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Dispersion of water into oil in a rotor–stator mixer. Part 2: Effect of phase fraction

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ABSTRACT

In Part 1 (Rueger and Calabrese, 2013), we monitored dilute water-in-oil dispersions in a batch Silverson L4R rotor–stator mixer to establish breakage mechanisms and develop a mechanistic basis for correlation of equilibrium mean drop size. In this study (Part 2) we consider the effect of water phase fraction under similar processing conditions, thereby requiring consideration of coalescence. Most of the work on the effect of phase fraction in stirred vessels was done with a low-viscosity continuous phase in turbulent flow with inertial subrange scaling ($d > \eta$). For that case drop size increases linearly with phase fraction, ϕ. In this study, viscous oils comprised the continuous phase, with water as the drop phase. The equilibrium DSD was measured in both laminar and turbulent flow conditions. The diameter of the largest drops was always less than the Kolmogorov microscale ($d < \eta$). A much greater increase (than the aforementioned linear relationship) in drop size with phase fraction was observed for $\phi \leq 0.05$; including cases where an oil soluble surfactant was present and where metal mixing head surfaces were rendered hydrophobic by treatment with silane functional groups. It is argued that this significantly greater dependence on ϕ is due to the flow field being locally laminar near the drops with coalescence rate being strongly affected by the collision efficiency, which depends on the viscosity of both phases. The presence of surfactant decreased drop size. The silane treatment decreased drop size; possibly by altering water drop interactions with mill head surfaces. Additional experiments were performed at higher phase fraction, where surfactant was required to stabilize the emulsion. The equilibrium drop size was found to plateau for $0.10 < \phi < 0.50$. The high phase fraction behavior is attributed to the competing rates of coalescence and breakage and their dependence on ϕ and drop size.

Keywords: Liquid–liquid dispersion; Drop breakup; Drop coalescence; Rotor–stator mixer; High-shear; Drop size; Phase fraction

1. Introduction

This work extends the study of Part 1 (Rueger and Calabrese, 2013), using the same liquid–liquid pairs and experimental procedures, to look at the effect of phase fraction on mean drop size for both laminar and turbulent flow. In Part 1, dilute dispersions of water in oil in a Silverson L4R batch, rotor–stator mixer were examined. The Part 1 results are prerequisite from a fundamental standpoint to first quantify the role of drop breakup without complications arising from drop–drop interactions and coalescence. However their use is of limited practical utility because the dispersed phase volume fraction was always $\phi = 0.001$.

Part 2, this paper, is concerned with the investigation of non-dilute dispersions, again with a viscous continuous phase, in both laminar and turbulent flow. The effect of phase fraction on equilibrium mean drop size is examined both for clean systems and as a function of continuous phase surfactant concentration. At higher water phase fraction, this oil soluble surfactant was required to stabilize the dispersion. Although they are more complex to analyze, concentrated surfactant-laden systems are more industrially relevant.

Other issues of interest in practical emulsification systems were also investigated. In some experiments, the role of heterogeneous coalescence was investigated as a function of phase fraction by rendering the rotor–stator mill head more

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Nomenclature

A	Hamaker constant
a	slope of the log-linear phase fraction function of Eq. (8)
a_v	interfacial area per volume
b	coefficient of phase fraction in Eq. (5)
c	intercept of the log-linear phase fraction function of Eq. (8)
C	particle collision rate (assuming equally sized particles)
C_1	constant in Eq. (5)
C_2	constant of order unity in Eq. (6)
$Ca = \mu_c \dot{\gamma} d/2\sigma$	Capillary number
d	drop diameter
D	rotor diameter
d_{32}	equilibrium Sauter mean diameter
k	constant in Eq. (1)
L	length scale of largest turbulent eddies
n	number of drops per unit volume
N	rotor rotation rate
P	collision efficiency
v	characteristic velocity difference across drop surface
$\overline{v'(d)^2}$	turbulent mean-square velocity difference across drop surface
t_c	time required to drain a film of fluid between two colliding drops
t_i	interaction time for a drop collision event
$We = \rho_c N^2 D^3/\sigma$	Weber number
$\dot{\gamma}$	characteristic shear rate
δ	clearance between rotor blade and inner stator wall (shear gap)
ε	energy dissipation rate per unit mass
η	Kolmogorov micro length scale of turbulence
$\lambda = \mu_d/\mu_c$	viscosity ratio
μ_c	continuous phase viscosity
μ_d	dispersed phase viscosity
ν_c	continuous phase kinematic viscosity
ϕ	phase fraction
σ	equilibrium interfacial tension

