Effect of Mass Transfer on Droplet Breakup in Stirred Liquid-Liquid Dispersions

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Population balances represent an effective framework for the analysis of rate processes in dispersed phase systems. Mainly, they are able to account for the dynamics of the dispersed phase because of particle breakup and agglomeration while concurrently accounting for the rate processes in single particles. The effectiveness of this framework depends on whether particle phenomena (such as breakage and agglomeration) may be regarded as independent of the rate processes themselves. Thus, for example, in liquid-liquid dispersions one may ask if droplet breakup and coalescence rates may themselves depend on rate processes such as mass transfer. There is very little information in the literature on measurement of drop breakup and coalescence rates even in the absence of mass transfer. In this connection, recent work by Narsimhan et al. (1980, 1984) has reported drop breakup rates in lean liquid-liquid dispersions in which coalescence may be neglected. Their determination of the breakup rates has been accomplished with the aid of a similarity theory. In the present context, it is of interest to ascertain whether the foregoing similarity theory is applicable to dispersions in which mass transfer of a solute is occurring. The primary objective of this note is thus an investigation of droplet breakup when a solute is transferring into the continuous phase.

Information about drop breakage pertains to the breakage rates of single droplets as well as the size distribution of daughter droplets arising out of a given breakage. Narsimhan et al. (1980) have formulated and applied a similarity theory to the population balance equation in order to recover the breakage rate of single drops as a function of drop sizes. In their latest work (1984) they have shown that their theory adapts reasonably well to data on transient drop size distributions obtained by direct photographic measurement. Narsimhan et al. (1984) have determined the transitional breakage probability as well as the daughter droplet size distribution from the breakage of a parent droplet. They have characterized the breakage rate as a function of drop sizes and other operational parameters in terms of generalized dimensionless groups. However, their experiments were limited to pure systems. The question then arises as to whether the similarity theory is also applicable for dispersed phase systems with solute in phase equilibrium with the continuous phase, as well as the effect of mass transfer, on drop breakage rate. The similarity theory proposed by Narsimhan et al. (1984) can be applied more universally if the breakage frequencies do not strongly depend on the transfer rates between the dispersed particles and the containing medium. The main theme of this paper is to verify the applicability of the above similarity theory in the presence of rate processes in droplets.

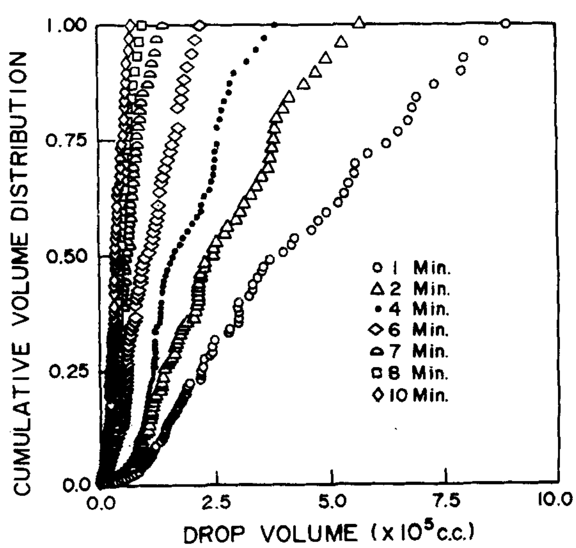

Figure 1. Drop size distribution vs. drop volume at various times.

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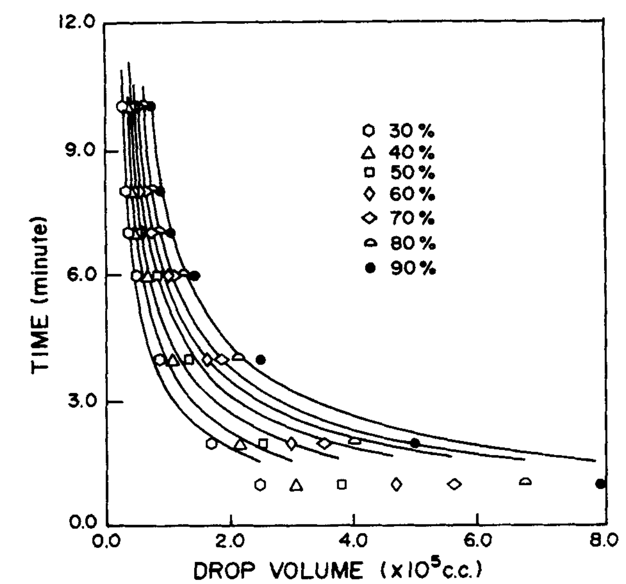

Figure 2. Stirring time vs. drop volume for fixed cumulative volume percentages.

