Coalescence in a Surfactant-less Emulsion under Simple Shear Flow

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Shear-induced coalescence is investigated in a neutrally buoyant, surfactant-less oil-in-water emulsion containing an electrolyte. Emulsion drops are large enough for Brownian motion–induced coalescence to be negligible. The emulsion is subjected to a simple shear flow in a tangential Couette apparatus with a rotating inner cylinder, and the evolution of the drop size distribution with time is obtained using optical microscopy and image analysis. The effect of varying the shear rate and the dispersed phase holdup is studied. The evolving drop size distributions become bimodal with increasing coalescence and are not found to be self-similar. A population balance model with an empirical coalescence efficiency (ratio of the actual coalescence rate to the Smoluchowski rate) function containing four fitting parameters describes the time evolution of the experimental drop size distribution reasonably well. The coalescence rate, inferred qualitatively from the measured drop size distributions at different times as well as obtained from the fitted coalescence efficiency, is found to increase with increasing shear rate and dispersed-phase holdup. The coalescence efficiency also increases with holdup, although it decreases with increasing shear rates. The fitted coalescence efficiency results indicate the existence of a critical drop diameter of 12 μm at which the coalescence efficiency is maximum. The computed magnitude of the coalescence efficiency is of the order of 10^{-2} for all cases and is about 100-fold larger than that obtained earlier for surfactant-stabilized emulsions. The results indicate that coalescence in surfactant-less emulsions is qualitatively different from that in emulsions containing surfactant. The experimental findings are discussed in the light of recent theories and experimental work in this field.
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Introduction

Emulsions are mixtures of immiscible fluids in which one of the fluids is present as fine drops (the dispersed phase) inside the other (the continuous phase). Such mixtures are encountered in various industrial processes and products. Important industrial processes involving emulsions include solvent extraction, melt blending of polymers, and secondary oil recovery to cite but a few.[1-3] Products in the form of emulsions include paints, cosmetics, food products, and cutting fluids for machinery. The efficiency of the processes and the properties of the products depend on the size distribution of the drops of the dispersed phase. The drop size distribution in turn is determined by a combination of the processes of drop breakup and coalescence. The focus of the present work is coalescence of drops that, in general, may be the result of Brownian motion (drop diameters < 1 μm), gravity-induced creaming or sedimentation (specific gravity of the continuous phase signifi-

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cantly different from that of the dispersed phase), and shear flow. In this study, we investigate shear-induced coalescence in an emulsion containing no surfactant. The drops are large enough (>2 μm) to eliminate Brownian motion, and the emulsion is neutrally buoyant to prevent creaming or sedimentation. Furthermore, the shear rate is sufficiently low, such that shear-induced drop breakup is negligible. An electrolyte (sodium chloride) is added to screen the electric double layer. Thus, we consider a system with no droplet breakup and in which coalescence occurs only as a result of shearing.

The simplest theory for predicting the coalescence rate for shear-induced coalescence is that proposed by Smoluchowski.[4] Based on the assumption that all drops move along streamlines and every collision results in coalescence, the theory yields the coalescence rate of drops of volume v and v' to be

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

Here γ is the shear rate and $n(v)$ is the number density of drops having volumes between v and $(v + dv)$. However, in practical systems not all collisions result in coalescence as a consequence of the hydrodynamic interactions between the colliding pair of drops, interactions of the pair with neighboring drops, and the stability of the liquid film between the colliding drops. The factors contributing to the reduction in coalescence are often lumped into a term known as the *coalescence efficiency* (ε) or the *stability ratio* ($W = 1/\varepsilon$). The coalescence efficiency is defined as the ratio of the actual coalescence rate (C) to the Smoluchowski rate[4] (C_S) and is expressed as

$$\varepsilon = \frac{C(v, v')}{C_S(v, v')} \tag{2}$$

A detailed description of the process of coalescence between drops in simple shear flow, along with a review of some of the recent literature in the field may be found in Nandi et al.,[5,6] Burkhart et al.,[7] and Leal.[8] Other important effects related to flow-induced coalescing emulsions (but not relevant to the present work) such as wall migration of drops and layered microstructuring of droplets arising from shear (shear rate differences between the wall and the bulk of the sheared fluid are large) have been addressed by Hudson[9] and Pathak et al.[10]

Here we describe some of the important theoretical and experimental work relevant to the shear-induced coalescence in emulsions and blends. Mousa and van de Ven[11] reported experimental results on shear-induced coalescence in surfactant-stabilized emulsions. An emulsion of silicone oil in water was sheared between rotating, parallel circular plates. The evolution of the average drop diameter with time was measured by the extinction of light passing through the sample. For the case when surfactants were not used to stabilize the emulsion, the coalescence efficiency first decreased with increasing shear rate and then showed a sharp increase beyond a critical shear rate. They proposed an empirical function to describe the dependency of the coalescence efficiency on the size of the colliding drops, of the following form:

$$\varepsilon = \begin{cases} \alpha_0[4q/(1+q)^2]^5 & \text{if } v \text{ and } v' \le v_c \\ 0 & \text{if } v \text{ and } v' > v_c \end{cases} \tag{3}$$

In the above equation, $q = (v/v')^{1/3}$ is the ratio of the diameters of the colliding drops, and v_C is the volume of the largest drop that can coalesce with other drops.

Vinckier et al.[12] studied shear-induced coalescence in a polymer blend. A high shear rate was applied to produce the emulsion. The shear rate was then stepped down to coalesce the drops. The increase of the volume-averaged diameter with time matched the predictions of the model of Chesters[13] for partially mobile interfaces. Increasing the dispersed-phase holdup resulted in a higher efficiency of coalescence. This was explained by hypothesizing that the disturbance arising from a coalescence event between two drops triggers coalescence of nearby pairs of drops. Increased holdups result in an increase in the number of proximate pairs and thus in an increased coalescence efficiency. This mechanism is supported by the work of Janssen,[14] which showed that shearing of emulsions tends to form strings of drops, each in contact with a pair of neighbors. In such a situation, a single coalescence event would result in coalescence of other drops along the string resulting from propagation of the disturbance caused by coalescence.

