Maximum Stable Drop Diameter in Stirred Dispersions

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Transient drop-size distributions of stirred dispersions undergoing breakage were experimentally measured at long stirring times. The results show that drops continue to break the entire duration of the experiment (at least up to 10 h) and force a reevaluation of the widely held concept of a maximum stable drop diameter, d_{max}. Transient distributions show the existence of self-similarity, which is the same as that observed in transient distributions obtained at short times (up to ~ 1 h, Sathyagal et al., 1995b) indicating that the nature of breakage does not change with time. The existence of similarity at long stirring times can be used to obtain good estimates of breakage rates of small drops by an inverse problem procedure.

Introduction

The characterization of stirred liquid-liquid dispersions by a maximum stable diameter is routinely accepted by academic as well as industrial researchers (Hinze, 1955; Shinnar and Church, 1960; Godfrey et al., 1989). The concept is a consequence of the relative increase in the interfacial tension force for a smaller drop over the forces of hydrodynamic origin that try to deform and break it. Thus drops of diameter less than $d_{\max}$ are said to survive forever, while those of larger diameter will break in due course of time; $d_{\max}$ is thus deemed to be the largest diameter for a drop that will survive breakage. The survival time of the drop decreases for diameters increasing above $d_{\max}$. Correlations relating the Weber number, a ratio of inertial to interfacial forces, to the maximum stable diameter have long existed in the literature. Coulaloglou and Tavlarides (1976) have listed a number of such correlations available in the literature. Calabrese et al. (1986) have discussed correlations which account for high viscosity dispersed phases. In recent years, there have been many articles in which models for $d_{\max}$ have been developed for viscous dispersed phases (Arai et al., 1977; Wang and Calabrese, 1986; Lagisetty et al., 1986; Kumar et al., 1992), for the effect of surfactants (Koshy et al., 1988a), for the effect of drag-reducing agents (Koshy et al., 1989), and for viscoelastic dispersed phases (Koshy et al., 1988b). In most studies on $d_{\max}$ in the literature, the experimental $d_{\max}$ values were determined by running the breakage experiment for a specified amount of time (usually 1 to 2 h) and observing the largest drop size at the end of time. The objective of this article is to present experimental evidence forcing a reexamination of the concept and to provide a fresh perspective on the same. The discussion that follows begins with an elucidation of the concept as originally conceived, its practical significance, followed by considerations which inspired the experiments reported in this work.

Concept of d_{max}

In a stirred liquid-liquid dispersion, mechanical energy is introduced into the system by means of a mechanical impeller. Drops may be subjected to hydrodynamic forces arising directly from viscosity and/or turbulent pressure fluctuations. We shall confine our discussion to situations in which experimentally determined drop sizes are not influenced by coalescence between droplets. Minimization of coalescence events can be accomplished by maintaining low dispersed phase fractions. [Of course one may under these circumstances envisage fluctuations in the size distribution by both breakup (particularly of drops of diameter exceeding $d_{\max}$) and coalescence occurring at very slow rates.] Furthermore, we shall not account for wetting effects of the impeller such as those observed by Kumar et al. (1991). The correlations and models for $d_{\max}$ have been based on the concept of drop breakage by turbulent pressure fluctuations as envisaged by Kolmogoroff (1949) and Hinze (1955) using the average energy dissipation rate per unit volume. Indeed from a probabilistic point of view, pressure fluctuations in excess of the

