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On the steady-state drop size distribution in stirred vessels. Part I: effect of dispersed phase viscosity

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Abstract

Previous studies on emulsification have used the maximum drop size (d_{max}) or Sauter mean diameter ($\bar{d}_{32}$) to investigate the effect of viscosity on the drop size distribution (DSD), however these parameters fall short for highly polydispersed emulsions. In this investigation (Part I) we studied the steady-state DSD of dilute emulsions using of silicon oils with viscosities varying across 6 orders of magnitude at different stirring speeds. Different emulsification regimes were identified; our modelling and analysis is centred on the intermediate viscosity range where interfacial cohesive stresses can be considered negligible and drop size increases with viscosity. The bimodal frequency distributions by volume were well described using two log-normal density functions. **In Part II¹ we expanded this study by using other continuous phases of different viscosity while keeping the Power number constant, thus examining the effects of viscosity ratio.**

Keywords: Emulsification, Viscosity, Droplet size distribution, Stirred vessel, Drop breakup

1. Introduction

The properties of emulsions are linked to their microstructure. One of the most important characteristics of its microstructure is their droplet size distribution (DSD) which has a direct impact on its rheological behaviour, sta-

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5 bility, and interfacial area. The DSD of emulsified products through mechan-
 6 ical mixing results from the breakup and coalescence of droplets. The latter
 7 becomes negligible for dilute emulsions and allows isolation of the break-up
 8 mechanism for its study.

9 Due to the complexity of turbulent fields a full theoretical description of
 10 the drop breakup process has not been possible. The breakup forces encoun-
 11 tered in a turbulent chaotic flow pattern will be different for all the drops;
 12 nevertheless it has been possible to determine the average size of the largest
 13 drops (of diameter d_{max}) that can withstand these disruptive forces. Hinze²
 14 determined through dimensional analysis that two dimensionless groups, the
 15 Weber number of the droplet (We_d) and the viscosity group (Vi_H), could
 16 describe the breakup process.

$$We_d = \frac{\tau d_{max}}{\sigma} \quad (1)$$

$$Vi_H = \frac{\mu_d}{\sqrt{\rho_d \sigma d_{max}}} \quad (2)$$

17 Where τ is the stress experienced by the drop of diameter d_{max} ; σ is the
 18 interfacial tension in-between the dispersed and continuous phase, and μ_d
 19 and ρ_d are the viscosity and density of the dispersed phase respectively. The
 20 breakup would occur when the We_d reached a critical value or critical Weber
 21 number (We_{crit}) **number** which is a function of Vi_H .

$$We_{crit} = C_1[1 - \psi(Vi_H)] \quad (3)$$

22 It has been theorized that for droplets larger than the Kolmogorov length

scale η (for isotropic homogeneous turbulence) the stress τ experienced by a drop is due to the kinetic energy fluctuations, this is known as the turbulent inertia regime. Kolmogorov's length scale and the stress due to the kinetic energy fluctuations are given by^{2,3}

$$\eta = \left(\frac{\mu_c}{\rho_c} \right)^{\frac{3}{4}} \epsilon^{-\frac{1}{4}} \quad (4)$$

$$\tau = C_2 \rho_c (\epsilon d_{max})^{\frac{2}{3}} \quad (5)$$

Where μ_c and ρ_c are the viscosity and density of the continuous phase. For inviscid dispersed phases ($Vi_H \rightarrow 0$) Equations 1, 3 and 5 yield $d_{max} = C_3 (\rho_c/\sigma)^{-3/5} \epsilon^{-2/5}$. Where ϵ is the energy dissipation rate per unit mass, which value depends on the location in the vessel. Authors like Zhou and Kresta⁴ have suggested that the the equilibrium drop size is determined by the maximum energy dissipation rate ϵ_{max} which is located in the impeller vicinity. There is much discrepancy on how to estimate ϵ_{max} as it depends on the method and assumptions used for its estimation⁵. One of the scaling parameters used in literature is the $\epsilon_{max}/\bar{\epsilon}$ ratio, where $\bar{\epsilon}$ is the mean dissipation rate and can be obtained from power draw P measurements

$$\bar{\epsilon} = \frac{P}{\rho_c V} \quad (6)$$

Where V is the volume of the vessel. For fully developed turbulence in a stirred vessel with a stirrer diameter D rotating at a speed N the dimensionless Power number ($Po = P \rho_c^{-1} N^{-3} D^{-5}$) becomes constant. Rushton et al.⁶ determined that $\bar{\epsilon} = C_4 N^3 D^2$. Combining Equations 1, 3 and 5 Shinnar and

41 Church⁷ concluded that for inviscid, diluted droplets larger than η

$$\frac{d_{max}}{D} = C_5 \left(\frac{\rho_c N^2 D^3}{\sigma} \right)^{-\frac{3}{5}} = C_5 \text{We}_S^{-\frac{3}{5}} \quad (7)$$

42 Note that the Weber number defined above is based on the stirrer and not
43 on the stress experienced by the droplet ($\text{We}_S = \rho_c N^2 D^3 \sigma^{-1}$).