Mishra et al.[15] studied shear-induced coalescence of a surfactant-less emulsion of pentadecane drops suspended in an aqueous solution of sodium chloride. The evolving drop size was measured using laser Doppler anemometry. The experimentally observed coalescence efficiency was close to the hard sphere predictions of Zeichner and Schowalter[16] and Feke and Schowalter.[17] The evolving drop size distributions were also self-similar, indicating that the coalescence efficiency was independent of drop size. The coalescence rate increased with shear rate and electrolyte concentration.

In a study of shear-induced coalescence in neutrally buoyant emulsions stabilized by a surfactant, we found that the coalescence rate decreases with shear rate.[5] In this case it was shown that the contact time required for coalescence of a pair of drops is large compared to the drainage time. Because the contact time is inversely related to the shear rate, an increase in the shear rate yields a smaller average contact time and thus a smaller coalescence frequency. The coalescence efficiency decreased with increasing holdup for all the shear rates studied. In the case of dilute emulsions (1% v/v dispersed phase) the coalescence efficiency was found to be independent of drop size and well described by a simple model. At higher volume fractions a modified form of Eq. 3 was found to describe the process.[6] The same expression is used in the analysis of data in the present work (Eq. 5) and the results for the two cases are compared.

Lyu et al.[18,19] sheared a polymer blend made of polystyrene and high-density polyethylene melt in the gap of a cone-and-plate device. A polystyrene–polyethylene block copolymer was used as the surfactant to stabilize the blend. The authors showed that suppression of coalescence is achieved as a result of steric repulsion between the block copolymer molecules adsorbed at the interfaces. Hudson et al.[20] reported the effect of temperature, capillary number, copolymer molecular weight, and concentration on the coalescence of a polymer blend stabilized by a block copolymer surfactant. The work identifies the importance of film deformation and Marangoni stresses in the various concentration windows of the surfactant. Similar to the results of Lyu et al.,[19] the effect of surfactant was found to saturate at low surfactant concentrations.

Yeung et al.[21] studied coalescence of high-viscosity bitumen drops in saline water (containing NaCl, $NaHCO_3$, and Na_2SO_4). The drops coalesced only when the collisions were oblique (off-centric). This observation was explained on the basis of a nonuniform charge distribution on the drop surface. When drop–drop collisions are off-centric, the drops slide past one another as the film between the drops thins. The film breaks only when two points on either side of the film, where the repulsive electrostatic charges are low, happen to cross each other.

A few experimental studies have focused on the coalescence of a pair of drops in a well-defined flow. Yang et al.[22] considered a pair of drops in a four-roll mill on two streamlines offset by a fixed distance in a system without surfactant. They found the coalescence process to be nonstochastic and the existence of a critical capillary number above which no coalescence occurs. The critical capillary number decreases with increasing offset and beyond an offset of about $0.06D$ it becomes zero. Thus, for a given system and a fixed shear rate no coalescence is possible between drops larger than a critical size. This is reflected in the model of Mousa and van de Ven[11] (Eq. 3).

The objective of this work is to study experimentally the effect of shear rate and the dispersed-phase holdup on the coalescence kinetics of a surfactant-less emulsion under carefully controlled conditions. A neutrally buoyant emulsion was used to suppress gravity-driven motion of the drops. Care was taken to ensure removal of the surface-active impurities from the liquids that made up the emulsion. Sodium chloride was added to exclude the effect of the electric double layer. Drop size distributions were measured to study the effect of the size of the colliding drops on the efficiency of coalescence. A population balance model with an empirical expression for the coalescence efficiency was used to analyze the data. The back-calculated values of the various parameters in the model were used to infer the importance of different processes in the coalescence of surfactant-less drops in simple shear flow.

Experimental

A mixture of chlorobenzene, tetrachloroethylene, silicone oil, and liquid paraffin oil was dispersed in a mixture of glycerol, water, and sodium chloride to form an emulsion. All chemicals with the exception of the silicone oils (Reliance Silicones, Navi Mumbai, India) and the double-distilled water (distilled in the laboratory) were obtained from S. D. Fine Chemicals (Mumbai, India) and were of high purity (spectroscopic grade). The silicone and paraffin oils are nonreactive with each other and mutually soluble. The advantage of using such an oil mixture is that the ratio of the low-viscosity silicone (20 cP) oil to the high-viscosity (10,000 cP) oil may be altered to vary the viscosity of the dispersed phase. The oils were individually purified of surface-active reagents by stirring them in contact with anhydrous silica gel in a glass beaker for 24 h. The amount of silica gel used was around 10 g per 100 mL of each of the chemicals. The pure liquid was decanted after the silica gel particles settled at the bottom of the beaker. This was then filtered twice through a 0.22 μm membrane filter paper (Sartorius) to remove any suspended particles. The two phases were thereafter tested for the presence of any surface-active impurity, as described below.

A 70-mL aliquot of the dispersed phase was slowly poured into a 100-mL glass beaker containing 30 mL of a mixture of glycerol, water (1:1 v/v), and 0.2 g of NaCl to prevent mixing of the two liquids and to produce two separate fluid layers. The aqueous phase was made heavier than the oil phase by adding a small excess of glycerol, so that it would remain at the bottom. The beaker containing the two layers, constituting the dispersed and continuous phases, was placed on a weighing balance. A du Nuoy ring, tied to a clean, washed, and dried thin cotton thread, was carefully lowered into the upper (oil) phase using a hand-operated wooden pulley. The weighing balance was set to zero when the ring was <1 mm above the interface. Thereafter, the ring was lowered carefully until it started to deform the interfacial film. The value registered by the balance increased as a result of the increasing deformation of the interfacial film. Beyond a point, it remained almost constant until the film broke. The maximum value registered on the weighing balance corresponded to the force arising from the interfacial tension (46 mN/m) and the weight of the film. The beaker and its contents were kept standing for 1 h and the procedure was repeated. This value was found to be 1% less than that noted before. The chemicals, used without treating with silica gel, gave a reduction of 9% of the original value. This indicated that our cleaning procedure removed most of the surface-active impurities. The same experiment was repeated with more (60 mL) of the aqueous phase, and less (40 mL) of the dispersed phase, and the difference between the reading on the weighing balance and the previous reading was again found to be $<1\%$. The addition of 0.08 g of the oil containing 1% of Tween 80 by weight reduced the reading on the balance by $>20\%$ of the original value. The above tests implied the near absence of surface-active impurities.

