Viscosity Effects in Miniemulsification via Ultrasound

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Introduction

Emulsions with submicron droplet size, so called miniemulsions or nanoemulsions, have found increasing attention in recent years due to their unique properties caused by their nanoscale drop size. As an example, miniemulsions can be employed in a polymerization technique (i.e., miniemulsion polymerization) to produce composite polymer nanoparticles.[1,2] Energy-intensive emulsification methods such as high-pressure homogenization and ultrasound have been widely used for preparation of miniemulsions and artificial latexes.[3] The mechanisms by which nanoscale drops are formed via these energy-intensive emulsification methods are of significant interest to academics, as well as industrialists working on the emulsification technologies.

Emulsion is the product of two simultaneous competing processes, disruption and coalescence of dispersed phase. To rupture droplets, sufficient energy must be applied to overcome the opposing Laplace pressure

$$\Delta p = \frac{2\sigma}{R} \tag{1}$$

where σ and R are interfacial tension and radius of droplet, respectively.

Taylor, in his pioneering work,[4] concluded that for very small drops, stresses due to inertia are smaller than those from viscosity. This theory was later completed by Kolmogorof who considered a turbulent wave scale which defines the boundary between inertia and viscous subranges. The formed eddies in a turbulent field produce smaller ones and this is repeated until the smallest eddies, named Kolmogorof eddies, at which their energy is dissipated as heat are formed. The dominating rupture forces can be distinguished as inertial force (for droplets bigger than Kolmogorof scale), or viscous force (for droplets smaller than this scale). The rupture force in both laminar and turbulent flows is a result of velocity gradient across the droplet. For inertia subrange, this force is $\rho_c\bar{u}^2$ where ρ_c is the continuous phase density, and $\bar{u}$ is the mean velocity difference across the droplet. For the viscous subrange, the exerted stress is $\mu_c G$, where μ_c is the dynamic viscosity of the continuous phase, and G is the strain rate.

Despite all recent advances in the understanding of relatively new sonication technology, the mechanism of drop formation by ultrasound is not clear yet. According to Li and Fogler,[5] drop formation in a sonication process starts with primary interfacial instability that leads to the rupture of droplets from the dispersed phase into the continuous phase. This is completed by a second transient cavitation that generates microstreaming, high-pressure shock wave resulting in very small droplets. The formation of nanoscale drops, however, may imply that shear stress generated in these devices could be the main cause for drop rupturing.

Traditionally, the occurrence of disruption has been judged by the ratio of disruptive energy over surface energy as a sole cohesive energy. This resulted in the introduction of two dimensionless terms, namely Weber number and capillary number, as follows

$$W_e = \frac{\rho_c\bar{u}^2 d_{max}}{\sigma} \tag{2}$$

$$\mathbb{C} = \frac{\mu_c G d_{max}}{\sigma} \tag{3}$$

In both regimes, the diameter of droplet decreases with a decrease in deforming stress until the deforming stress cannot break the droplet any further. This droplet is usually referred to as $d_{\max}$, which is the maximum stable droplet diameter. The aforementioned equations are only applicable to dilute emulsions where drop coalescence is unlikely and effective viscosity of emulsion is dominated by the viscosity of the continuous phase.

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It is usually assumed that breakup can occur only if the aforementioned numbers exceed a "*critical value*". Hinze[6] suggested an empirical treatment for data correlation in the inertia subrange when dispersed phase viscosity contributes to drop stability. The critical Weber number was suggested to take a form of

$$W_{e_{crit}} = C(1 + f(\mu)) \tag{4}$$

where C is a constant and $f(\mu)$ is the viscosity function. The viscosity function decreases to zero for low-viscosity dispersed phase so that C represents W_{ecri} for inviscid drops. Many investigators have unanimously confirmed that the average drop size in the inertia subrange increased with dispersed phase viscosity in a way similar to what was suggested by Hinze.[7,8]

The effects of viscosity on the size of miniemulsion drops in the viscous subrange have been barely studied in the literature. Bentley and Leal[9] conducted a sophisticated research on the contribution of the viscosity ratio, defined as $\lambda = \mu_d/\mu_c$, into critical capillary number for drop rupture in the viscous subrange, and found a U-type relationship between the two. The occurrence of a U curve for critical capillary number vs. viscosity ratio is quite intriguing. One may expect that drop size should show a minimum with viscosity ratio at some point. While there exist extensive data in the literature regarding the critical capillary number in the viscous subrange at which drop rupturing occurs, only few reports[10] appear to have considered the variations in the size of resulting drops with viscosity ratio. To the best of authors' knowledge, there is no data in the literature on viscosity effects in emulsification at nanoscale. In this communication, we aim to investigate viscosity effects in ultrasonication to evaluate the existing theories. A series of silicon oil was used to be able to alter the viscosity of the disperse phase uniformly.

