Factors Affecting Coalescence Frequency of Droplets in a Stirred Liquid-Liquid Dispersion

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Liquid-liquid dispersions are commonly used for separations and reaction systems, because the added interfacial area due to dispersion aids in mass transfer and chemical reaction rates. Transient coalescence experiments have been performed for a wide range of dispersed-phase fractions and impeller speeds. A similarity transformation of the experimental drop-size distribution is possible for most of the experiments. The drop-size-dependent coalescence frequency is obtained from an inverse problem procedure previously developed. Over the range of drop sizes encountered in our experiments, the coalescence frequency increases with increases in the size of the coalescing drops, the dispersed-phase fraction, and the impeller speed. For a disperse-phase system of neutrally buoyant droplets of benzene/carbon tetrachloride in water, the coalescence frequency is $K(v, v') = 3.72(10^{-3})\phi^{1.42}N_2^{0.52}(v^{1/2} + v'^{1/2})$ *as a function of dispersed-phase fraction,* ϕ*, impeller speed,* N_2*, and volumes of the coalescing droplets,* v *and* v'*. The results are compared with previous models for the coalescence frequency. Models predicting an eventual decrease in coalescence rates with drop size are disqualified unless this decrease occurs beyond the sizes observed in our experiments.*

Introduction

Liquid-liquid dispersions have important engineering applications. They are commonly used in separation and reaction processes where the added surface area due to dispersion facilitates mass transfer. Tatterson et al. (1991) stated that an understanding of the processes that affect drop-size distributions in liquid-liquid dispersions was one of the top ten issues in mixing technology. The same article stated that failure to understand processes that affect mixing, such as liquid drop-size distribution, currently costs the U.S. chemical process industry from $1 billion to $20 billion per year. The potential for significant cost savings and the diversity of the applications warrants a fundamental study into the dynamics of liquid-liquid dispersions.

Drop-size distributions are affected by two characteristic processes, drop breakage and coalescence. In this article we will investigate how various physical factors such as the dispersed-phase fraction and the impeller speed affect the droplet coalescence frequency. In order to do this we will use the inverse problem framework for extracting the coalescence frequency from experimental drop-size distribution measurements. This framework is explained in detail elsewhere (Wright and Ramkrishna, 1992; Wright, 1991; Wright et al., 1990; Tobin et al., 1990). The inverse problem framework has been applied successfully to determine the agglomeration or aggregation frequency for diffusion-limited cluster-cluster aggregation in two and three dimensions (Wright et al., 1992). The inverse problem takes advantage of the self-preserving size distributions first noticed by Friedlander and associates (Friedlander, 1977; Wang and Friedlander, 1966). In this article the similarity distribution for one physical system (benzene-carbon tetrachoride droplets in water) is found to be "universal." A universal similarity distribution for a particular physical system means that the similarity distribution is identical even though the dispersed-phase fraction and impeller speed has been altered. However, the similarity distributions for another physical system (acetophenone in water) do not display universal behavior. Impeller speed and dispersed-phase fraction appear to change the similarity distribution for that dispersion. In fact, similarity is not always observed for this system. This

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article will investigate these observations further. It will also compare the experimental results with models for the coalescence frequency that are found in the literature.

The population balance framework (Ramkrishna, 1985) gives a convenient framework for the investigation of coalescence of liquid droplets. For a purely coalescing system, the population balance leads to the Smoluchowski (or population balance) equation. Let $n(v,t)dv$ be the number of droplets of volume $(v,v+dv)$ at time t per *unit volume of dispersed phase.* The evolution of $n(v,t)$ can be written as:

$$\frac{\partial n(v,t)}{\partial t}=\frac{1}{2}\int_0^v K^s(v-v',v',\ldots)n(v-v',t)n(v',t)dv' - \int_0^\infty K^s(v,v',\ldots)n(v,t)n(v',t)dv' \qquad (1)$$

The first term on the righthand side of the equation represents the rate of accumulation of drops of size v from the coalescence of two smaller droplets. The second term represents the rate of loss of particles of size v by their coalescence with all other particles. $K^s(v,v',\ldots)$ is the effective coalescence frequency. Equation 1 does not presuppose any type of closure hypothesis for the population balance equation. See Ramkrishna (1985), Wright et al. (1990), Wright (1991), and Wright and Ramkrishna (1992) for more information on the closure hypothesis in the population balance. If we adopt the commonly used first-order closure hypothesis:

$$K^s(v,v',\ldots)n(v,t)n(v',t)=K(v,v')n(v,t)n(v',t)$$

then the effective coalescence frequency $K^s(v,v',\ldots)$ becomes the commonly used coalescence frequency, $K(v,v')$, that depends only on the size of the drop pair. Use of this closure hypothesis indicates that only the two droplets that coalesce affect the coalescence rate, not necessarily a valid assumption.

We will only summarize the pertinent results of the inverse problem methodology in this article. The computational aspects of the inverse problem are extremely important and may be found elsewhere (Wright and Ramkrishna, 1992).

The self-preserving or similarity distribution for coalescing populations enables us to extract the coalescence frequency (or an effective coalescence frequency) from measurements of the drop-size distribution as a function of time. If the extracted coalescence frequency is found to be a function only of the drop size of the two coalescing drops then we know that the commonly used closure hypothesis is valid. The observation of a similarity distribution makes the solution of the population balance for the coalescence frequency a tractable problem by separating the "size" dependence and the time dependence.

Let $F(v,t)$ be the cumulative volume fraction of droplets under size v at time t:

$$F(v,t)=\int_0^v vn(v,t)dv$$

Similarity is observed if

$$F(v,t)\rightarrow f(z) \quad \text{or} \quad n(v,t)=\frac{f'(z)}{z}\frac{1}{S(t)^2} \qquad (2)$$

where z is the similarity variable and is equal to $z=v/S(t)$ and $S(t)$ is the average droplet volume.

$$S(t)=\frac{M_2(t)}{M_1(t)} \quad \text{where} \quad M_k(t)=\int_0^\infty v^k n(v,t)dv \qquad (3)$$

The scaling size $S(t)$ has been chosen for reasons discussed by Wright and Ramkrishna (1992). Similarity distributions have been observed for a whole host of other agglomerating systems. They were first observed in aerosols and have more recently been observed in cluster-cluster aggregation. We have reported the observation of similarity distributions in the coalescence of liquid drops previously (Tobin et al., 1990; Wright et al., 1990). In Tobin et al. (1990) we also reported that the drop-size distributions found in Konno et al. (1987) also appear to show similarity.

