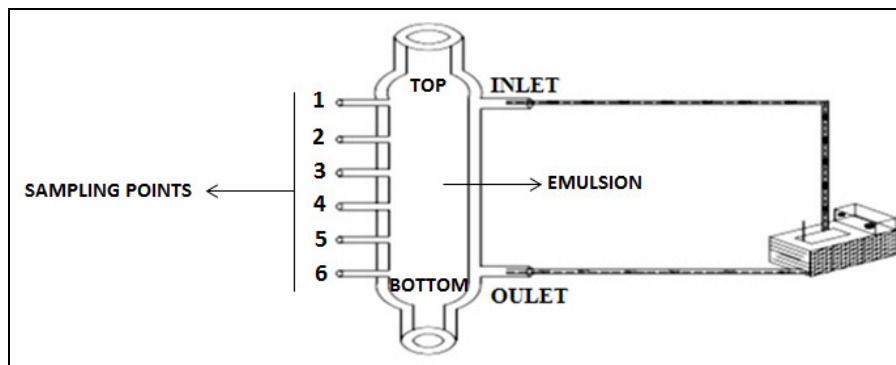


Figure 1: Experimental set-up used during sedimentation tests, including a separator vessel connected to the thermostatic bath. The emulsion samples were collected regularly at three sampling points (the second- depth of 4 cm, fourth- depth of 13 cm and sixth- depth of 22 cm) and analyzed for water content and droplet size distribution

Table 1: Experimental conditions obtained from the sedimentation experiments at depth of 4 cm.

WC (%)	Initial - $d_{4,3}(\mu\text{m})$ ^{*1}	Final - $d_{4,3}(\mu\text{m})$ ^{*2}	VE (mm/minute)
T = 25 °C ± 2 °C			
10	3.3	2.3	1.73
20	8.4	5.4	0.78
30	20.8	16.6	0.73
40	25.2	16.1	0.49
50	44.0	34.9	0.40
T = 40 °C ± 2 °C			
10	3.5	2.5	2.95
20	8.3	5.7	1.70
30	21.0	7.2	1.12
40	25.4	17.9	0.54
50	43.8	45.4	0.45
T = 60 °C ± 2 °C			
10	3.6	2.2	3.64
20	8.1	4.3	2.17
30	20.6	13.6	1.69
40	25.3	21.5	0.80
50	44.3	42.1	0.49

*1 t=0 min. *2 after 120 min.

According to Grimes (2012), the interface positions of the W/O emulsion can be depicted using an axial spatial coordinate, z , which is taken to be zero at the top of the separator and extends in a positive direction to the bottom of the separator. In this case, the direction of the gravitational force is along the positive z -direction. Figure 2 shows a typical curve for the displacement of the oil/emulsion interface with time. The zone settling velocity is defined as the gradient of the linear (or linearized) part of this curve.

After placing the sludge batch in the vessel, the following behavior was observed: afterwards placing the emulsion in the vessel, an interface is formed,

separating the clear oil not containing suspended solids in the upper part and settling emulsion in the lower part. In the region below the interface, all emulsion particles settle at the same rate, so that the interface is also displaced at the same rate. Simultaneously at the bottom of the vessel, emulsion with a higher concentration accumulates. With time, an ever-larger fraction of the emulsion particles become part of the concentrated emulsion. Finally, the emulsion-oil interface approaches to the region of concentrated emulsion and its rate of displacement starts to decrease gradually. The use of different concentration allows the experimental determination of the relationship between the emulsion concentration and the zone settling velocity. Figure 3 depicts the oil/emulsion interface evolution in function of temperature and water content of the emulsion. Taking into account the error bars, one may conclude that these experiments exhibit a good reproducibility.

