

Droplet breakup in concentrated emulsions

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(Received 10 July 2000; final revision received 26 October 2000)

Synopsis

In this paper we report an experimental study on the conditions for droplet breakup in concentrated emulsions under simple shear flow. We present a set of experiments where the ratio between drop and matrix viscosity was varied from 0.1 to 22 and the volume fraction ranged from 0% to 70%. It was observed that the critical shear rate for breakup decreased by more than an order of magnitude for the most concentrated emulsions. Further, drops with viscosity ratio of 22 were seen to rupture in simple shear as soon as the emulsion concentration was raised to 40%. All these effects were conveniently explained by means of a mean field model which assumes simply that breakup of a droplet in a concentrated emulsion is determined by the average emulsion viscosity rather than the continuous phase viscosity. © 2001 The Society of Rheology. [DOI: 10.1122/1.1333001]

I. INTRODUCTION

The dispersion of a liquid into a second immiscible liquid is an important operation associated with many industrial processes as occurring in food processing, pharmaceutical manufacturing, polymer blending, and chemical engineering. In many of these operations the use of high volume fractions of the dispersed phase is more the rule rather than the exception. An important parameter during processing of such highly concentrated emulsions is the (average) drop size. The smaller the size, the more stable the resulting emulsion and the larger the total interfacial area, which is the scaling parameter for mass transfer and chemical reactions. For the design of processing equipment is thus important to be able to estimate the average drop size for a specific set of processing conditions and emulsion properties.

The average size of a group of drops subjected to a flow field is determined by two processes: breakup and coalescence. If the flow strength exceeds a certain critical value the drops will rupture and the average drop size decreases. On the other hand, if the flow is slow enough and the concentration is not too low, the collision of pairs of drops can result in coalescence, which will increase the average drop size. In this paper we will focus on the breakup process only.

Breakup of single droplets has been the subject of many investigations since the early work of Taylor (1934). Usually three different breakup mechanisms are discerned [see e.g., de Bruijn (1989)]. A droplet in a velocity field of which the magnitude is slowly increased will split into two daughter drops (binary breakup). Capillary breakup, on the other hand, occurs if the drop has no time to adapt its shape to the rapidly varying flow field. This then results in a highly elongated shape on which perturbing ripples develop.

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The last mechanism is tipdropping, where small droplets are released at the pointed ends of a parent drop. Tipdropping is caused by a nonuniform surfactant distribution and can be prevented by a proper choice of the surfactant. Here we will restrict ourselves to binary breakup.

For isolated drops the conditions for binary breakup are governed by the interplay between the viscous force of the matrix fluid τ_m and the Laplace pressure σ/a , where σ denotes the interfacial tension and a refers to the undeformed drop radius. It has been shown that breakup depends on two dimensionless quantities: the force ratio or Capillary number $Ca \equiv \tau_m a / \sigma$ and the ratio between drop to matrix viscosity $\lambda = \eta_d / \eta_m$. For each viscosity ratio there is a Capillary number above which the drop will rupture. This critical Capillary number is of order unity for viscosity ratios close to one and increases steadily as λ decreases. At the other end, for $\lambda > 1$, the critical Capillary number rapidly increases and reaches an asymptote for $\lambda \approx 3.8$. This means that isolated drops cannot breakup in shear flows if $\lambda > 3.8$. The master curve for single droplet breakup is usually referred to as the Grace curve [Grace (1982)] and can be written as

$$Ca_{\text{crit}} = f_{\text{Grace}}(\lambda). \quad (1)$$

In more concentrated systems, however, this relation cannot be expected to hold without modification. Droplets interact frequently with their neighbors, which will destabilize the drops and thus the critical breakup curve is expected to shift toward smaller Capillary numbers. The question is how much.

Despite its obvious industrial relevance there is only a limited number of studies concerning this problem. In fact, the most detailed work on the effect of concentration on interdroplet interaction, hydrodynamic stresses, and breakup are the recent numerical studies by Loewenberg and Hinch (1996) and Loewenberg (1998). They presented a three-dimensional simulation of a concentrated emulsion in shear flow using a boundary integral formulation, which allows for a disordered dynamic microstructure. They calculate how the average (normal) forces and the drop deformation and orientation change with increasing Capillary number for volume fractions up to 30%. From their simulations it follows that the critical Capillary number decreases by about 20% at maximum, which suggests that the effect of concentration on breakup is relatively small (at least for volume fractions from 0% to 30%).

