

13th European Conference on Mixing
London, 14-17 April 2009

Effect of dispersed phase viscosity on solid-stabilized emulsions

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Abstract. The time required to efficiently stabilize viscous oil droplets with finely powdered material during agitation has been investigated. The experimental work relied on silicone oils of varying viscosities (50 to 5000 cSt) dispersed in distilled water with a Rushton turbine ($D=6,5$ cm) under controlled conditions (Volume = 0,6 L, 0-17 kW/m³, and constant agitation time). The solid phase was iron powder in the size range 20-50 microns. Each experiment consisted in wetting the powder with water, dispersing the oil/water phases for a given time and conditions, and to record the amount of oil stabilized after stopping agitation. Emulsification in controlled conditions shows that the viscosity of the dispersed phase acted as a damping factor for particle anchoring at the o/w interface and plays an important role during the emulsification process, a role that has never been demonstrated. Furthermore, the emulsification results indicate the existence of a dispersed phase viscosity limit for a given agitation time beyond which emulsification becomes impossible. A relation between the emulsified oil volume, the phase viscosity ratio, mixing power density, and agitation time was also proposed for the studied systems so to predict emulsification feasibility and stability using highly viscous dispersed phase. The results from this investigation will support the design of processes for the generation of solid-stabilized emulsions involving extra-heavy oils.

Keywords. Pickering emulsions, emulsification, experimental, mixing

1. INTRODUCTION

Studies on emulsions stabilized solely by solid particles (Pickering emulsions) are increasingly reported in the literature for their scientific interest and clear potential for industrial applications, especially cosmetics and oil industries where potential applications are numerous. The preparation and properties of solid stabilized emulsions have been reviewed in details by Aveyard et al. [1]. Some general rules concerning solid stabilized emulsions have also been summarized by Arditty et al. [2]. They can be listed as follows: the solid particles used must partially wet both phases; the continuous phase of the preferred emulsion is the one in which the particles are preferentially dispersed, where the oil/water ratio plays an important role; the particle size must be considerably smaller than the emulsion droplet and the interactions between the particles must be weak (flocculation) to obtain efficient stabilization.

The particles wettability is the central property governing the creation and stabilization of such emulsions [1, 3]. As a general rule, an hydrophobic particle (contact angle $\theta > 90^\circ$) favors a water-in-oil emulsion while an hydrophilic particle (contact angle $\theta < 90^\circ$) generates an oil-in-water emulsion. However, this rule may be broken depending on the number of layers the solid particles will form at the oil-water interface. Based on energy and maximum capillary pressure considerations, Kaptay [4] showed that for an emulsion stabilized by a single layer of particles, the contact angle for o/w emulsions must be $15^\circ < \theta < 90^\circ$ and for w/o emulsions, the contact angle must be $90^\circ < \theta < 165^\circ$. For emulsions stabilized by a double layer of particles, o/w emulsions are stable for contact angle values of $15^\circ < \theta < 129.3^\circ$ and w/o emulsions are stable for contact angles values of $50.7^\circ < \theta < 165^\circ$. Furthermore, the interval of optimum contact angle, for both single and double particles layer appears to be between 70° and 86° for o/w emulsions and between 94° and 110° for w/o emulsions.

Previous experiments [2] showed that emulsions can be prepared in a vessel where the constituents are mixed by hand or with a mixer. It has been shown that the surface coverage of the particles increases as the mixing intensity increases [2]. A possible explanation is that the high energy of agitation may promote a more efficient particle anchoring at the o/w interface (considering that agitation intensity can modify the adsorption parameters). Arditty et al. [2] used different oil viscosities (ranging from 10 cP to 350 cP) to study solid stabilized emulsions, but found no apparent effect of o/w ratio on the generation of the emulsions. Their experiments were conducted with nano-sized particles only.