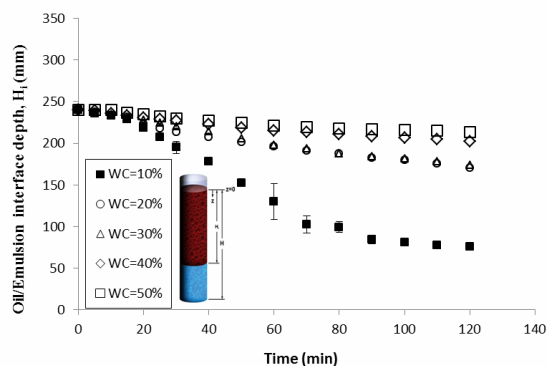


Figure 2: Depths of the oil/emulsion interfaces of emulsions with different WC at an experimental temperature of 25 °C (±2 °C).

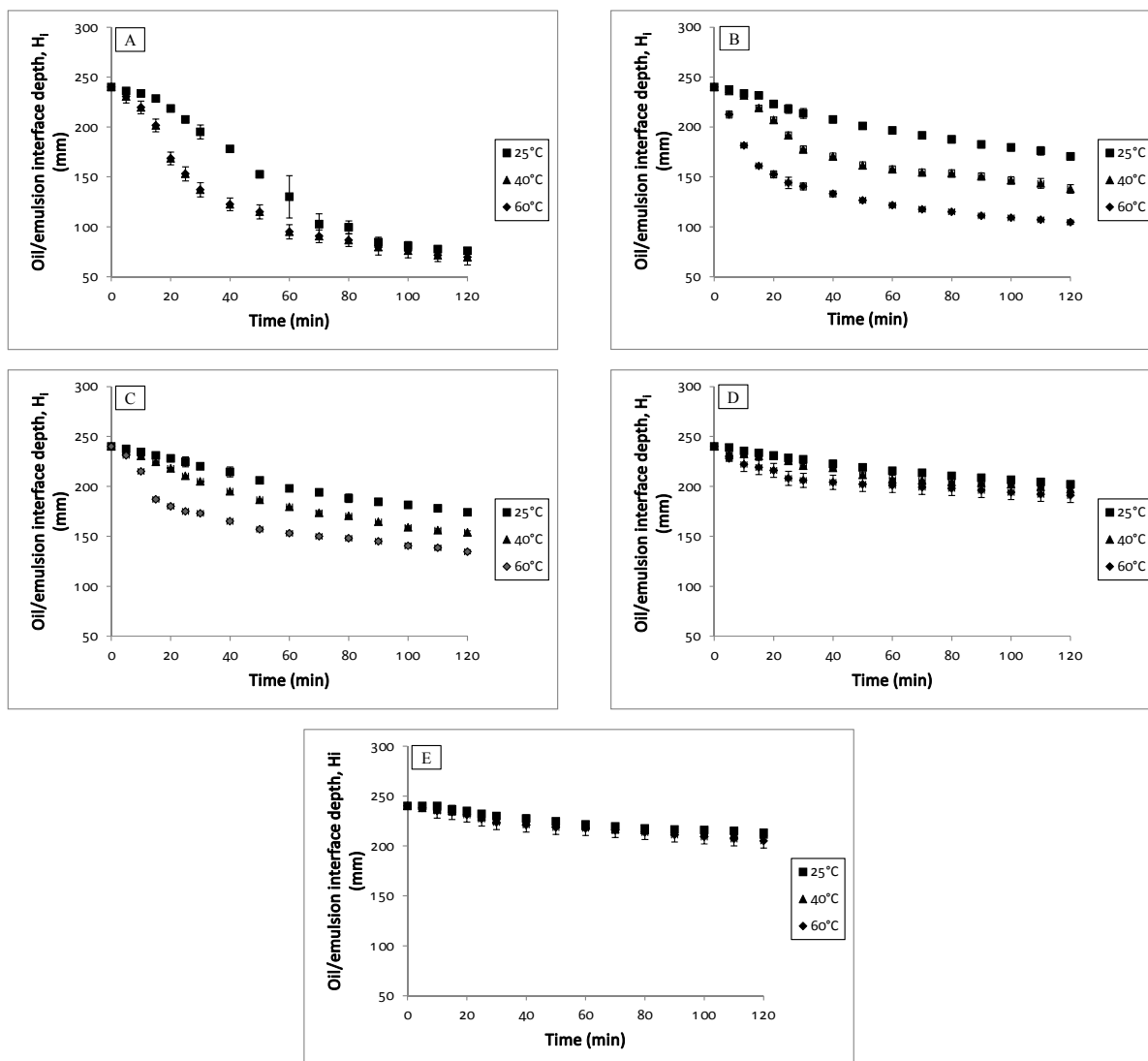


Figure 3: Depths of the oil/emulsion interfaces of emulsions with different WC at different experimental temperature. A) $WC=10\%$, B) $WC=20\%$, C) $WC=30\%$, D) $WC=40\%$ and E) 50% .

The heat treatment may accelerate the separation of water-oil emulsions due to the decrease of continuous phase viscosity in according with Eqs. (1) and (2). In this way temperature has an important role in the mechanisms of sedimentation and coalescence between droplets. From Figure 3, it can be observed that as the temperature was increased, there was a significant variation in the behavior of the system, especially for water contents below 30%. In contrast for WC of 40% and 50% very low rates of sedimentation and coalescence between the droplets was observed. Figure 3 also shows that for water contents above 30% the emulsion presents a high stability, even at higher temperatures.

Correlation for the Effect of Water Content on the Settling Velocity

The water content is one of the most important parameters for the stability of petroleum emulsions. To include the effect of phase concentrations on the settling velocities of complex mixtures, Richardson and Zaki (1954) proposed an empirical correlation Eq. (3). Figure 4 reports the experimental values of the settling velocities as a function of the water content WC and temperature. A well-defined decrease in the settling can be observed with the increase of WC . Moreover, settling velocities increased with the temperature enhancement.