The emulsion was made using a sonifier (Branson 450). The continuous phase contained 0.75 L of glycerol and 30 g of NaCl in 1 L water (double-distilled water made in the laboratory). The dispersed phase consisted of 0.307 g of low-viscosity silicone oil (20 cP), 0.06042 g of high viscosity silicone oil (10,000 cP), 0.6246 g of liquid paraffin, and 1.1439 g of chlorobenzene, mixed with every 1 g of tetrachloroethylene. The specific gravity of the dispersed phase was equal to that of the continuous phase (1.119 ± 0.002). The viscosity ratio of the dispersed-phase viscosity (3.2 cP) to the continuous-phase viscosity (5.1 cP) was 0.63. The sonifier settings were manipulated by trial and error to yield emulsions that did not have drops with diameters < 2 μm. This was done to prevent the occurrence of Brownian motion–induced coalescence. The temperature during formation of the emulsion in the sonifier was maintained at the ambient temperature (24 ± 1°C) by circulating water around the container holding the emulsion.

The initial drop size distributions for the three holdups are plotted in Figure 1. All drop size distributions are plotted on a volume fraction basis with $(\pi D^3/6) f(D) dD$ being the volume fraction of drops in the size range $(D, D + dD)$. The distributions are normalized by the total volume fractions (ϕ) for comparison. Error bars indicate the standard deviations over all six data sets studied. The plot shows that the distributions for 1 and 2% are very similar, but the 4% case is slightly different. The reason for this is that the control over the drop size

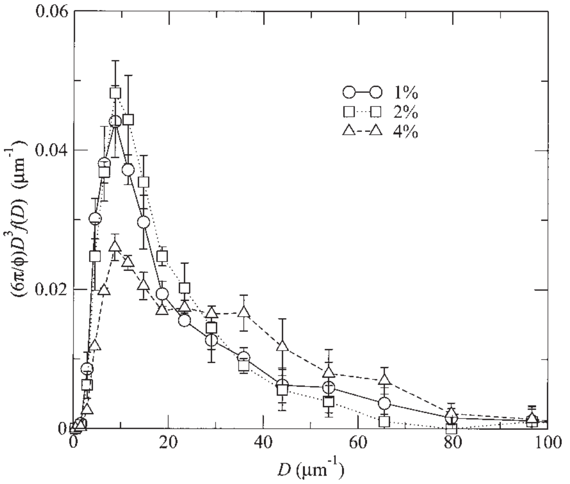

Figure 1. Initial volume density distributions for three holdups.

distribution by changing sonification parameters is not easily achieved.

Experiments to study the kinetics of shear-induced coalescence were carried out at three dispersed phase holdups and two shear rates for each case. The emulsion was sheared in the gap between concentric cylinders (Taylor–Couette flow). The diameter of the inner cylinder was 5.75 cm and the gap width was 0.28 cm. Details of the apparatus are reported in Nandi et al.[5,6] The droplet size distribution was measured by withdrawing a small quantity of the emulsion from the shear cell and diluting it to an approximate dispersed-phase holdup of 0.3–0.5%. The diluent had the same composition as that of the continuous phase but with some added surfactant (Tween 80, 0.02% by weight). The lowering of the dispersed phase holdup as well as the presence of the surfactant prevented further coalescence. The diluting solution containing water and the surfactant was equilibrated with the dispersed oil phase for a day before the experiment. This prevented dissolution of the oil drops into the diluting fluid. Thereafter, drops of the diluted emulsion were placed on a glass slip, covered with a coverslip, and photographed under an optical microscope. Various combinations of objectives were used to measure a wide range of drop sizes (1–500 μm). The drop sizes were measured from the pictures using image analysis software (Image-Pro plus). A minimum of 14,000 drops was measured for each sample to obtain statistically correct drop size distributions.

The maximum drop diameter encountered in all the runs was <500 μm. For the maximum shear rate (~ 21.5 s^{-1}) the capillary number (~ 0.001) corresponding to the largest drop (~ 500 μm) is two orders of magnitude smaller than the critical capillary number (for simple shear flow) needed to break the drops (~ 0.8). The critical capillary number corresponding to the viscosity ratio (~ 0.63) of the emulsion system is obtained from the Grace curve.[14] This confirms that drop breakup is negligible for all the experiments.

Theoretical Analysis

The time evolution of the drop size distribution of a purely coalescing emulsion system is given by the population balance equation

$$\frac{\partial n}{\partial t} = \frac{1}{2}\int_0^v \varepsilon C_S(v, v - v')dv' - \int_0^\infty \varepsilon C_S(v, v')dv \quad (4)$$

where $n(v)$ is the number density of drops of volume between v and $(v + dv)$ and $C_S(v, v')$ is the Smoluchowski coalescence rate given by Eq. 1 for drops of size v and v'. An assumption in the above equation is that only pairwise collisions are considered. If all collisions result in coalescence, $\varepsilon = 1$. However, as will be seen below from the experimental results, $\varepsilon \ll 1$ and depends on the size of the colliding drops, the shear rate, and the dispersed-phase holdup.

Here, we assume the same form for the coalescence efficiency that was used in the previous work for studying the coalescence in surfactant-stabilized emulsions.[6] The expression is a generalization of the form assumed by Mousa and van de Ven[11] and is given by

$$\varepsilon = \alpha_0\left[\frac{4q}{(1+q)^2}\right]^C\left[1 + \left(1 - \frac{D_i}{D_C}\right)^2\right]^{-m} \times \left[1 + \left(1 - \frac{D_j}{D_C}\right)^2\right]^{-m} \quad (5)$$

In the above equation, D_i and D_j are the diameters of the colliding drops. The first two terms on the right-hand side of the expression are the same as those reported by Mousa and van de Ven.[11] The second term captures the dependency of the coalescence efficiency on the diameter ratio ($q = D_i/D_j$) of the colliding drops. The value of the exponent C indicates the strength of the dependency of the coalescence efficiency on the size ratio. The last two terms account for the fact that there may be a critical drop diameter (D_C) at which the coalescence efficiency is maximum or minimum, depending on the value of m. For $m > 0$, it is clear that $[1 + (1 - D/D_C)]^{-m} \leq 1$, and attains its maximum value at $D = D_C$. Thus, in this case the maximum in the coalescence efficiency is achieved when $D_i = D_j = D_C$ (Eq. 5). For a given chemical system the prefactor α_0 is an overall coalescence efficiency term, which is assumed to depend only on the shear rate and holdup. The parameters of the model (α_0, C, m, D_C) are obtained by a regression procedure applied to the experimental drop size distributions as described below.