Experimental

Materials

Sodium dodecyl sulfate ($C_{12}H_{25}OSO_3Na$; SDS) was obtained from Sigma-Aldrich and was of 99% purity. Silicon oils of 0.65, 5, 10, and 100 cSt were obtained from Sigma-Aldrich. Mixtures of these oils were also prepared to provide oils with intermediate viscosities. Deionized water was obtained from an ELGA PURELAB Option water purification system.

Apparatus

A digital sonifier model 450 from BRANSON Ultrasonic Corp. with the maximum output of 400 watts (with frequency of 19.850–20.050 KHz) was used for producing miniemulsions. Emulsions were prepared using amplitude of 70%.

Measurement

A Nano ZS particle sizer (ZEN3600, MALVERN instruments) at a fixed scattering angle of 173°, and with laser wavelength of 633 nm was used for measuring droplet-size average (d_z) and distribution. The reproducibility of the results was good, within ±5.0%, which improved with increasing surfactant concentration. Viscosities of the silicon oils and miniemulsions were measured using an ARES rheometer. The interfacial tensions of the oils and water containing surfactant were measured by the pending drop method using FTA200 tensiometer.

Method

An aqueous solution of the surfactant in the water phase was prepared. A primary mixture was produced using a certain concentration of SDS in water as the aqueous phase followed by addition of the oil. The overall volume of the emulsion was 40 cm^3. The mixture was placed in a 50 cm^3 beaker, and the sonication horn was immersed in the solution. A small emulsification vessel was chosen to avoid long circulation times and produce homogeneous mixing in the vessel. Samples were always taken from the vicinity of the tip of the horn where the highest rate of energy dissipation occurred.[11] To maintain the emulsification temperature constant, the beaker was placed in a water bath cooled with ice. Furthermore, sonication was conducted in 2 s time intervals followed by a pause of 20 s after each interval. The active ultrasonication time was 180 s. The emulsification temperature was kept constant within 15.0 ± 2.0°C.

Results and Discussion

To study the effects of dispersed phase viscosity on drop size, four silicon oils with viscosities of 0.65, 5, 10, 100 cSt were used. Mixtures of the oils were also made to form oils with intermediate viscosities in the same range. Miniemulsions may degrade by diffusional degradation (Ostwald ripening). The solubility of the silicon oil in water is extremely low so that diffusional degradation can be eliminated. The physical properties of oils are given in Table 1. Preliminary experiments indicated that the steady-state drop size was achieved in less than 3.0 min for all oils viscosities including the highest viscosity oils. Therefore, a time interval of 3.0 min was considered for duration of sonication. To eliminate drop coalescence, experiments were carried out using dispersed phase ratio of 0.5 vol %. Two sets of experiments were conducted. In set A, the SDS concentration of 1.0 g/l was used. In set B, a higher surfactant concentration (2.5 g/l SDS) was used to enhance drop rupturing. This concentration is around the critical micellar concentration of SDS at which the minimum interfacial tension is achieved.

Figure 1 shows average drop size vs. viscosity ratio for emulsions produced in the presence of 1.0 and 2.5 g/l SDS. The viscosity of water phase was not significantly affected by the presence of SDS (0.000107 Pa s), especially at low concentration, so it was taken as that of pure water (0.001 Pa s). The data points for the sets fall on two similar curves. The interesting point is that plotting the z-average size vs. viscosity ratio result in a U-curve graph. The average drop size sharply decreases with increasing viscosity ratio in the lower range, reaches a minimum around the viscosity ratio of 1.0, and then starts increasing at a lower rate for both concentrations of surfactant used. This finding is in line with the statement that in a simple shear field with a low-