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average can occur locally so that drops of the order of the maximum stable diameter may undergo breakage. Meneveau and Sreenivasan (1991) have experimentally determined the distribution of the energy dissipation rate in turbulent flows. Their measured distributions are intermittent and very spiky in nature, with instantaneous energy dissipation rates far exceeding the average value. Their results also indicate that the dissipation rates become increasingly intermittent with an increase in the flow Reynolds number. Thus the concept of the maximum stable diameter does not altogether preclude breakage of drops below that size. It stands to reason that the likelihood of fluctuations far in excess of the average must drop sufficiently to let drops of size below $d_{\max}$ survive indefinitely. The extent to which drop sizes can dip below $d_{\max}$ is an issue that has not been addressed in the literature, since it has become more or less taken for granted that $d_{\max}$ should represent the size of the largest drop that can be encountered in a stirred dispersion after allowing sufficient time for breakage. Consider, for example, the evolution of drop-size distributions in which the dispersed fraction is maintained at a level sufficiently small to exclude the effects of coalescence. If sufficient time is allowed to elapse, however, the possibility of appearance of drops with diameter smaller than $d_{\max}$ cannot be ignored. Such an experiment would be of interest to determine whether, on providing for longer periods of observations, significant breakage can occur at sizes below diameter $d_{\max}$, and if so the extent to which time scales of observation must be stretched.

Evolution of Drop-Size Distribution in Purely Breaking Dispersion

The temporal evolution of drop-size distributions in a lean liquid-liquid dispersion due to droplet breakage has been studied by Narsimhan et al. (1980, 1984) and by Sathyagal et al. (1996). An interesting aspect of such transient size distributions is the observation of scaling behavior (Ramkrishna, 1974; Narsimhan et al., 1980, 1984; Sathyagal et al., 1996), by which is meant that the dynamic size distributions when plotted on a suitable dimensionless scale collapse into a single time-invariant distribution. The scaling observed in the above studies may be described simply as being with respect to a scaled time ζ obtained by dividing real time by the average "survival" time of the drop. The average survival time which depends on the size of the drop may be defined as the reciprocal of the breakage rate of drops of that size. As pointed out earlier, the drop-size distribution in such an experiment must feature as the largest size drops of diameter $d_{\max}$ if drops of diameter below $d_{\max}$ were not to break at all; this observation must be valid at least over time scales comparable to the survival times of drops slightly larger than those with diameter $d_{\max}$. However, the objective of this investigation has been to examine the size distributions at considerably larger times. It would also be interesting to see if the scaling behavior, a manifestation of some underlying regularity in the breakage process, persists at the larger times.

Experimental

As mentioned above, most experiments to determine $d_{\max}$ have typically been carried out for 1 or 2 h. There has been some indication in the literature, however, that drop breakage continues up to longer times. Konno et al. (1983) conducted experiments with *o*-xylene—CCl_4 as the dispersed phase and their results indicate that drops continued to break for up to 5 h. They have not made any comments on the apparent discrepancy with the literature on $d_{\max}$. Baldyga and Bourne (1995) have recently conducted drop breakup experiments in a jet mixer with recirculating flow. Their experimental measurements (only $d_{\max}$ was measured) at 1, 5 and 24 h indicate that significant breakup occurs between 1 and 5, and also between 5 and 24 h. The dependence of $d_{\max}$ on the Weber number, however, changed continuously with time from $We^{-0.6}$ to $We^{-0.82}$. The authors explained the changing value of this exponent by invoking a change in the breakage mechanism as time progresses—at short times, drops break by average pressure fluctuations, and at long times, they break due to rare but very intense pressure fluctuations (Meneveau and Sreenivasan, 1991). These considerations predict that with change in mechanism of breakup, the exponent should change from -0.6 to 0.92.

The aim of the present study is to obtain detailed experimental measurements (not just $d_{\max}$) from 1 to 10 h to study the effect of long stirring times on the mechanism and the nature of drop breakage. The experiments of transient breakage in liquid-liquid dispersions were conducted in a 14-cm dia. mixing vessel of standard configuration. A Rushton turbine impeller (5 cm dia.) was used to provide the agitation. A diagram of the mixing vessel is shown in Figure 1. The impeller was driven by a variable speed Lightnin motor, which gives very accurate control of the stirrer speed.