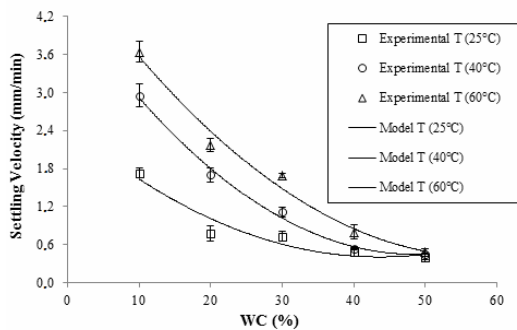


Figure 4: Experimental settling velocities as a function of water content and temperature.

Following the format of Equation (4), the results presented in Figure 4 can be fitted according to the Equation (5).

$$V_E = k(1 - 0.01 WC)^n \quad (5)$$

In Equation (5) V_E is the experimental sedimentation velocity (calculated from the gradient of the linear (or linearized) part of this curve) and the water content (WC) is expressed in percentage by volume of water in the mixture or the emulsion. The adjusted values of k and n for V_E are presented in Table 2 as a function of temperature. Due to the effects of surfactant adsorption, asphaltene/resin interaction, the system droplets can flocculate and form agglomerates. In this sense, the values of k adjusted from the experimental values are not expected to be those predicted by the original Richardson-Zaki correlation, which was obtained from results of sedimentation and fluidization of solid particles (Frising *et al.*, 2008). The values of n in Table 2 are always greater than 2, which suggests that a stronger hinderance

effect is produced by the highly concentrated population of water droplets as compared with the relatively smaller effect of increasing sizes (exponent 2 in Equations (1) and (2), for example).

