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Insight into the Emulsification Process Effect on Particles Distribution in Pickering Emulsions: A Series of Rheological and Gravimetric Tests

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This work aims to develop a method to quantify the particles distribution in Pickering emulsions. Particle stabilized oil-in-water emulsions of different formulations were produced with different emulsification processes. These emulsions were then centrifugated to separate the oily from the aqueous phase. Successive rheological and gravimetric tests on the same aqueous phases provide information about the silica fraction adsorbed at the emulsion's interfaces and the particle interfacial concentration. The emulsification process changes the average droplet size of the emulsion, and results also show that the silica fraction in the dispersed phase and the silica interfacial concentration are modified. Moreover, the silica behaviour may be dictated by the nature of the stirrer, the time and the shear speed of the emulsification process.

1. Introduction

Particle stabilized emulsions, otherwise known as Pickering emulsions, are claimed to be very stable against coalescence. As a consequence, this behaviour has not only drawn the scientists' attention but has also promoted the development of new products (Tang et al., 2015; Foo et al., 2017). Pickering emulsions thus appear to be an interesting alternative in comparison to the classic surfactant stabilized emulsions (Monazzami et al. 2016).

The properties and the stabilization of these emulsions are affected by the repartition of the particles inside the system. The particles can be adsorbed at the oil/water droplet interface or be located mainly inside the dispersed phase (Ganley and van Duijneveldt, 2017). In the last case, a gel of particles is generally encountered (Velandia et al., 2021). Intermediate situations are also obtained depending on the water/oil/particles contact angle.

It becomes then pertinent to use techniques to determine the repartition of the particles in these systems. Different microscopic techniques can be applied such as confocal microscopy (Dai et al., 2008), cryoTEM (Bao Y. et al., 2019), AFM (Tatry et al., 2020), Raman (Wei et al., 2019). But these techniques lead to qualitative data rather than quantitative ones.

In this paper, we develop and describe a method to measure the amount of particles in contact with the droplets as well as the particle content in the continuous phase. The method is based on the separation of the dispersed phase from the continuous phase of the emulsion. The analysis of the resultant particles residue in the continuous phase is obtained first by measuring its viscosity and then by weighing after drying the suspension. A mass balance approach gives access to the particle content in contact with the droplets. Another aim of the paper is to study the impact of the emulsification process on the repartition of the particles inside oil-in-water emulsions.

2. Results and discussion

2.1 Emulsions preparation and average droplet size characterization

Three batch emulsification processes, involving three different stirrers, were mainly studied in order to monitor the process effect on particle distribution within the emulsions. The dispersion systems included ultrasonic homogenizer (UL), rotor-stator homogenizer (UT), and Rushton turbine blender (RT). The studied emulsions were prepared for two different fractions of paraffin oil (20% V/V and 50% V/V) and two different fractions of silica in the aqueous suspension (1 wt.% and 4 wt.%, relatively to water phase). The main process and formulation parameters are synthesized in Figure 1.

The silica aqueous suspensions, in which the paraffin oil is dispersed, contained partially hydrophobic silica particles dispersed into deionized water. The paraffin oil was provided by Fisher Scientific. The silica particles, HDK H30, were supplied by Wacker Chemie AG. Based on the data sheet of the supplier, it was an hydrophobized silica with 50% of the silanol groups grafted by organosilanes. However, our analysis pointed out a greater hydrophobic behavior of the silica with surfaces properties closed to that of other silica with 70% of hydrophobized silanol groups. The particle size was equal to 20 nm from TEM measurements but the DLS measurements indicated larger particle size when dispersed in water (diameter of around 600 nm).

The suspensions were prepared as follows: first, the required amount of silica powder was added to a predefined volume of deionized water, then the silica was dispersed by means of a magnetic stirrer for at least 48 h, and finally, the suspension was subject to an ultrasonic homogenization process for 20 min, at 20 kHz and 20 % of the maximum power. The ultrasonic probe corresponds to model 550 from Fisher Scientific. This treatment was applied before all three emulsification processes, namely ultrasonic homogenizer (UL), rotor-stator homogenizer (UT), and Rushton turbine blender (RT).