Before beginning each experiment, the apparatus was thoroughly cleaned and rinsed. The apparatus was then dried before it was used in the experiment. To start the experiment, 1,700 mL of water (which had earlier been equilibrated with the dispersed-phase organic liquid) was added to the glass vessel. The water used in the experiments was distilled and deionized before being filtered through a Millipore water system. The organic phase (previously equilibrated with water) was added to the vessel through the sampling port while the stirrer speed was maintained at the speed required for the experiment. In each experiment, 10 mL of the organic phase was added, corresponding to a dispersed-phase fraction of 0.58%.

Small samples of the dispersion were removed at regular intervals from the stirred vessel with a micropipette, placed on a microscope slide and stabilized with a couple of drops of sodium dodecyl sulfate (SDS) surfactant. Images of the dispersion were captured from a microscope with a video camera and stored for analysis with an image analyzer. The images were then processed using a Cambridge Instruments Q570 Image Analyzer to obtain the drop sizes. Approximately 120 images were taken at each experimental time, and approximately 3,000 drops were measured to construct a good estimate of the size distribution.

Experiments were conducted with various dispersed-phase systems and at different stirred speeds. Four different dispersed-phase systems were chosen. Small amounts of carbon tetrachloride were added to some of the organic phases to make a neutrally buoyant dispersion. The physical properties of the experimental systems used are shown in Table 1. For the remainder of this article, the silicone oil will be referred to by its nominal viscosity in centistokes (as provided by the