Experimental studies, however, show that at higher volume fractions the effect of concentration on breakup can be quite pronounced. Wieringa *et al.* (1996) considered an 80% oil-in-water emulsion and follow the change in drop size distribution after emulsification in a colloid mill. Their experimental results were compared with a population balance model in which breakup is predicted using a critical Capillary number based on the emulsion viscosity. The model predictions agreed well with the experiments, which confirms the idea that breakup is caused by the *average* emulsion stress rather than the local stress in the continuous phase layers.

The subject of the present work is to present a systematic study on droplet breakup in (highly) concentrated emulsions at different viscosity ratios in simple shear flows. The results will be interpreted in terms of a simple mean field scaling model, which is presented in Sec. II.

II. SCALING THEORY

To a first approximation, the forces exerted on a single droplet immersed in a concentrated emulsion can be considered as being proportional to the viscosity of the surrounding emulsion (mean field approximation). We therefore propose to use the breakup

relation as given in Eq. (1) but then with a rescaled critical capillary number $Ca^* = \tau_{em}a/\sigma$ and a rescaled viscosity ratio $\lambda^* = \eta_d/\eta_{em}$. This can be written as

$$\eta_{r,em}Ca_{cr} = f_{Grace}(\lambda/\eta_{r,em}), \quad (2)$$

where $\eta_{r,em} = \eta_{em}/\eta_m$ is the relative emulsion viscosity. We thus expect the points on the Grace curve to shift both downwards and to the right if the emulsion concentration increases. Note that these shifts can be as large as a factor of 10^2 for emulsions with 70% volume fraction dispersed phase. In applying the above mean field approximation we neglect possible collective breakup effects in which flow instabilities generated by breakup of one droplet induce breakup of neighboring drops. Shear thinning effects which also affect the local force balance near a droplet, on the other hand, are taken into account by this approach if the emulsion viscosity is evaluated at the critical shear rate.

III. EXPERIMENT

A. System selection

Breakup can be studied either by direct observation of a drop in a well defined flow field (as is done for all single drop experiments) or by observing the change in drop size distribution [Wieringa (1996)]. In this paper we choose the optical observation technique since it has the advantage that it not only gives a direct relation between drop size and critical shear rate but that visual information also is available about droplet interactions leading to breakup. The problem, however, is that for volume fractions above 10% the emulsions become opaque unless the refractive index of water and oil phases are exactly matched. In addition, the density of the two phases must be also matched to prevent creaming effects. Further requirements are that the systems should be stable and that coalescence is suppressed as much as possible. Moreover, the viscosity of the continuous phase should be such that breakup occurs within the experimental window (typically between 0.1 and 100 s⁻¹).

We therefore developed a system consisting of silicon oil drops in an aqueous phase mixture of 29 wt % polyacrylicacid solution +25 wt % hexyleneglycol +26 wt % distilled water +20 wt % dobanol 91-8 surfactant. All aqueous components were completely insoluble in the oil phase. The surfactant is added in excess such that effects related to a nonuniform or nonconstant interfacial concentration are minimized. Tipdropping is not observed with this surfactant. The polyacrylicacid ($M_w = 90\,000$, 25% in water, ex Acros) serves to increase the viscosity, whereas the hexyleneglycol and water are used to decrease the density and match the refraction index. The viscosity, refraction index, and density (all at 25.0 °C) of the aqueous phase were measured to be 0.340 Pa s, 1.4040, and 1.024 g/cm³, respectively. Silicon oils of different viscosity (Baysilone, ex Bayer) were used to create a set of emulsions with viscosity ratios of $\lambda = 0.1, 0.26, 1.0, 2.6, 10,$ and 22. Although the refraction index of these oils was fairly independent of the molecular weight, in some cases minor corrections to the aqueous phase composition were needed to create perfectly transparent emulsions. Marker drops were created by adding a small amount of colorant (Fluka Scarlet Red) to the oil phase.