The energy of attachment of a particle to a liquid-liquid interface is related to the interfacial tension γ_{ow} and the particle contact angle θ at the interface [3]. The energy needed to remove a particle of radius b from this interface is estimated using:

$$E = \pi b^2 \gamma_{ow} (1 \pm \cos(\theta))^2 \quad (1)$$

where the minus sign is for removal into the water phase and the plus sign is for removal in the oil phase. The maximum stability of the particle at the oil-water interface is attained at 90° , the angle corresponding to the maximum energy value necessary to move the particle in which it is preferably wetted [5].

The contact angle of a particle is the key parameter governing solid stabilized emulsions. Many well documented methods already exist regarding direct measurement of a liquid contact angle to solid surface [6]. However, those methods are often found to be inadequate when dealing with porous solid particles. Capillary rise techniques have also been proposed [7] [8] [9] [10] [11] but always with some limitations such as the structure of the solids bed inside the capillary, the experimental requirements, the accuracy, the unknown solids structure inside the bed, its porosity, and many others.

Following along the line of Hey and Kingston [5] and pushing further their reasoning implies that when dealing with highly viscous oil, the viscous forces within the drop could create resistance to the particle penetration into the interface. Consequently, the particle would need more time to achieve its stability contact angle, thus indicating that the processing time would play an important role in creating solid stabilized o/w emulsion using highly viscous oils. In a process design perspective based of making use of solid stabilized emulsions, the resulting time effect is clearly an important parameter that has to be investigated.

In a context where extra-heavy oil has to be emulsified and stabilized with solid particles, the purpose of this work is to investigate the effect of the oil viscosity on the processing time required to stabilize oil droplets with powders of diameter in the 10-50 micron range.

2. MATERIALS AND METHOD

The experiments were conducted using a 600 ml baffled stirred vessel (8 cm in diameter) with a single off-centered shaft equipped with a Rushton turbine (6.5 cm in diameter). Emulsions were prepared using 83.3 wt% of distilled water, 12.5 wt% of oil and 4.2 wt% of iron powder. The powder was systematically added to the water phase first. Then, oil was slowly poured on the water surface. The oils used were Dow Corning 200R Silicon oil with viscosities of 50 cSt (density of 0.96 g/cm^3), 350 cSt (density of 0.97 g/cm^3), 1000 cSt (density of 0.97 g/cm^3) and 5000 cSt (density of 0.97 g/cm^3). Preliminary testing was done using Fisher Silicon oil of 50 cSt (density of 0.96 g/cm^3). Distilled water was used as the continuous phase. The distilled water conductivity was $1990 \text{ }\mu\text{S/cm}$ at 25°C (corresponding to 0.1 wt% of NaCl in distilled water) with a pH of 6.57. The powders used Atomet 95 hydrophillic iron powders provided by QMP (Montreal) with Fe content of +99.9%, D_{50} of $34 \text{ }\mu\text{m}$ and particle density of 2.25

g/cm^3 . The size distribution of the iron powder was determined using a Mastersizer S (Malvern Instruments, UK)

Iron powders were chosen for their contact angle value (hydrophilic) and density in order to facilitate the oil layer thickness measurements. The high density of the powder attached at the o/w interface increases the droplets weight, thus increasing the sedimentation of the emulsions. This phenomenon prevents creaming of droplets and makes the oil/water interface height measurements more accurate. Because of the low oil dispersed phase fraction, the overall mixing fluid density and viscosity are considered to be equal to those of the water. As a result, Reynolds numbers (Re) were computed for each of the mixing intensities and compared with the emulsified oil %. In this context, Re is also used as dimensionless agitation speed, since only N is varying with emulsified oil %. Also, it is assumed that the fabricated emulsions are all destroyed by shear forces in the vessel during mixing. Indeed, the energy required to remove a particle from the interface is of the order of $\sim 10^{13}$ J and the mixing energy shearing the oil droplets is $\sim 10^1$ J. If the particles are removed from the o/w interface, the emulsions will eventually be destroyed.