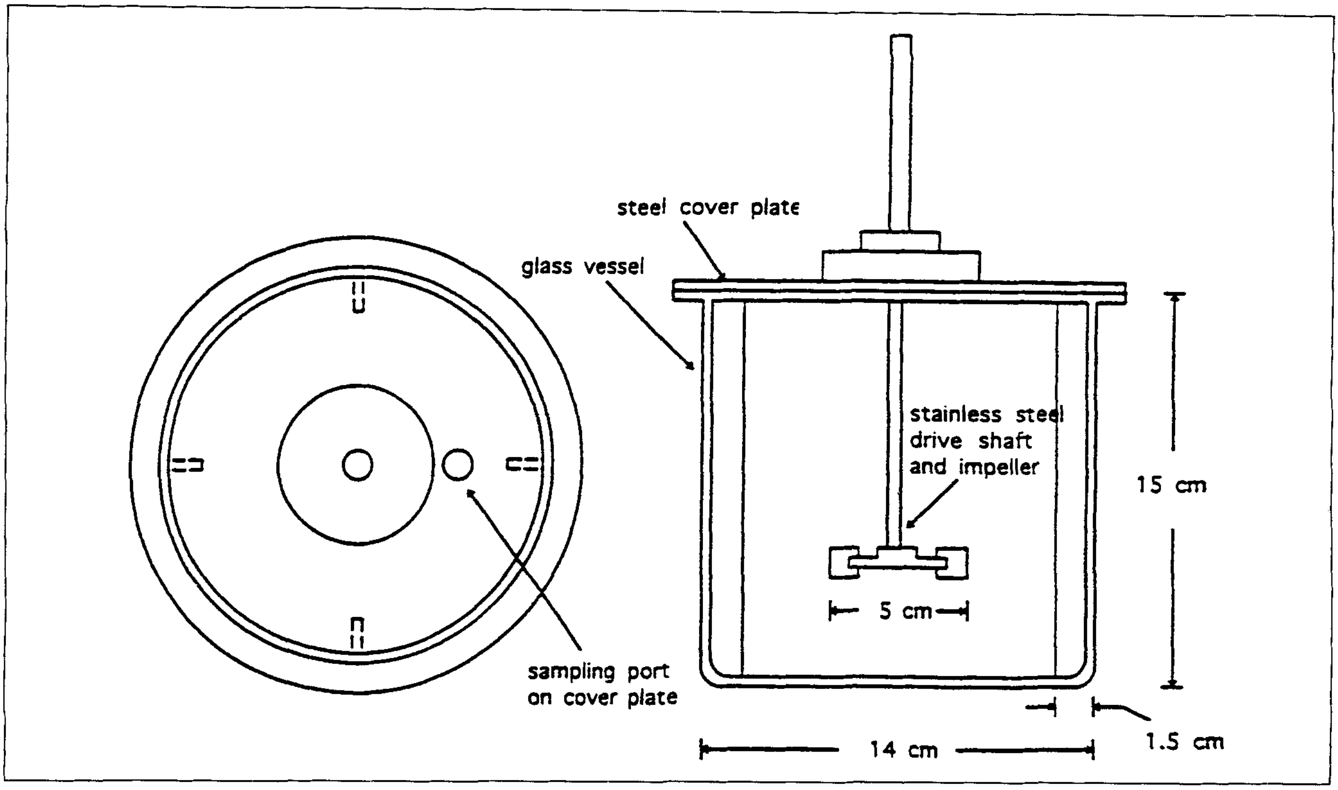

Figure 1. Mixing vessel used in experiments.

manufacturer). Details of the viscosity and interfacial tension measurements are given in Sathyagal et al. (1996). Experiments at various stirrer speeds (typically 350, 400 and 500 rpm) were conducted for each of the systems.

Results and Discussion

The data from the image analysis system in the form of a list of drop diameters was converted into size distribution curves using kernel density estimation techniques. Details of these techniques are given in Silverman (1986). Cumulative volume fraction curves were also calculated from the image analysis data.

Figure 2 shows experimental cumulative volume fraction $[F(v, t)]$ curves for some of the systems studied. These curves are typical of the data obtained in all the experiments conducted in this study. The figures show that the curves move consistently to the left with time. This clearly indicates that the drops continue to break throughout the 8 to 10 h course of the experiments. This stands in direct contrast to the experiments reported in the literature on $d_{\max}$, where it was typically assumed that drop breakage no longer occurred after 1 to 2 h. Table 2 compares some $d_{\max}$ values obtained from the correlation of Calabrese et al. (1986) with the largest drop size seen at the end of the experiments in this study. From this table, it can be seen that the $d_{\max}$ values are much larger than the drop sizes seen in these experiments. The rate at which the curves move to the left decreases with time. This is consistent with the notion that the breakage rate of smaller drops is lower than that of the larger drops.

Table 1. Physical Properties of Liquids Used in Breakage Studies

System	Composition w/w %	Viscosity cp	Interfacial Tension mN/m
Benzene–Carbon Tetrachloride	73–27	0.74	35.0
Heptane–Carbon Tetrachloride	44.7–55.3	0.72	42.0
Acetophenone	100	1.6	17.4
Dimethylpolysiloxane (20 cs) Carbon Tetrachloride	87.6–12.4	11.3	36.2

As mentioned earlier, the experiments have been conducted with a very low dispersed-phase fraction to minimize drop coalescence. Although the drops continue to break, even at the long times at which these experiments have been conducted, the total drop number density (number of drops per unit volume of dispersion) is sufficiently low to neglect drop coalescence. The negligible effect of drop coalescence in these experiments can also be inferred from the fact that the transient drop-size distributions (such as those shown in Figure 2) collapse very well into a single curve under the similarity transformation for drop breakage. Figure 3 shows a time-invariant similarity distribution obtained from the transient-size distribution data. The similarity variable ζ on the x-axis is defined as $t\Gamma(v)/\Gamma(v_{\text{ref}})$, where $\Gamma(v)$ is the breakage frequency of drops of size v, and v_{ref} is a reference volume representing a drop size present in the system. Function $f(\zeta)$ in the similarity group $\zeta f'(\zeta)$ plotted on the y-axis is the transformed cumulative volume fraction $[f(v, t) \rightarrow f(\zeta)]$.