B. Emulsion preparation

The general procedure was to create a 70% stock emulsion by slowly adding oil to the aqueous phase under constant stirring. Emulsions of the desired concentration were then obtained by dilution. In this way the drop size distribution was kept constant within each viscosity ratio series. The stock emulsions of $\lambda \geq 1$ remained stable for weeks. For the lower viscosity ratio systems no stable concentrated stock emulsions could be obtained

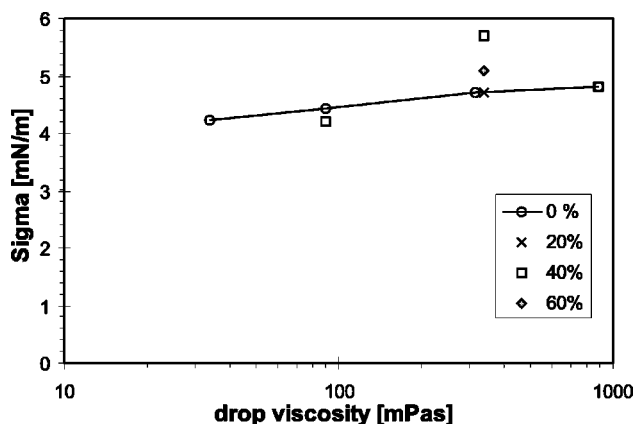


FIG. 1. Equilibrium interfacial tension of colored marker drops in emulsions of different volume fractions. The full line corresponds to the interfacial tension of single drops.

and each emulsion was prepared independently prior to the measurements. The volume fraction range for these emulsions was restricted to an upper limit of 30%. For the 30% low viscosity ratio emulsions coalescence was observed occasionally during shear.

C. Characterization methods and measurement equipment

The interfacial tension was measured using a fully automated apparatus in rising drop set-up (I.T. Concept, France). The method is based on a fit between the measured shape and that predicted by the classical Laplace equation of capillarity. Since the numerical evaluation of the fit is fast (10–20 measurements/s) dynamic aspects of the interfacial tension can also be measured. Figure 1 shows the interfacial tension for drops with different viscosities (full line). It can be seen that the interfacial tension slowly increases with increasing drop viscosity and ranged from 4.24 to 4.8 mN/m. To check whether the emulsion concentration had an effect on the interfacial tension we also measured the interfacial tension at different emulsion concentrations. It is clear from Fig. 1 that within measurement errors, the interfacial tension is independent of the concentration. The data point at 340 mPa s and 40% concentration was disregarded here.

Information about possible elastic effects in the interfacial layer can be obtained by applying periodic variations of the surface area and observing the phase shift with the interfacial tension. In our case, however, these measurements are complicated by the relatively high viscosity of the drop and matrix fluids which tend to mask the (small) surface elastic forces. If the drop is inflated too fast, for example, the interface will flatten what is interpreted by the software as an apparent interfacial tension increase. In extreme cases these effects will cause the apparent interfacial tension to run *ahead* of the applied changes in area, which shows up as phase angles between 45° and 90°. Because of these considerations no reliable surface elasticity data could be obtained with our emulsion systems. If, however, we assume that the viscous effects always tend to increase the surface elastic modulus, then we can take our measurements (typically 5 mN/m) as an upper limit of the surface elastic modulus.

Drop size distributions were obtained by diluting a sample of the emulsion in a mixture of glycerin and surfactant to a final volume fraction of about 10%. In that way the refractive index difference increased and separate drops became visible. The diluted sample was then placed between parallel glass slides which were separated by a spacer of

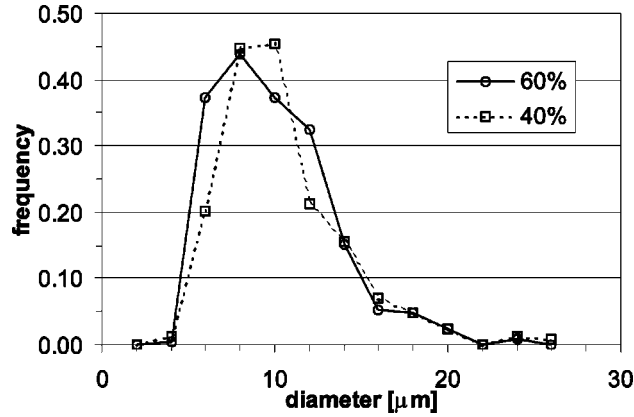


FIG. 2. Drop size distribution of an emulsion with viscosity ratio 1.0. The two curves refer to volume fractions of 40% (squares) and 60% (circles).

about 100 μm to prevent drop squeezing. This system was viewed by a microscope equipped with a video camera and the size distribution was evaluated off-line by measuring the diameter of each individual drop. Typically 200–300 drops taken at three different positions were measured for each size distribution.