44 Sprow⁸ proposed that the average drop sizes $\bar{d}_{pq}$ are proportional to the
45 maximum diameter.

$$\bar{d}_{pq} = C_6 d_{max} \quad (8)$$

46 Where $\bar{d}_{pq}$ is

$$\bar{d}_{pq} = \left[\frac{\int_0^\infty f_n(d_i) d_i^p dd_i}{\int_0^\infty f_n(d_i) d_i^q dd_i} \right]^{\frac{1}{p-q}} \quad (9)$$

47 For $p = 3$ and $q = 2$ the Sauter mean diameter $\bar{d}_{32}$ can be obtained. The
48 $\bar{d}_{32}$ is specially useful as it links the interfacial area to its volume through
49 $a_v = 6\phi/\bar{d}_{32}$. Where a_v is the interfacial area and ϕ the emulsion's volume
50 fraction.

51 Equation 8 made d_{max} and $\bar{d}_{32}$ interchangeable and has been widely used
52 but several values for C_6 have been reported in literature. Nishikawa et al.⁹
53 found $C_6 = 0.45$ and Calabrese et al.¹⁰ found $C_6 \approx 0.6$ for moderate viscous
54 oils and $C_6 \approx 0.5$ for highly viscous due to the broadening of the DSD as
55 μ_d increases. Li et al.¹¹ obtained bimodal DSD using a rotor-stator mixer
56 and found $C_6 = 0.16$. Liu and Li¹² emulsified four crude oils with different
57 viscosity using a batch rotor-stator mixer as they took samples at different
58 time intervals. They obtained bimodal DSD and found that C_6 was inde-

pendent of time but that C_6 decreased as μ_d increased and the distribution broadened. The aforementioned studies suggest that Equation 8 should be used with caution if a mechanistic model based on d_{max} is applied to viscid materials.

Other mechanistic and empirical models apart from Equation 7 have been suggested and many have been summarized by Singh et al.¹³.

The three paper study by Calabrese et. al.^{10,14,15} has been the most important to describe the effect of μ_d and σ for viscid dispersed phases. For their mechanistic model Calabrese et al.¹⁰ and Wang and Calabrese¹⁴ balanced the disrupting and the surface and viscous cohesive energies

$$\frac{\bar{d}_{32}}{D} = C_7 \text{We}_S^{-\frac{3}{5}} \left[1 + C_8 \text{Vi}_C \left(\frac{\bar{d}_{32}}{D} \right)^{\frac{1}{3}} \right]^{\frac{3}{5}} \quad (10)$$

Where their dimensionless viscosity group Vi_C is the ratio of the viscous energy of the dispersed phase to the surface energy ($\text{Vi}_C = \mu_d N D (\rho_c / \rho_d)^{1/2} \sigma^{-1}$). If $\text{Vi}_C \rightarrow 0$ Equation 10 reduces to Equation 7; on the other hand if Vi_C is very large, the interfacial forces become negligible and Equation 10 reduces to

$$\frac{\bar{d}_{32}}{D} = C_9 \left(\frac{\rho_c}{\rho_d} \right)^{\frac{3}{8}} \left(\frac{\mu_d}{\mu_c} \right)^{\frac{3}{4}} \text{Re}^{-\frac{3}{4}} \quad (11)$$

Where Re is the Reynolds number $\text{Re} = \rho_c N D^2 \mu_c^{-1}$. As noted by the authors as μ_c is contained within Re thus Equation 11 has no dependency on μ_c . Calabrese et al.¹⁰ performed a long series of experiments using five silicon oils (SiOils) as dispersed phase within the $9.60 \times 10^{-2} \text{ Pa s}$ to $1.05 \times 10^1 \text{ Pa s}$ viscosity range in distilled water in the absence of surfactant; σ was constant for all the SiOils and water $\sigma = 3.78 \times 10^{-2} \text{ N m}^{-1}$. Equation 10 was able

80 to describe the results obtained by Arai et al.¹⁶ and most of their own re-
 81 sults, except the ones obtained with two most viscous SiOils (4.43 Pa s and
 82 10.5 Pa s). For these two **silicon oils** **SiOils**, their results were well-correlated
 83 by¹⁰

$$\frac{\bar{d}_{32}}{D} = 2.1 \left(\frac{\mu_d}{\mu_c} \right)^{\frac{3}{8}} \text{Re}^{-\frac{3}{4}} \quad (12)$$

84 The droplet size dependency on μ_d for these SiOils was approximately half
 85 of the one in Equation 11 despite the large Vi_C . This equation suggests that
 86 there is a μ_c dependency, but the authors did not perform any experiments
 87 to prove such dependency.

88 In the second part of these studies, Wang and Calabrese¹⁴ changed σ
 89 systematically by using different methanol in water solutions for SiOils in the
 90 1.0×10^{-3} Pa s to 1.0 Pa s μ_d range and 1.0×10^{-3} N m⁻¹ to 4.5×10^{-2} N m⁻¹
 91 for the σ range. They found that as μ_d increases the influence of σ decreases.

92 The DSD may be represented by frequency or density distribution curves
 93 $f(d_i)$ or by their cumulative curves $F(d_i)$. For emulsions these are commonly
 94 by number ($f_n(d_i)$ and $F_n(d_i)$) or by volume ($f_v(d_i)$ and $F_v(d_i)$). Two emul-
 95 sions may have different DSDs despite having the same mean droplet size.
 96 There have been numerous attempts to describe the droplet size distribu-
 97 tions obtained in stirred vessels and in rotor-stators; some of the distribution
 98 functions used are summarized in Table 1.

