Suppression of Coalescence in Surfactant Stabilized Emulsions by Shear Flow

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A study of the shear flow-induced coalescence in a surfactant stabilized, neutrally buoyant emulsion is presented. Evolving drop size distributions are obtained by image analysis. The shear induced coalescence is well described by a population balance model with the coalescence rate taken to be proportional to the Smoluchowski coalescence rate. The coalescence efficiency (ratio of the actual rate to the Smoluchowski rate) is extracted from the experimental data and is found to be independent of drop size. Both theory and experiment show a reduction in the coalescence rate with increasing shear rate. The effect suggests a simple means of stabilizing suspensions during storage.

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Coalescence of drops in sheared emulsions (liquid-liquid dispersions) is of considerable importance in the manufacture of several food and cosmetic products, paints, and polymer blends. Simultaneous coalescence and breakage of drops during processing determines the final drop size distribution which may have a significant impact on product properties [1,2]. Besides its practical significance, understanding of coalescence kinetics provides an input to theoretical descriptions of aggregation processes which have been widely studied [3]. Most emulsion systems contain surfactants (surface active molecules) which stabilize the thin films between colliding drops and thus reduce the extent of coalescence. The focus of this Letter is flow-induced coalescence in such systems; a simple shear flow is used with a uniform shear rate that is low enough to preclude drop breakup, and the density of the dispersed phase is matched with that of the continuous phase to minimize gravity induced creaming.

The classical theory of Smoluchowski [4] gives the coalescence rate for drops of different sizes in shear flow as

$$C_s(v, v') = \frac{\gamma}{\pi}[(v)^{1/3} + (v')^{1/3}]^3 n(v)n(v'), \quad (1)$$

where $C_s(v, v')$ is the coalescence rate between drops of volume v and v', γ is the shear rate, and $n(v)$ is the number density of drops of volume v. Smoluchowski's [4] theory is based on the assumption of instant coalescence upon collision of two drops and no hydrodynamic interaction between drops so that drop trajectories are taken to coincide with flow streamlines.

Subsequent studies have considered the various complexities that arise from the binary collision of drops in a sheared emulsion, such as hydrodynamic interactions, flow within the colliding drops, drop deformation during collision and thinning of the film of continuous phase between the drops, the interfacial mobility of the liquid-liquid interface, and charge effects [5–8]. Inclusion of such effects leads to a reduction of the coalescence rate compared to the predictions of Smoluchowski's [4] theory. Results of analysis and experiments are commonly expressed in terms of the coalescence efficiency (ε) which is the ratio of the actual coalescence rate to that predicted by Smoluchowski's [4] result. The actual coalescence rate is then

$$C(v, v') = \varepsilon C_s(v, v'), \quad (2)$$

where the efficiency, in general, depends on the shear rate, the sizes of the colliding droplets, and the properties of the emulsion.

Experimental validation of the theories for coalescence in sheared emulsions is sparse. Vinckier *et al.* [9] studied shear induced coalescence in a polymer blend emulsified at a high shear rate and reported the variation of volume average drop diameter with time. Evidence of the slowing of the coalescence process with increasing shear rate can be extracted from the data presented; however, this is based on average drop size measurements. Mishra *et al.* [10] subjected an emulsion of pentadecane in salinated (using NaCl) water to Couette flow and measured the evolving drop size distribution using Laser Doppler anemometry. Their results for variation of the average drop diameter with time follow the predictions of Zeichner and Schowalter [5] and Feke and Schowalter [6] for hard spheres subjected to shear flows. Here the coalescence rate increases with the shear rate.

Mousa and van de Ven [11] sheared a surfactant stabilized emulsion between two circular plates. They back-calculated the coalescence efficiency using a population balance analysis applied to experimental measurements of the average diameter from light transmittance through the emulsion sample. The following dependence of the coalescence efficiency on drop sizes was assumed:

$$\varepsilon = \alpha_0[4q/(1 + q^2)]^5, \qquad v, v' < v_m, \quad (3)$$

where $q = (v/v')^{1/3}$ is the ratio of the diameter of the colliding drops, and v_m is the maximum volume of drops that can coalesce with other drops. While the prefactor (α_0) was found to decrease with increasing shear rates, the overall effect of shearing was to increase the coalescence rate. Again, the results are based on measurements of average diameter. The shear rate is also not uniform in the system.