The drop size distributions for $\lambda = 1.0$ emulsions at volume fractions of 60% and 40% are shown in Fig. 2. Both distributions have similar shapes and result in a volume to surface average diameter d_{32} , of about 15 μm (where $d_{pq} = \sum n_i d_i^p / \sum n_i d_i^q$). The observed polydispersity, here defined as d_{43}/d_{32} , is 1.10 in both cases. For other systems similar results were obtained.

A Haake RS 150 rheometer was used for all viscosity measurements. The emulsion viscosities were measured in constant shear rate mode, using the plate–plate geometry. The shear rates were varied between 0.12 and 50 s^{-1} , corresponding to the experimental shear rate range in the breakup measurements. Only the curves with decreasing shear rate were recorded to exclude shifts in the viscosity curve due to breakup. For each emulsion measurements were performed using two gap sizes (0.40 and 0.25 mm) to allow for a slip layer correction if necessary [Yoshimura and Prud'homme (1998)].

An example of the measured viscosity curves for the $\lambda = 1.0$ emulsions is given in Fig. 3. It can be seen that with increasing concentration the emulsion viscosity increases and that the higher concentration emulsions show profound shear thinning effects. With increasing viscosity ratio the viscosity curves shift upward as is shown in Fig. 4.

Breakup measurements were performed in a high precision counter rotating Couette cell with a radial swing of only 1.5 μm [de Haas *et al.* (1998)]. The inner radius of the Couette cell is 100 mm and the gap width and depth are 2.2 and 8.0 mm, respectively. The rotation of the inner and outer cylinder is controlled such that the position of the stationary layer can be shifted without affecting the shear rate. The shear rates were checked by independent measurements and could be varied between 0.01 and 100 s^{-1} . A digital camera (Sony XC-75/75CE) connected to an optical system allowed for direct observation of the droplets during flow. The view is in the shear plane (top view). All breakup measurements were performed under thermostatted conditions at 25.0 ± 0.1 $^{\circ}\text{C}$.

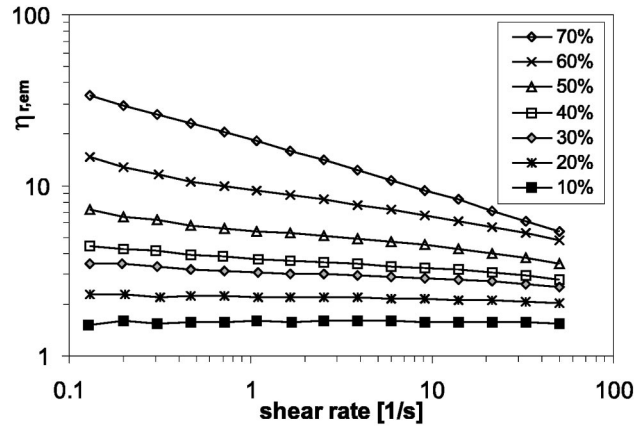


FIG. 3. Relative viscosity curves of $\lambda = 1.0$ emulsions for volume fractions between 10% and 70%.

D. Measurement procedure

Emulsions with a predetermined volume fraction of dispersed phase were prepared by dilution of the stock emulsion followed by gentle mixing. Air bubbles were allowed to escape before the emulsion was introduced in the Couette cell. A preshear of 50 s^{-1} was applied for 10 min. Then a colored silicon oil marker drop was inserted below the emulsion surface by direct injection from a syringe. Typical drop radii range from 40 to $300 \mu\text{m}$. Next, the shear rate was slowly increased until breakup occurred and the initial drop size and critical shear rate were recorded. This procedure was repeated with 10–20 different drops for each emulsion. No differences could be detected between freshly introduced drops and drops which had been ruptured previously.

IV. RESULTS

In Fig. 5 we plotted the critical shear rates for breakup versus the reciprocal drop radius for a $\lambda = 1.0$ emulsion of different volume fractions. The figure shows that the product of $\dot{\gamma}$ and a is constant and decreases with increasing volume fraction. The

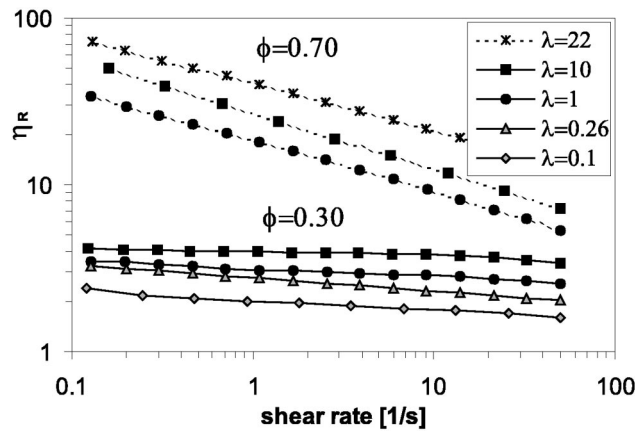


FIG. 4. Relative viscosity for emulsions with different viscosity ratios: (dotted lines) volume fraction 0.70; (full lines) volume fraction 0.30.