99 Multimodality has been explicitly mentioned by several of authors listed
 100 in Table 1^{9,23,25,26,28,29} while others^{10,14} found that the DSD broadens as μ_d
 101 increases. The broadening has been attributed to a change in the droplet
 102 breakup mechanism from bursting towards stretching by several of the afore-
 103 mentioned authors.

Table 1: Types of Distributions used by Several Authors to fit the DSD.

	Function(s)
$F_n(d_i)$	Normal ^{9,10,17}
	Log-normal ^{10,18,19}
$f_n(d_i)$	Log-normal ^{13,20}
	Fréchet ^{11,21}
$F_v(d_i)$	Schwarz and Bezemer ⁸
	Normal ^{10,14,18,22}
	Multiple Normal ⁹
	Log-normal ^{10,23}
$f_v(d_i)$	Normal ^{24,25}
	Log-normal ²⁶
	Generalized Gamma ²⁷

Figure 1 shows the viscosity ratio of the dispersed and continuous phase used in some of the most relevant studies in the field in chronological order. Despite the numerous studies on emulsification using stirred vessels and rotor-stators, it becomes evident that the effect of viscosity on polydispersity has not been addressed.

When bimodality is present, regularly one or several of the four approaches listed below is used

- Fit to the cumulative distribution. As noted by Pacek et al.²³, cumulative distributions tend to smooth out detailed variations.
- Truncate the distribution that does not follow the trend^{25,30}
- Nishikawa et al.⁹ used two normal density functions to fit the distribution by number and three to describe the one by volume.
- Convert the distribution by volume to a distribution by number^{10,11,21} which diminishes the contribution of the large drops.

Figure 1: Viscosity ratio μ_d/μ_c in relevant experimental studies on emulsification^{1,8–11,13,14,16–22,24–29}. The extended line for the study of Calabrese et al.¹⁰ implies that different equations were used to fit each viscosity ratio range (see Eqs. 11 and 12).

Calabrese et al.¹⁰ found that a linear-normal distribution by number or volume could describe their DSD for low to moderate (1.0×10^{-3} Pa s to 5.0×10^{-1} Pa s) dispersed phases. But for their high-viscosity oils (5.0 Pa s to 10 Pa s) the largest 1% of the drops contained 70% of the emulsions volume, therefore their data could only be represented using a log-normal distribution by number.

Zhou and Kresta³¹ used four different types of impeller at different impeller speeds and off-bottom clearances and measured to study the DSD of very dilute emulsions. They classified their DSD into four categories and suggested different distribution functions for each case: (1) Long tail distribution represented by a normal distribution; (2) double peak distribution by

129 superimposing two normal distributions; (3) skew distribution which could be
 130 represented by a Poisson distribution, an exponential distribution, a Gamma
 131 distribution or two superimposed normal distributions; and (4) skew-normal
 132 distribution which can be approximated by a normal distribution.

133 Chatzi et al.²⁹ attributed the scarce amount of literature reporting bi-
 134 modality on the inaccuracy of the photographic methods while Laso et al.²⁸
 135 noted that in photographic methods the observers tend to neglect small
 136 droplets and focus on the larger ones. The DSD analysis before 1990 included
 137 techniques such as Coulter counter⁸, photograph image analysis^{10,14,16,17,24,25,28}
 138 and microscopy⁹.

139 In our previous study²⁷ we studied the effect of μ_d on the $f_v(d_i)$ for rotor-
 140 stator mixers using a multiple fit Generalized Gamma function. The DSD
 141 obtained in the aforementioned study showed two distinctive peaks which
 142 could be fit as the mode of the daughter drops Mo_d and the mode of the
 143 satellite drops Mo_s of each distribution was easily obtainable. The present
 144 study resulted more challenging as the $f_v(d_i)$ of the two types of daughter
 145 droplets were merged together in most of the DSD and the trends are more
 146 difficult to quantify.

147 In Part I of this study, the combined effects of μ_d and N of dilute emulsions
 148 (1 v.%) with an excess of surfactant—to hinder cohesive interfacial forces—on
 149 the droplets size and DSD are studied. Throughout this investigation we
 150 intend to broaden the understanding of the droplet breakup process by pro-
 151 viding a characterization of the $f_v(d_i)$ as bimodality arises for viscid dispersed
 152 phases.

153 In Part II¹, we investigated the effect of μ_c on the DSD for experiments

at constant Po ; according to the theory reviewed in this section, the drop size and DSD should be independent of μ_c if Po is constant, and if emulsification occurs in the turbulent inertia regime; however this is was not the case. Part II¹ offers an explanation by discussing the limitations of the Kolmogorov $-5/3$ energy spectrum.

The narrow bars in Figure 1 (for the current studies: Parts I and II¹) represent the experimental range while the thick bars represent the range on which modelling was undertaken.

2. Materials and equipment and methods

2.1. Materials

Nine 200 Fluid XX Silicone Oil (dimethyl siloxane, Dow Corning, Michigan, U.S.A.) where “XX” stands for their nominal dynamic viscosity in centistokes [cSt], which will be used to facilitate discussion. **Silicon Oils (SiOil)** **SiOils** are available over a wide range of viscosity, their shear viscosity is independent of shear rate and their densities and interfacial tensions are similar for most of them. Four additional SiOils with intermediate viscosities labelled as 2800 cSt, 4500 cSt, 7600 cSt and 50 000 cSt were obtained by mixing. The list of the SiOils and relevant properties are listed in Table 2.