A rest period of 30 minutes was observed prior to the start of mixing, so as to ensure that oil had uniformly distributed itself at the water interface. The results of preliminary experiments clearly indicated the necessity of such a rest period in order for the very viscous oil to freely distribute at the interface, without trapping water and/or air. The 30 minute period was then imposed to all the experiments for uniformity purpose. Emulsions were made at different mixing intensities (0 to 17 kW/m^3) for different viscosities and different agitation time, and the emulsified oil volume fraction was measured as a function of mixing intensity for each of the mentioned oil viscosities. The mixing process consisted of mixing the system a given time at a given mixing intensity, followed by a rest period for dispersed oil to coalesce and emulsions to stabilize, and then mixing again at given time at higher mixing intensity and so on. Since the geometry of the vessel remains constant, the percentage of emulsified oil volume was measured by comparing oil height 3 minutes after the end of each mixing stage.

3. EMULSIFICATION RESULTS AND DISCUSSION

The effect of agitation time on emulsified oil fraction was first studied for different Re at constant o/w viscosity ratio (ratio of 48). This first study was done using Fisher silicon oil of 50 cSt. Figure 1 shows that for a given Re , a maximum volume of oil can be emulsified and that this maximum is reached for an agitation time of 10 seconds. For a given Re , the same oil fraction will be emulsified for an agitation time of 10 seconds than for an agitation time of 300 seconds. This indicates that dispersed oil droplets size remains constant after 10 seconds of agitation. For a constant powder concentration, more droplets can be created and stabilized. This can be seen in Figure 1, where emulsified oil volume % with agitation time appears linear for agitation times smaller than 10 seconds. Even though data are too limited to fully conclude a linear behaviour, a large volume of oil has been emulsified within that time frame, as compared to the rest of the timeframe/overall timeframe of the experiment.

The graph suggests a very narrow time period of less than 10 seconds where stabilization of solid stabilized emulsions can be studied. Following those results, an agitation time of 10 seconds was always used in the subsequent trials since it allows enough oil-solids contact time for droplets stabilization. Also, the same figure shows that the maximum emulsified oil volume increases as Re increases, suggesting a potential role of viscosity in the process. Indeed, since Re is inversely proportional to kinematic fluid viscosity, an increase in Re would imply a decrease in viscosity, and by the results shown in Figure 1, an increase in maximum emulsified oil volume for the studied system.

The effect of Re on emulsified oil fraction was studied for different o/w viscosity ratios using Dow Corning silicon oil of different viscosities. Results are shown in Figure 2. It can be

noted that, for a given agitation time and mixing conditions, emulsification results may slightly differ using different silicon oils. For example in Figure 1, emulsified oil volume percentage reached almost 80% for 10 seconds of agitation for Re around 8000 with Fisher silicon oil of 50 cSt (o/w viscosity ratio of 48). In Figure 2, however, 80% emulsification can be reached for 10 seconds of agitation using Dow Corning silicon oil of 50 cSt (o/w of 48) only if Re is superior to approximately 30,000. This results is not surprising, since oil type as been know as a parameter influencing solid stabilized emulsions [3].