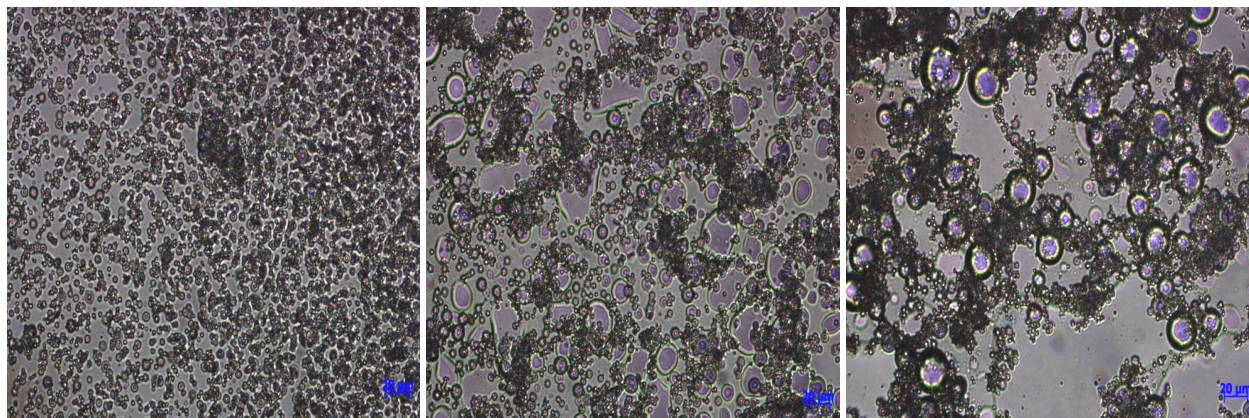
Table 2: Values of k and n obtained by the adjusted from the experimental values by Richardson-Zaki correlation for temperatures of 25, 40 and 60 °C.

Temperature (°C)	k	n
25	2.28	3.22
40	4.37	3.92
60	5.15	3.48

Figure 5 shows examples of microscopic images of emulsions used for the droplet size distribution (DSD) measurements. It was also noted that several droplets have a remarked deformation, resulting from effects of surfactant adsorption, interaction between asphaltenes/resins, flocculation or agglomeration of the droplets and the influence of stabilization mechanisms in emulsions.

The results confirm that the DSD is highly dependent on the WC in the emulsion, and the average water droplet size decreased from 44 μm at the WC of 50% to 3.3 μm at the WC of 10%. The average water droplet size decreased significantly when the WC of emulsion was less than 30%. Figure 6 shows the average droplet size as a function of water content at temperatures of 25, 40 and 60 °C. In this temperature range, only a slight influence on the average droplet sizes was observed, while WC exhibited an almost linear dependence. A good linear correlation ($R^2=0.945$) between droplet mean size and WC was achieved using Equation (6).

$$d_{4,3} = 0.986 WC - 9.104 \quad (6)$$



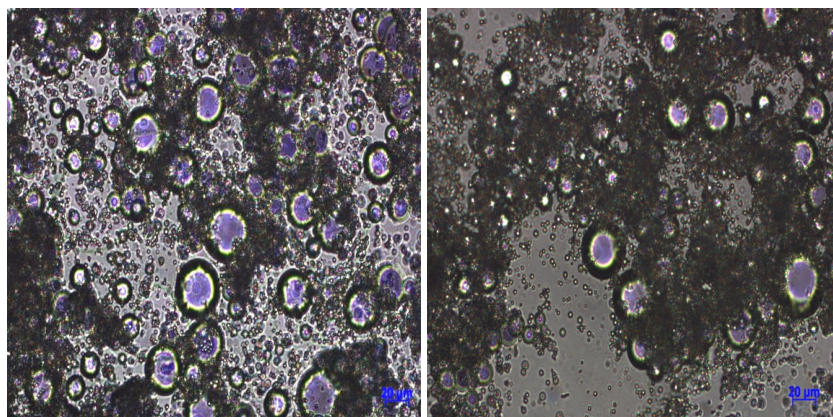


Figure 5: Optical microscopic pictures in the initial phase of the sedimentation tests for all the WC (10%, 20%, 30%, 40% and 50% respectively) for emulsion at a temperature of 25 °C (± 2 °C) with a magnification of 200-fold (x200).

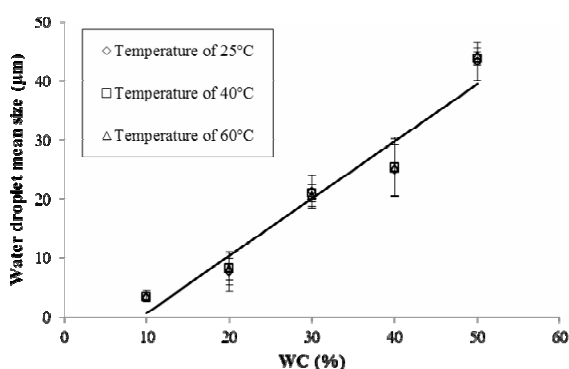


Figure 6: Mean water droplet size (diameter $d_{4,3}$ (µm)) versus water content (v/v) of THE emulsion at temperatures of 25, 40 and 60 °C.