Only some effective coalescence frequencies can yield a similarity distribution; thus, the observation of similarity places constraints on the identification of the effective coalescence frequency that generated the self-similar size distribution. The mathematics yield the constraints (Wright and Ramkrishna, 1992):

$$K^s(xS,yS,\ldots)=S(t)^\lambda b(x,y) \qquad (4)$$

where $x=v/S(t)$ and $y=v'/S(t)$ and $b(x,y)$ is a function only of the scaled volumes. The implication of the above relationship is that if similarity is observed, the myriad possible dependencies of the effective coalescence frequency must reduce to that in Eq. 4. If the commonly used closure hypothesis were used and the coalescence frequency was a homogeneous function of the drop volumes then Eq. 4 would reduce to:

$$K^s(xS,yS,\ldots)=K(xS,yS)=S(t)^\lambda K(x,y) = S(t)^\lambda b(x,y) \qquad (5)$$

λ is then the degree of homogeneity of the coalescence frequency.

The implication of Eq. 5 is that if the first-order closure hypothesis is valid and the coalescence frequency is assumed to be homogeneous then $K(x,y)=b(x,y)$.

The observation of similarity places another constraint on the evolution of the average drop volume, $S(t)$, such that:

$$\frac{dS(t)}{dt}=\langle b\rangle S(t)^\lambda \qquad (6)$$

where $\langle b\rangle$ is a constant equal to the expected value of $b(x,y)$. From Eq. 6, then a plot of $S(t)^{(1-\lambda)}$ vs. time (t) should yield a straight line (for $\lambda\neq 1$). The slope of that line allows the determination of $\langle b\rangle$. Given the constraints of similarity, the population balance transforms to:

$$\langle b\rangle zf'(z)=\int_0^z dxf'(x)\int_{z-x}^\infty dy\frac{f'(y)}{y}b(x,y) \qquad (7)$$

The inverse problem consists of extracting the unknown function $b(x,y)$ from the experimentally determined similarity distribution, $f'(z)$, as well as determining the unknown parameters, $\langle b \rangle$ and λ. Knowledge of $\langle b \rangle$, λ, and $b(x,y)$ allow us to reconstruct the coalescence frequency, $K^s(v,v', \ldots)$.

Experimental Procedure

The experiments are performed in a 2.4 L glass mixing vessel. The vessel is 12.7 cm in diameter with four glass baffles 1.3 cm wide fused to the vessel wall. A six-bladed Rushton impeller 5 cm in diameter is used. During the course of the experiments, a glass cover plate is clamped to the vessel. Samples of the dispersion are withdrawn through a small sealable hole in the cover plate by an auto pipette with a tip opening 5 mm in diameter. A 50 μL sample of the dispersion is withdrawn. The sample is immediately placed on a slide which contains a small amount of 1% sodium dodecyl sulfate (SDS) solution. SDS is a surfactant that stabilizes the sample against coalescence and drop breakup. The entire sampling procedure takes about one second. The dispersed phases used are neutrally buoyant, so buoyancy effects do not affect the coalescence frequency and also there is no driving force for coalescence within the auto pipette. The continuous phase was deionized water at least 24 h old.

After the sample is collected a computerized image analysis system was used. The image analysis system determined the diameter of the drops and allowed the size distribution to be computed.

A study was performed to investigate the efficacy of the experimental procedure. There are two issues to resolve. Does the surfactant stop the coalescence and breakup of the dispersed-phase droplet? Does the sampling procedure alter the drop-size distribution? The surfactant was found to be quite sufficient at stabilizing the drop-size distribution against coalescence and breakup. A dispersion of benzene/carbon tetrachloride was stirred at 800 rpm for our hour. The dispersed-phase fraction was $\phi = 0.25$. A sample of the dispersion was withdrawn and placed on a slide which contained two drops of 1% SDS solution. The sample was observed under the microscope for 30 min. No droplet movement, coalescence, or breakup was observed. To further demonstrate, a 25% dispersion of benzene/carbon tetrachloride in 10^{-3} M solution of SDS in water (approximately equivalent to that present normally on the slide with the sample) was stirred for several hours at 800 rpm. Several samples were withdrawn. The impeller speed was reduced to 200 rpm. Samples of the dispersion were taken 5, 10, and 15 min after the impeller speed reduction. Each of the size distributions was identical with the distribution at 800 rpm within experimental uncertainty. The surfactant stabilized the distribution against coalescence and breakup even under the vigorous 200 rpm stirring.

To investigate the applicability of the sampling procedure, another study was undertaken. The study consisted of sampling a 25% dispersion of benzene/carbon tetrachloride in water which had been stirred for two hours at 600 rpm with different orifice diameter auto pipettes. One orifice diameter was 3 mm and the other was the standard 5 mm. We found that changing the orifice diameter did not affect the measured drop size distribution (Wright, 1991). If laminar shear of the sample withdrawal significantly affected the drop-size distribution then we would anticipate that varying the Reynolds number into the auto pipette by varying the orifice diameter would affect the measured drop-size distribution. If drops of certain sizes were screened out of the sample then changing the orifice diameter would change the size of the screened drops and again change the drop-size distribution. We conclude that the proposed sampling procedure allows measurement of drop-size distributions that are free from the effects of laminar shear and screening effects even at relatively high dispersed phase fractions.

Interval of Pure Coalescence

We envisage experiments to extract the coalescence frequency. These experiments are transient experiments in which no significant droplet breakage occurs for a certain length of time. Drop breakup can be minimized by initially making a dispersion of small drops via agitation at a high impeller speed, which is drastically reduced after the formation of these small drops. The small drops will be too small to break at the new lower turbulence intensity until they have grown via coalescence for some time. The determination of the length of time that pure coalescence (coalescence in the absence of significant drop breakup) dominates the evolution of the transient-size distribution is the focus of this section.

In order to determine the length of time of pure coalescence, t_{pc}, it is necessary to examine drop breakup in more detail. We will follow the view of drop breakup first proposed by Kolmogoroff (1949), further expounded by Hinze (1959), and later yet by Shinnar (1961). Let us assume that our droplets are larger than the microscale of turbulence, η. In this case the droplet will oscillate about its spherical equilibrium shape. If the deformations in the shape are large, the droplet will be unstable and break up. In order to become unstable, the kinetic energy of these oscillations must be sufficient to overcome the gain in surface energy due to drop breakup. The kinetic energy of the oscillating droplet is assumed to be proportional to $\rho_d \overline{u^2(d)} d^3$ where $\overline{u^2(d)}$ is the mean square velocity fluctuations between two diametrically opposite points on the surface of the droplet. The minimum gain in the surface energy is approximately proportional to σd^2. The value of the ratio of these two energies is the Weber number,

$$We = \frac{\rho_d d \overline{u^2(d)}}{\sigma}$$

The critical value of this ratio at which breakup occurs is dependent upon the details of the breakup process (which may be viewed as the conversion of turbulence energy into new surface energy) and may be expected to be a constant characteristic of the physical system.