hydrophobic, thereby changing water drop interaction with solid surfaces. Another issue is that of possible drop adherence to low-shear surfaces. Experiments were performed with additional low-shear solid surface area present in the mixing volume to test its effect on drop size.

Except for hydrophobic treatment of solid surfaces, the materials, methods, and procedures used to acquire the Part 2 data were similar to those employed in Part 1 (Rueger and Calabrese, 2013). These details are only repeated here to the extent necessary.

2. Theory

For non-dilute systems, the drop size distribution (DSD) of an emulsion or dispersion is, in general, determined by a dynamic equilibrium between the rates of drop coalescence and breakage (Coulaloglou and Tavlarides, 1977; Leng and Calabrese, 2004). 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 $\phi < 0.01$). The advantages of a dilute system 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 deformation field, the imposed disruptive stress must be greater than the cohesive stress(es) (Hinze, 1955). The disruptive stress decreases with decreasing drop size and the cohesive stress due to interfacial forces increases. Once the eroding 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 as summarized in Part 1 (Rueger and Calabrese, 2013) (in Table 1 for turbulent flow and the discussion of Grace's (1982) work for laminar flow). Having discussed breakup fully in Part 1, it is now necessary to discuss coalescence phenomena.

Homogeneous coalescence occurs via a sequential procedure involving at least two drops. First, drops must collide, forming a thin film of continuous phase between them. The film must drain and finally rupture (Coulaloglou and Tavlarides, 1977). Based on this mechanism, the coalescence rate can be expressed as the product of the collision rate and a collision efficiency, which is the probability that a collision will result in coalescence. Chesters (1991) provided methods for a first-estimate of the collision rate per unit volume, C, and the collision efficiency, P, for a monodisperse system. The collision rate is given by

$$C = kvd^2n^2 \tag{1}$$

k is a flow-dependent constant, v is a characteristic velocity between two points separated by a distance d in the flow field, and n is the number of drops per unit volume ($n \sim \phi/d^3$). For turbulent flow, v is the square root of the turbulent mean-square velocity difference, $v = \sqrt{\overline{v'(d)^2}}$ (listed in Table 1 of Part 1 (Rueger and Calabrese, 2013)). For sub-Kolmogorov inertial flow where $d < \eta$, but not $d \ll \eta$ (it is called "fine-scale turbulence" in Chesters' paper (1991)), $v \sim (\varepsilon/\nu_c)^{1/2} d$. Substituting into Eq. (1), along with $\varepsilon \sim N^3D^2$ for constant power number, the collision rate for sub-Kolmogorov inertial flow can be scaled by Eq. (2).

$$C \sim \frac{N^{3/2} D \phi^2}{d^3 \nu_c^{1/2}} \tag{2}$$

For viscous simple shear flow, v is the product of the characteristic shear rate and the drop diameter. From Part 1 (Rueger and Calabrese, 2013), the characteristic shear rate in laminar flow is $\dot{\gamma} \sim ND/\delta$, where δ is the width of the shear gap or distance from the tip of the rotor blade to the inner wall of the stator. Substituting into Eq. (1), the collision rate can be scaled by Eq. (3).

$$C \sim \frac{ND\phi^2}{d^3\delta} \tag{3}$$

It is interesting to note that in these expressions, $C \propto \phi^2/d^3$ for both viscous simple shear and sub-Kolmogorov inertial turbulent flow. These are the two flow field types most appropriate to this study, as was established by mechanistic analysis in Part 1 (Rueger and Calabrese, 2013).