The experimental emulsion system used in this study comprises 1% (by volume) chlorobenzene (analytical grade, Glaxo Chemicals, India) dispersed in a mixture of glycerol (LR grade, Merck, India), double distilled water, and sodium chloride (Loba Chemie, India), using TWEEN-80 (spectroscopic grade, SD Fine Chemicals, India) as the surfactant. The sodium chloride masks the ionic impurities and suppresses the electric double layer. The continuous phase and dispersed phase densities were matched to within ± 0.005 g/cm^3 to minimize buoyancy driven motions. The continuous phase was equilibrated with pure chlorobenzene prior to the experiment. The viscosities of the continuous and dispersed phases are $\mu_c = 0.69$ mPa s and $\mu_d = 3.3$ mPa s, respectively (measured using an Ostwald capillary viscometer), and the equilibrium interfacial tension is $\sigma = 16.9$ mN/m (measured using a drop volume tensiometer, Kruss DVT-10).

Emulsions were prepared in a 1 ℓ beaker fitted with baffles, using a shrouded turbine impeller. Emulsions were stirred for sufficient time (2.5 h) to ensure a steady state drop size distribution, and also the establishment of equilibrium of the surfactant in the two liquid phases. These emulsions were then sheared in a tangential Couette apparatus with the inner cylinder rotating (Fig. 1). The critical rotational speed of the inner cylinder for transition to the Taylor-Couette flow for the system is 50 rad s^{-1} (48 rpm), and the apparatus is sufficiently long to prevent longitudinal instabilities ($L/(R_1 - R_2) > 20$) [12]. The transient evolution of the drop size distribution was studied by withdrawing samples of the emulsion at specific time intervals and diluting these using a specific amount of the continuous phase containing a large quantity of surfactant, so as to prevent any coalescence during the sampling. The droplet size distributions were obtained by analysis of digital images taken with a CCD camera (SONY 94C) mounted on an optical microscope (Olympus BX60). Various combinations of lenses were used to count drops in the diameter range 2 to 100 μm, using an image analysis package (Image-Pro Plus). A sufficiently large number of drops were counted (>15 000) such that counting more drops gave no change in the distribution. Other checks on the accuracy of the method included measuring the drop size distributions of two samples from the same emulsion batch and taking samples from the top, bottom, and middle ports of the apparatus. The distributions were essentially identical in all cases.

The critical capillary number for breakup of the largest drop due to shear flow in the system (viscosity ratio $\mu_c/\mu_d = 0.2$) is $Ca^* = \gamma^* a_{\max} \mu_c/\sigma = 0.7$ [13,14], so that the critical shear rate is $\gamma^* = 9.4 \times 10^4$ s^{-1} where the radius of the largest drop is obtained from measurements as $a_{\max} = 38$ μm. The reported experiments are carried out at shear rates which are 3 orders of magnitude lower than the critical shear rate, hence, no drop breakup occurs, and drop deformation due to shear flow is negligible. Furthermore, the ratio of the collision rate due to buoyancy induced creaming to that due to shearing for the lowest shear rate studied is 10^{-8}, and the ratio of the collision rate due to Brownian motion to that due to shearing is 4×10^{-3}.

The normalized (with respect to the initial volume average diameter) volume average diameters are plotted against the time of shearing for different shear rates in Fig. 2. All experiments were repeated at least 4 times and the average values are shown with the error bars indicating the typical standard deviation of the measurements. The slopes of the plots decrease with increasing shear rate, clearly showing the reduction in coalescence rate with shearing. The evolution of the nondimensional volume average diameters with time for the same emulsion in a

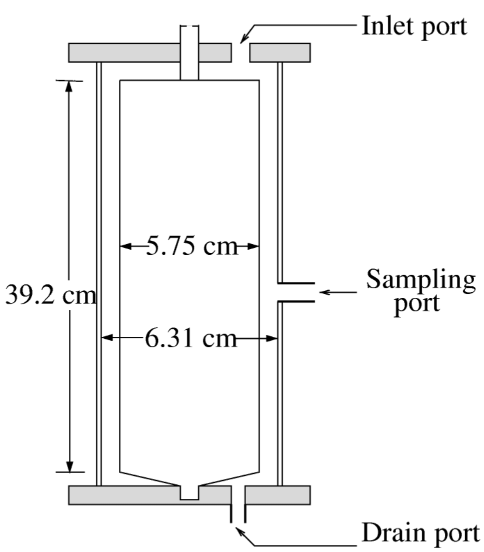

FIG. 1. Schematic diagram of the tangential Couette flow assembly.