Equation 4 was discretized after substituting the Smoluchowski collision rate (Eq. 1) and nondimensionalized to

$$\frac{\partial \bar{N}_i}{\partial \bar{t}} = \frac{1}{2}\sum_{j=1}^{i-1} \bar{\varepsilon}[(\bar{v}_{i-j})^{1/3} + (\bar{v}'_j)^{1/3}]^3 \bar{N}_{i-j}\bar{N}_j - \sum_{j=1}^{\infty} \bar{\varepsilon}[(\bar{v}_i)^{1/3} + (\bar{v}'_j)^{1/3}]^3 \bar{N}_i\bar{N}_j \quad (6)$$

where $\bar{N}_i$ is the nondimensionalized number concentration ($\bar{N}_i = N_i/N_{T0}$) of drops having volume $\bar{v}_i$, N_{T0} is the total number concentration of drops at the beginning of the experiment ($t = 0$), and N_i is the actual number concentration of drops with volume v_i. $\bar{v}_i = v_i/v_0$ is the volume of a drop nondimensionalized by the number-average volume at the beginning of the

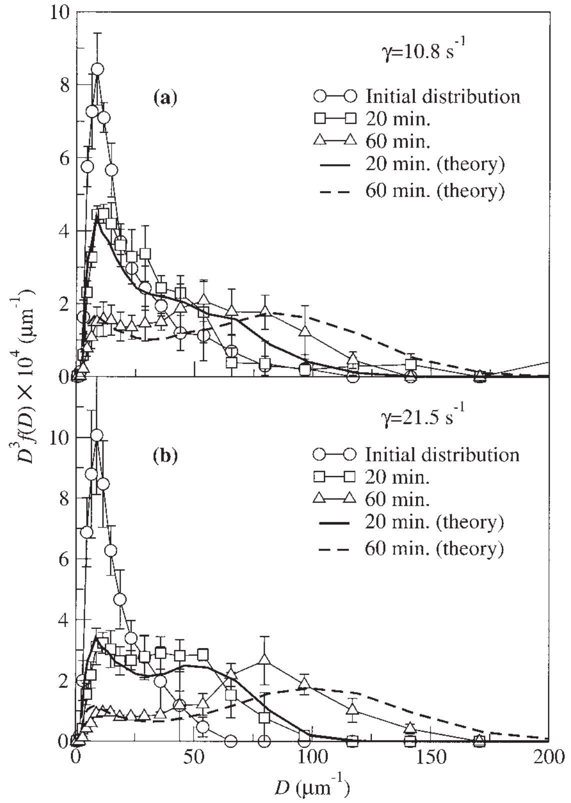

Figure 2. Volume density distributions for two shear rates at 1% holdup.

Symbols denote experimental measurements and thick lines are the predicted distributions using the parameters of the coalescence efficiency function given in Table 1 as indicated in the legend.

experiment (v_0), $\bar{t} = \alpha_0 t \gamma \phi / \pi$ is the nondimensionalized time, and $\bar{\varepsilon} = \varepsilon / \alpha_0$.

The nondimensionalized population balance equation (Eq. 6) was solved using the experimentally measured size distribution of the starting sample ($t = 0$) as the initial condition. Model parameters were optimized using an exhaustive search algorithm to match the computed distribution to the measured one, at each time. Details are given in an earlier paper.[6]

Results and Discussion

The measured drop size distributions at different times for varying shear rates and dispersed-phase holdups are shown in Figures 2–4. The symbols are experimentally obtained values, averaged over a minimum of three runs, with error bars showing the standard deviation of the experimental data. The drop size distribution broadens with time, whereas the value of the peak decreases. For the lowest shear rate (10.8 s^{-1}) and the lowest holdup (1%) (Figure 2a), a shoulder is seen to develop in the distribution after 20 min and after 60 min it evolves into a second peak. Doubling the shear rate (Figure 2b) shows formation of the second peak in about 20 min. The magnitude of the primary peak for both cases diminishes with time, but remains at the same value of the drop diameter. The secondary peak broadens and moves to higher drop diameters. The peak broadening is faster at the higher shear rate, indicating the rate of coalescence is higher at higher shear rates. The time variation of the drop size distribution for a 2% holdup of dispersed phase at two different shear rates is broadly similar to that obtained for 1% (Figures 3a and 3b). That is, the primary peak height reduces and the second peak broadens and shifts to higher diameters with time. The process is much faster at 2% holdup compared to 1% holdup and the distribution is evolved to a similar extent but at a shorter time. At a dispersed-phase holdup of 4% (Figure 4a), the evolution of the drop size distribution is qualitatively similar to the 1 and 2% holdup cases only for the lower shear rate (10.8 s^{-1}). At the higher shear rate (21.5 s^{-1}, Figure 4b), a second peak is obtained in the drop size distribution within 2 min. However, this peak, unlike that in the previous cases, does not broaden as it moves to higher diameters. This indicates a change in the kinetics of the coalescence process, which is quantitatively elucidated below.

In all cases in which bimodal distributions are obtained the minimum in the distribution between the two peaks occurs close to a drop diameter of $D = 20$ μm. This depletion indicates a maximum in the coalescence rate for drops of size close to 20 μm, independent of shear rate and holdup.

