THE EFFECT OF PHASE FRACTION ON DROP SIZE DISTRIBUTION IN A HIGH SHEAR MIXER WITH A VISCOUS CONTINUOUS PHASE

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Abstract. Much of the previous work on the effect of phase fraction on equilibrium drop size distribution (DSD) in stirred vessels was done with a low-viscosity continuous phase under turbulent flow with inertial subrange scaling, where the equilibrium drop size is greater than the Kolmogorov microscale, $\eta$. In that case the maximum stable drop size, $d_{\text{max}}$, at low to moderate holdup, increases linearly with respect to the phase fraction, $\varphi$ [1, 2, 3]. In this study viscous oils comprised the continuous phase, with water as the drop phase. The equilibrium DSD in a batch rotor-stator mixer was measured for laminar flow and turbulent flow with $d_{\text{max}} < \eta$. A much greater increase (than the previous linear relationship) in drop size with phase fraction, $\varphi$, was observed for all cases studied for phase fractions less than 0.05, including cases where surfactants were added and where the high-shear surfaces were rendered more hydrophobic by coating with silane functional groups. It is believed that this significantly greater dependence on phase fraction is due to the flow field being locally laminar around coalescing drops with the coalescence rate being strongly affected by the collision efficiency, which is a function of the continuous and dispersed phase viscosities. Below $\varphi = 0.05$, the equilibrium drop size had a log-linear dependence on phase fraction which plateaus above $\varphi = 0.05$. This is attributed to the competing rates of coalescence and breakage and their dependence on phase fraction and drop size.

Keywords: Mixing, Phase fraction, Drop breakup, Coalescence.

1. INTRODUCTION

The drop size distribution (DSD) of an emulsion is, in general, determined by a dynamic equilibrium between the rates of coalescence and breakage of drops [4, 5]. There is a much greater understanding of breakage than of coalescence phenomena because drop breakage in emulsions can be studied independently of other effects by using a dilute dispersed phase (usually $\varphi < 0.01$). The advantages of using a dilute dispersion are that the continuous phase flow field is essentially unchanged from that of a pure fluid except on the drop scale, and that coalescence is negligible due to the rarity of drop-drop collisions. For a drop to break up in a given shear field, the imposed dispersive stress must be greater than the cohesive stress(es) [5]. The dispersive stress decreases with decreasing drop size and the cohesive stress due to interfacial phenomena increases. Once the drops reach a certain size, they will no longer break up and the equilibrium drop size is reached. Since breakup is due to stresses that the continuous phase exerts on individual drops, different flow regimes have been analyzed separately. For laminar flow, Grace [6] performed individual drop breakup experiments in idealized flow fields such as simple shear flow and pure extensional flow. The results of which can be compared to practical mixing processes using the idea that the appropriate characteristic shear rate in a mixing system is proportional to the impeller rotation rate [7].

Drop breakup in turbulent flow can be broken into 3 sub-regimes according to the drop size, $d$, relative to the Kolmogorov microscale, $\eta$; the length scale of the smallest turbulent eddies. For a low-viscosity continuous phase, almost all of the breakup studies have been for drops influenced by inertial subrange eddies; that is where $d$ is greater than $\eta$, but less than the turbulent macroscale, $L$. Using the theory of local isotropy in turbulent flow and equating the dispersive and cohesive stresses, a correlation was developed [8, 9] for the maximum stable
drop size, $d_{\text{max}}$, in a turbulent system using inertial subrange scaling ($L \gg d \gg \eta$).

\[
d_{\text{max}}/D \sim We^{-3/5}
\]

(1)

where, \[ We = \rho_c N D^2 / \sigma \]

$D$ is the impeller or rotor diameter, $\rho_c$ is the continuous phase density, $\sigma$ is the interfacial tension, and $We$ is the Weber number, the ratio of inertial to interfacial forces in the system. This expression has been extensively verified experimentally. Equation (1) applies to inviscid drops for which internal viscous resistance to deformation is negligible. Similar expressions were developed for the other 2 sub-regimes [10, 11], the sub-Kolmogorov inertial regime (where the ultimate drop size is less than the Kolmogorov microscale, but still large enough that inertial forces play a role in drop breakup) and the sub-Kolmogorov viscous subrange (where the ultimate drop size is much less than the Kolmogorov microscale), but experimental verification has been limited.