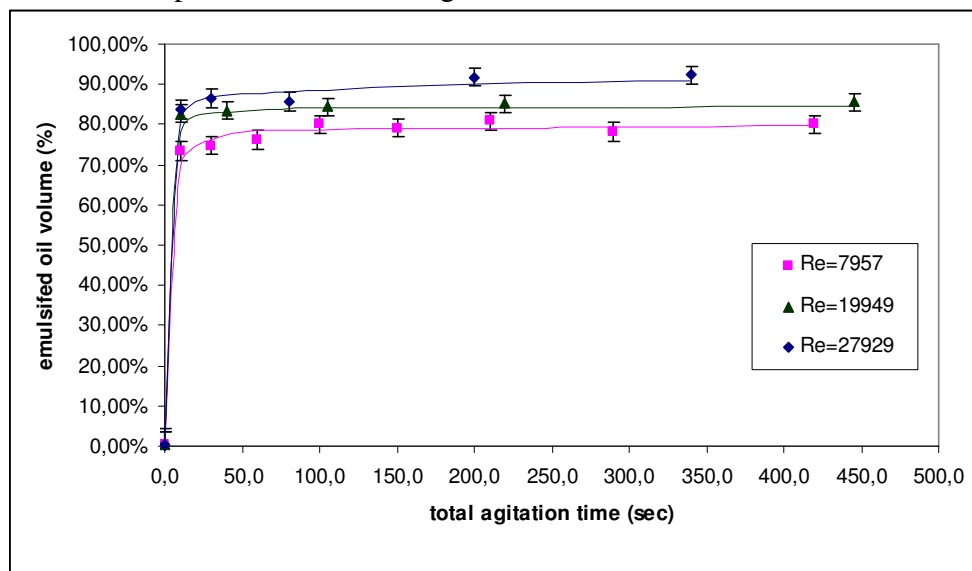


Figure 1 – Emulsified oil volume % as a function of agitation time for different Reynolds numbers at constant o/w viscosity ratio ($p = 48$) using Fisher silicon oil.

The existence of a minimum threshold value of Re was noted above which emulsification becomes possible. This can be seen in Figure 2, when the curves deviate from zero at a specific Re. In this case, this would suggest that a minimum Re needs to be reached in order to perform emulsification. As can be noted, Figure 2 shows that this threshold appears to be independent of o/w viscosity ratio. Since this minimum threshold value appears to be in the range of 5000, this would indicate that, since the vessel used is cylindrical, that turbulent flow needs to reach in order to create solid stabilized emulsions. This is not surprising, since the dispersed phase needs to be properly sheared and the dispersed particles need to gain enough momentum to properly adhere at the o/w interface.

In addition, Figure 2 shows that emulsified oil fraction increases with Re, as expected. As previously mentioned, this trend was also seen earlier in Figure 1. However, Figure 2 also shows that the rate (slope) decreases as the o/w viscosity ratio increases, indicating that the dispersed phase viscosity is affecting the emulsion formation process. Moreover, this effect is clearly seen for o/w viscosity ratio of 970 in Figure 3. Indeed, Figure 3 shows that, for different Re, under the studied system conditions, the emulsified oil volume percentage decreases as the oil/water viscosity ratio increases (in our case, for constant water viscosity, the emulsified oil volume percentage decreases as the oil viscosity increases). Furthermore, Figure 3 suggests a convergence towards a limiting o/w ratio (asymptotic value), one for which apparently no emulsions (i.e. 0% emulsified oil volume) would be possible. This asymptotic value can be seen as an upper threshold value, one for which below emulsification is possible. The viscosity would then act as a barrier preventing emulsification using solid particles as a stabilizing agent.

Following these observations, the o/w viscosity limit ratio was predicted by performing a simple linear regression (weighted least square method) on the emulsified oil volume fraction

as function of o/w viscosity ratio for different Re. The value of o/w viscosity limit ratio, corresponding to the o/w viscosity ratio beyond which no oil is emulsified, were computed and plotted as a function of Re. Results shown in Figure 4 indicate that, for the studied system and for an agitation time of 10 seconds, the o/w viscosity limit ratio tends towards an asymptotic value of ~1250-1400. Hence, it is believed that, for 10 seconds of mixing, it would not be possible to create an o/w emulsion, with the current o/w fraction, with an o/w viscosity ratio beyond 1400. For the studied system, this would correspond to a silicon oil viscosity of ~1440 cSt. This leads to believe that viscosity of the dispersed phase slows down the particle penetration process at the o/w interface, thus slowing down the emulsion stabilization process,

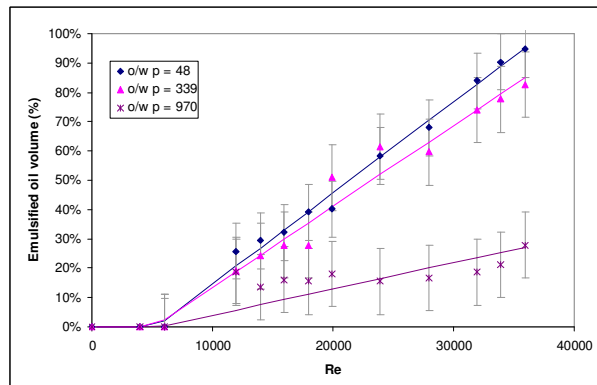


Figure 2 – Emulsified oil volume % as a function of Reynolds number for different o/w viscosity ratio p (agitation time of 10 seconds) using Dow Corning silicon oil.