The densities ρ_d were taken as given by the provider. The viscosities μ_d were measured using a DV2T Viscometer (Brookfield Vicometers, Essex, UK). The refractive index n_{ri} of SiOils were determined using a RFM390 Refractometer (Belling-ham and Stanley Ltd, Kent, UK).

Calabrese et al.¹⁰ raised some concerns about some high viscosity SiOils behaving as Boger fluids: shear viscosity independent of shear rate but with

Table 2: Density ρ_d , viscosity μ_d and refractive index n_{ri} for the SiOils used at 25 °C.

SiOil [cSt]	ρ_d [kg m ⁻³]	μ_d [Pa s]	n_{ri} [-]
0.65	750	4.88×10^{-4}	1.375
10	934	9.58×10^{-3}	1.399
50	960	4.91×10^{-2}	1.402
350	970	3.28×10^{-1}	1.403
1000	970	9.47×10^{-1}	1.404
*2800	970	2.75×10^0	1.404
*4500	970	4.34×10^0	1.404
*7600	970	7.36×10^0	1.404
10 000	970	1.05×10^1	1.404
12 500	970	1.33×10^1	1.404
30 000	970	2.93×10^1	1.404
[†] 50 000	970	4.88×10^1	1.404
100 000	970	1.06×10^2	1.404

*Obtained by mixing the 1000 and 10 000 cSt SiOils.

[†]Obtained by mixing the 30 000 and 100 000 cSt SiOils.

178 a an extensional viscosity dependent on extensional strain rate. The exten-
179 sional properties of the 1000, 10 000, 30 000 and 100 000 cSt SiOils were inves-
180 tigated using a HAAKE CaBer (Thermo Fischer Scientific, Massachusetts,
181 USA). All the SiOils behaved as Newtonian fluids under the experimental
182 strain rates. This study can be consulted in the Supplementary material
183 attached to this paper.

184 As continuous phase we used a 1.0 wt.% sodium laureth sulfate (SLES)
185 aqueous solution. The surfactant used was Texapon N701 (Cognis, Hert-
186 fordshire, UK) which contains approximately 70% concentration by weight
187 of SLES and approximately 30% water and impurities. SLES is an anionic
188 surfactant with molar mass and density equal to 420 g mol⁻¹ and 1030 kg m⁻³
189 respectively. El-Hamouz³² determined that its critical micelle concentration

190 is $8.4 \times 10^{-2} \text{ g L}^{-1}$, the concentration used in this investigation is approxi-
 191 mately 120 times higher.

192 The interfacial tension were measured using a K11 Mk4 Tensiometer
 193 (KRUSS, Hamburg, Germany) with a 9.545 mm platinum-iridium ring. Mea-
 194 suring the interfacial tension for SiOils above a 1000 cSt was not possible with
 195 this method because the tensiometer overestimates the maximum lamella
 196 height and breaks it. The σ between the 0.65 cSt, 10 cSt and 350 cSt SiOils
 197 and the continuous phases are shown in Table 3. The interfacial tension
 198 **increases** for the two most viscous SiOils is very similar, therefore the inter-
 199 facial tension for the SiOils with viscosities greater than 350 cSt was assumed
 200 constant, as done by Calabrese et al.¹⁰ and Hall et al.²⁶.

Table 3: Interfacial tensions of the SiOils and the continuous phases. The percentages represent one standard deviation.

SiOil [cSt]	σ [mN m ⁻¹]
0.65	$6.08 \pm 1.2\%$
10	$9.25 \pm 3.0\%$
350	$9.43 \pm 3.9\%$

201 2.2. Equipment

202 A 6-bladed pitched turbine inclined 45° with $D = 4.83 \times 10^{-2} \text{ m}$ was used
 203 as impeller. The turbine was coupled with a RW20 (IKA-WERKE, Staufen,
 204 Germany). The tank had a diameter T of $1.37 \times 10^{-1} \text{ m}$ ($D/T \approx 0.35$) and
 205 four baffles. The size of the baffles, clearance and the height of the liquid
 206 were $T/10$, $T/3$ and T respectively. The volume of the vessel V was 1.97 L.

207 The DSD was obtained using an off-line laser diffraction particle size
 208 analyser, the Mastersizer 3000 (Malvern Instruments, Malvern, UK), which
 209 allows to measure drops in the $10^{-3} \mu\text{m}$ to $3 \times 10^3 \mu\text{m}$ range.

210 2.3. Method

211 2.3.1. Emulsification

212 Once the continuous phase was poured into the vessel, the desired rota-
213 tional speed of the impeller was fixed using a CT6 Hand-Held Tachometer
214 (Compact Instruments, Lancashire, UK) and 20 mL of SiOil were injected
215 in the impeller vicinity using a syringe. The concentration of the SiOil was
216 1.0% by volume.

217 The emulsification time for all experiments was 24 h and steady-state was
218 verified by comparing the DSDs obtained after 24 h and 72 h for the 10 and
219 10 000 cSt SiOils for $N = 8.33 \text{ s}^{-1}$.

220 As seen in Table 2, μ_d was varied across several orders of magnitude. The
221 effect of μ_d and N was assessed by emulsifying the SiOils listed in Table 2
222 in the Water/SLES solution at five different N : 8.33 s^{-1} , 10.0 s^{-1} , 11.7 s^{-1} ,
223 13.3 s^{-1} and 15 s^{-1} .