Table 1. Physical Properties of Silicon Oils

Oil	Viscosity*10^3		Density	Interfacial tension γ [mN/m]		
					Water with SDS	
cSt	Kinematic (v)[m/s^2]	Dynamic (μ) [Pa.s]	ρ* [Kg/m^3]	Air	1 g/l	2.5 g/l
100	0.1	96.50	965	20.9	7.5	3.8
37	0.0375	35.90	958	–	–	–
10	0.01	9.30	930	20.1	7.4	3.6
7.4	0.00758	6.97	920	–	–	–
5	0.005	4.55	910	19.7	7.2	3.4
1.7	0.00172	1.44	835	–	–	–
1.07	0.00107	0.84	783	–	–	–
9.98	0.00099	0.76	762	–	–	–
0.87	0.00087	0.65	740	–	–	–
0.65	0.00065	0.49	760	15.9	5.6	2.1

*Density of the oil mixtures were obtained by interpolation.

interfacial tension, the maximum energy transfer occurs when the viscosity of both liquids are equal.[12]

Behrend et al.[13] used water containing various concentrations of stabilizer as continuous phase to study the effect of continuous phase viscosity on the size of droplets obtained by sonification. They reported increasing droplet size with viscosity ratio for the range of $\lambda = 3$ and 60, at various phase ratios. The viscosity ratios smaller than one were not reported. Kumar et al.[10] studied the variation of drop size with viscosity ratio in the viscous subrange for a conventional stirred vessel. The drop size, however, was in the order of few hundred microns. The drop size initially reduced with viscosity ratio, but remained constant within the viscosity ratio range of 3.0–12.0. The results obtained in this study clearly show that the average diameter of nanodrops starts to increase with viscosity ratio, after seemingly a plateau within viscosity ratio of 1.0–5.0 is achieved.

Now we investigate how drop sizes can be predicted by the theory. According to Kolmogorof,[14,15] the size of the Kolmogorof length scale in turbulent fields can be estimated by

$$l_w = \left(\frac{v_c^3}{\varepsilon}\right)^{\frac{1}{4}} \tag{5}$$

where ι_w is the Kolmogorof (turbulent) wave length, υ_c is the kinematic viscosity of continuous phase, and ε is the energy dissipation per unit of mass. The estimated Kolmogorof length scale for the system under study is 3.0 μm, which is much larger than the average size of the resulting drops. This confirms that viscous subrange is predominant in the system under study.

Solving Eq. 3 for viscous subrange considering $G = C(\varepsilon/v)^{1/2}$ gives

$$d_{max} = C\sigma(\rho_c\mu_c\varepsilon)^{-0.5}\mathbb{C}_{crit} \tag{6}$$

where C_{crit} is the critical capillary number, which was obtained from the study performed by Bentley and Leal.[9] Figure 2 shows the critical capillary number versus viscosity ratio for different values of α, which specifies the relative strength of the strain rate and vorticity in the flow. Simple shear corresponds to $\alpha = 0$, while $\alpha = +1$ indicates pure-straining. The velocity gradient tensor of $\alpha = 0.4$, whose pattern is similar to that of drop size, was used for calculations. The critical capillary number decreases moderately in the lower range of viscosity ratio, $1.0 > \lambda$, remains almost constant in the intermediate range, $1.0 < \lambda < 7.0$, and then sharply increases in the higher range, $\lambda > 7.0$. According to the map, no drop burst is possible for viscosity ratio higher than 13 and 46.6 for $\alpha = 0.2$ and $\alpha = 0.4$, respectively.

The lines projected in Figure 1 illustrates the average droplet size vs. viscosity ratio, calculated using Eq. 6, for two surfactant concentrations used. In the construction of this curve it was assumed that $d_{max} \sim d_z$. Calculations were carried out according to the following procedures. The interfacial tensions for four pure oils were measured and found to increase with viscosity of the oils, but decrease in the presence of the surfactant at the interface. They are tabulated in Table 1. The interfacial tensions were fitted with exponential correlations $\sigma = 0.009\mu_d^{0.054}$ and $\sigma = 0.005\mu_d^{0.110}$ for SDS concentration of 1.0 and 2.5 g/l, respectively. These correlations were used to estimate interfacial tensions of the oil mixtures. The effective viscosity of miniemulsions with