Emulsion Settling Profiles

For each overall water content and fixed temperature, experimental average values of water content within three different regions of the gravity settler produces approximate profiles of WC as a function of time (Figures 7 and 9). According to the results presented above, the water content plays an important role in the sedimentation results. As predicted by the Richardson-Zaki correlation, higher settling velocities are expected at low WC values. In order to verify how the WC evolves along the sedimentation time and space, emulsion settling profiles were plotted as 3D graphs, considering time and position in the vessel. The analyses were performed for two cases where the settling rates are especially significant: emulsions with an initial water content of 10 and 20%. Figure 7 shows the settling profiles of W/O emulsions with an initial WC of 10% at different

temperatures. According to these profiles, water droplets accumulate at the bottom of the vessel. At low temperature (Figure 7A), the sedimentation process is clearly slow, and the water droplets have time to accumulate in the middle of the vessel. At this position, the coalescence of the droplets is likely to occur (this is clear in Figure 8A). Conversely, at higher temperatures (Figures 7B and 7C), the accumulation of water at the bottom occurs quickly; in such a way that there is no significant water accumulation in the middle of the vessel and no coalescence (see Figures 8B and 8C). It seems that at higher temperatures, the droplets may settle faster from the top to the bottom with negligible coalescence effects in the middle of the vessel. As a consequence, emulsion WC profiles at the top and middle of the vessel should be similar.

Figure 8 shows the average droplet size profiles along the sedimentation runs for each temperature. As discussed before, sedimentation results at 25 °C are clearly different in the higher temperature cases. At low temperature (Figure 8A) the water droplets may settle and coalesce, yielding larger droplet sizes in the middle of the vessel. In opposition, the average droplet size in the middle of the vessel remains relatively constant. Note that, even though the droplet sizes involved in these tests are quite small, the sedimentation occurs with time, and water can be accumulated quickly at the bottom of the vessel, as shown previously in Figure 7.

Figures 9 and 10 show the settling and droplet size distribution profiles of the emulsions with initial water content of 20%. As expected, the water sedimentation is a slow process at low temperatures (Figure 9A), and the water content at the top of the vessel remains essentially unchanged with time (up to 80 min).

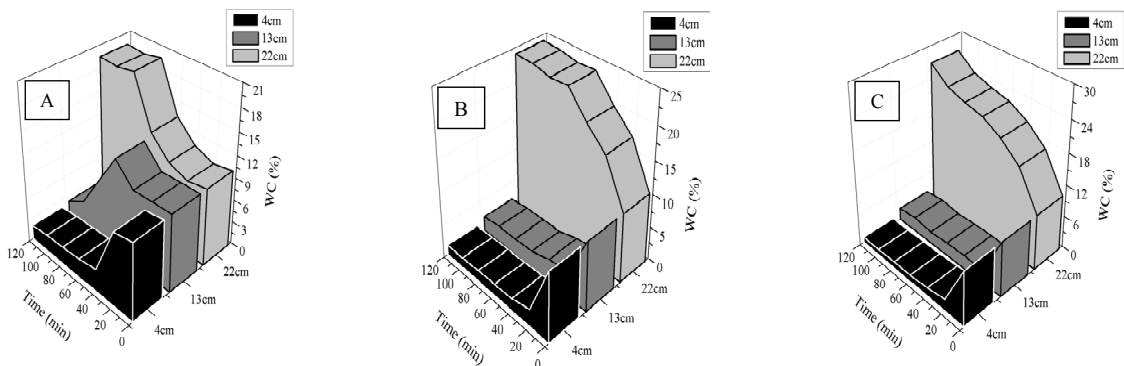


Figure 7: Emulsion sedimentation profiles of water content with time and depth in the separator vessel, for a water content of 10% at the temperatures of 25 °C (A), 40 °C (B) and 60 °C (C).