224 The total number of emulsions prepared was 65, nevertheless the emul-
225 sions prepared with 7600 cSt and 10 000 cSt SiOil for the lowest stirring
226 speeds (8.33 s^{-1} and 10.0 s^{-1}) could not be analysed because the largest
227 droplets were beyond the measuring limit of the instrument and due to the
228 large diameter span of the DSD spreading across three orders of magnitude.

229 2.3.2. Droplet Size Analysis

230 Samples were taken at the impeller vicinity using a syringe with a modi-
231 fied larger hub not to cause further droplet break up. Samples were analysed
232 right after sampling to ensure that no changes in the DSD would occur,
233 despite that emulsion stability was verified for a period of 72 h after emulsi-
234 fication. At least three samples were analysed for each emulsion. Drops of

the sample were added to the Hydro EV dispersion units until reaching an obscuration rate of about 5-11%.

The analysis model chosen in the instrument's software was "General purpose" to ensure that bimodal effects were not suppressed. Three measurement cycles of 30 s were performed for the emulsions containing the 0.65 cSt -2760 cSt SiOils whereas measurement cycles of 300 s were needed for the most viscous SiOil. This was necessary due to the polydispersity of the droplets, increasing the analysis time allowed consistency in the measurements for the same sample. The n_{ri} for the dispersed phases are the ones listed in Table 2 and the absorption index used was 1×10^{-3} as recommended by Malvern for transparent droplets under the microscope.

3. Results and discussion

3.1. Phenomenology

In this section some of the results will be presented to show the effect of μ_d and N on the shape of the DSD. Two different behaviours were found for the 0.65 -10 000 cSt SiOils and the 12 500-100 000 cSt SiOils. In the former μ_d range, droplet size increased with μ_d and decreased with N ; for the latter viscosity range, the maximum droplet size was independent of μ_d and N .

The effect of μ_d for the SiOils in the 0.65 cSt -10 000 cSt viscosity range for $N = 11.7 \text{ s}^{-1}$ is shown in Figure 2a in a semi-log plot. As expected, the droplet size increases with μ_d and the DSD broadens. The 0.65 cSt, 10 cSt and 50 cSt SiOils yielded monomodal distributions while the rest were bimodal, presumably due to a change in the drop breakup mechanism that produces satellite droplets.

High speed image processing of drop breakup events have shown that drop breakup is seldom a binary process^{33–36}. Andersson and Andersson³⁴ observed that prior to breakup, droplets stretch and acquire a dumbbell shape with two spherical ends connected by a cylinder and that the liquid threats could be even longer than 20 times their original diameter. Eastwood et al.³³ and Nachtigall et al.³⁵ found that the drops stretch several times their original diameter and that this stretching increases with the viscosity of the dispersed phase. The appearance of a secondary type of drops was attributed to breakup of dumbbell-shaped drops: (1) large daughter drops correspond to the spherical ends of the dumbbell-shaped drops and (s) small daughter drops to the breakup of the cylinder in-between the ends.

Figure 2b shows the effect of N on the DSD for the 1000 cSt SiOil. As expected the droplet size decreases with N . This is true for the daughter and satellite droplets.

Figure 2: Examples of the resulting DSD of systems emulsified. (a) DSD for SiOils for in the 0.65 cSt -10 000 cSt viscosity range for $N = 11.7 \text{ s}^{-1}$. (b) DSD for the 1000 cSt SiOil for different N . The shadowed areas represent one standard deviation from the mean.

Figure 3 shows the DSD for the second type of behaviour encountered where the maximum drop size is independent of μ_d (see Fig. 3a) and N (see Fig. 3b).

Figure 3: Examples of the resulting DSD of systems emulsified. (a) DSD for SiOils for in the 10 000 -100 000 cSt viscosity range for $N = 11.7 \text{ s}^{-1}$. (b) DSD for the 100 000 cSt SiOil for different N . The shadowed areas represent one standard deviation from the mean.

Figure 4 shows the $\bar{d}_{32}$ as a function of μ_d with N as parameter. The vertical dashed delimits the two types of behaviours mentioned above. For the first type of behaviour (left of the dashed line), where d_{max} is μ_d and N dependent, $\bar{d}_{32}$ increases with viscosity and levels off before decreasing sharply despite d_{max} increasing. This behaviour is due to the appearance of satellite drops, which amount increase with μ_d as was previously shown in Figure 2a. Furthermore the curves for different N are parallel.

The $\bar{d}_{32}$ for the SiOils with viscosity equal and above 12 500 cSt were plotted at the right side of the dashed line in Figure 4; this zone is characterized by d_{max} being independent of μ_d and by a decrease in N dependency; all the curves seem to converge at the maximum μ_d .

Figure 4: Effect of μ_d on the $\bar{d}_{32}$ with N as parameters.

Equation 8 was tested for our emulsions using the 95th percentile as an approximation of d_{max} . Figure 5 shows the evolution of the $\bar{d}_{32}$ to d_{max} ratio. It can be seen this ratio was constant for our monomodal emulsion while decreasing with μ_d for our bimodal distribution. No clear trend was found for the most viscous SiOils; as explained above, these had a different behaviour. However, this plot reveals that assuming a constant $\bar{d}_{32}/d_{max}$ result in a tenfold-miscalculation in this region.