Finally, the emulsification was produced by mixing the oily and aqueous phases in a batch mode. The stirring time was fixed to 20 min for UL and RT, while a duration of 10 min was applied with the rotor-stator homogenizer UT. The volume of the prepared emulsions was equal to 70 mL. For each emulsion type, 3 specimens were prepared, tested and analyzed in order to assess the reproducibility and reliability of the data. The following results were the average of the analysis of the 3 samples.

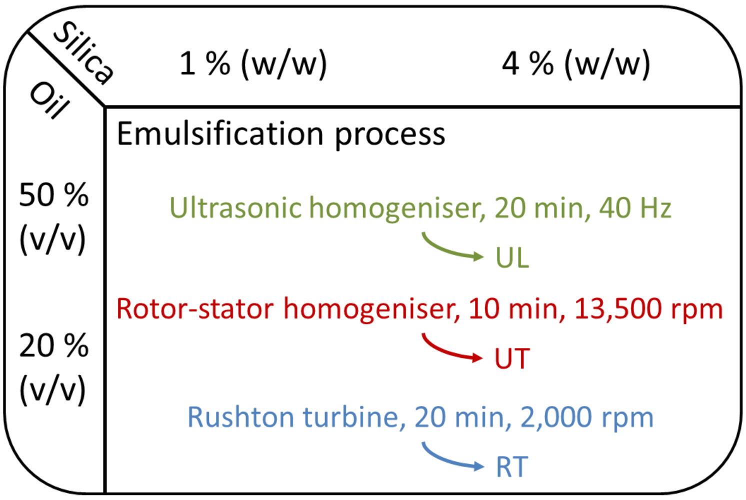

Figure 1: Composition, formulation and emulsification process parameters of the studied emulsions.

The average droplet size (d_{50}) of the emulsions was then measured using a static light scattering technique (SLS) and the Fraunhofer diffraction model to calculate the granulometric distribution of the droplets size, *via* the Malvern MasterSizer 2000 equipment and software. The emulsion type was determined from the behavior of a drop of emulsion in distilled water and in paraffin oil. For all prepared emulsions, a drop from the emulsion dispersed into water and remained as a drop into oil, indicating oil-in-water emulsions, regardless of the formulation and process used (Binks and Lumsdon, 2000).

2.2 Experimental materials balance

In order to obtain information about the silica particles distribution within the emulsion, and thus about the emulsification process, an experimental materials balance is proposed (Figure 2). It is based on a centrifugation method followed by rheological and gravimetric analysis. Centrifugation was applied at 3,000 rpm for 30 minutes to best separate the emulsions while avoiding coalescence. Special attention was given to the emulsions d_{50} before and after centrifugation, which remained unchanged for all the systems.

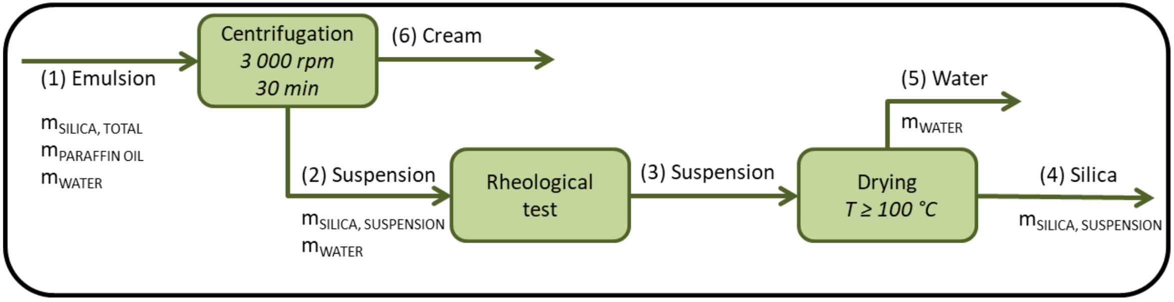

Figure 2: Block diagram describing the experimental material balance steps.