Coalescence occurs via a sequential procedure involving at least two drops. First, two drops must collide, forming a thin film of continuous phase between them. The film must drain and finally rupture [4]. Based on this mechanism, the coalescence rate can be expressed as the product of the collision rate and a collision efficiency, the probability that a collision will result in coalescence. Chesters [12] provided methods for a first-estimate of the collision rate per unit volume, $C$, and the collision efficiency, $P$, for a monodisperse system.

\[
k = kv d^2 n^2
\]

(2)

$k$ is a flow-dependent constant, $v$ is a small-scale, flow-dependent characteristic velocity between two points a distance $d$ apart, and $n$ is the number of drops per unit volume ($n \sim \phi / d^3$). According to Chesters [12], $v \sim d$ for both simple shear flow and fine scale turbulence ($d \approx \eta$). With these substitutions, $C \sim \phi^2 / d^3$.

\[
P = \exp(-t_c / t_i)
\]

(3)

$t_c$ is the time required to drain the film so that it is thin enough for rupture to occur and $t_i$ is the interaction time brought about by each collision event.

Equations (2) & (3) are general and apply to any flow regime. A significant amount of work has been done with turbulent flow with $L \gg d \gg \eta$. Coulaloglou and Tavlarides [4] developed expressions for the coalescence and breakage rates for this case.

A number of authors [1, 2, 3] have published relationships (which reduce to equation (1) at the dilute limit) for the maximum stable drop size which can be approximated as follows.

\[
d_{\text{max}}/D = C_1 (1 + b \phi) We^{-3/5}
\]

(4)

$C_1$ is a system-dependent constant and $b$ ranges from about 1 to 10. This functional dependence of the drop size on phase fraction in the "inertial subrange" has been attributed to turbulence damping, coalescence, or both depending on the study [5].

Equation (4) is an accepted way to quantify the effect of phase fraction on the equilibrium drop size. However, this relation should not be expected to be generally valid since it was developed and validated using inertial subrange scaling in turbulent flow. The mechanism of coalescence can be different if the flow is laminar or if the drops are smaller than the Kolmogorov microscale, making the flow locally laminar. In the "inertial subrange" the coalescence mechanism originates from the fact that drops are brought into contact and moved apart by eddies of the size of the drops [13]. The coalescence mechanism is different if the flow field around the drop is locally laminar - a criterion which covers both sub-Kolmogorov turbulent systems and laminar systems.

Using equation (3) and arguments for the interaction time and film drainage time, the collision efficiency for monodisperse, deformable drops in viscous simple shear flow can be approximated by [12]:

\[
P = \exp\left(-C_2 (\mu_d / \mu_c) C_{ad}^{3/2} (2\pi \sigma d^2 / A)^{1/3}\right)
\]

where, \[ C_{ad} = \mu_c \gamma d / 2\sigma \]

(5)
C₂ is an unknown constant of order 1, μ_d is the dispersed phase viscosity, μ_c is the dispersed phase viscosity, Cₐ_d is the drop phase Capillary number, σ is the interfacial tension, A is the Hamaker constant (material-dependent and related to the van der Waals force, but typically about 10⁻²⁰ J), and ̇γ is the characteristic shear rate.

The predicted inverse dependence on viscosity ratio, λ, in Equation (5) has been qualitatively verified experimentally [14, 15, 16, 17] with studies of coalescence in shear fields which were too weak to cause any breakage events. These authors present their results in terms of λ, yet it should be noted that dependency on λ alone is too simplistic. In Equation (5), P ~ \exp(-μ_dμ_c^{1/2}), revealing that increasing either μ_d or μ_c individually decreases the collision efficiency.

Film drainage is primarily dependent on interface mobility [12]; that is, the ability of the drop surface to move with the film as it is squeezed out between colliding drops. Increasing μ_d decreases interface mobility, thereby increasing drainage time. Meanwhile, collision force increases with increasing μ_c, promoting coalescence. However, film drainage rate decreases with increasing μ_c, hindering coalescence, yet only in proportion to the steepness of the velocity profile within the film. If the interface was completely mobile, then there would be no decrease of film drainage rate with increasing μ_c.

2. EXPERIMENTAL METHODS

Water was dispersed into a viscous mineral oil, Crystal Oil, in a Silverson L4R batch rotor-stator mixer equipped with a slotted stator head and a 2 liter glass vessel (Figure 1). The equilibrium DSD was determined for laminar and sub-Kolmogorov turbulent "clean" (no surfactant) flows, surfactant-laden laminar flows, and flows where the high-shear surfaces had been treated with a hydrophobic silane group.

The viscosity as a function of temperature was measured using a "TA Instruments Advanced Rheometer 2000," which is a thermally-controlled cone-and-plate device. The interfacial tension was measured using the pendant drop method and a semi-empirical correlation [18] which relates the shape of a drop hanging from a capillary tip to the ratio of the interfacial to the gravitational/buoyant forces. The range of available equilibrium interfacial tensions was found to be from 6.16 to 54.8 mN/m.