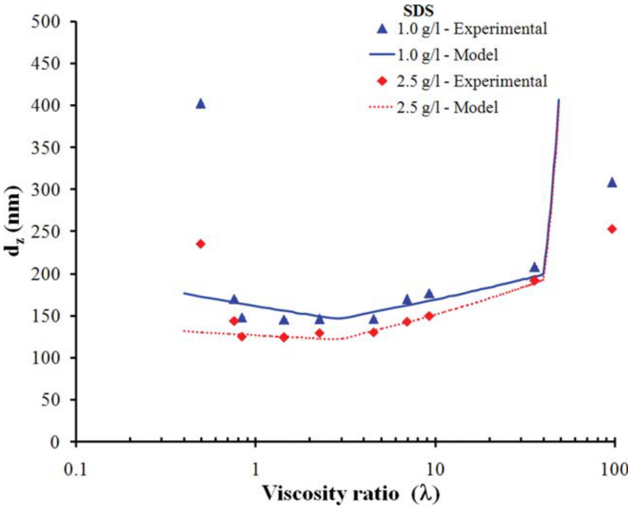

Figure 1. z-average drop diameter vs. viscosity ratio for miniemulsions prepared with 0.5 vol % oil/water ratio and SDS concentrations of 1.0 and 2.5 g/l.

Symbols represent experimental data and lines represent the model predictions using Eq. 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

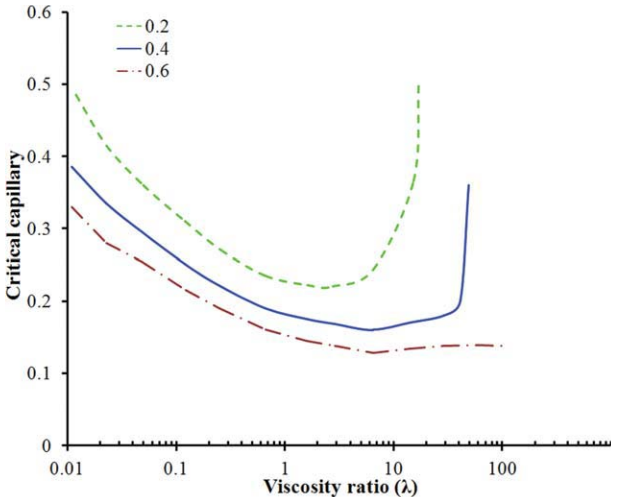

Figure 2. Critical capillary in flows with different α, velocity gradient tensor, dash line for $\alpha = 0.2$, and solid line for $\alpha = 0.4$ (data from Bentley and Leal[9]).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.5 vol % oil ratio was measured and found to be the same as that of water (0.001 Pa.s). This confirms that at such a low-phase ratio, the effective viscosity of emulsion is dictated by the continuous phase viscosity. The critical capillary number curve ($\alpha = 0.4$) was divided into several intervals and then fitted with appropriate correlations. The average energy dissipation rate was found to be around 7350 m^2/s^3 (for the lightest oil used). It was assumed that the whole sonication energy was transferred to the emulsions during emulsification. The emulsification constant C, was arbitrarily taken to be 0.012 and 0.025 for the low and high SDS concentrations, respectively. These values, which are within the range of values used by other investigators, provide satisfactory fits to the data.

It appears from Figure 1 that the predicted values can fairly well reproduce the experimental data for the intermediate viscosities, but only qualitatively for the lower and higher ends. Drop rupturing via sonication occurred until viscosity ratios as high as 100 were reached. Sonication beyond this range proved to be inefficient. Drop rupturing did not occur at viscosity ratio of 390 as drops as large as 4.0 μm in diameter remained in the dispersion after sonication time of 180 s (not shown). The theoretical prediction of drop size variation with viscosity ratio, as shown in Figure 1, appears to be qualitatively sound.