In locally isotropic flow, the average mean-square velocity between two points is given by (Shinnar, 1961):

$$\overline{u^2(r)} = c_1 \epsilon^{2/3} r^{2/3} \quad r >> \eta \tag{8}$$

where ϵ is the energy dissipation per unit mass of the fluid, and η is the Kolmogoroff length scale of the small energy dissipating eddies.

$$\epsilon = KN^3 D^2$$

where N is the impeller speed, D is the diameter of the impeller, and K is a dimensionless constant dependent on the geometry of the vessel and agitator only.

From these relationships, the dependence of the maximum stable drop size on the impeller speed can be obtained as:

$$d_{\max} \sim N^{-6/5} \tag{9}$$

At steady state, the maximum stable drop size will be approximately the observed maximum sized drop. Actually, following Shinnar (1961), we let $d_{\max}$ be the diameter at which $F(v,t) = 0.9$ and $d_{\min}$ is the diameter in which $F(v,t) = 0.1$.

The relationship between the observed maximum droplet diameter and the impeller speed has been experimentally verified by several investigators. The impeller speed step down experiments of Konno et al. (1988) support the $-6/5$ relationship. Their experiments were performed for neutrally buoyant o-xylene and carbon tetrachloride in 0.1 M NaCl/water solution at dispersed-phase fractions of $\phi = 0.01$, 0.02, and 0.05. Shinnar and Church (1960) also confirmed the relationship for a 5% dispersion of molten wax in hot water.

Steady-state experiments of a dispersion of benzene and carbon tetrachloride were performed for six different impeller speeds and five different dispersed-phase fractions. The experiments consisted of allowing the dispersion to come to a steady-state drops-size distribution by agitating at a constant impeller speed for several hours. The maximum drops size, $d_{\max}$, was determined. The maximum diameter can be correlated to impeller speed and dispersed-phase fraction. The following correlation was determined:

$$d_{\max} = 10^{6.85 \pm 0.75} N^{-1.30 \pm 0.15} \phi^{0.56 \pm 0.1} \tag{10}$$

This is a confirmation of Eq. 9 for the systems of interest to us. Further experimental results can be found in Wright (1991).

Let us visualize the events in a liquid-liquid dispersion. At steady state, droplet coalescence and droplet breakage are in dynamic equilibrium. There exists a maximum observed diameter, $d_{\max}$, and a minimum observed droplet diameter, $d_{\min}$. If a droplet significantly larger than $d_{\max}$ is formed by coalescence that droplet has a high probability of being broken in a short period of time. Likewise if a droplet significantly smaller than $d_{\min}$ is formed it will coalesce, as further droplet breakage is unlikely. In this way a steady-state drop-size distribution is maintained. Our picture of what happens during an impeller speed shift down emerges. Initially, the system is at steady state and the drop-size distribution is maintained. After a step change in the impeller speed to a new lower agitation rate there exists a length of time in which the drop-size distribution changes predominantly due to pure coalescence (no significant drop breakage) which is denoted t_{pc}. Droplet breakup is insignificant because the new lower turbulence intensity is not sufficient to overcome the surface forces and cause drop breakup. After this interval of pure coalescence, there is a period of time in which drop breakup and coalescence occur simultaneously because some of the droplets move into the range in which drop breakup may occur.

The question remains as to how one may identify the stage at which coalescence has produced drops of the critical size which may break. Shinnar (1961) noticed that the ratio of the maximum droplet diameter $d_{\max}$ $[F(v,t) = 0.9]$ to the minimum drop diameter, $d_{\min}$, for a 5% dispersion of wax in water at steady state was approximately 2.

$$\frac{d_{\max}}{d_{\min}} \sim 2 \tag{11}$$

The previous steady-state experiments described by Eq. 10 also confirm Shinnar's observation for the ratio of $d_{\max}$ to $d_{\min}$. The actual experimental observation led to an average value of $d_{\max}/d_{\min} = 2.43$. We take this as experimental confirmation of Shinnar's observation for systems of interest to us.

We are now in a position to develop an expression of the maximum droplet diameter for the interval of pure coalescence, d_{pc} which can be related to the maximum droplet diameter at the original higher impeller speed via Eqs. 9 and 11.

$$d_{pc} = \frac{d_{\max}(t=0)}{2} \left(\frac{N_1}{N_2}\right)^{1.2} \tag{12}$$

where $d_{\max}(t=0)$ is the maximum droplet diameter observed at the initial steady state, N_1 is the initial impeller speed at that steady state, and N_2 is the final impeller speed after the step down. The time interval of pure coalescence, t_{pc}, can be determined from the above relationship and $d_{\max}(t_{pc}) = d_{pc}$. If $d_{\max}(t) < d_{pc}$, we are in the interval of pure coalescence. If $d_{\max}(t) > d_{pc}$, we are in the time interval of simultaneous droplet breakup and coalescence. Equation 12 gives a conservative estimate of the interval of pure coalescence since it assumes that the smallest droplets in the new steady-state size distribution at the lower impeller speed will break.

From these relationships we are able to determine the minimum impeller speed shift that is necessary to cause the development of a transient pure coalescence interval.

$$\left(\frac{N_1}{N_2}\right)_{\min} = 1.78$$

If the impeller speed shift is larger than 1.78, a time interval of pure coalescence is possible. If the impeller speed shift is less than 1.78, then transition to the new steady state will occur via simultaneous droplet breakage and coalescence only.

Pure Coalescence Experiments—Benzene Carbon Tetrachloride in Water

Transient pure coalescence experiments are needed to identify the coalescence frequency. Fourteen transient experiments were performed with a neutrally buoyant mixture of benzene and carbon tetrachloride dispersed in water at five different dispersed-phase fractions ($\phi = 0.01$, 0.05, 0.10, 0.15, and 0.25) and at two different final impeller speeds of $N_2 = 200$ and 400 rpm. The physical properties of the dispersions are given in Table 1.