The continuous phase of the emulsion is recovered after centrifugation and its rheological behaviour is then characterised. As these rheological tests are non-destructive, it is also possible to measure the silica particles concentration of the recovered phase *via* a gravimetric test and so to verify, in a direct way, the information obtained with the rheological characterisations. Indeed, the rheological behaviour of a suspension is related to its particle concentration (Quemada, 1977). Therefore, it is possible to build a standard curve relating the silica fraction suspended in water to the viscosity of the aqueous suspension (Figure 3).

The standard silica aqueous suspensions were prepared following the preparation process previously described in section 2.1 and their viscosity was measured using a strain-controlled rheometer with a parallel-plate geometry. The viscosity behaviour of the suspension may be modelled by means of Eq (1), where η is the silica suspension's viscosity, η_F is the distilled water's viscosity, φ is the silica fraction and φ_M^{Eff} is an adjustable parameter related to the maximum packing fraction of the droplets.

$$\eta = \eta_F \left(1 - \frac{\varphi}{\varphi_M^{Eff}}\right)^{-2} \tag{1}$$

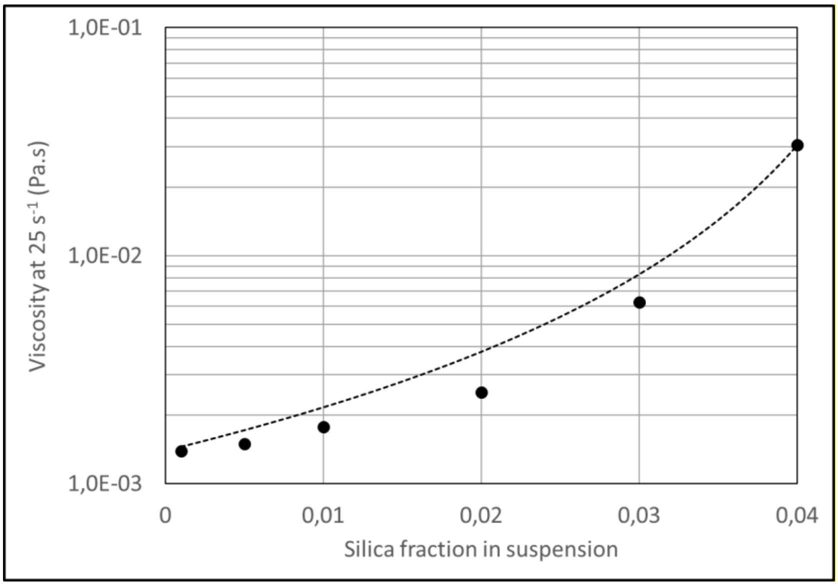

Figure 3: Viscosity of the silica aqueous suspension as a function of the silica concentration (points). Rheological modelling of a silica aqueous suspension as a function of its silica concentration (line).

2.3 Control of the particle distribution by the emulsification process

Table 1 shows the mass fraction of silica adsorbed by the emulsion droplets (Adsorbed silica) and the average diameter of the droplets (d_{50}) for emulsions prepared with 1 and 4 % of silica and with the three emulsification processes (Figure 1). The adsorbed silica fraction is calculated as follows

$$Adsorbed\ silica = \frac{m_{SILICA,TOTAL} - m_{SILICA,SUSPENSION}}{m_{SILICA,TOTAL}} \tag{2}$$

where $m_{SILICA,TOTAL}$ denotes the total mass of silica introduced in the emulsion and $m_{SILICA,SUSPENSION}$ refers to the mass of silica remaining in the aqueous continuous phase, *i.e.* non adsorbed on the droplets (Figure 2).

This fraction is over 60 % for all the processes and formulations, which means that more than half of the whole quantity of silica particles is adsorbed at the interfaces. This behaviour is the consequence of the relative hydrophobicity of these particles, with a high affinity for the oil phase.

Table 1: Fraction of silica adsorbed by the emulsion droplets (Adsorbed silica) and average diameter of the droplets (d_{50}). 20: emulsions with 20 % of paraffin oil; 50: 50 % of paraffin oil. RT: Rushton turbine, UT: Rotor-stator, UL: Ultrasonic homogeniser.