Theory

Since the similarity analysis has already been elaborated elsewhere (Narsimhan et al., 1980, 1984) we will only recount briefly here the development for predicting the transition breakage probability.

The evolution of drop size distribution in a batch vessel with negligible coalescence is described by

$$\frac{\partial F(v,t)}{\partial t} = \int_v^\infty \Gamma(v')G(v,v')\partial_v F(v',t) \tag{1}$$

Narsimhan et al. (1980) have assumed that $G(v, v')$ should be of the form

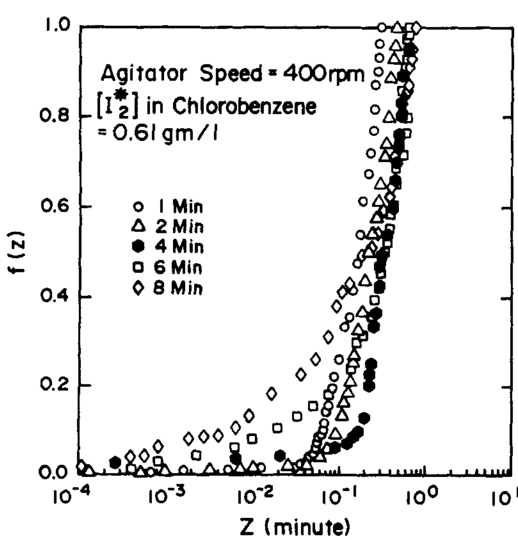

Figure 3. Cumulative volume distribution vs. similarity variable.

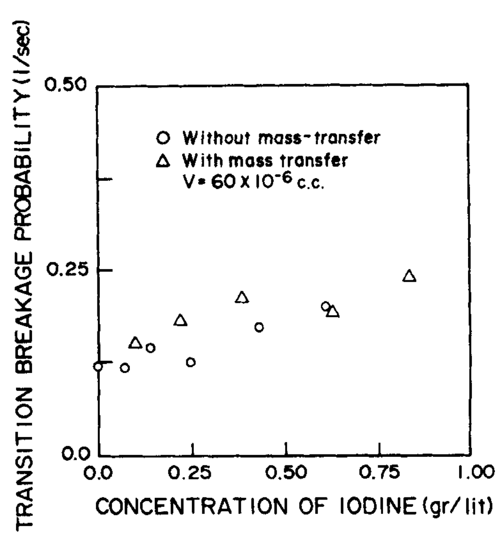

Figure 4. Effect of solute concentration on transition breakage probability.

$$G(v,v') = g\frac{\Gamma(v)}{\Gamma(v')} \tag{2}$$

which contains the hypothesis of similar breakage. Equation 2 admits a similarity transformation of the form

$$F(v,t) = f(z) \quad \text{and} \quad z = \frac{\Gamma(v)}{\Gamma(v_o)}t \tag{3}$$

where v_o is same reference drop volume. Equation 3 recasts Eq. 1 in the form

$$\phi(z) = \Gamma(v_o)\int_z^\infty \phi(z)g(z/\xi)\,d\xi \tag{4}$$

where $\phi(z) = z(df/dz)$. A similarity check can be established by plotting $f(z)$ vs. z where all the transient drop size distributions will merge to a single curve. In order to solve Eq. 4 for $\phi(z)$ it is necessary to know $\Gamma(v_o)$ and g. We follow the same procedure (Narsimhan et al., 1984) to obtain $\Gamma(v_o)$ and it has also been similarly assumed that g follows a beta distribution that contains three parameters. Thus,

Table 1. Estimated Values of Transition Breakage Probability $\Gamma(v_o)$ and Parameters of Daughter Drofplet Distribution Function

I_2 in Chlorobenzene g/L	$\Gamma(v_o)$* 1/s	Parameters r	s	x_o	I_2 in Chlorobenzene g/L	$\Gamma(v_o)$* 1/s	Parameters r	s	x_o
0.0	0.852	3.42	3.42	0.4	—	—	—	—	—
0.071	0.817	3.56	3.2	0.42	0.1	0.911	3.0	3.0	0.41
0.141	0.86	3.5	3.5	0.4	0.22	1.13	3.16	3.22	0.36
0.248	0.978	4.27	3.68	0.39	0.382	1.352	3.63	3.41	0.4
0.61	1.15	3.7	3.2	0.52	0.627	0.97	3.8	4.21	0.43
—	—	—	—	—	0.837	1.41	3.22	4.01	0.47