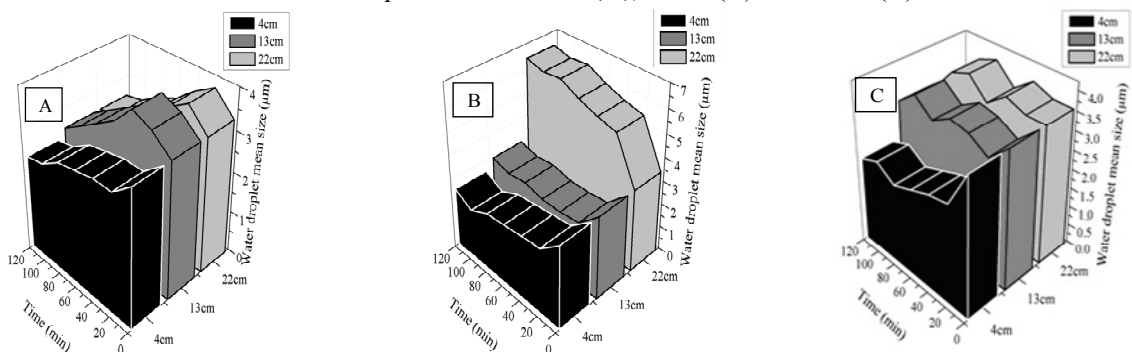


Figure 8: Emulsion sedimentation profiles of water droplet mean size with time and depth in the separator vessel, for a water content of 10% at the temperatures of 25 °C (A), 40 °C (B) and 60 °C (C).

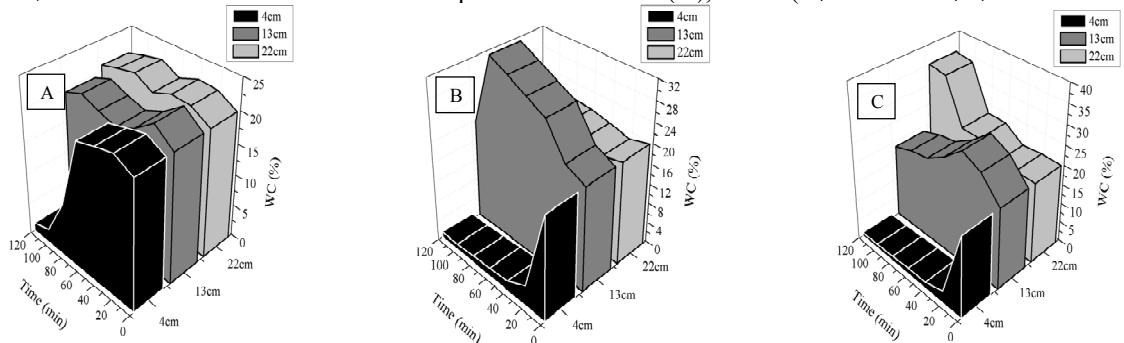


Figure 9: Emulsion sedimentation profiles of water content with time and depth in the separator vessel, for a water content of 20% at the temperatures of 25 °C (A), 40 °C (B) and 60 °C (C).