We examine more closely the results from a single transient experiment before looking at the entire set of experiments. Figure 1 shows the transient cumulative volume fraction distributions for a transient experiment for a 5% dispersion of benzene carbon tetrachloride. The dispersion was initially stirred at 1,200 rpm for two hours. The impeller speed was reduced to 400 rpm at $t = 0$. The size distribution was measured as a function of time for 120 min. The impeller speed reduction is sufficient to cause an interval of pure coalescence. At 1,200 rpm steady state, $d_{\max} = 108.3$ μm. By Eq. 12, $d_{\max}$ can grow

Table 1. Physical Properties of the Liquid-Liquid Dispersions (Tobin, 1992)

System	Density g/cm^3	Viscosity cp	Interfacial Tension dyne/cm
Benzene/Carbon Tetrachloride (83.9 mol% Benzene, 16.1 mol% Carbon Tetrachloride)	1.074	0.7	35
Acetophenone	1.028	1.6	17

to 202 μm before significant drop breakage can occur; $d_{\max}$ is 197.2 μm at 40 min and 207.7 at 60 min, thus indicating that the time interval for pure coalescence is just beyond 40 min. Beyond 40 min, drop breakup and droplet coalescence are both possibly occurring because the droplets have grown to a size where drop breakage is probable.

Equation 2 is the similarity transformation we are looking for. In Figure 2, we have plotted the cumulative volume fraction $F(v,t)$ vs. the similarity variable z for the various transient size distributions in the interval of pure coalescence. The size distributions vs. the similarity variable overlay each other.

A total of 14 transient experiments were performed at nine different conditions (that is, different impeller speeds and dispersed-phase fractions) with this dispersed-phase system. Similar analyses as that performed on this last set of data were completed on each transient experiment.

All of the transient experiments showed similarity behavior. In fact, all the similarity distributions for all the experiments remarkably overlay each other, indicating a universal similarity distribution for this dispersed-phase system. Figure 3 shows the similarity transformation of the experimental data as a plot of the transformed number density function $f'(z)/z$ vs. the similarity variable z for different dispersed-phase fractions and impeller speeds. In the 14 transient experiments performed, the average droplet size $S(t)$ in the interval of pure coalescence ranged from $5\times(10^{-5})$ μL to 0.2 μL which represents a 4,000-fold increase in the average droplet volume.

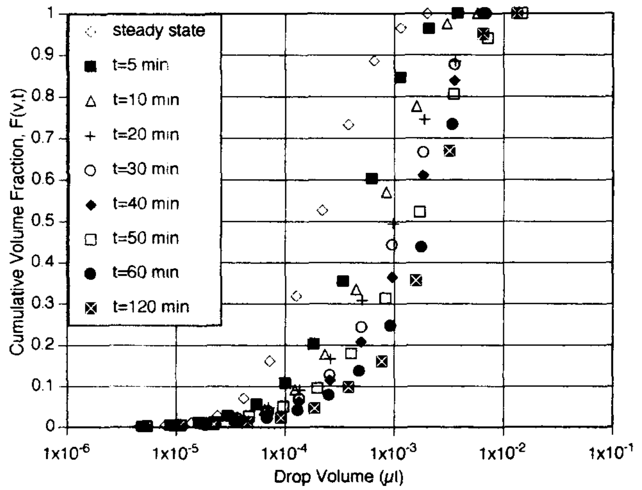

Figure 1. Transient drop-size distributions for 5% dispersion of benzene carbon tetrachloride in water.

Impeller speed reduced from 1,200 rpm (steady state at $t=0$ min) to 400 rpm.

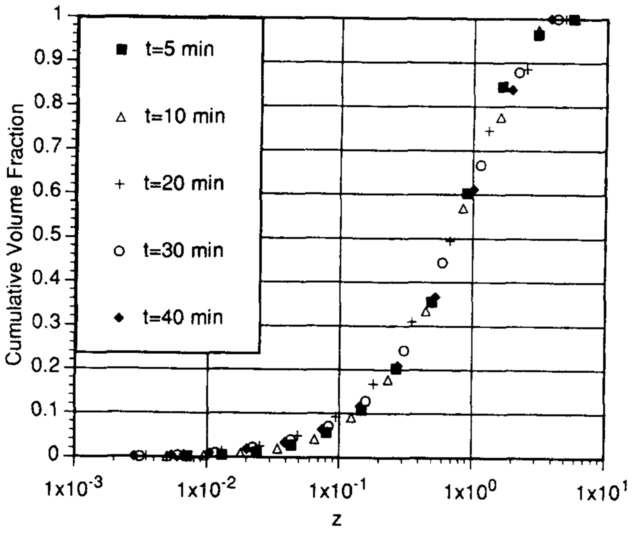

Figure 2. Similarity transformation of transient distributions for data in Figure 1.

Similarity variable z is the ratio of droplet volume v to the average drop volume at time t ($S(t)$).

The existence of this universal similarity distribution for this dispersion indicates that the drop-size dependence, dispersed-phase fraction dependence, and the impeller speed dependence for the effective coalescence frequency are separable. It means that the effective coalescence frequency can be written as:

$$K^s(v,v',\ldots)=G(\phi)H(N_2)J(v,v',\ldots)$$

where G, H, and J are functions of their arguments yet to be determined.

Equation 6 gives the evolution of the average droplet volume $S(t)$ as a function of time. The universal similarity distribution leads to the conclusion that λ must be the same for all the

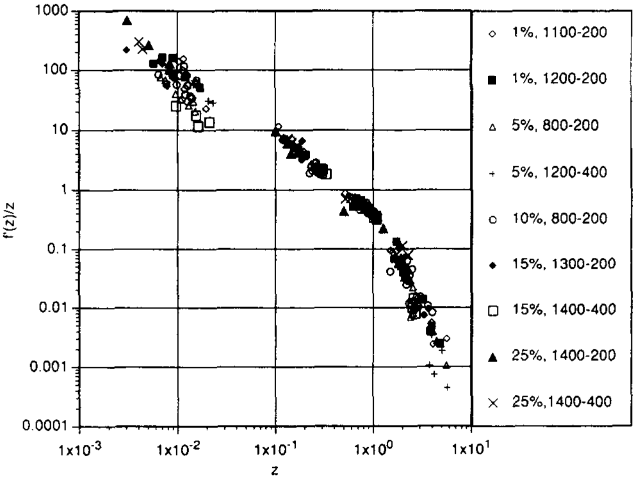

Figure 3. Universal similarity distribution for benzene carbon tetrachloride experiments as a function of dispersed-phase fraction and impeller speed reduction.

The legend refers to first % dispersed-phase fraction, and then impeller speeds before and after impeller speed reduction.