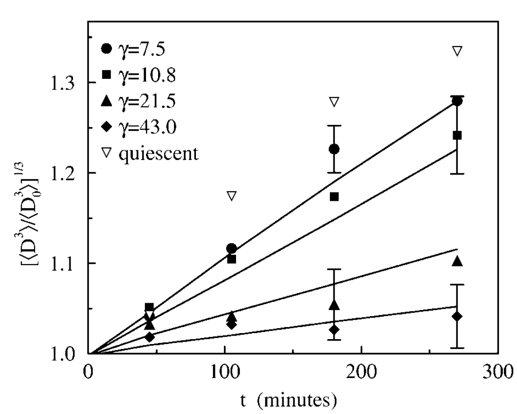

FIG. 2. Variation of the normalized volume average diameter with time for emulsions (1 vol % dispersed phase) subjected to different shear rates (γ). Points are experimental data and solid lines are the corresponding theoretical predictions using a different fitted value of the coalescence efficiency (ε) for each shear rate. The volume average diameter for a standing emulsion is also shown.

quiescent state (Fig. 2) shows that the coalescence rate is the highest in this case. The high coalescence rate results because drops cluster upon contacting each other in gentle collisions generated due to various causes (e.g., slow flows produced by handling, weak Brownian motion, and slow buoyancy driven creaming). Clusters once formed in the quiescent system do not break [15]; consequently, contact times between drops are very large compared to the sheared emulsions and this results in a high probability of coalescence as discussed below [Eq. (6)].

The population balance equation for emulsions, for the case of a coalescence efficiency varying with colliding drop sizes, is given by [16]

$$\frac{\partial n}{\partial \tau} = \frac{1}{2}\int_0^v g(v - v', v')\bar{C}s(v - v', v')n(v - v')n(v')\,dv' - \int_0^\infty g(v, v')\bar{C}s(v, v')n(v)n(v')\,dv', \quad (4)$$

where $\tau = \alpha_0 \gamma t$ is the rescaled time; $\bar{C}s = C_s(v, v')/\gamma$ is the rescaled coalescence rate. In the above, we take $\varepsilon = \alpha_0 g(v, v')$, where $g(v, v')$ accounts for the dependence of the coalescence efficiency on the sizes of the colliding drops. The above equation is applicable only for coalescence resulting from binary collisions, and this assumption is valid for the experimental system in which a low volume fraction of dispersed phase (1%) is used. The initial drop size distribution, obtained experimentally for each case, was taken as the initial condition, and the evolution of the drop size distribution with rescaled time was computed using a fourth order Runge-Kutta algorithm with step size correction. The size dependence of the coalescence efficiency was taken to be

$$g(v, v') = \left[\frac{4q}{(1 + q)^2}\right]^C \{1 + [1 - (v/v_c)^{1/3}]^2\}^{-m} \times \{1 + [1 - (v'/v_c)^{1/3}]^2\}^{-m}, \quad (5)$$

where v_c is a critical drop volume at which the efficiency is maximum, and C and m are constants. This is a generalization of the expression used by Mousa and van de Ven [11] [Eq. (3)]. The coalescence efficiency prefactor (α_0) for a given shear rate (γ) was calculated by finding the rescaled time (τ) at which the least square error between the computed distribution and experimental distribution was minimum for assumed values of the parameters C, m, and v_c. The volume fraction density, defined as $D^3 f(D)$, where $f(D)$ is the number density of drops of diameter D, was used in the computation of the least square error. Carrying out an exhaustive search minimization of error in the ranges $C \in [-4.0, 4.0]$ in steps of 0.5, $m \in [-1.0, 2.5]$ in steps of 0.5, and $v_c^{1/3} \in [2.41, 65.29]$ μm in steps of 3.90 μm, the best fit was obtained for $C = 0$ and $m = 0$. This indicates that the coalescence efficiency is independent of the size of the drops, and the only parameter of the model is $\varepsilon = \alpha_0$. Figure 3 shows a comparison between the theoretically predicted distributions, obtained using the average of the fitted values of ε for a given shear rate, and the experimentally measured distributions. The experimental distributions are averages over four runs and the error bars give the standard deviation. There is good agreement between the theoretical predictions and experimental results.

Figure 4 shows the average coalescence efficiency values expressed as a product with the shear rate ($\varepsilon\gamma$) for different shear rates. The error bars are based on an average over different runs and for different times during a run. The graph also shows the central result of the paper that the coalescence rate (εC_s) decreases sharply with shear rate in the range of shear rates studied. Thus coalescence is suppressed by gentle shearing. A few experiments conducted at a higher rate ($\gamma = 64.5$ s^{-1}) show a slight increase in the coalescence rate. However, the flow is in the Taylor-Couette regime at this shear rate.