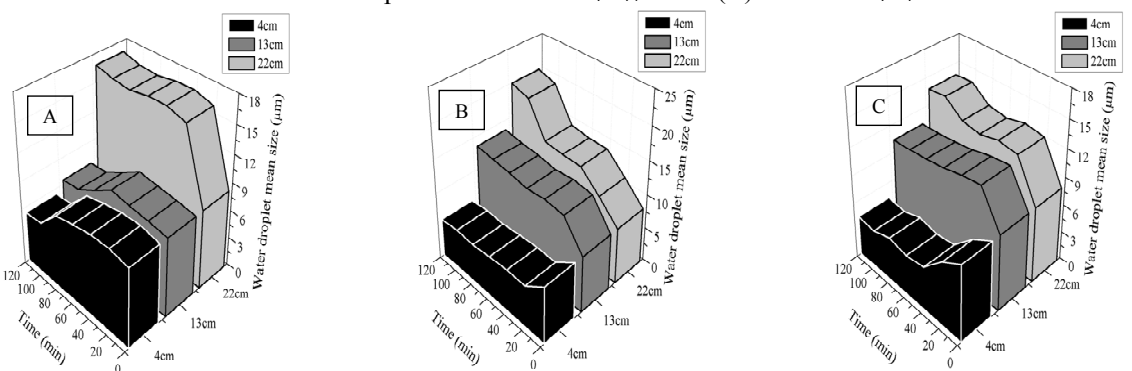


Figure 10: Emulsion sedimentation profiles of water droplet mean size with time and depth in the separator vessel, for a water content of 20% at the temperatures of 25 °C (A), 40 °C (B) and 60 °C (C).

Conversely, raising the temperature to 40 or 60 °C, the water droplets settle quickly and then the top of the vessel becomes dehydrated (Figures 9B and 9C). Also, from these figures at higher temperatures, one may note that the water accumulates in the middle of the vessel, indicating that coalescence of droplets plays a role, and the droplets may then settle and accumulate at the bottom.

Note from Figure 10A that the average droplet sizes in the top and middle of the vessel remain constant during the first 80 min for the run at 25 °C. Additionally, a significant increase of the droplet sizes occurs when the water droplets come from the middle to the bottom of the vessel, revealing that the water droplets settle and coalesce in the bottom at controlled rate, in such a way that the droplet sizes at the bottom of the vessel remain high with time. On the other hand, for those experiments carried out at 40 and 60 °C, distinct droplet populations can be observed from the top to the bottom of the vessel, indicating that the coalescence of the droplets is likely to occur in the middle and in the bottom of the vessel.

According to the previous discussion and comparing the emulsion settling profiles of emulsions with $WC=10\%$ and $WC=20\%$ (Figures 7 and 9), one may note that the low water content case yielded faster emulsion resolution, allowing for the fast accumulation of water droplets in the bottom. These results agree with the Richardson-Zaki correlation, which takes into account the strong effect of the water content on the settling velocity.

As a final remark it should be emphasized that the approach adopted in this work was based on a simple experimental apparatus and relied on standard emulsion characterization techniques such as Karl Fischer titration analysis and optical microscopy. Additional investigation focused on non-dilute systems should be encouraged. In this case, the use of more specialized equipment able to deal with opaque mixtures is mandatory such as those based on the infrared transmission and backscattering spectroscopy (Xu *et al.*, 2013).

CONCLUSIONS

The settling velocity of water-oil emulsions was experimentally analyzed as a function of water content and droplet sizes. Water content from 10% to 50% and temperatures from 25 °C to 60 °C were evaluated. A Richardson-Zaki type correlation was used to calculate the settling velocities as a function of the water volume fraction. Droplet size distribu-

tions at different positions and times were used to study the phenomena of sedimentation and coalescence. The results showed that a stronger hinderance effect is produced by a higher concentration of particles, as compared with the relatively smaller effect of increasing droplet sizes. Additionally, the higher stability of the concentrated emulsions was in good agreement with the low settling velocities predicted by the Richardson-Zaki correlation, which was able to describe the experimental results obtained.

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NOMENCLATURE

V_{STOKES}	sedimentation velocity (m/s)
ρ_d	density of the dispersed phase (kg/m ³)
ρ_c	density of the continuous phase (kg/m ³)
g	gravitational constant (m/s ²)
d	particle diameter (m)
μ_d	dynamic viscosity of the dispersed phase (Pa.s)
μ_c	dynamic viscosity of the continuous phase (Pa.s)
ϕ	volume fraction of the dispersed phase (-)
WC	water content (%)
n	experimentally determined constant (-)
$d_{4,3}$	average droplet size by volume (µm)
DSD	drop size distribution (-)
V_E	experimental sedimentation velocity (mm/minute)
W/O	water-in-oil emulsion (-)

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