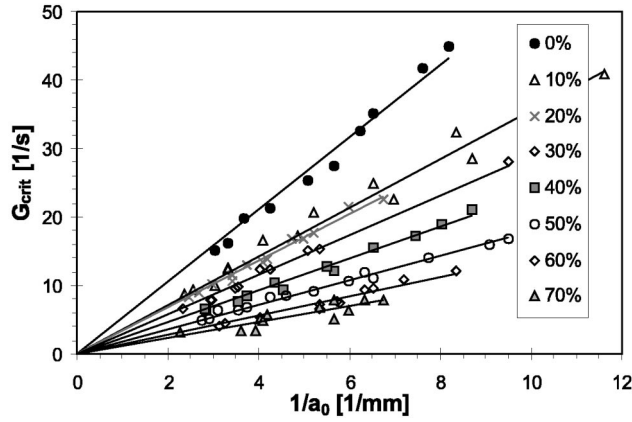


FIG. 5. Shear rate above which breakup occurs vs the reciprocal drop radius for $\lambda = 1.0$ emulsions with different volume fractions.

uncertainty in $\langle \dot{\gamma}a \rangle$ is approximately 10%. Figure 6 shows how the critical Capillary number, calculated as $\eta_m \langle \dot{\gamma}a \rangle / \sigma$, varies with the viscosity ratio for emulsions of different volume fractions. The thick gray line represents the Grace curve for single drop breakup. Figure 6 shows that breakup indeed is easier in concentrated emulsions (the curves shift downward). The reduction in the critical Capillary number for 70% emulsions is about a factor of 10. Further, Fig. 6 shows that for the more concentrated emulsions breakup is possible far above the limiting viscosity ratio for single drop breakup, $\lambda \approx 4$.

To test the validity of our mean field approximation [Eq. (2)] we re-evaluate the breakup data by using the rescaled variables λ^* and Ca^* , as explained in Sec. II. Note that this implies that for each data point in Fig. 5 the emulsion viscosity at the corresponding shear rate should be taken into account. Figure 5 then effectively transforms to a plot of the critical shear stress versus the reciprocal drop radius and the corrected critical Capillary number is obtained as $Ca^* = \langle \eta_{em}(\dot{\gamma}) \dot{\gamma}a \rangle / \sigma$. This evaluation proce-

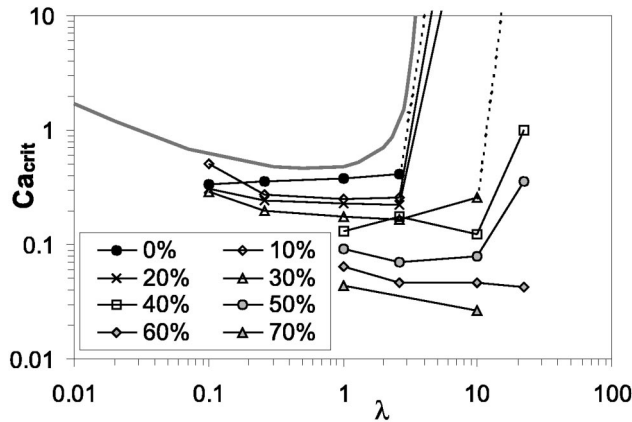


FIG. 6. Critical Capillary number for emulsions of different viscosity ratio and different volume fractions. The thick gray line is the Grace curve and the dotted lines mark the viscosity ratios above which no breakup was observed.