Figure 5: $\bar{d}_{32}$ to d_{95} ratio as a function of μ_d . The error bars represent one standard deviation from the mean.

Even though the experimental viscosity range used by Calabrese et al.¹⁰

is included in our study, we did not observe a low viscosity d_{32} -plateau for the viscosity range where, according to their mechanistic model, interfacial forces are the primarily force resisting drop breakup. As explained by Wang and Calabrese¹⁴, this is attributed to the lower interfacial tensions in our systems as the systems emulsified by Calabrese et al.¹⁰ were surfactant-free.

3.2. Drop size

The drop size analysis was performed using the mode of the daughter drops Mo_d , alternatively d_{max} could be used; but we considerer the former statistically more significant and is consistent with our previous work²⁷. In Section 3.3 the DSD will be standardized by Mo_d ($f_v(d_i/Mo_d)$) and it will become evident that $Mo_d \propto d_{max}$ and why this was used. The analysis in this Section was only performed for the SiOils thinner than the 12 500 cSt SiOils.

Figure 6 shows the mode of the daughter droplets Mo_d as a function of μ_d . This curve shows a steady increase of Mo_d with μ_d for each N compared to the $\bar{d}_{32}$ shown previously where a plateau and decrease were observed. The comparison in-between Figures 4 and 6 show that $\bar{d}_{32}$ is not the best measure of central tendency to elucidate the drop break-up mechanism when the DSD are multimodal.

However, it can be noticed that the data obtained by the thinnest SiOil (0.65 cSt) does not follow the same trend as the thicker SiOils. This is attributed to its different properties (see Table 2) and σ (see Table 3); furthermore Figure 2a shows that this oil produced a broader DSD than the other subsequent oils which also yielded monomodal distributions. Following Equation 7, the $Mo_d D^{-1} We_S^{3/5}$ against μ_d should collapse the data-

Figure 6: Effect of μ_d on the Mo_d with N as parameters.

320 points creating a master-curve. As shown in Figure 7, this standardization
 321 successfully collapses the data points for different N , furthermore the curve
 322 resembles the ones presented by Calabrese et al.¹⁰ and Wang and Calabrese¹⁴
 323 where a drop size-plateau (interfacial forces dominate) is followed by a drop
 324 size increase (as viscous forces become important). This Figure aids in de-
 325 limiting the boundary of our study to the 10 cSt - 10 000 cSt SiOils where
 326 viscous cohesive forces dominate.

Figure 7: Dimensionless standardized Mo_d as a function of μ_d .

327 A fit was performed for the emulsions with SiOils in the 10 cSt -10 000

328 cSt viscosity range with a fixed $Mo_d \propto N^{-1.2}$ dependency.

$$\frac{Mo_d}{N^{-\frac{6}{5}}} = A_1 \mu_d^{A_2} \quad (13)$$

329 The values of the fitting constants, their 95% Confidence Interval and p -value
330 are listed in Table 4.

Table 4: Fitting parameters for Equation 13.

Parameter	Coefficient	p -value
A_1	$4.64 \times 10^3 \pm 2.94\%$	5.1×10^{-59}
A_2	$0.365 \pm 3.29\%$	1.4×10^{-31}

331 The coefficient of determination R^2 and the mean absolute error MAE of
332 the fit were 0.986 and 5.39% respectively. Our dependency on μ_d disagrees
333 with most mechanistic models found in literature; the models proposed by
334 Arai et al.¹⁶ and Calabrese et al.¹⁰ state that $A_2 = 0.75$ and the model
335 proposed by Davies³⁷, $A_2 = 0.6$. For their most viscous oils, Calabrese
336 et al.¹⁰ could not fit their results using their mechanistic model and proposed
337 an empirical correlation with $A_2 = 3/8$ (Eq. 12), which is very similar to
338 the value found throughout our investigation. In our previous study on the
339 effect of dispersed phase viscosity in rotor-stators²⁷ we found $A_2 = 0.375$,
340 suggesting that A_2 is independent of the mechanical stirred apparatus used.

341 3.3. Droplet size distribution modelling

342 The DSD were normalized by Mo_d to show the changes in the shape of
343 the DSD. Figure 8a shows the effects of μ_d for constant N and Figure 8b
344 shows the effect of N on the DSD for the 1000 cSt **Silicon Oil SiOil**. **The**
345 **former** Figure 8a shows that the DSDs become broader and that the amount

346 of satellite drops increase with μ_d . The latter Figure 8b shows that for our
 347 experimental range, there is no important DSD-shape dependency on N .
 348 Therefore Equation 8 holds for different N but not for μ_c for a given SiOil.
 349 Both Figures show that $Mo_d \propto d_{max}$, the 95th percentile d_{95} of all the DSD
 350 was $d_{95} = 1.54Mo_d$ with a standard deviation of 6.54%.

Figure 8: Normalized DSD $f_v(d_i/Mo_d)$ (a) for different SiOils for $N = 13.3 \text{ s}^{-1}$ and (b) for the 1000 cSt SiOil for different N .