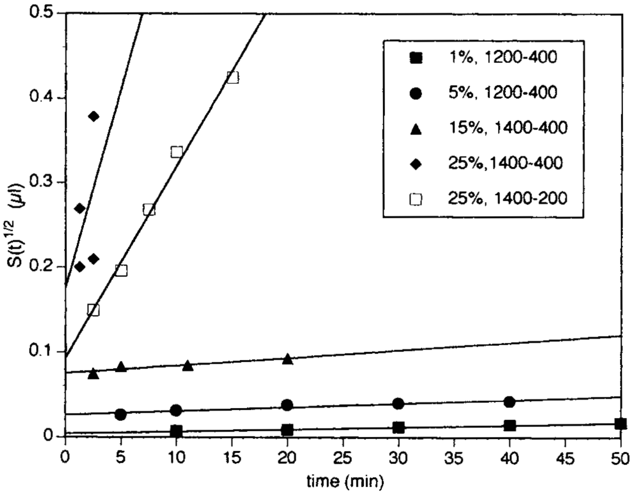

Figure 4. Similarity implies that the average droplet volume $S(t)$ evolve in time so that $S(t)^{(1-\lambda)}$ is linear vs. time.

For benzene carbon tetrachloride, $\lambda = 0.5$. The slope of the line is proportional to $\langle b \rangle$.

experiments. Fitting the $S(t)$ evolution data to Eq. 6 yields $\lambda = 0.5 \pm 0.1$. A plot of $S(t)^{1/2}$ vs. time for a wide variety of the experimental data is shown in Figure 4 which clearly displays the required linear trends. The slope of the line is proportional to $\langle b \rangle$, the expected value of $b(x,y)$. As one would expect, $\langle b \rangle$ increases substantially as the dispersed-phase fraction increases. The expected value of $b(x,y)$ was correlated as:

$$\langle b \rangle = 6.69 \times 10^{-3} \phi^{1.42} N_2^{0.52}$$

The overall coalescence rate increases substantially as the dispersed-phase fraction increased. For a 1% dispersion, the interval of pure coalescence was 50 min. For the same impeller speeds, the interval of pure coalescence decreased to 2.5 min for a 25% dispersion.

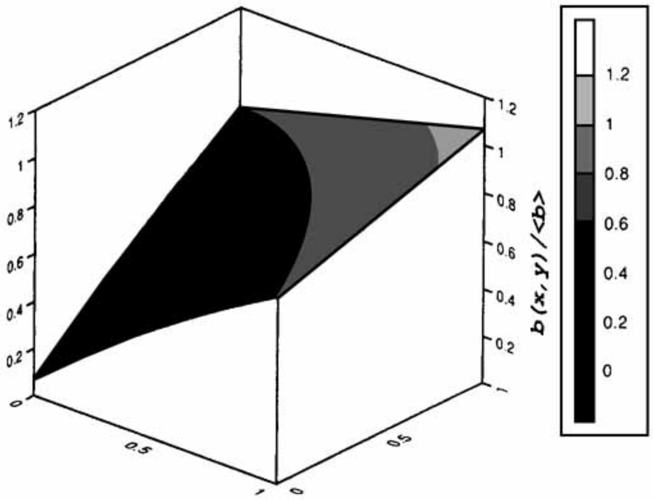

Figure 5. Three-dimensional representation of the scaled coalescence frequency, $b(x,y)$ vs. scaled drop size, x and y determined from the inverse problem.

Note that the frequency is a monotonically increasing function of drop size.

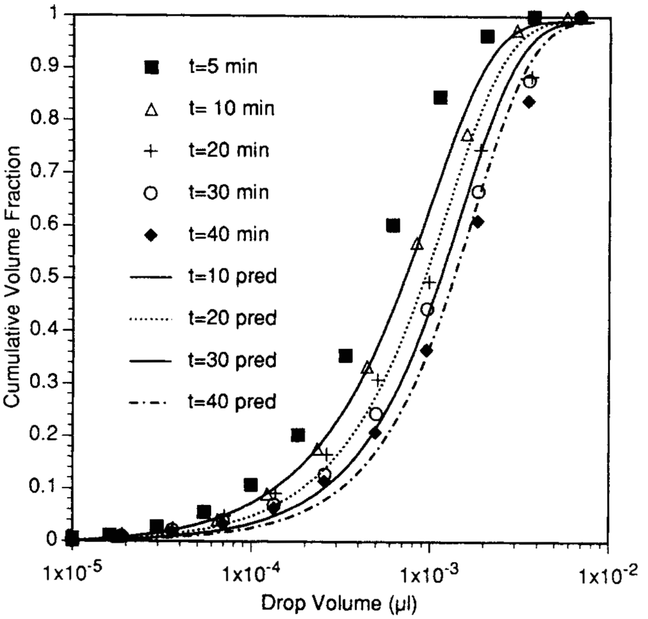

Figure 6. Predictions of the homogeneous approximation to the coalescence frequency.

The universal similarity distribution for a dispersion of benzene and carbon tetrachloride in water can be represented by:

$$f'(z) = 0.9294 z^{0.0304} \exp(-3.5127z) + 1.7857 z^{0.9114} \exp(-1.5464z) \quad (13)$$

The scaled coalescence frequency, $b(x,y)$, was determined numerically. Figure 5 shows a three-dimensional representation of $b(x,y)$. It is important to note that $b(x,y)$ and thus the effective coalescence frequency K^s increases with increases in the scaled drop sizes, x and y.

A homogeneous approximation for the coalescence frequency can be attempted. The procedure is dependent on the details of the inverse problem and is found elsewhere (Wright and Ramkrishna, 1992; Wright et al., 1992; Wright, 1991). The function $b(x,y)$ can be approximated as:

$$b(x,y) = 0.555 \langle b \rangle (x^{1/2} + y^{1/2}) \quad (14)$$

The validity of the homogeneous approximation to the extracted frequency can be determined by numerically solving the population balance equation with the homogeneous approximation and comparing the results with the experimental size distributions. This was done for the experiment with five percent dispersion at an impeller speed of 400 rpm following a step-down from 1,200 rpm. The results are shown in Figure 6. The homogeneous approximation predictions are seen to be within the experimental uncertainty. Since we are able to determine a reasonable homogeneous approximation, we can write a simplified form for the coalescence frequency for ben-

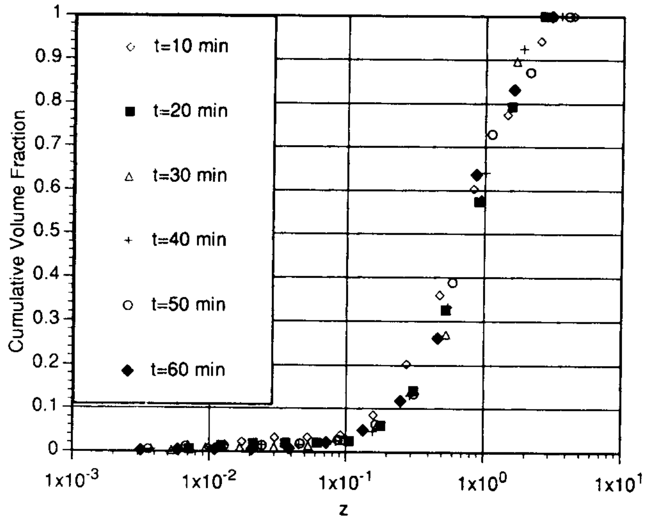

Figure 7. Similarity distribution of 1% dispersion of Acetophenone in water.