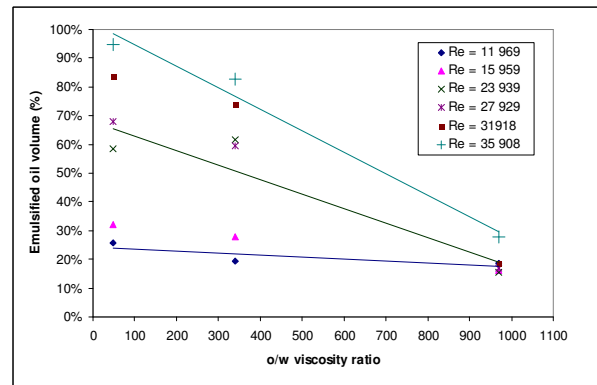


Figure 3 – Emulsified volume (%) of oil for o/w emulsions for different o/w viscosity ratios for different Reynolds numbers (agitation time of 10 seconds) using Dow Corning silicon oil.

up to a point where stabilization becomes impossible within the timeframe of agitation. To stabilize the emulsion, the particle needs to penetrate the o/w interface up to a point where it reaches a contact angle (stability contact angle) that will create stability through energy considerations. In that case, the viscosity of the disperse phase would act as a damping factor to particle penetration, up to a point where it would eventually become a barrier to particle penetration. It is worth noting that the emulsification with 5000 cSt oil was never successful during our experiments in the specified conditions.

The energy densities in the vessel were then calculated using the mixing power densities \mathcal{E} for a mixing time of 10 seconds. Figure 5 shows that the emulsified oil volume varies linearly with the square root of the energy density, the slope being a function of o/w viscosity ratio. The following relation can be derived:

$$V_{o/w} = c_E \sqrt{\mathcal{E} \Delta t} \quad (2)$$

where $V_{o/w}$ is the volume of emulsified oil, \mathcal{E} the mixing power density, Δt the agitation time and c_E an emulsification coefficient function of the o/w viscosity ratio p , defined as:

$$p = \frac{\mu_d}{\mu_c} \quad (3)$$

where μ_d is the viscosity of the dispersed phase (oil) and μ_c the continuous phase (water).

From (2), it can be seen that the emulsified oil volume depends on \sqrt{t} , in agreement with a capillary rise phenomenon. From the oil droplet perspective, when encountering a particle at the o/w interface, the oil will tend to engulf the solid particle when it comes in contact with it. The oil flow will then act as capillary rise, not only engulfing the particle, but also penetrating through the pores of the particle. For this flow behaviour, the viscous force will then cause a time delay for the complete attachment of the particle at the interface, thus affecting the

stability and formation of the emulsion. The capillary rise kinetics is described by the Washburn equation (Siebold, A., et al. [11]). A capillary rise h is linear with \sqrt{t} and inversely proportional to $\sqrt{\eta}$. This capillary rise effect would also indicate why previous work made by Arditty et al. [2] exhibited no effect of viscosity. Apart from the fact that Arditty et al. [2] did not make experiments for o/w viscosity ratio beyond a value of 350, the capillary effect is faster as the radius of the capillary is getting smaller. While Arditty et al. [2] experimented with nano-sized particles, our experiments dealt with micron-size particles. Therefore, the capillary effect is longer, since the viscosity of the fluid and that the capillary rise takes place on a larger surface due to particle size, making it more likely to observe experimentally the effect of viscosity. Overall, the combination of low viscosity and very small particle size explains why previous works lacked the proper resolution, phenomenon wise, to adequately observe the effect of viscosity, especially the dispersed phase viscosity, during solid-stabilization of emulsions.