Property	Silica content	RT20	RT50	UT20	UT50	UL20	UL50
Adsorbed silica	4 %	0.70 ± 0.07	0.86 ± 0.08	0.66 ± 0.07	0.99 ± 0.05	0.70 ± 0.01	0.63 ± 0.01
	1 %	-	-	-	0.63 ± 0.04	0.77 ± 0.02	0.67 ± 0.01
d_{50} (µm)	4 %	126 ± 13.2	81 ± 1.9	56 ± 1.2	74 ± 0.2	5 ± 1.4	8 ± 0.8
	1 %	-	-	55 ±12.6	70 ± 8.6	7.2 ±1.2	18 ±5.8

The emulsions d_{50} appears to be controlled by the energy supplied to the system. The most energetic process, *i.e*. UL, produces the smaller droplet sizes, with an average diameter smaller than 10 µm, compared to RT and UT generating droplet sizes between 55 and 126 µm.

The smallest silica surface concentration (Γ) is also for the UL emulsion (Figure 4). Indeed, at a constant composition, the lower the droplet size, the higher the interfacial area. Consequently, the d_{50} of emulsions controls the surface concentration of the silica particles bound to the interfacial area, Γ, which is calculated as shown in Eq(3).

$$\Gamma = \frac{m_{SILICA,TOTAL} - m_{SILICA,SUSPENSION}}{A_{INTERFACIAL}} \tag{3}$$

where $A_{INTERFACIAL}$ represents the total interfacial area created by all the droplets. It is estimated from the dispersed phase fraction and the droplet diameter (d_{50}). The silica surface concentration Γ is around 0.1 g/m^2 for the most energetic process, *i.e.* UL, while it is over 0.4 g/m^2 for the less energetic processes.

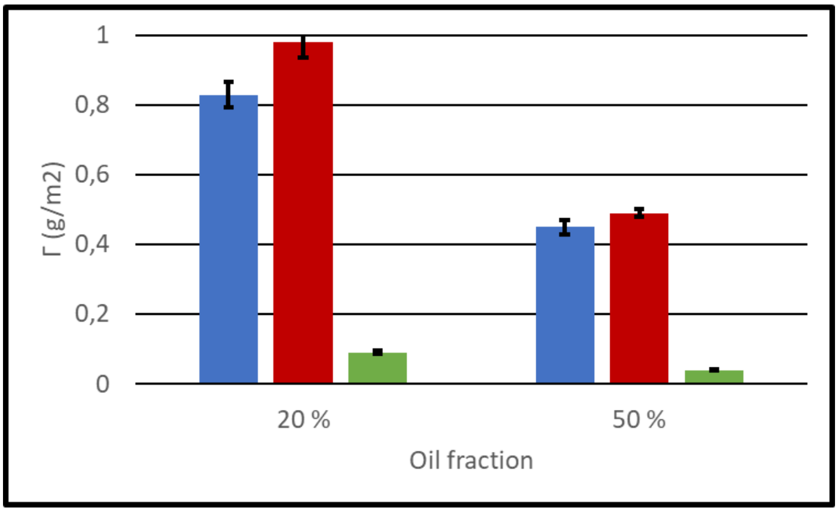

Figure 4: Silica surface concentration (Γ) for the emulsions containing 4 % of silica particles. Blue: RT process; red: UT process; green: UL process.

On the other hand, the energy supplied to the system with a same stirring device can also be modified *via* the process time. For example, the energy supplied by the rotor-stator homogeniser UT during 10 minutes of emulsification is around 1.3 x 10^{10} J/m^3, during 20 minutes it is around 2.5 x 10^{10} J/m^3 and during 30 minutes it is around 3.8 x 10^{10} J/m^3. Figure 5 represents the parallel evolution of Γ and d_{50} with the emulsification time. As shown in Figure 5, at a fixed silica content, the longest process time produces the smallest d_{50}, and so the highest interfacial area.