Impeller speed was reduced from 1,100 rpm to 200 rpm at $t=0$.

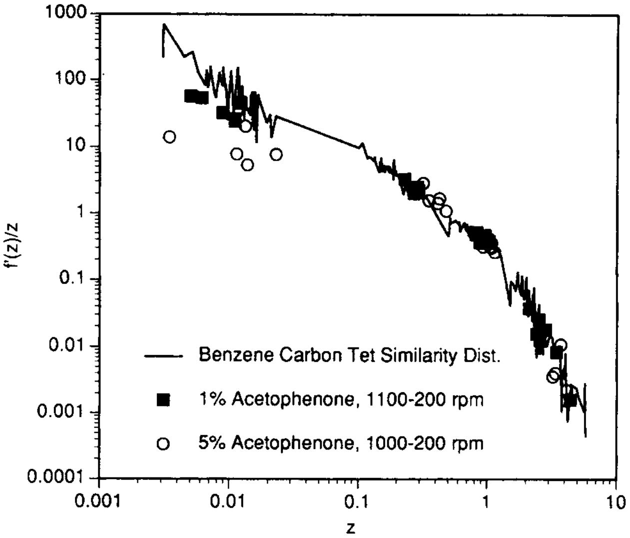

Figure 8. Comparison of similarity distributions from benzene carbon tetrachloride and acetophenone experiments.

zene carbon tetrachloride droplets in water. Our pure coalescence data suggest that:

$$K(v,v') = 3.72\times 10^{-3}\phi^{1.42}N_2^{0.52}(v^{1/2}+v'^{1/2}) \qquad (15)$$

where ϕ is the dispersed-phase fraction, N_2 is the final impeller speed in rpm, and v and v' are droplet volumes in microliters.

Pure Coalescence Experiments—Acetophenone in Water

The universal similarity distribution for the benzene and carbon tetrachloride experiments was quite unexpected. The question arose as to whether the universal similarity distribution is actually universal across physical systems. In order to investigate this possibility, a series of experiments with a different dispersed phase was performed. The disperse phase chosen was acetophenone. Acetophenone is nearly neutrally buoyant in water with a density of 1.03 g/mL at 298 K.

Five pure coalescence experiments with a dispersed phase of acetophenone were performed. Two with a 1% dispersion and three with a 5% dispersion of acetophenone in water. Two of the experiments exhibited similarity behavior. Three did not. [The mathematics in the analysis of self-similarity establishes only "feasibility." Whether or not self-similarity can be actually attained during evolution (in which the assumption of pure coalescence is sustained) depends on the initial condition and the analysis of what class of initial conditions does indeed provide for self-similar behavior (if it does at all) is an extremely difficult problem. Thus, we have relied on experiments to establish whether the feasibility of self-similar behavior is exploited by the initial conditions in the experiments. It is therefore not surprising when in a small number of cases self-similarity is not attained.] The two experiments that showed similarity behavior were both performed with a final impeller speed of 200 rpm. One of the two was with a 1% dispersion and the other was with a 5% dispersion. A plot of the transient pure coalescence size distributions vs. the similarity variable is shown in Figure 7 for a 1% dispersion undergoing an 1,100 to 200 rpm impeller speed reduction.

The similarity distribution is not universal for this dispersed-phase system. The similarity distributions for 1% dispersion and 5% dispersion are clearly distinct. They do resemble fairly closely the distribution found for benzene carbon tetrachloride but there are significant differences. Figure 8 shows the benzene carbon tetrachloride universal similarity distribution and the two acetophenone similarity distributions. While the distributions are almost identical for large z values, they vary significantly at small z. This is precisely where differences in the coalescence frequency are manifest.

The techniques used for determination of the coalescence frequency for the benzene carbon tetrachloride experiments can be used for the determination of the coalescence frequency for the two cases that showed similarity behavior. For a 1% acetophenone in water dispersion with a final impeller speed of 200 rpm, the homogeneous approximation for the coalescence frequency is:

$$K(v,\ v') = 4.71\times 10^{-5}(v^{0.25}+v'^{0.25}) \qquad (16)$$

For a 5% acetophenone dispersion in water with a final impeller speed of 200 rpm, the homogeneous approximation for the coalescence frequency was determined to be:

$$K(v,\ v') = 9.24\times 10^{-5}(v^{0.05}+v'^{0.05}) \qquad (17)$$

The impeller speed does appear to control the ability of the acetophenone experiments to exhibit similarity, since none of the three experiments performed at $N_2 = 400$ rpm show similarity. This result indicates that the impeller speed and the size dependence of the coalescence frequency must be interrelated in such a way that the higher impeller speeds reduce the likelihood of observing similarity behavior. The effect that the dispersed-phase fraction has on the coalescence frequency of acetophenone is unclear. From the two experiments that exhibit similarity, it appears that the size dependence of the coalescence

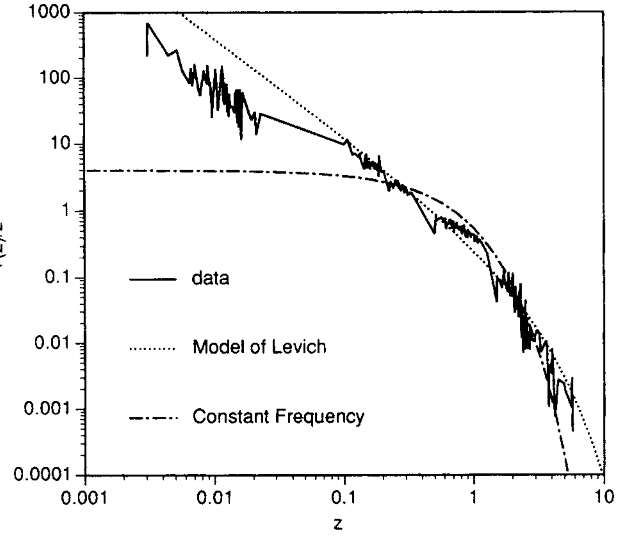

Figure 9. Comparison of benzene carbon tetrachloride similarity distribution with similarity distributions determined from Levich's model for turbulent coagulation (sum frequency) and the constant frequency.