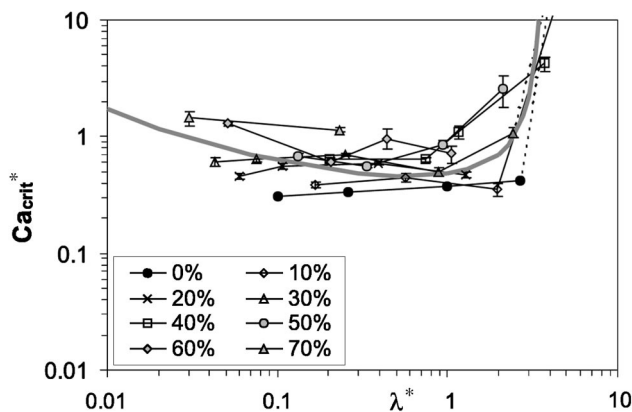


FIG. 7. As in Fig. 6 but now with the rescaled quantities $Ca_{crit}^* = \eta_{r,em} Ca_{crit}$ and $\lambda^* = \lambda / \eta_{r,em}$.

ture becomes especially important for the higher concentration range where the emulsions are shear thinning. The resulting plot is shown in Fig. 7 from which it can be seen that all curves now collect close to the Grace curve. The figure also contains error bars which reflect the smallest and largest possible slopes in the $\langle \eta_{em} \dot{\gamma} \rangle$ versus $1/a$ plots.

V. DISCUSSION

We performed experiments in which the breakup of marker drops in concentrated emulsions was investigated as a function of viscosity ratio and concentration. Because of the relatively large size of the marker drops, our model system is strictly speaking not representative for a concentrated emulsion. However, since in typical (polydisperse) emulsion systems the largest drops always break first, our results are still thought to be applicable for emulsions with a broad size distribution. From Fig. 7 it is evident that the scaling relation Eq. (2) groups all data close to the master curve for single drop breakup. This suggests that the emulsion viscosity is indeed the dominating scaling parameter in these experiments and that pairwise interaction and collective breakup effects are, at most, second order effects. This is corroborated by the observation that in experiments in which two or more marker drops interacted, breakup did not occur unless those drops were already close to their critical shear rates. Such interactions of marker drops were frequently observed after a number of breakup events of a large parent droplet. A similar observation was made by Loewenberg and Hinch (1997). They simulated the collision of two deformable drops just below the critical breakup shear rate and found that the drops adjusted their shape in the neutral direction rather than breaking up.

A closer inspection of the data for the single droplet experiments (0% emulsion in Figs. 6 and 7) shows a small downward deviation of this data with respect to the Grace curve. It appears that this deviation is systematic and cannot be explained by uncertainties in the critical shear rates since these were particularly small in this case (of the order of the size of the symbols in Fig. 7). Surfactant induced effects are at first sight unlikely as an explanation since surfactant layers tend to stabilize drops against breakup [the dilution effect would increase the interfacial tension near the waist which would increase the critical Capillary number, see Janssen *et al.* (1994)]. However, surfactant effects can be quite complicated and a decrease in the critical Capillary number due to small amounts of surfactants has been observed before [Hu *et al.* (2000)].

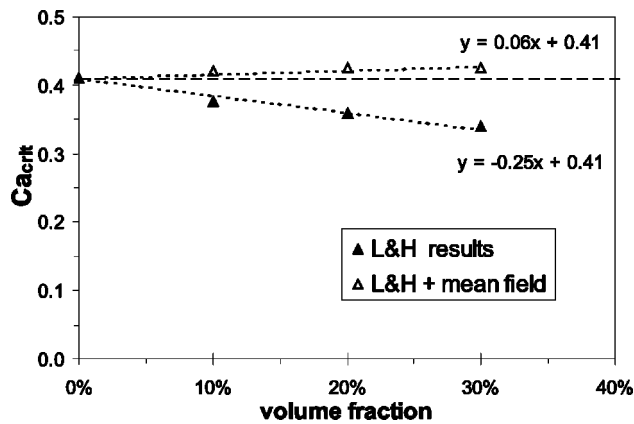


FIG. 8. Loewenberg and Hinch's numerical predictions for the volume fraction dependency of the critical Capillary number (filled symbols). The open symbols refer to the same data but then corrected using the mean field approximation [Eq. (2)]. The dashed line is the prediction for the dilute limit ($Ca_{crit} = 0.41$ for $\lambda = 1$).