Figure 3, which is typical of all the experiments conducted in this study, shows two main features of the breakup process studied here. First, it shows that the drop breakup is self-sim-

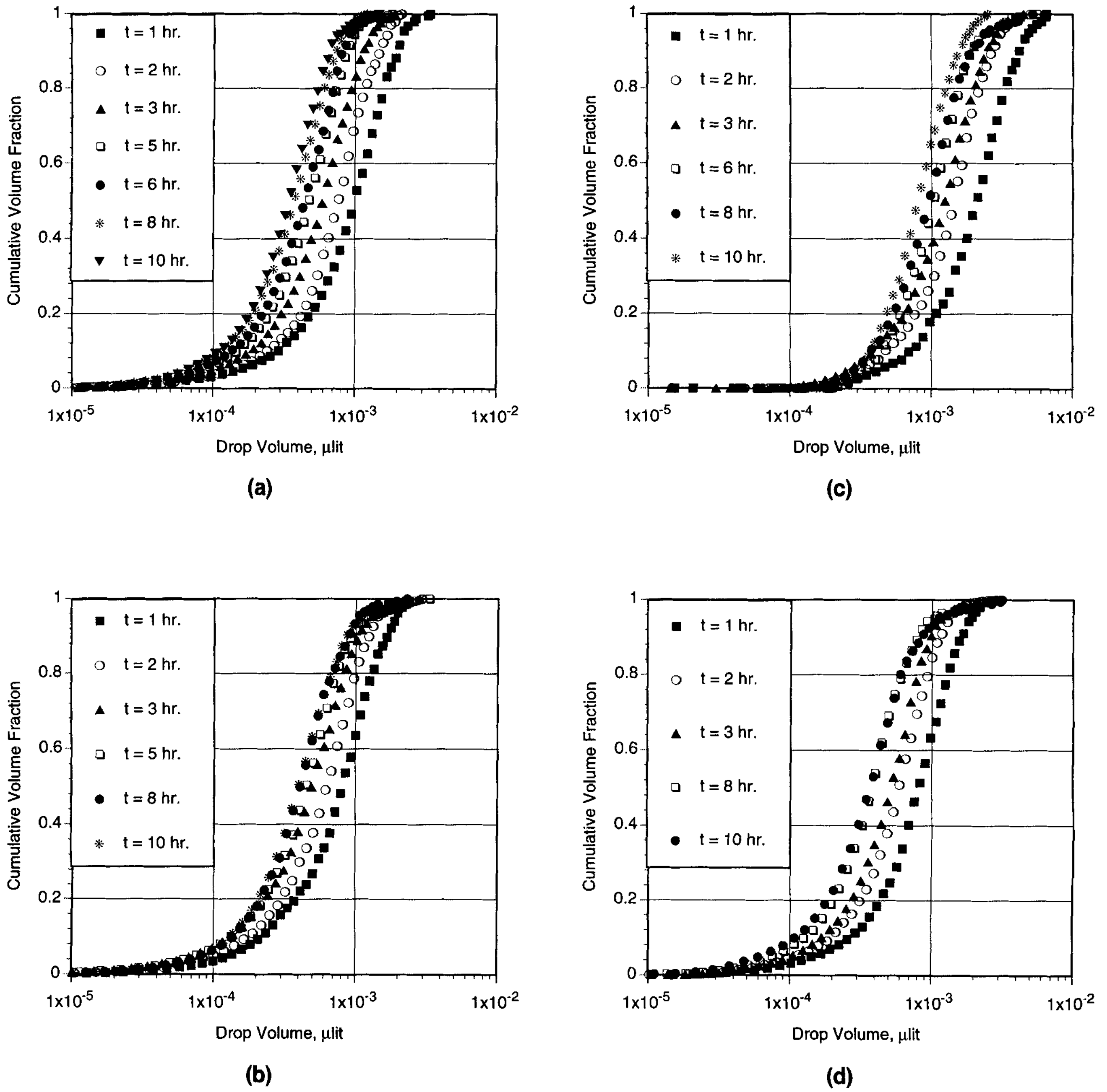

Figure 2. Experimental drop-size distributions for various systems.

(a) System: benzene-CCl_4 at 400 rpm; (b) system: acetophenone at 300 rpm; (c) system: heptane-CCl_4 at 400 rpm; (d) system: 20 cs oil-CCl_4 at 500 rpm.