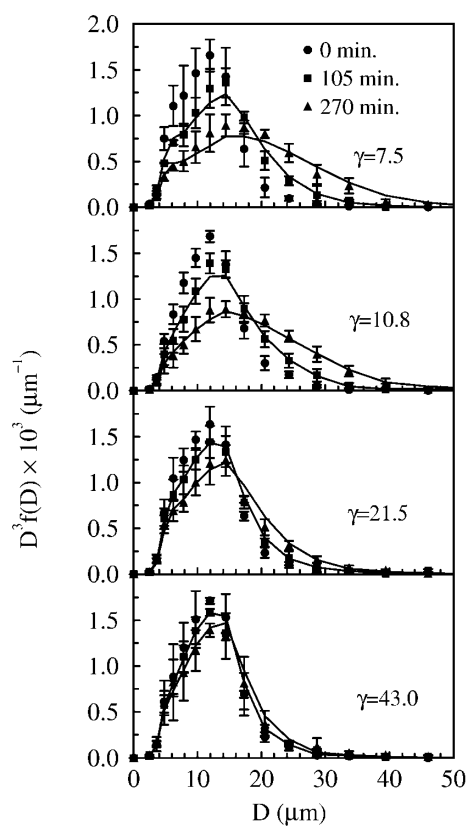

FIG. 3. Points are the experimentally obtained volume fraction density distributions for emulsions (1 vol% dispersed phase) subjected to different shear rates (γ), and error bars show the standard deviation of the measurements. Solid lines are the distributions for 105 and 270 min obtained from theory using fitted values of the coalescence efficiency (ε).

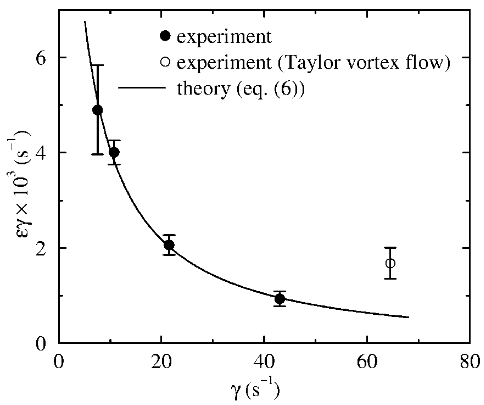

FIG. 4. Product of the fitted values of the coalescence efficiency (ε) with the shear rate (γ) versus the shear rate (γ).

The above result can be explained on the basis of the processes controlling the coalescence between colliding drops. The drops experience mutual hydrodynamic forces when they are far apart; when they are closer, lubrication forces in the liquid film separating them dominate and in this stage the drops may flatten due to the applied forces [7]. Both far-field hydrodynamic interactions and film drainage are dependent on the sizes of the colliding drops and the applied shear rate [8]. In the absence of surfactant, if the film thins to a sufficient extent during the collision, it breaks resulting in coalescence. Surfactants, however, greatly stabilize such thin films, sharply reducing the coalescence efficiency [17]. In addition, experiments of coalescence of drops with a flat interface show a log-normal distribution of film breakage times [18,19]. It is this stochastic process that appears to dominate in our experiments and, as a consequence, the coalescence efficiency is independent of drop sizes. The time of contact during a collision reduces with shear rate and this produces a faster than linear decrease in the probability of film breakage and, consequently, the coalescence rate decreases with shear rate.

Consider a simple model to describe this process. Taking the distribution of the film breakage time (t_b) for a pair of drops in contact with each other to be log-normal [$P(\ln t_b)$], and the drop-drop contact time to be $1/\gamma$ [7], the probability of coalescence is

$$\varepsilon = \int_0^{\ln(1/\gamma)} P(\ln t_b)\, d\ln t_b = \frac{1}{2}\,\mathrm{erfc}\left\{\frac{\mu_b + \ln\gamma}{\sqrt{2}\,\sigma_b}\right\}, \quad (6)$$

where $\mu_b = 4.35$ and $\sigma_b = 1.99$ are the mean and standard deviation of the distribution, which were obtained by fitting to the data in Fig. 4. Predictions of Eq. (6), shown as a solid line in Fig. 4, are in very good agreement with experimental data. The mean film breakage time obtained from the fitted parameters is $e^{\mu_b} = 77.6$ s indicating that the film between colliding drops is highly stable, as proposed. The model of Chesters [7] which does not account for the stochastic film breakage process predicts an efficiency that is 2 orders of magnitude higher than that obtained above.

This Letter demonstrates a simple experimental method of obtaining the coalescence efficiency in sheared, surfactant stabilized emulsions. The method is particularly suited for such systems considering that fewer than one in 10^3 collisions result in coalescence, and that the process is stochastic. The results show a significant *decrease* in the coalescence rate by gentle shearing for the system studied. The model presented indicates that the observed effect of suppression of coalescence by shearing is not an isolated case for the system studied but may be common in surfactant stabilized emulsions. The results have implications for practical applications involving the stabilization of emulsions during prolonged storage.

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