By further comparing Figs. 6 and 7 it can be seen that the order of appearance of the volume fraction curves is reversed. This effect is particularly evident for the 70% curve which moves from a critical Capillary number of about 0.03 in Fig. 6 to $Ca^* = 1.5$ in Fig. 7. For the other emulsions the effects are smaller and decrease with decreasing volume fraction. This means that the mean field approximation overestimates the effect of the emulsion viscosity. Reanalyzing our data in fact showed that if an “effective” emulsion viscosity is used, which is 20%–25% lower than the actual emulsion viscosity, the collapse of data in Fig. 7 is improved considerably. A similar overestimation of the mean field approach could also be deduced from the simulation results of Loewenberg and Hinch (1996). Figure 8 shows their predictions for the critical Capillary number (closed symbols) together with these data after application of our mean field correction [Eq. (2), open symbols]. It is clear that also in this case the mean field approach overestimates the correction needed to transform the critical breakup data of concentrated emulsions back to the dilute limit (dashed line in Fig. 8). In this case the correction is about 20% overestimated, which agrees well with our experimental findings.

The explanation for the apparent overestimation of the mean field scaling is that in this approach the drop is assumed to be immersed in a continuous medium with a viscosity equal to that of the emulsion, whereas in reality the drop is always surrounded by a continuous phase layer with a much lower viscosity. This low viscosity layer may act as a slip layer which lowers the interfacial stress such that a higher shear stress is needed for breakup.

VI. CONCLUSION

In this paper we studied the breakup of drops in emulsions consisting of two immiscible Newtonian fluids by direct visual observation. We observed that the critical Capillary number for breakup decreased by more than an order of magnitude for the most concentrated emulsions. Moreover, drops with viscosity ratio $\lambda > 4$, which are known not to break in single drop experiments, did show breakup at elevated emulsion concentrations.

All these effects were conveniently explained by means of a mean field model, which assumes simply that breakup of a droplet in a concentrated emulsion is determined by the

average *emulsion* viscosity rather than the continuous phase viscosity. A more detailed analysis of our data showed that the mean field model slightly overpredicted the stress at which breakup occurred. This deviation was thought to be caused by the continuous phase layer close to the drop, which impairs the transmission of stresses from the bulk to the drop interface. Both the analysis of our experimental data and that of the simulations by Loewenberg and Hinch (1996) suggest that the stress transmission efficiency is about 80%. An improved estimate of the critical breakup Capillary number can thus be obtained by introducing this efficiency factor in Eq. (2).

ACKNOWLEDGMENTS

We acknowledge Jan Benjamins from Unilever Research Vlaardingen for his help with the interfacial tension measurements and the European Community for the financial support (Project No. BE 4322).

References

- de Bruijn, R.A., "Deformation and breakup of drops in simple shear flows," Ph.D. thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1989.
- Grace, H. P., "Dispersion phenomena in high viscosity immiscible fluid systems," *Chem. Eng. Commun.* **14**, 225–277 (1982).
- de Haas, K. H., van den Ende, D., Blom, C., Altena, E. G., Beukema, G. J., and Mellema, J., "A counter-rotating Couette apparatus to study deformation of a sub-millimeter sized particle in shear flow," *Rev. Sci. Instrum.* **69**, 1391–1397 (1998).
- Hu, Y. T., D. J. Pine, and L. G. Leal, "Drop deformation, breakup and coalescence with compatibilizer," *Phys. Fluids* **12**, 484–489 (2000).
- Janssen, J. J. M., A. Boon, and W. G. M. Agterof, "Influence of dynamic interfacial properties on droplet breakup in simple shear flow," *AIChE J.* **40**, 1929–1939 (1994).
- Loewenberg, M., "Numerical simulation of concentrated emulsion flows," *J. Fluids Eng. Trans. ASME* **4**, 824–832 (1998).
- Loewenberg, M. and E. J. Hinch, "Numerical simulation of a concentrated emulsion in shear flow," *J. Fluid Mech.* **321**, 395–419 (1996).
- Loewenberg, M. and E. J. Hinch, "Collision of two deformable drops in shear flow," *J. Fluid Mech.* **338**, 299–315 (1997).
- Taylor, G. I., "The formation of emulsions in definable fields of flow," *Proc. R. Soc. London, Ser. A* **146**, 501–523 (1934).
- Wieringa, J. A., van Dieren, F., Janssen, J. J. M., and Agterof, W. G. M., "Droplet breakup mechanisms during emulsification in colloid mills at high dispersed phase volume fractions," *Trans. Inst. Chem. Eng., Part A* **74A**, 554–561 (1996).
- Yoshimura, A. and R. K. Prud'homme, "Wall slip corrections for Couette and parallel disk viscosimeters," *J. Rheol.* **32**, 53–67 (1988).