Table 2. d_{max} Values of Calabrese et al. (1986) vs. Largest Drop Sizes at Long Times in Experiments

System	Stirrer Speed rpm	d_{max} of Calabrese et al., μm	Largest Drop Exp. μm
Benzene–CCl_4	350	249.6	164.2
Benzene–CCl_4	400	213.0	141.5
Benzene–CCl_4	500	163.2	101.2
Acetophenone	250	244.0	225.2
Acetophenone	300	196.0	175.8
Heptane–CCl_4	400	237.3	189.9
Heptane–CCl_4	500	181.8	144.7
20 cs silicone oil–CCl_4	500	180.6	181.4

ilar which indicates that similar breakage events occur during the course of the experiment; second, the choice of similarity variables, which involves time explicitly, suggests that the breakup process continues through the experiment and may continue for even longer stirring times. The similarity distributions obtained in this study compare very well with those obtained by Sathyagal (1994) at short times (approximately up to 1 h). One such similarity distribution, obtained under the same experimental conditions as those used for Figure 3, is shown in Figure 4. A comparison of Figures 3 and 4 shows that even for two separate experiments, the similarity distributions at short and long times are very similar in shape. The ζ values in the two similarity distributions are different be-

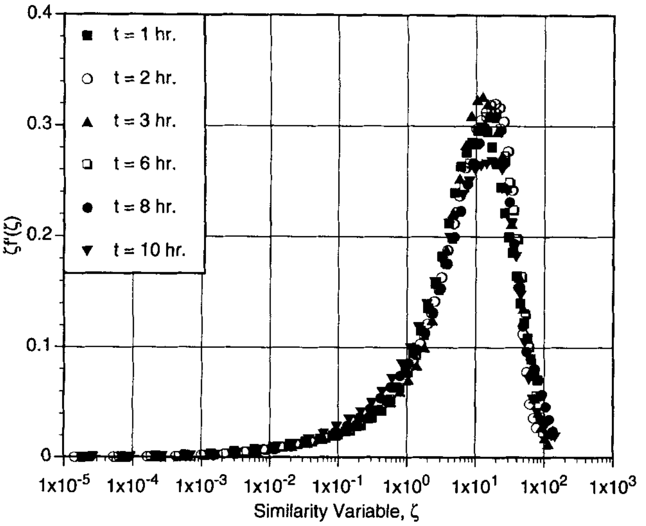

Figure 3. Similarity distribution for the system benzene-CCl$_4$ at 350 rpm at long times.

cause the reference volume v_{ref}, which corresponds to a representative drop size present in the system (Sathyagal et al., 1995), is smaller for a long-time experiment (Figure 3).

We will now show that the two similarity distributions are actually identical. Consider that the transient distribution in Figure 3, obtained at 60 min, is replotted in Figure 4 using the v_{ref} value employed in Figure 4. Since Figure 4 already shows that the transient distributions obtained at 15, 30, 45, and 75 min are self-similar, the transient distribution obtained at 60 min will also have to be self-similar; therefore, when replotted on Figure 4, it will coincide with the similarity distribution for a short-time experiment. All other transients in Figure 3 are self-similar to that obtained at 60 min; hence, these too, if replotted using the value of v_{ref} employed in Figure 4, will coincide with the similarity distribution in Figure 4. Thus, the transient distributions obtained by Sathyagal (1994) over a 15- to 75-min period and those obtained in the present study over a 1- to 10-h period collapse in to a single self-similar distribution. The fact that the similarity distributions for the short time and those in the present study are identical confirms that *similar* breakage events occur over the *entire period* of these experiments.