The dispersion experiments were conducted by injecting ultrapure water into 2 liters of Crystal Oil FG (viscosity of 18 or 93 cP). Because of the large amount of viscous energy dissipation, a high rate of heat removal was required necessitating sophisticated temperature control (Figure 2). The oil was first brought to thermal equilibrium at the lowest mixing speed, 3900 rpm, then the water was injected below the mixing head. After allowing 2.5 hours for the drop size to reach equilibrium, a sample of the emulsion was withdrawn and the mixing speed was increased to 5900 rpm. At 2.5 hour increments this was repeated for mixing speeds of 7300 and 9000 rpm. Soon after withdrawal, samples were placed on glass slides and imaged via optical microscopy, using a "Watec America Corp. LCL-902K" camera. These images were analyzed using a purpose developed automated image analysis macro in ImageJ. Enough images were collected so that the number of drop counts exceeded 1000, the number needed for reasonable statistical confidence [19].

3. RESULTS AND DISCUSSION

The flow regime was determined by reference to work done by Padron [20] who measured Power numbers, N_P, for this mixer. By observing where N_P becomes independent of Reynolds number, the flow transition (Re ~ 1000) from laminar to turbulent flow can be
determined. The Kolmogorov microscale, \( \eta = (\nu^3/\varepsilon)^{1/4} \), where \( \varepsilon \) is the local energy dissipation rate and \( \nu \) is continuous phase kinematic viscosity, was estimated from the power draw data (\( N_P = 2.1 \)) using the impeller swept volume approach [5]. \( \eta \) ranged from 40 to 75 \( \mu \text{m} \) which is always larger than the drop size reported below in turbulent flow.

In this study, the Sauter mean diameter, \( d_{32} = \Sigma d_i^3/\Sigma d_i^2 \), is used to represent drop size, as is customary in liquid-liquid dispersion studies.

3.1 Clean or surfactant free systems

Figures 3 & 4 show that for both laminar and turbulent flow with \( d_{32} < \eta \), the effect of phase fraction on the drop size is log-linear, and is well-represented by:

\[
\log(d_{32}(\varphi)) = a \ln(\varphi) + b
\]

It does not make sense to compare the data of Figures 3 & 4 directly with previous data for which turbulent inertial subrange scaling is valid because the coalescence mechanisms are fundamentally different (for example, bouncing occurs in inertial collisions [12]).

Equation (6) is a clear departure from the prevailing notion that equation (4) describes the effect of phase fraction on drop size. Since equation (4) applies to a turbulent coalescence mechanism, it should not be expected to describe the data in the current study. Equation (5), although derived for the specific case of viscous simple shear flow, is a reasonable first-approximation for the coalescence rate in flows which are locally viscous for both the laminar and turbulent data (\( d_{32} < \eta \)) presented in Figures 3 & 4.

Table 1 was constructed using the approximations of Chesters [12] in equation (5). It is only intended to convey qualitative information since there are many simplifying assumptions, such as the coalescing drops being of equal size. Sample values were chosen near the middle of the ranges applicable to the data of Figures 3 & 4, and the shear rate used in the Capillary number is approximated by the nominal shear rate in the rotor-stator gap.

\[
\dot{\gamma} = ND/\delta
\]

\( N \) is the rotor speed (ranges from 3900 to 9000 rpm), \( D \) is the rotor diameter (2.8 cm), and \( \delta \) is the distance between the rotor tip and the stator (0.185 mm).

<table>
<thead>
<tr>
<th>Sample Values; ( d = 8 \mu \text{m}, \sigma = 54.8 \text{mN/m}, \text{rotor speed} = 5900 \text{rpm} )</th>
<th>( \mu_d ) (cP)</th>
<th>( \lambda )</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Laminar,} ( \mu_c = 93.3 \text{ cP} )</td>
<td>93</td>
<td>9.3</td>
<td>0.62</td>
</tr>
<tr>
<td>\text{Turbulent,} ( \mu_c = 18.1 \text{ cP} )</td>
<td>0</td>
<td>0.02</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 1. Table of approximate values of collision efficiency. This table shows that the viscosities play a controlling role in determining the probability that a collision event will result in coalescence.

Bolded columns indicate the results that correspond to Figures 3 & 4.