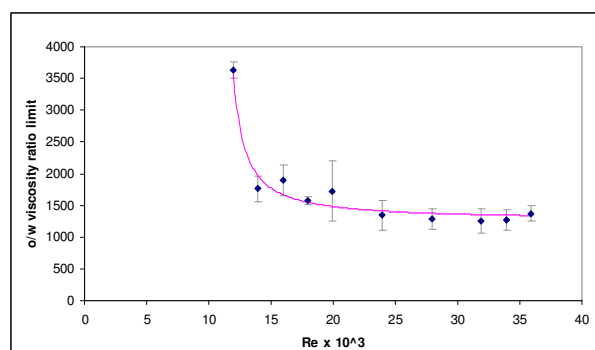


Figure 4 – Predicted emulsified oil ratio limit as a function of Reynolds number Re for 10 seconds of mixing.

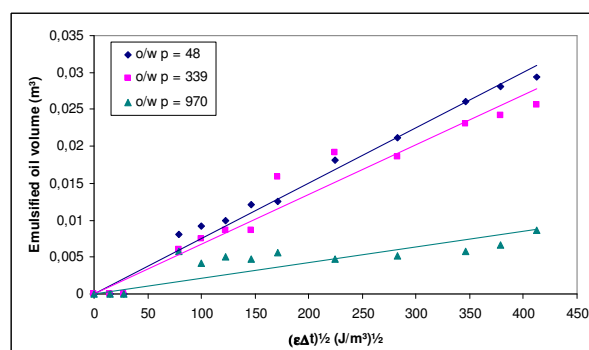


Figure 5 – Emulsified oil volume as a function of mixing power density with time $\epsilon\Delta t$ for corresponding o/w viscosity ratio p .

Figure 6 shows the values of c_E as a function of o/w viscosity ratio. It can be seen that the value of c_E decreases as the o/w viscosity ratio increases, again leading to o/w viscosity limit ratio. A linear prediction gives an o/w viscosity limit ratio of ~ 1250 - 1400 . This range is roughly the same as the one previously found, indicating that the linear behaviour holds, and leading to confirm this value as the o/w viscosity limit ratio for our system. The presence of this o/w limit confirms our hypothesis, namely that the dispersed phase viscosity acts as a barrier to emulsification. A possible explanation is that the limit is governed by equilibrium between the anchoring time needed for the particle to attach itself at the interface and the shear forces in the fluid that can remove the particle from the interface. Furthermore, in order to reach maximum stability contact angle or even a minimum stability contact angle, the particle needs to overcome the viscous forces within the oil droplet in order to achieve the associated penetration length. This phenomenon is even more present with the rather large iron particles used here (30 microns) and might explain why Arditty (Arditty et al. [2]) did not observe such an effect.

The dampening effect created by the viscous dispersed phase will affect the emulsion stability by creating a competition between two phenomena: limited coalescence and viscous penetration. If the coalescence rate is such that the particle does not have sufficient time to properly attach itself at the interface, the emulsion will not be created even though the proper wetting conditions are present. Subsequently, using a linear relation between c_E and P as shown in Figure 6, it is possible to write:

$$c_E = c_0 \left(\frac{1}{p} - \frac{1}{p_c} \right) \quad (4)$$

where c_0 is a number describing the system conditions and p_c the o/w viscosity limit ratio. Note that equation (4) is coherent with a capillary rise phenomena, since $h \propto 1/\sqrt{\eta}$ and in our case, $\eta = \mu_d$, and $c_E \propto 1/\sqrt{\mu_d}$. Since c_0 is proper to the system, it is believed that it will increase with the agitation time. Equation (2) then becomes:

$$V_{o/w} = c_0 \left(\frac{1}{p} - \frac{1}{p_c} \right) \sqrt{\varepsilon \Delta t} \quad (5)$$

Furthermore, knowing that $Re \propto \sqrt{\varepsilon}$, equation (5) becomes:

$$V_{o/w} = c_1 \left(\frac{1}{p} - \frac{1}{p_c} \right) Re \sqrt{\Delta t} \quad (6)$$