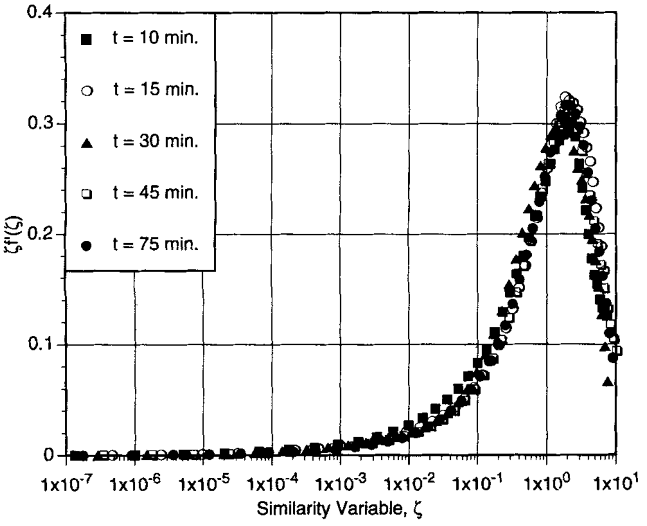

Figure 4. Similarity distribution for the system benzene-CCl$_4$ at 350 rpm at short times (Sathyagal, 1994).

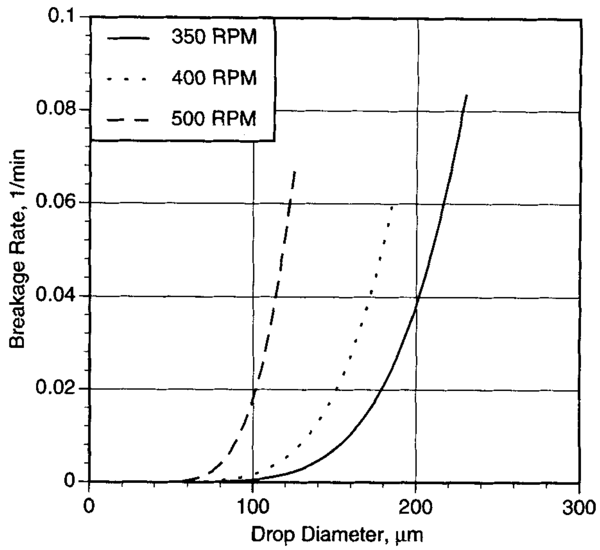

Figure 5. Drop breakage rates determined from the inverse problem at different stirrer speeds for the benzene-CCl$_4$ system.

The existence of similarity can be used to determine the drop breakage rate and daughter drop distributions via an inverse problem procedure as described by Sathyagal et al. (1995). The similarity distributions obtained in this study were used to evaluate the drop breakage functions. The drop breakage rate functions for all the experimental conditions in this study were found to be nonpower law functions, consistent with the results obtained by Sathyagal et al. (1996). A typical result for the drop breakage rate is shown in Figure 5. The breakage rate curves are very similar to those obtained by Sathyagal et al. (1996). The breakage rate increases strongly with stirrer speed and drop diameter. It must be noted that these drops have a nonzero, though small, breakage rate. Such long-time experiments, by sampling more breakage events of the small drops compared to the short-time experiments, could provide better estimates of the breakage rate of small drops.

Conclusion

Drop breakage experiments conducted over long times (approximately 10 h) show that the drop-size distribution evolves continuously toward smaller drop sizes. This indicates that drops continue to break over the course of the experiment, and challenges the notion of the existence of a maximum stable drop diameter $d_{\max}$ at least over the time scales of the current experiments.

The transient drop-size distributions obtained in these long-time experiments show the existence of self-similarity. The similarity distributions obtained are identical to those obtained under the same experimental conditions at short times. This leads to the conclusion that apparently the nature of drop breakup (distribution of daughter drops) at long times does not differ from that observed at short times. Baldyga and Bourne (1995) have proposed, however, that the mechanism of breakup changes at long times. From our experiments in stirred dispersions, however, it does not appear that breakage of the smaller droplets occurs by a different mechanism.

The similarity distributions obtained here have been used to evaluate drop breakage functions via an inverse problem (Sathyagal et al., 1995a). The breakage rates of the small drops are nonzero but small in magnitude.

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