Self-similarity of the evolving drop size distributions was tested using the analysis of Swift and Friedlander.[23] The cumulative oversize number fraction ($1 - N_v/N_T$) was plotted

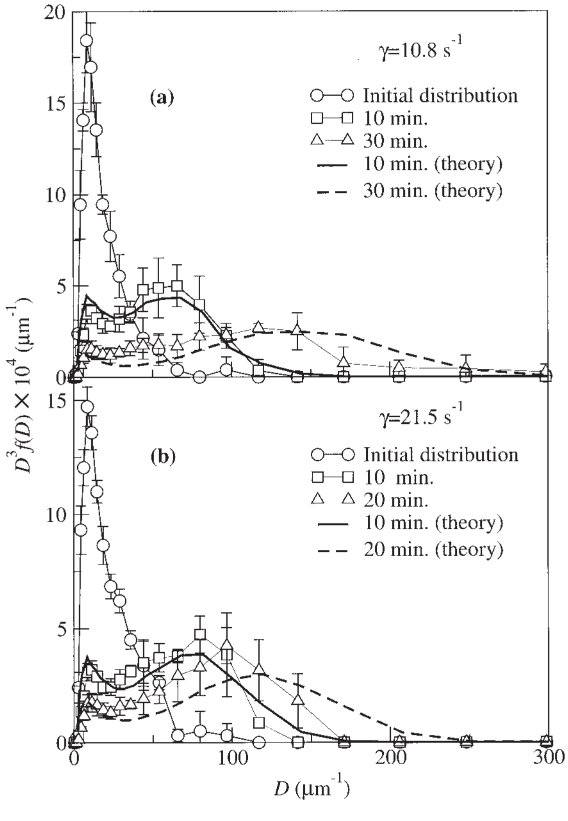

Figure 3. Volume density distributions for two shear rates at 2% holdup.

Symbols denote experimental measurements and thick lines are the predicted distributions using the parameters of the coalescence efficiency function given in Table 1 as indicated in the legend.

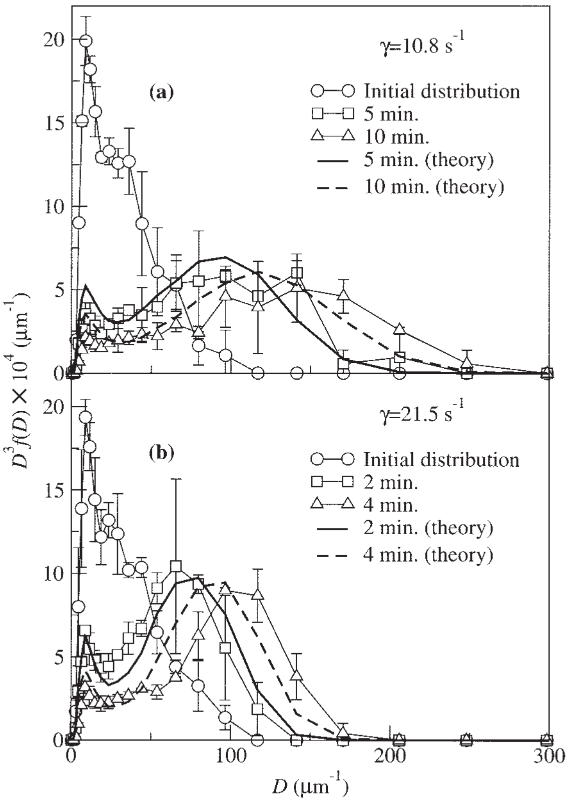

Figure 4. Volume density distributions for two shear rates at 1% holdup.

Symbols denote experimental measurements and thick lines are the predicted distributions using the parameters of the coalescence efficiency function given in Table 1 as indicated in the legend.

against the normalized drop volume ($v_i/\langle v\rangle$) for all the holdups. Here,

$$N_v = \sum_{k=1}^{i} N_k \qquad N_t = \sum_{j=1}^{\infty} N_j$$

and $\langle v\rangle = N_T/\phi$. The plots revealed a lack of self-similarity in the distributions for all the cases. A typical plot for 1% holdup and a shear rate corresponding to 21.5 s^{-1} is shown in Figure 5. The lack of self-similarity indicates that the coalescence efficiency depends on the size of coalescing drops.

The time evolution of the nondimensionalized volume-average diameter is plotted in Figure 6. The symbols are the experimental data and error bars indicate the standard deviation over three runs. The rate of coalescence, which can be inferred from the slope of the curves, decreases with time for all cases. There are two reasons why this occurs. First, larger drops have larger flattened surfaces in the collision zone as a result of lower surface tension forces.[13,20] Chesters[13] showed that this results in an increased time for drainage of the liquid from the continuous-phase film separating the drops. Second, the trajectory calculations of Wang et al.[24] show that smaller drops travel along streamlines that are distorted by the larger ones. Thus, when collisions are off-centric the smaller drops travel around the large drops rather than collide with them. A reduction in the average coalescence rate with time is a consequence of both effects. The experimental results and the above reasoning are also consistent with the experimental results of Mishra et al.,[15] Vinckier et al.,[12] and Hudson et al.[20] Further, unlike a surfactant-stabilized emulsion coalescing in a simple shear

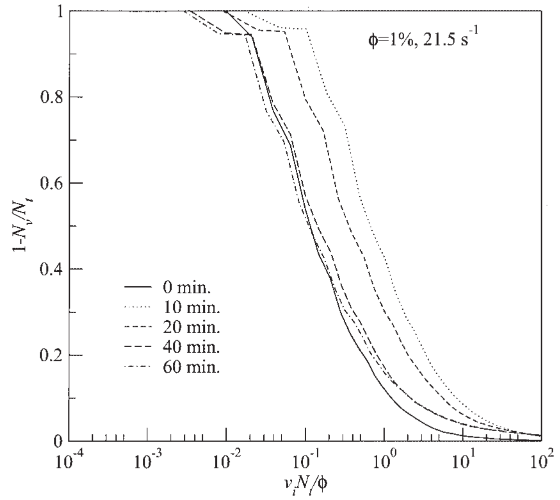

Figure 5. Scaled cumulative distribution for 1% holdup at a shear rate of 10.8 s^{-1}.

The distributions show a lack of self-similarity, indicating a coalescence efficiency that is dependent on the sizes of the drops.