Drop-size distribution data contain valuable information regarding the mechanism of drop rupturing. Earlier reports on drop-size distributions in the inertia subrange have shown that the mechanism of drop breakup may also be affected by alteration in the viscosity of the drop.[16] For dispersions with a low-viscosity dispersed phase it has been found that drops *burst* and several smaller drops of comparable size are obtained.[17,18] Whereas for high-viscosity drops, rupturing occurs via *stretching* leading to formation of bimodal distributions.[7,17,18]

The results obtained in this work for the viscous subrange clearly point to a change in the pattern of evolution of drops-size distributions with viscosity ratio. Figure 3 presents typical time evolution of drop-size distributions for a low-viscosity oil phase, 0.65 cSt, and a high-viscosity silicon oil, 100 cSt (viscosity ratios of 0.49 and 96.50, respectively). The drop-size distribution is monomodal during sonification for the lower viscosity ratio, whereas it becomes bimodal during sonication for the higher viscosity ratio before practically evolves to a monomodal distribution at a later time. With increasing viscosity ratio, the mechanism of drop rupturing appears to shift from *stretching* toward *erosive* (stripping of small satellite droplets from the mother drop) forming a large number of small droplets and a bimodal drop-size distribution. The continuous erosion of drops eventually leads to formation of unimodal drop-size distribution. This is a common assumption in two-phase mixing that drop breakup occurs in the high-shear regions, in the vicinity shear producing source, while drop coalescence occurs close to the vessel walls where the intensity of mixing is low. In this work, a small emulsification vessel was used to eliminate heterogeneity in drop rupturing and drop coalescence

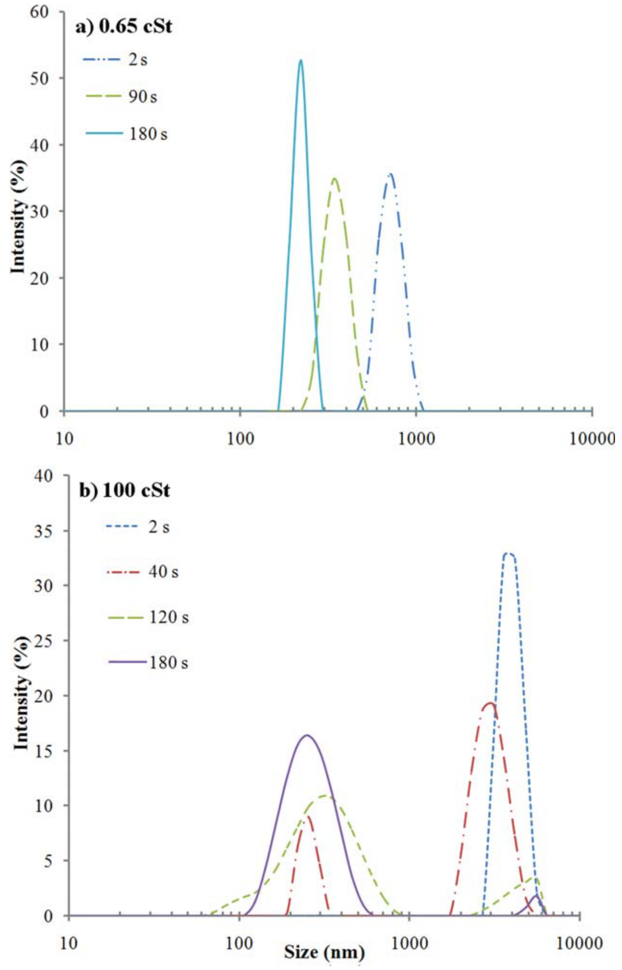

Figure 3. Time evolution of drop-size distribution for (a) 0.65 cSt, and (b) 100 cSt silicon oils.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

caused by long circulation times.[11] It is worth noting that, however, circulation time may not affect the mechanisms by which drop rupturing occurs (i.e., the pattern of evolution of drop-size distribution remains the same), but only influences the time at which the steady-state drop-size distribution is achieved. This pattern was found to be different from that in the inertia subrange in which drop-size distribution remains bimodal or very skewed as mother drops cannot be further broken to the size of satellite droplets within the emulsification time span.

Conclusion

While the existing theory points to a decreasing trend in drop size with viscosity, as well as an occurrence of a minimum in the lower range of viscosity ratio, the experimental data available in the literature either have focused on the higher range of viscosity ratio or have not elucidated on such a trend. In this communication, the effects of viscosity of the dispersed phase on the size of drops formed by emulsification via sonication were investigated. The experimental results show a significant reduction in the size of drop with increasing viscosity of the dispersed phase till the midrange viscosities, followed by a sharp increase at the higher viscosities. It is suggested that the theory developed for viscous drop rupturing can be applied to nanodrop formation via sonication. Drop rupturing mechanism appeared to change with viscosity ratio. Drops underwent stretching at low viscosity, but erosion at high-viscosity ranges.

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