The most striking feature of Table 1 is the extremely strong dependence of the collision efficiency on viscosity. To avoid confusion about the flow regime, only the dispersed phase viscosity was changed on either side of the table, but it should be remembered that equation (5) shows that collision efficiency follows: \( P \sim \exp(-\mu_d\mu_c^{1/2}) \).
3.2 Clean or surfactant free systems with treated surfaces

For some experiments the mixing head, consisting of the surfaces that were exposed to high shear rates, was treated with dimethyldichlorosilane in toluene, in order to modify the hydrophobicity so that the effect of the interaction between the dispersed phase and the metal surfaces could be examined. The results of these experiments are plotted in Figure 5. In addition to the increase in the variability of the data, it appears that there is no effect of the treatment at dilute volume fractions ($\phi < 0.001$) with no surfactant, but that at non-dilute concentrations the drop size decreases slightly. These data can also be modeled by equation (6). This suggests the possibility of a heterogeneous coalescence mechanism whereby the dispersed phase's interaction with the high-shear surfaces promotes coalescence. This is based on the idea that the treatment slightly reduces the total amount of coalescence occurring via interaction with the metal surfaces, thus reducing the drop size.

3.3 Surfactant systems

For some experiments an oil-soluble surfactant, Tergitol NP-4, was added. The critical micelle concentration (CMC) in Crystal oil was $1 \times 10^{-3}$ mol/L, as measured by the pendant drop technique. This is the concentration at which the equilibrium interfacial tension became independent of surfactant concentration. Experiments were performed at initial surfactant concentrations of $0.01 \times$ CMC, $0.1 \times$ CMC, and $1 \times$ CMC. Bulk surfactant concentration decreases as interfacial area increases.

Figure 6 shows that surfactant data follow the same log-linear behavior as both the clean laminar and turbulent flow experiments. Similar plots to Figure 6 can be made for all three surfactant concentrations and, while greater amounts of surfactant were found to reduce the drop size and decrease the value of $a$ in equation (6), they all have the same log-linear functionality.

It can be concluded that surfactants reduce the interfacial tension, but they do not change the underlying phenomena. They facilitate breakage by reducing the free energy driving force for cohesion. It appears, for this system, that the surfactant lowers the drop size by lowering the interfacial tension and does not necessarily provide an additional physical barrier to coalescence, as reported by Lobo and Svereika [21] for hexadecane oil-in-water emulsions.

3.4 High Concentration systems

The previously presented data are restricted to $\phi < 0.05$. It was not possible to achieve complete dispersion for clean systems above this volume fraction. However, the addition of a sufficient amount of surfactant allowed us to acquire data in stable dispersions up to $\phi = 0.5$. This was done at a surfactant concentration of $1 \times$ CMC.

Figure 7 shows that $d_{32}$ follows equation (6) initially, but then plateaus at higher phase fractions. This is attributed to the competing rates of breakage and coalescence. The rate of breakage, since it only involves one drop, is approximately independent of phase fraction except for its effect on emulsion viscosity, yet it does increase with drop diameter. This is because: (1) drops only break if they are too large to be stable in the deformation field and (2) drops that are much larger than the threshold of stability undergo catastrophic rather than
binary breakage [9].

The rate of coalescence depends on both phase fraction and drop size. In equation (2), increasing the phase fraction significantly increases the collision rate. However, increasing the drop diameter decreases both the collision rate in equation (2) and the collision efficiency in equation (5). The interpretation of Figure 7 is that, at first, increasing $\phi$ only increases the collision rate, but as drop diameter starts to increase, both collision rate and collision efficiency decrease and the breakage rate increases.

4. CONCLUSIONS

Sauter mean diameter increases according to Equation (6) when $0.001 < \phi < 0.05$ invalidating the widely held notion that $\phi < 0.01$ is the limit for defining a dilute (non-coalescing) system, at least for the systems covered in this study. There is a much greater dependence of drop size on phase fraction than was previously reported for turbulent flow with $L >> d >> \eta$. This is because the flow conditions in this study are locally laminar around the drops (either the flow was laminar or $d_{32} < \eta$) resulting in drop collisions governed by viscous rather than inertial forces.

There is apparently a much higher rate of coalescence when the flow is locally laminar, at least at the continuous and dispersed phase viscosities of this study. Based on work done by others [12, 14, 15, 16, 17], the coalescence rate in these systems is believed to be the result of sufficiently low values of $\mu_c$ and $\mu_d$ in flows that were locally laminar around the drops.

Adding surfactants and treating the mill head surfaces with a hydrophobic silane decreased the drop size, but did not qualitatively change the functionality. This implies that the same coalescence phenomena are occurring, but are reduced in their effectiveness.

Finally, at large volume fractions the drop size plateaus (at least in the presence of surfactants). Just as the initial increase of the drop size is attributed to an increase in collision frequency, the plateauing is attributed to the effect of increasing the drop size: decreased collision frequency, decreased collision efficiency, and increased drop breakage rate.

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5. REFERENCES