The DSDs were modelled by fitting two log-normal distributions functions
 $(p(d_i/Mo_d))$ to the Mo_d -standardized DSD by volume. The $p(d_i/Mo_d)$ were
 normalized so that the sum of the frequencies equals 100%. The equations
 of the log-normal distribution, its normalization and the mixing rule of the

two distributions are given by

$$p\left(\frac{d_i}{Mo_d}\right) = \frac{1}{s_z \sqrt{2\pi} \left(\frac{d_i}{Mo_d}\right)} \exp \left\{ -\frac{\left[\ln \left(\frac{d_i}{Mo_d} \right) - \bar{z} \right]^2}{2s_z^2} \right\} \quad (14)$$

$$f_v\left(\frac{d_i}{Mo_d}\right) = 100 \times \frac{p\left(\frac{d_i}{Mo_d}\right)}{\sum p\left(\frac{d_i}{Mo_d}\right)} \quad (15)$$

$$f_{v,T}\left(\frac{d_i}{Mo_d}\right) = (1 - \phi_s) f_{v,d}\left(\frac{d_i}{Mo_d}\right) + \phi_s f_{v,s}\left(\frac{d_i}{Mo_d}\right) \quad (16)$$

Where s_z is the standard deviation of $\log(d_i/Mo_d)$, $\bar{z}$ is the arithmetic mean of $\log(d_i/Mo_d)$, ϕ_s is the volume fraction of the satellite drops; and $f_{v,T}(d_i/Mo_d)$, $f_{v,d}(d_i/Mo_d)$ and $f_{v,s}(d_i/Mo_d)$ are the standardized frequency distribution by volume for the whole DSD, the daughter drops and the satellite drops respectively.

The expression for the mode Mo of a log-normal distribution function is $Mo = \exp(\bar{z} - s_z^2/2)$, therefore in the case of the Mo_d -standardized DSD we obtain $\bar{z} = s_z^2/2$ reducing the number of fitting parameters for $f_{v,d}(d_i/Mo_d)$.

To fit the Mo_d -standardized DSDs the following assumptions were made:

- The standard deviation of the daughter droplets $s_{z,d}$ is independent of μ_d and N as Mo_d/d_{max} is constant (see Fig. 8).
- The modes of both types of droplets are equidistant

$$\begin{aligned} \bar{z}_s &= \ln Mo_s + \frac{s_{z,s}^2}{2} \\ &= A_4 + \frac{s_{z,s}^2}{2} \end{aligned} \quad (17)$$

- The standard deviation of the satellite droplets is N -independent (see Fig. 8b), but has a power-law dependency on μ_d :

$$s_{z,s} = A_5 \mu_d^{A_6} \quad (18)$$

- As ϕ_s for the monomodal distributions is zero, increases with μ_d , the daughter droplets disappeared in short μ_d -interval and is N -independent; we used a cumulative Weibull distribution to describe the effect of μ_d on ϕ_s

$$\phi_s = 1 - \exp \left[- \left(\frac{\mu_d}{\beta} \right)^\alpha \right] \quad (19)$$

Where α and β are fitting parameters.

Under these considerations listed above, the DSD were fitted for $s_{z,d}$, A_4 , A_5 , A_6 , α and β using the least absolute error in-between the experimental and modelled DSDs. The values obtained for the fit are shown in Table 5. Some examples of the fits are shown in Figure 9.

Table 5: DSD fit parameters.

Parameter	Coefficient
$s_{z,d}$	0.40
A_4	-0.87
A_5	0.80
A_6	0.15
α	1.4
β	2.0

The value we obtained for $s_{z,d}$ is considerably larger than the ones of Chen and Middleman²⁴ and Wang and Calabrese¹⁴ who reported values of 0.23 and 0.24 respectively.

Figure 9: Random fitting examples to Mo_d -standardized DSD: (a) 350 cSt SiOil and $N = 8.33 \text{ s}^{-1}$; (b) 2760 cSt SiOil and $N = 11.7 \text{ s}^{-1}$; (c) 5370 cSt SiOil and $N = 10.0 \text{ s}^{-1}$ and; (d) 10000 cSt SiOil and $N = 13.3 \text{ s}^{-1}$.

Figure 10 shows the values of ϕ_s if it is allowed to fit “freely”, while the line represents Equation 19 with its corresponding fit parameters found in Table 5. This Figure shows that a cumulative Weibull distribution is adequate for describing the ϕ_s dependency on μ_d . Furthermore, it depicts why Equation 13 was not applicable for the thickest SiOils: the trend-line suggests that $\phi_d \approx 0$ for $\mu_d > 30 \text{ Pa.s}$.

It is interesting noticing that the two DSD are equidistant, in our previous

Figure 10: Volume fraction of satellite drops ϕ_s as a function of dispersed phase viscosity μ_d using water/SLES as continuous phase for five different stirring speeds.

study on the effect of viscosity in rotor-stators²⁷ we found the same Mo_d dependency on μ_d , but we found that the small droplets decreased with μ_d which was not the case for stirred vessels. The reason, a priori, is unknown.

The goodness of the fit can be assessed by comparing the $\bar{d}_{32}$ obtained with the fit with the experimental one. In the first subfigure a N -standardized $\bar{d}_{32}$ as a function of μ_d is shown; provided that Equation 8 is applicable for different N and that $d_{max} \propto N^{-6/5}$. It can be observed that our fit follows the trend of the experimental data. The second Figure uses direct comparison. The R^2 and MAE are 0.82 and 12.2% respectively.

4. Conclusions

A wide number of SiOils with μ_d ranging across 6-orders of magnitude were emulsified to study the changes in the steady-state drop break-up mechanism. Three different regimes were observed, namely (1) the one where interfacial forces dominate and which has been described by Hinze², Chen and Middleman²⁴, Calabrese et al.¹⁰ and Calabrese et al.¹⁵ and many others.