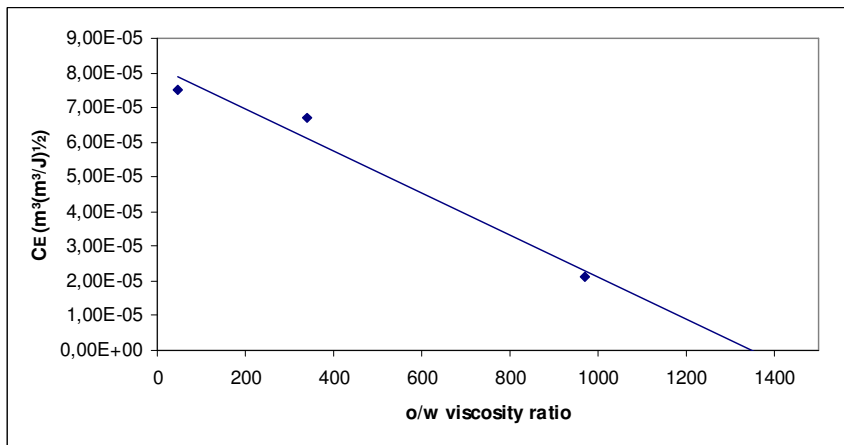


Figure 6 – Values of cE as a function of o/w viscosity ratio.

The results shown in Figure 2, Figure 3, and Figure 5 all corroborate the above relation. Therefore, using relations (5) and (6), for the studied system, it is possible to predict the emulsified oil volume for o/w emulsion for an emulsification time of 10 seconds. The identical results obtained with this second approach make us comfortable about the results previously obtained, regarding the existence of an o/w viscosity limit ratio for emulsification using solid particles. For the studied system and for the stated agitation time, this value of viscosity ratio is in the range 1250-1400.

The existence of o/w viscosity ratio limit may also be related the stability of solid stabilized emulsions. If solid stabilized emulsions have been formed, then the dispersed- or the continuous phase viscosity may act as a damping factor to the removal of particles located at the oil-water interface. In the limit situation were the o/w limit ratio has been reached, the particle would become very difficult to remove, making the solid stabilized emulsion very difficult to destroy. The o/w viscosity ratio may also contribute to the stability of solid stabilized emulsions, especially in the case of w/o emulsions typically encountered in heavy crude oil processing. However, this would require further investigations.

4. CONCLUDING REMARKS

The role of the dispersed phase viscosity in solid stabilized o/w emulsions was also studied. Experiments were conducted for a series of o/w viscosity ratio under different mixing intensities for a fixed agitation time. Results showed that the dispersed phase viscosity ratio

plays a role in the emulsion stabilization, as the volume of emulsified oil reduces as the dispersed phase viscosity increases under identical mixing conditions. The emulsification time is believed to play a critical role in the stabilization of highly viscous o/w emulsions, as the viscosity of the dispersed phase introduces a damping factor for particle anchoring at the o/w interface. This phenomenon is believed to become increasingly important with particles above the micron size such as the ones used in the present study and has never been reported in the literature, where published studies use much smaller particles in the nm range. Furthermore, for a given agitation time, it would appear that a o/w viscosity upper limit ratio exists, suggesting the presence of a viscosity barrier for solid stabilized emulsification at constant mixing intensities. The design of applications related to solid-stabilized emulsions will probably have to integrate the time parameter for solid particles anchoring at a o/w interface when very viscous oils are present such as those found in the industrial world. The agitation time would then become critical in application dealing with emulsification or demulsification in fields such as the oil industry.

Finally, experiments showed that a relation exists between emulsified oil volume, o/w viscosity ratio, power density (or Reynolds number) and agitation time. The results presented above also suggest the presence of a capillary action between the dispersed phase (oil) and the particle at the interface. Further experiments will be needed to fully validate the observations presented, as for the time influence of on the emulsification coefficient c_E is not known.

5. ACKNOWLEDGEMENT

The financial contribution of Total SA is gratefully acknowledged.

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