The experimental similarity distribution is explained by neither model.

frequency, as measured by the exponents obtained for the homogeneous approximation, decreases as the disperse-phase fraction increases. From the experiments that do not yield similarity behavior, the trend is less clear since the qualitative behavior such as the increasing breadth of the size distributions are similar for both dispersed-phase fractions.

The feasibility of a homogeneous form of size dependence for the coalescence frequency in both the systems studied indicates the possibility of identifying parameters associated with this form from dynamic size distribution data in pure coalescence experiments.

Comparison of Results with Literature Models

The benzene carbon tetrachloride experimental results are compared with the predictions of previously derived models for the coalescence frequency. The similarity distributions, $f'(z)/z$, for the sum frequency model $K(v,v')=C(v+v')$ for turbulent coagulation developed by Levich (1962), and the constant coalescence frequency $K(v,v')=K$ are shown in comparison in Figure 9. The data plotted in that figure is the universal similarity distribution from benzene carbon tetrachloride experiments. It can clearly be noted that the constant coalescence frequency does not adequately represent the data. It is clear that the coalescence frequency must be dependent upon the size of the droplet pair since the experimental similarity distribution does not coincide with the similarity distribution for the constant frequency. The sum frequency model of Levich also does not adequately represent the data.

Several models have been developed based on the idea that the coalescence frequency $K(v,v')$ can be modeled as the product of a collision frequency, ω_c, and a coalescence efficiency after collision, η_c. In these models the collision frequency is determined based on kinetic theory type arguments and give rise to expressions like (Muralidhar, 1988; Coulaloglou and Tavlarides, 1977):

$$\omega_c \propto (v^{1/3}+v'^{1/3})^{7/3} \tag{18}$$

Table 2. Various Models for the Coalescence Efficiency

Model	Coalescence Efficiency
Coulaloglou and Tavlarides (1977) (and Muralidhar, 1988, Dynamic Deformation Model)	$\eta_c=\exp(-k_1R^4)$
Muralidhar (1988) Rigid Drop Model	$\eta_c=1-\dfrac{C_1R^{4/3}}{C_2+C_3R^{4/3}}$
Muralidhar (1988) Static Deformation Model	$\eta_c=\dfrac{1-\exp(-k_1R^4)}{1-\exp(-k_2R^4)}$

Several models for the coalescence efficiency are found in Table 2. In that table, R is the equivalent drop radius and is defined by:

$$\frac{1}{R}=\frac{1}{R_1}+\frac{1}{R_2}$$

where R_1 and R_2 are the radii of the drop pair.

It is possible to model the coalescence efficiency as a constant, and to use Eq. 18 for the collision frequency and solve the population balance equation for the similarity distribution. Figure 10 shows the constant efficiency model similarity distribution compared to the similarity distribution from the benzene carbon tetrachloride experiments. This model similarity distribution is closer than the sum and/or constant frequency models, but the data clearly do not overlay the model distribution for small z values. If we assume the collision frequency described above is valid, then our experimental data do not support the conclusion that the coalescence efficiency is independent of drop size. The coalescence frequency is evidently a function of the size of the drop pair. The mixing vessel used in coalescence rate studies is shown in Figure 11.

Our experimental results lead to the conclusion that the

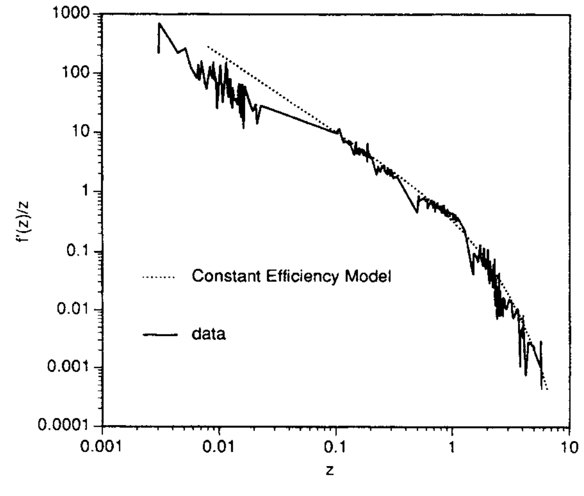

Figure 10. Comparison of benzene carbon tetrachloride similarity distribution with similarity distribution determined from the constant efficiency model.