Figure 11: Goodness of the fit to the DSDs. (a) shows the N -standardized experimental and modelled $\bar{d}_{32}$ and (b) the goodness of the predicted $\bar{d}_{32}$.

(2) The regime where the drops' viscous resistance dominates which has been mainly described by Davies³⁷, Calabrese et al.¹⁰ and Wang and Calabrese¹⁴. In this regime bimodal drop size distributions were observed for the SiOils in the 50-350 cSt range. Bimodality was also observed in the same μ_d range in our study on the effect of viscosity in rotor-stators²⁷. (3) For very high μ_d we observed that the maximum drop sizes decrease and become independent of N ; furthermore the steady-state $\bar{d}_{32}$ of these emulsion were smaller than the ones obtained for the 10 cSt SiOils.

To describe the effect of μ_d on the drop sizes we used the Mo_d , which was shown to be a better parameter than $\bar{d}_{32}$ while being proportional to d_{max} for all the experimental μ_d and N . The drop size correlated well with $\mu_d^{-0.365}$, which is in agreement with our previous work²⁷, while being in disagreement with the work of Davies³⁷, Calabrese et al.¹⁰, Wang and Calabrese¹⁴ and Vankova et al.¹⁸; the first three of these studies were done in the absence of surfactant, while the latter was performed did use surfactants. The sutler

413 dependency of the DSD on μ_d could not been explained by any mechanistic
414 model.

415 Finally a methodology to fit the bimodal DSD by volume using two log-
416 normal distributions was proposed. The fit proposed could predict the $\bar{d}_{32}$
417 reasonably-well.

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433 tribution in stirred vessels. part ii: effect of continuous phase viscosity;
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Nomenclature

Latin symbols

$\bar{d}_{32}$	Sauter mean diameter [μm]
$\bar{d}_{pq}$	generalized mean drop size [μm]
$\bar{z}_d$	arithmetic mean of $\log(d_i/Mo_d)$ of the daughter drops [-]
$\bar{z}_s$	arithmetic mean of $\log(d_i/Mo_d)$ of the satellite drops [-]
A_i, C_i	i th constants [-]
a_v	interfacial area [m^2]
C_g	glucose concentration [mol L^{-1}]
D	diameter of the stirrer [m]
d_i	diameter of the drop class i [μm]
d_{95}	95th percentile [μm]
d_{max}	diameter of the largest drop [μm]
F_n	cumulative distribution by number [%]
f_n	frequency distribution by number [%]
F_v	cumulative distribution by volume [%]
f_v	frequency distribution by volume [%]
$f_{v,d}$	fitted frequency distribution by volume of the daughter drop distribution [%]
$f_{v,s}$	fitted frequency distribution by volume of the satellite drop distribution [%]
$f_{v,T}$	fitted frequency distribution by volume of the whole distribution [%]
MAE	mean absolute error [%]
Mo_d	mode of the daughter drops [μm]
Mo_s	mode of the satellite drops [μm]
N	impeller speed [s^{-1}]
n_{ri}	refractive index [-]
P	power [W]
$p(d_i)$	probability density of the drop class i [m^{-1}]
R^2	coefficient of determination [-]
$s_{z,d}$	standard deviation of $\log(d_i/Mo_d)$ of the daughter drops [-]
$s_{z,s}$	standard deviation of $\log(d_i/Mo_d)$ of the satellite drops [-]
T	diameter of the tank [m]
V	Volume of the vessel [m^3]

Greek symbols

α	parameter in the Weibull function [-]
β	parameter in the Weibull function [-]
ϵ	energy dissipation rate per unit mass [$\text{J kg}^{-1} \text{s}^{-1}$]
ϵ_{max}	maximum energy dissipation rate per unit mass [$\text{J kg}^{-1} \text{s}^{-1}$]
η	Kolmogorov length scale [m]
μ_c	dynamic viscosity of the continuous phase [Pa s]
μ_d	dynamic viscosity of the dispersed phase [Pa s]
$\bar{\epsilon}$	mean energy dissipation rate per unit mass [$\text{J kg}^{-1} \text{s}^{-1}$]
ϕ	volume fraction of the dispersed phase [-]
ϕ_s	volume fraction of the emulsion's satellite drops [-]
ρ_c	density of the continuous phase [kg m^{-3}]
ρ_d	density of the dispersed phase [kg m^{-3}]
σ	interfacial tension [N m^{-1}]
τ	stress [Pa]

Dimensionless numbers

Po	Power number. $Po = P\rho^{-1}N^{-2}D^{-5}$
Re	Reynolds number. $Re = \rho_cND^2\mu_c^{-1}$
Vi_C	Calabrese's viscosity group $Vi = \mu_dND(\rho_c/\rho_d)^{1/2}\sigma^{-1}$
Vi_H	Hinze's viscosity group $Vi = \mu_d\rho_d^{-1}\sigma^{-1}d_{max}^{-1}$
We_{crit}	critical Weber number for drop breakup.
We_d	Weber number of the droplet $We_d = \tau d_{max}\sigma^{-1}$
We_s	Weber number of the stirrer $We_s = \rho_cN^2D^3\sigma^{-1}$

Abbreviations

DSD	droplet size distribution
SiOil	silicon oil
SLES	sodium laureth sulfate

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