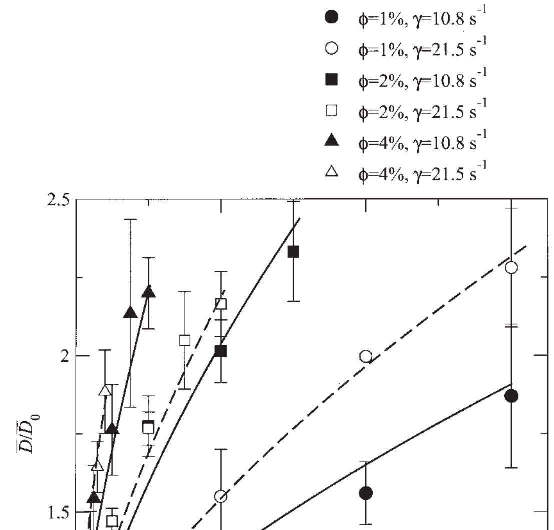

Figure 6. Variation of dimensionless volume average diameter with time for all holdups and shear rates vs. time.

Symbols are the experimental values and lines are the model predictions obtained using the fitted parameters given in Table 1.

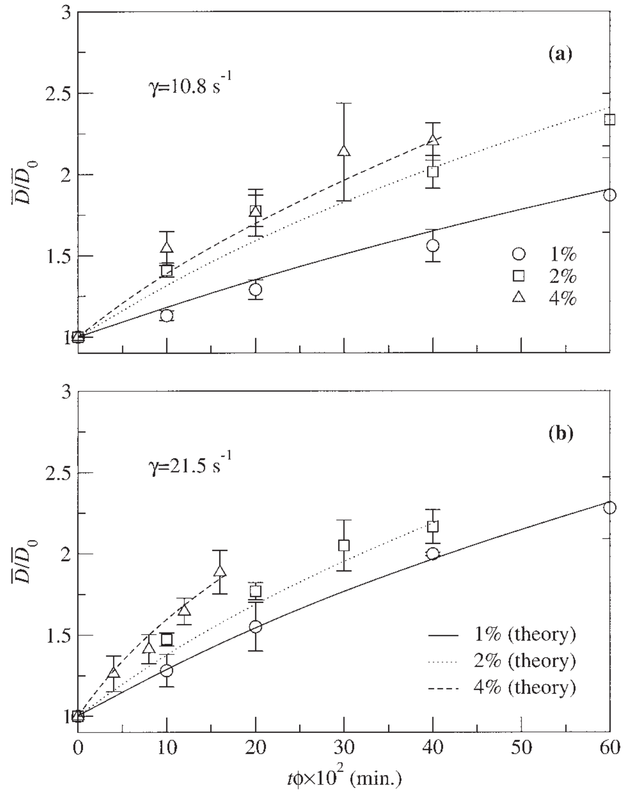

Figure 7. Dimensionless volume average diameters vs. time scaled by the dispersed phase holdup for different shear rates as indicated.

flow,[5,6,18,20,25] the coalescence rate in the present case increases with shear rate (Figure 6). Finally, the results show a very significant increase in the coalescence rate with volume fraction of the dispersed phase. Because the initial drop size distributions for the holdups studied are nearly the same, the increased coalescence rate is essentially attributed to a greater number of drops present per unit volume with increasing holdup.

We now scale the data from Figure 6 with respect to the dispersed-phase holdup (Figures 7a and 7b) and the shear rate (Figures 8a, 8b, and 8c). The scaling is based on the dimensionless population balance equation (Eq. 6) in which the time (t) is made dimensionless by the product of the shear rate and the dispersed phase holdup. Figure 7 shows the variation of the nondimensionalized volume-average diameter ($\bar{D}/\bar{D}_0$) with time scaled by the volume fraction. At the lowest shear rate (Figure 7a), the scaled diameter increases with increasing volume fraction for a fixed value of $t\phi$, which indicates that the average coalescence efficiency increases with volume fraction. For an emulsion stabilized by a surfactant the coalescence efficiency was found to decrease with increasing dispersed-phase holdup.[6] The increase in the coalescence efficiency with holdup is consistent with the results of Vinckier et al.[12] and with the proposed mechanism of enhanced coalescence probability arising from the disturbances generated by coalescence of nearby pairs. The trend of increasing coalescence efficiency with holdup is unchanged upon increasing the shear rate (Figure 7b), although in this case, the differences between the various dispersed-phase holdups are smaller.

Figure 8 shows the variation of the normalized volume-average diameter with time scaled by the shear rate, for different volume holdups. For all cases, the volume-average diameter is lower for the higher shear rate at fixed $t\gamma$, indicating that the average coalescence efficiency decreases with increasing shear rate. This can be explained by the Chesters[13] model for deformable drops in shear flow: As the shear rate increases, the interaction time between drops ($\sim 1/\gamma$) decreases. The diameter of the flattened region between colliding drops also increases with shear rate as a result of increased hydrodynamic forces pressing the drops together, and the drainage of the film separating the drops slows. Both phenomena together contribute to a decrease in the coalescence efficiency as shear rate increases.

The coalescence efficiency function (Eq. 5) was fitted to the evolving size distribution using the procedure detailed earlier. The fitted parameters (α_0, C, m, and D_C) for all the cases are given in Table 1. The lines in the volume density distribution curves (Figures 2–4) are the simulated distributions, using the tabulated values of the parameters. There is reasonable agreement between the predictions and experiments in all cases. The peak positions are well predicted at the intermediate time for all cases. At the final time, the predicted position of the second peak is at slightly higher diameters for the 1 and 2% holdups, whereas it is at lower diameters for the 4% holdup. The minimum in the computed distributions is at about 20 μm for all cases, in agreement with experiments. The predicted variation of the nondimensionalized volume-average diameter with time (lines in Figures 6–8) is also in good agreement with