*v_o = 500 × 10^{-6} cm^2; agitator speed 6.67 rps
System: chlorobenzene in 0.1 N KI solution

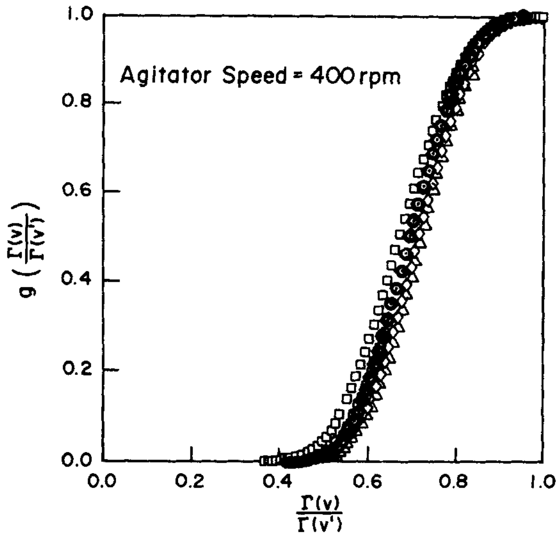

Figure 5. Dimensionless daughter drop size distribution.

$$g(x) = \frac{(r+s-1)!}{(r-1)!(s-1)!}\int_0^{(x-x_o)/(1-x_o)} \xi^r(1-\xi)^s\, d\xi \quad (5)$$

The details for estimating r, s, v_o, and $\Gamma(v_o)$ can be found in the work of Narsimhan et al. (1984).

Experimental Method

A glass vessel of 13 cm dia., and 14 cm height, with four symmetrically placed baffles and optical windows for photographing the dispersion was used in this study. The agitator was driven by a Fischer Stedi-Speed stirrer with speed control. An Olympus OM-2(N) 35 mm camera with autobellows and a 80 mm focal length $f/4$ macro lens was used to take the photographs of the droplet swarm. The necessary arrangements for obtaining good photographs of droplets sample are discussed elsewhere (Narsimhan et al., 1984).

The system used 0.1N KI aqueous solution-chlorobenzene-iodine where chlorobenzene was the dispersed phase and iodine was the transferring solute. Iodine obeys the following distribution law at 27°C:

$$\frac{[I^*_{KI}]}{[I^*_{ChB}]} = 0.025 \quad (6)$$

The volume fraction of dispersed phase was maintained at 0.2% in each run. In order to avoid any stray light, the photographs were taken in the dark. Care was taken to avoid measuring the sizes of those drops adhering to the side of the optical window. Drop size distribution was measured by analyzing the photograph by means of an Eyecom image processing system with PDP-11 microprocessor.

Results and Discussion

A typical plot of cumulative drop volume distribution function $F(v, t)$ vs. drop volume v at various times is shown in Figure 1. Figure 2 displays the plot of time vs. drop volume with cumulative volume percentages as parameters. The solid lines in Figure 2 indicate the curves best fitted to the experimental points through least squares. In Figure 3 $f(z)$ vs. z is plotted where $[z = \Gamma(v)t/\Gamma(v_o)]$. Except at large times the transformed distributions do merge into a single curve, supporting similarity. The