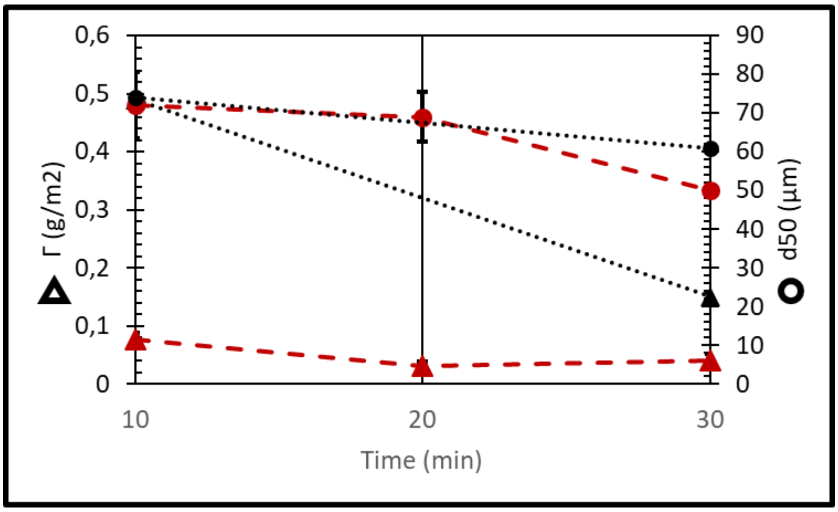

Figure 5: Values of Γ and d_{50} for emulsions containing 50 % of paraffin oil prepared with the rotor-stator homogeniser during different emulsification times. Dots: d_{50}; triangles: Γ; red-dashed lines: emulsions containing 1 % of silica; black-dotted line: emulsions containing 4 % of silica.

The Γ values for the rotor-stator homogeniser thus diminishes with the stirring time. The increase of the interfacial area (due to the reduction of the d_{50}) cannot fully explained this temporal reduction of Γ. The more plausible explanation comes from the fact that some silica can be ejected from the interfaces to the bulk of the emulsion. This aspect was already reported for Pickering emulsions during the emulsification processes under strong shearing (Ganley and van Duijneveldt, 2016). This desorption of the silica is observed for both silica contents.

For a mechanical mixer, such as a Rushton turbine RT, the energy supplied to the system can also be modified by changing the stirring speed, while keeping the process time constant. It was observed that increasing the stirring speed of the rotor-stator homogenizer from 13,500 rpm (1.3 x 10^{10} J/m^3) to 24,000 rpm (7.3 x 10^{10} J/m^3) modified the fraction of adsorbed silica from 0.66 to 0.77, respectively. Also, the d_{50} of the emulsion was modified from 56 µm to 40 µm. Therefore, the distribution of the silica particles at the interfaces changes too.

3. Conclusions

A method coupling rheological measurements and mass balance was developed to quantify the silica distribution in Pickering emulsions. In order to obtain information about the effect of the emulsification process, a Rushton turbine, a high-shear homogeniser and an ultrasonic homogeniser were used to disperse paraffin oil into a silica suspension, for 20 % V/V and 50 % V/V of oil and for 1 % wt. and 4 % wt. of silica. The nature of the stirrer determined the emulsions d_{50}. The ultrasonic probe produced emulsions of average diameter of 10 µm while the two other agitation systems led to droplets size of 56 – 126 µm. The method developed here was based on the separation of the emulsion phases, followed by a series of rheological and gravimetric tests. Significant information about the particles distribution in emulsion can be obtained thanks to this method. First, regardless of the stirrer nature, the systems adsorbed over 60 % of the total silica. However, the silica interfacial concentration was around 0.1 g/m^2 for the most energetic process, *i.e.* UL, while it was over 0.4 g/m^2 for the less energetic processes. Also, it was possible to modify silica distribution by changing the process time. For the high-shear homogeniser, the silica interfacial concentration and the d_{50} of the emulsion decreased by increasing the emulsification time. Finally, the stirrer speed may also control the silica distribution, so that the highest speed lead to an adsorbed silica fraction around 0.80. The method developed in this paper gives an insight of the effect of the emulsification process on the silica particles distribution in the emulsion. Furthermore, it could be inferred that the process controls the distribution of particles between the oil droplets and the bulk.

Future work will address the validation of the methodology with other methods such as confocal microscopy. The preliminary microscopy results compare well with the data presented here, thus improving and confirming the significance of our method.

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