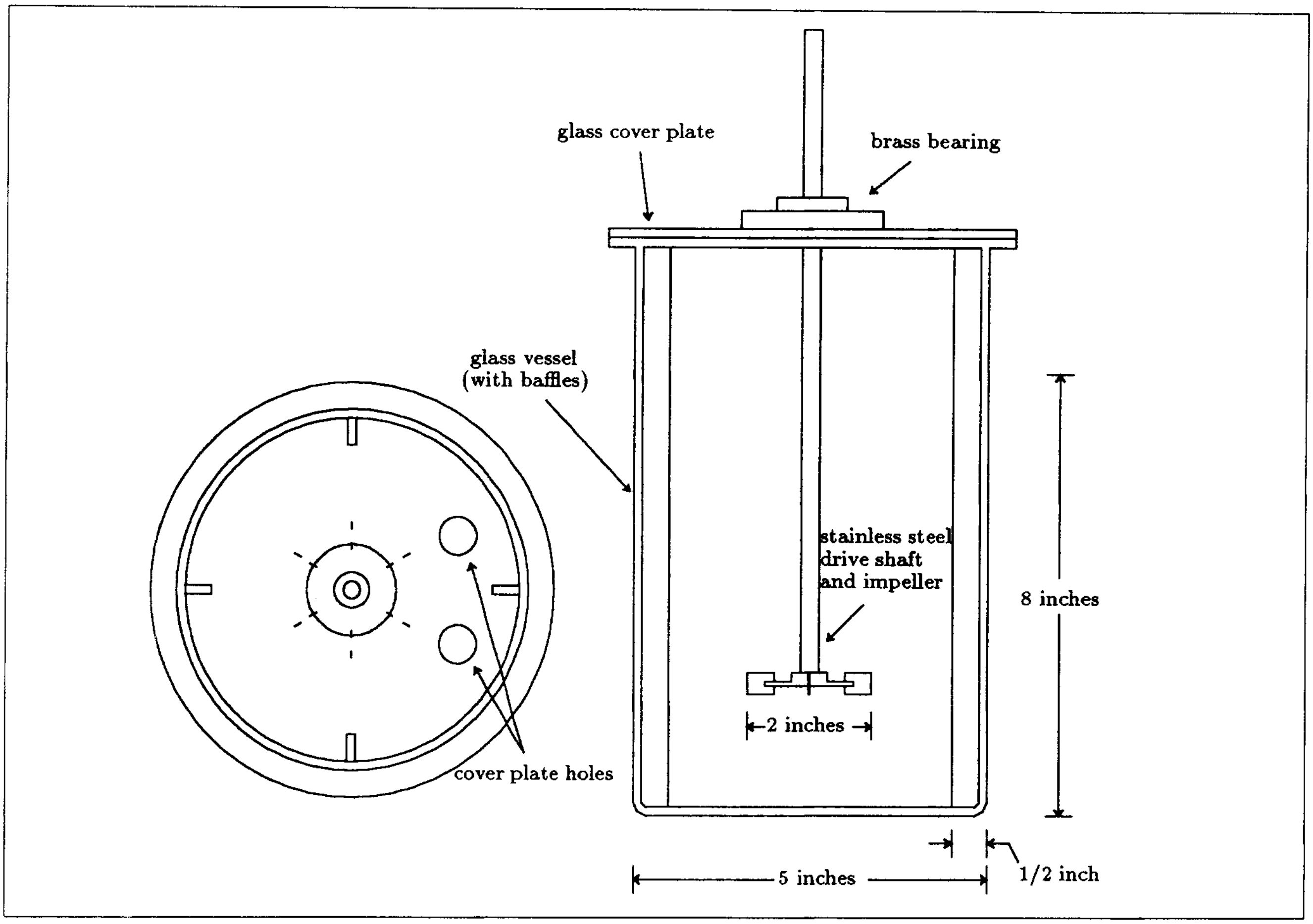

Figure 11. Details of the mixing vessel used in coalescence rate studies.

coalescence frequency is a monotonically increasing function of the size of the drop pair at least over the drop-size range over which it could be measured. A close inspection of the models listed in Table 1 for the coalescence efficiency as well as the collision frequency expression indicates that only the static deformation model of Muralidhar and Ramkrishna (1986) can potentially yield a monotonically increasing function of drop size. The models of Coulaloglou and Tavlarides (1977), the dynamic deformation model of Muralidhar and Ramkrishna (1988), and that of Kumar et al. (1993) all show an eventual drop in coalescence frequency with drop size for different reasons. Whether or not such an eventual drop in the coalescence rate actually does occur in practice is an issue that cannot be settled decisively by the inverse problem approach. This is because the approach is inherently constrained by the requirement of pure coalescence which may not be met if the drop sizes for which such a reversal occurs will also permit drop breakup. The power of the inverse problem technique, however, lies in its ability to isolate the two complex processes of coalescence and breakup allowing more reliable estimates of the coalescence rate for the permissible drop-size range. This merit is not shared by methods that rely on inverting dynamic dispersion data in which both coalescence and breakup occur.

Conclusions

Transient pure coalescence experiments have been performed and along with an inverse problem procedure allow us to extract the size specific coalescence frequency as a function of impeller speed and dispersed-phase fraction. Experiments have been performed with disperse-phase fractions up to 25%. The benzene carbon tetrachloride experiments yield a universal similarity distribution with respect to changes in impeller speed and disperse-phase fraction. The time interval for pure coalescence decreases drastically as the disperse-phase fraction increases.

Since the extracted coalescence frequency, K^s, can be approximated as a time-independent homogeneous frequency, the first-order closure hypothesis appears plausible for these experimental results with the benzene-carbon tetrachloride mixture. The closure hypothesis was not clearly affected by our manipulation of the dispersed-phase fraction and impeller speed. We venture the conclusion that self-similar behavior is a powerful attribute of coalescing systems in spite of our difficulties with the acetophenone-water system. The problem appears to stem from the considerably lower interfacial tension of this pair; the drops (especially the larger ones) showing a readiness to spread could possibly present a distorted image to the size-measurement technique adopted by us.

The results here lead to the conclusion that the coalescence frequency is a strong function of the size of the droplet pair. If we take the idea of the coalescence frequency being the product of the collision frequency and a coalescence efficiency, then we must conclude that the coalescence efficiency is a function of the size of the drop pair. The coalescence frequency is found to be a monotonically increasing function of the size of the drop pair. After analyzing several models for the coalescence frequency it is found that the static deformation model of Muralidhar (1988) allows a monotonically increasing coalescence frequency with drop size.

Since the results presented here belong only to two chosen systems, generalization to all systems is clearly not warranted. Our emphasis has been more on a rational methodology for the investigation of coalescence phenomena than on generating a general correlation. It is hoped that this article will stimulate further effort along these directions for other physical systems of interest.

Acknowledgment

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Notation

$b(x,y)$ = similarity of scaled coalescence frequency
$\langle b \rangle$ = expected value of $b(x,y)$, constant
$d_{\max}$ = maximum stable drop size at a specific impeller speed, μm
$d_{\min}$ = minimum stable drop size at a specific impeller speed, μm
d_{pc} = maximum diameter for the interval of pure coalescence, μm
D = agitator diameter, m
$f(z)$ = cumulative volume fraction vs. similarity variable
$f'(z)$ = scaled volume fraction density
$F(v,t)$ = cumulative volume fraction
$K(v,v')$ = coalescence frequency of drops of volumes v and v', $\mu L^2/s$
K^s = effective coalescence frequency
$M_i(t)$ = ith moment of the number density function
$n(v,t)$ = number density of drops of size v at time t, μL^2
N_1 = initial impeller speed, rpm
N_2 = final impeller speed, rpm
$S(t)$ = scaling function for similarity, average droplet size, μL
t_{pc} = time interval of pure coalescence, s
$\overline{u^2(r)}$ = mean-square velocity fluctuation for turbulence, m^2/s
v = droplet volume, μL
We = Weber number
z = similarity variable, $z = v/S(t)$

Greek letters

ϵ = turbulence energy dissipation per unit mass of fluid, Nm/kg
η = Kolmogoroff characteristic length scale of turbulence, m
λ = constant, pseudo-degree of homogeneity of K^s
ν_c = kinematic viscosity of the continuous phase, *cSt*
ρ_d = density of the dispersed phase, g/cm^3
σ = interfacial tension, dyne/cm
ϕ = dispersed-phase fraction

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