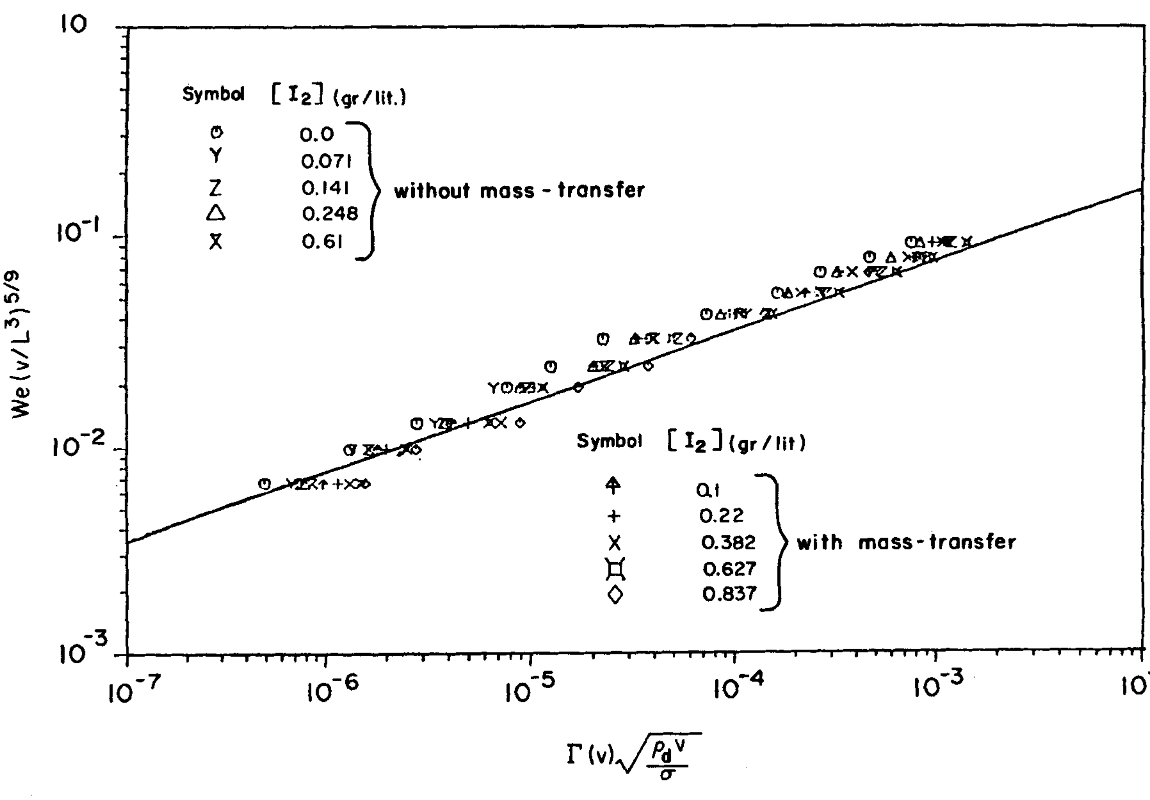

Figure 6. Dimensionless correlation of transitional breakage probability.

deviation at large times could be attributed to the error in estimating $\Gamma(v)/\Gamma(v_o)$ for small drop volumes. From Figure 4 it is found that in the absence of mass transfer the transition probability of breakage remains independent of the concentration of solute inside the drop. On the other hand, with mass transfer in effect, the breakage frequency, although weak, increases with the solute concentration.

Daughter droplet size distribution

Through an unconstrained multivariable optimization scheme the three parameters r, s, and x_o for $g(x)$ and the other parameter $\Gamma(v_o)$ have been estimated using similarity plots (Narsimhan et al. 1984). The values of estimated r, s, x_o, and $\Gamma(v_o)$ are given in Table 1. Figure 5 depicts the plot of estimated daughter droplet size distribution with and without mass transfer.

Correlation for transition breakage probabilities

Figure 6 displays a plot of $\Gamma(v)\sqrt{(\rho_d v/\sigma)}$ vs. $We(v/L^3)^{5/9}$ from which the transition breakage probability of drop of volume v can be estimated with given parameter values and experimental conditions. The experimental data were correlated by the following equation,

$$\Gamma(v)\sqrt{\frac{\rho_d v}{\sigma}} = 6.25\, Wc^{3.18}(v/L^3)^{1.77} \qquad (7)$$

The correlation coefficient was found to be 0.91, and 92.11% of total variation was explained by the fitted correlation. The coefficient and power of the correlated Eq. 7 differ insignificantly from the existing correlation for a pure system (Narsimhan et al. 1984), ensuring that variations of solute concentrations in the dispersed phase with and without mass transfer have no role in altering the transition breakage probability to any appreciable extent.

It is to be noted that larger drops tend to break up sooner with time scales smaller than that of mass transfer so that the breakage rate of smaller droplets is more likely to be affected by mass transfer. The present paper does not show significant effects for the breakup of even small drops.

We are thus led to the important conclusion that although from a qualitative point of view mass transfer effects could have the potential (as for example by interfacial turbulence) to influence drop deformation and breakup, they have very little significance for the breakage functions $\Gamma(v)$ and $G(v, v')$.

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Notation

- F = cumulative drop volume distribution
- g = cumulative daughter droplet distribution for "similar" breakage
- G = cumulative daughter drop size distribution
- L = impeller diameter, m
- N = agitator speed, s^{-1}
- r, s = parameters of beta distribution
- t = time, s
- v = volume of droplet, m^3
- v_o = reference volume, m^3
- We = $N^2L^3\rho_c/\sigma$, Weber number
- x = ratio of transitional breakage probabilities of daughter and parent drops
- x_o = parameter of beta distribution
- z = similarity variable

Greek letters

- Γ = transition breakage probability, s^{-1}
- ρ = density, kg/m^3
- σ = interfacial tension, $kg/m \cdot s$

Subscripts

- c = continuous phase
- d = dispersed phase

Literature Cited

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