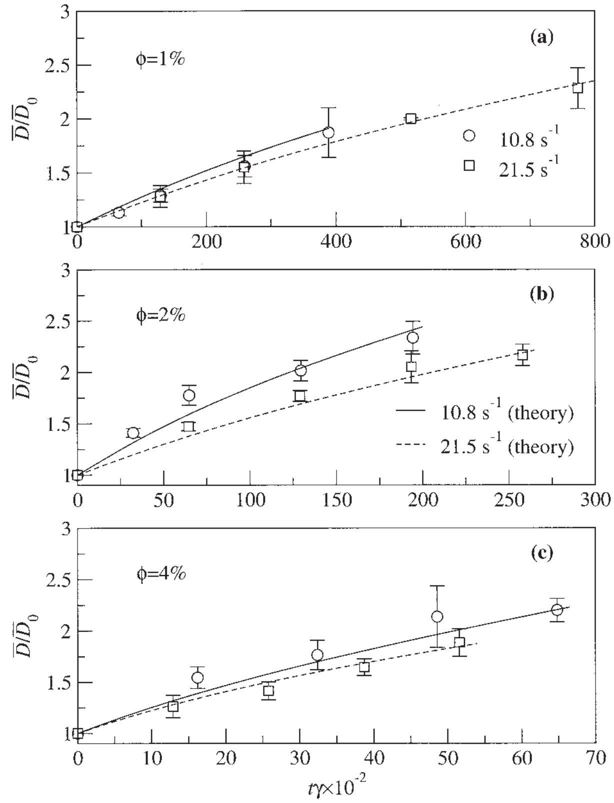

Figure 8. Dimensionless volume average diameters vs. time scaled by the shear rate for different dispersed-phase holdups as indicated.

Table 1. Parameter Values of the Coalescence Efficiency Function (Eq. 5) for Different Shear Rates and Dispersed-Phase Holdups Obtained by Fitting to Measured Drop Size Distributions

ϕ (%)	γ (s^{-1})	α_0	C	m	D_C (μm)
1	10.8	1.4×10^{-2}	0.0	0.25	12.0
1	21.5	9.9×10^{-3}	0.0	0.25	12.0
2	10.8	2.2×10^{-2}	0.0	0.25	12.0
2	21.5	1.5×10^{-2}	0.0	0.25	12.0
4	10.8	3.7×10^{-2}	0.0	0.25	12.0
4	21.5	4.1×10^{-2}	0.0	0.50	12.0

experimental data. The model thus gives a good description of the coalescence process over a wide range of system parameters.

Consider next the values of the fitted parameters given in Table 1. The value of C in all cases is found to be zero, indicating that the size ratio of the colliding drops is not important for determining the coalescence efficiency, unlike the case of emulsions with surfactant. Instead, there exists a critical drop diameter (D_C) at which the coalescence efficiency is highest, given that the exponent m is positive. The value of D_C is the same for all cases studied ($D_C = 12$ μm) and the value of the exponent m is the same ($m = 0.25$) for all cases, except for one (holdup of 4% and shear rate of 20.8 s^{-1}). This implies that the effects of dispersed-phase holdup and shear rate on the efficiency are essentially embodied in the prefactor α_0, and that the functional dependency of the coalescence efficiency on diameters of the coalescing drops is independent of the shear rate and holdup. The latter suggests that the functional dependency of the efficiency on the drop diameters arises from pairwise drop interactions resulting from significant drop deformation; moreover, multidrop interactions, which are important at higher holdups, do not play a significant role in determining the functional dependency on size. The fitted values of the prefactor (α_0) indicate that the coalescence efficiency decreases with shear rate and increases with volume fraction. These results confirm the inferences drawn from the analysis of the variation of the mean diameter with time data (Figures 7 and 8).

The parameter values obtained here differ significantly from those for emulsions containing surfactant analyzed using an efficiency function that is same as the one used in this work. For example, for a surfactant-stabilized emulsion at 1% holdup Nandi et al.[6] obtained $C = 0$ and $m = 0$, indicating that the coalescence efficiency is independent of size of the colliding drops. This is in contrast to the result for the surfactant-less system in which the same dependency of the efficiency on drop diameters was obtained at high and low holdups. The difference between the two cases is because coalescence in the surfactant laden emulsion is dominated by the requirement of large contact times for coalescence, and thus drop sizes, which determine the time of drainage, are not important. At a holdup of 5%, the parameters for the surfactant-laden system were $C = -1.5$, $m = 0.5$, and $D_C = 18.5$ μm. The negative value of C implies that dissimilar sized drops are more likely to coalesce, and the positive value of m indicates that coalescence is favored for drops of diameter 18.5 μm. In contrast, for the present case at 4% holdup, $C = 0$, $m = 0.25$, and $D_C = 12$ μm, indicating that drops of diameter 12 μm are most likely to coalesce.

The coalescence efficiency expressions, plotted vs. the drop diameters for $\phi = 1\%$, $\gamma = 20.5$ s^{-1}, and $\phi = 4\%$, $\gamma = 20.5$ s^{-1} are shown in Figures 9a and 9b, respectively. The two cases differ in the magnitude of the prefactor α_0 and the exponent m (Table 1), and thus the behavior is qualitatively similar. In both cases the coalescence efficiency is the highest when both coalescing drops have diameters of 12 μm. This result implies a low coalescence efficiency for both very large and very small drops. The lower coalescence efficiency for larger drops is qualitatively explained by Chesters[13] as stated above and is consistent with the experimental results of Yang et al.[22] The lower coalescence efficiency for small drops (<12 μm) interacting with small drops has not been reported previously but is also seen for surfactant-stabilized emulsions.[6] Theoretical simulations by Kumar et al.[26] report similar find-

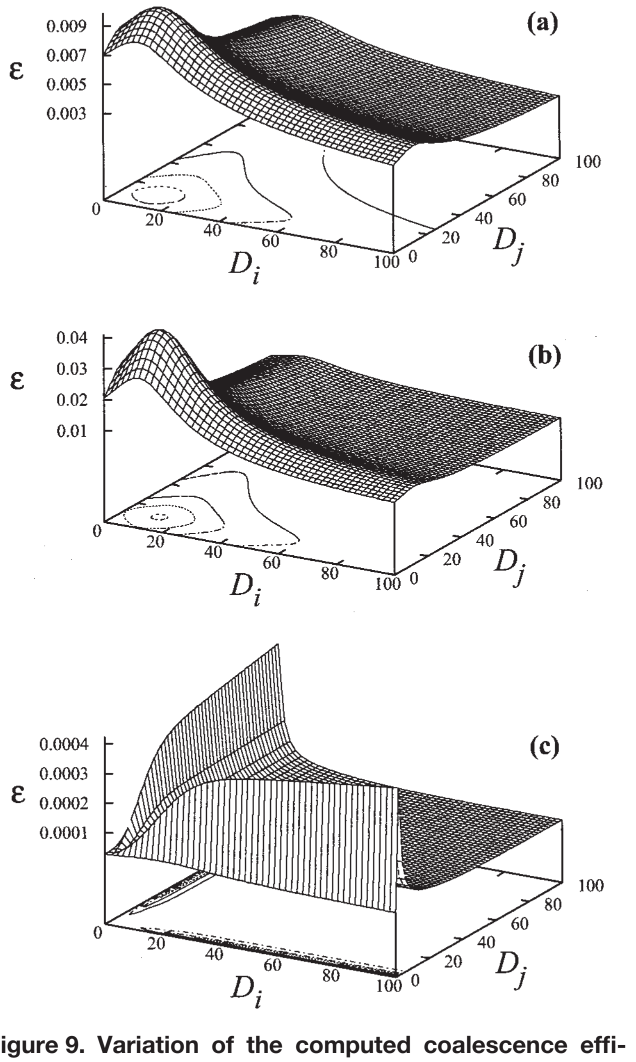

Figure 9. Variation of the computed coalescence efficiency (ε) (Eq. 5) with the diameters of the colliding drops (D_i, D_j) in μm at a shear rate of 21.5 s^{-1} for different cases.

The contours correspond to tic-mark values. (a) 1% holdup, surfactant-free using the parameters given in Table 1; (b) 4% holdup, surfactant-free using the parameters given in Table 1; (c) 5% holdup surfactant stabilized using parameters obtained in Nandi et al.[6]

ings for coalescence in stirred emulsions. A complete understanding of this phenomenon requires a more detailed study.

The magnitude of the coalescence efficiency increases with holdup but is of the order 10^{-2} for both cases. The coalescence efficiency for the case of a surfactant-stabilized emulsion ($\phi = 5\%$, $\gamma = 20.5\ \mathrm{s}^{-1}$), calculated using the parameters obtained by Nandi et al.,[6] is shown in Figure 9c for comparison. The graph indicates that coalescence is significant only when one of the pair of colliding drops is small (2 μm) and the other is large (>20 μm). Further, the magnitude of the coalescence efficiency is about 100 times smaller than the case without surfactant at similar holdup and shear rate values (Figure 9b).

The model of Chesters[13] yields a coalescence efficiency, $\varepsilon \approx 1$, for 12 μm drops with partially mobile interfaces using the following properties: interfacial tension of 46 mN/m, viscosity of the continuous phase of 5.1 mPa·s, and Hamaker constant of 0.46×10^{-20} J for the water layer trapped between oil on both sides. The back-calculated value of the coalescence efficiency is thus about two orders of magnitude smaller than that from the theory. This difference may be explained using the recent work of Nandi et al.,[27] which experimentally showed that the hydrodynamic drainage of the film between colliding liquid–liquid interfaces is retarded when salt (sodium chloride) is present in the aqueous film. The retardation is explained by the development of an interfacial tension gradient in the film stemming from the negative adsorption of the salt at the interface. A similar effect could reduce the coalescence efficiency in the present system where sodium chloride is present in the aqueous film between colliding drops. Incorporating this effect (salt at the interface) into the framework of this work in a quantitative manner is not feasible, given the current state of understanding. Further studies need to be done to quantitatively understand the dynamics of the formation of an interfacial tension gradient in the presence of salts.

We end the discussion by summarizing the similarities and differences between the present case (emulsion without surfactant) and previously reported data for a surfactant-stabilized emulsion.[5,6] For the emulsion with surfactant, the coalescence efficiency is independent of the size of the drops at low dispersed-phase holdup (1%) in contrast to the result obtained for surfactant-less emulsions. The overall coalescence efficiency (α_0) for the surfactant-stabilized emulsion is two orders of magnitude lower than that in the present case. Also, in contrast to the present surfactant-less system, the high film stability in the presence of surfactants results in a reduction of the coalescence rate with increased shear rate. The coalescence efficiency decreases with increasing shear rate for both kinds of emulsions. Further, the coalescence efficiency decreases with increasing dispersed-phase holdup in surfactant-stabilized emulsions, whereas for the surfactant-less emulsion the opposite trend is observed. The functional dependence of the coalescence efficiency on the colliding drop diameters is significantly different for the two systems. The results indicate significant qualitative differences in the coalescence in emulsions with and without surfactant.

Conclusions

A neutrally buoyant emulsion, containing an electrolyte was subjected to a tangential Couette flow in the simple shear regime. The chemicals used in making the emulsion were made free of surface-active impurities and tested to verify their absence. Drop size distributions were measured using optical microscopy and image analysis. Emulsions were made by sonification and care was taken to ensure that the initial sample did not have very small drops to ensure that Brownian motion–induced coalescence was negligible. The sonification conditions were also controlled to obtain nearly the same initial distribution for the different holdups studied.

Studies were conducted for varying shear rates and dispersed-phase holdups. Unlike emulsions containing surfactants, an increasing shear rate and dispersed-phase holdup both resulted in an enhancement in the coalescence rate. The evolving distributions were bimodal in all cases. On scaling the distributions, self-similarity was absent, suggesting that the coalescence efficiency was dependent on the drop sizes.

A population balance model, which included an empirical equation for describing the coalescence efficiency, was used to back-calculate the coalescence efficiency and its dependence on the size of colliding drops. The model gave a reasonably good description of the evolution with time of the drop size distribution and the volume-average drop diameter. The coalescence efficiency was found to increase with dispersed-phase holdup and to decrease with increase in the shear rate. These trends are in qualitative agreement with previous experimental and theoretical results. The coalescence efficiency calculated from the model of Chesters[13] was two orders of magnitude larger than the efficiency back-calculated from experiments ($\varepsilon \cong 10^{-2}$). This was explained in terms of the effect of interfacial tension gradients arising from the salt in the film. The back-calculated parameters for the coalescence efficiency showed the existence of a critical diameter ($D_C = 12\ \mu$m) at which the coalescence was maximized.

This work provides qualitative experimental confirmation for many of the theoretical predictions in the literature. It shows the generality of the proposed coalescence efficiency model that was previously found to satisfactorily describe the behavior of surfactant-stabilized emulsions. The differences in the shear-induced coalescence in surfactant-stabilized emulsions and those without surfactant are highlighted. The results provide new insights into coalescence in sheared surfactant-free emulsions.

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