Influence of Dynamic Interfacial Properties on Droplet Breakup in Plane Hyperbolic Flow

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Droplet breakup in laminar flows is important in emulsification processes and polymer blending. The influence of surfactants on droplet deformation and breakup in a plane hyperbolic flow was studied experimentally in an opposed-stream device. As in the case of simple shear flow, the inhomogeneity of the surfactant distribution along the droplet interface has a pronounced effect. Our results are qualitatively consistent with other numerical studies for droplet breakup in an axisymmetric elongational flow. Also a striking similarity is noted with other experimental observations for the deformation and breakup of polymeric drops in a quasi-steady-plane hyperbolic flow. The critical capillary number for droplet breakup in the experiments correlates with the interfacial viscoelasticity, and a reformulation of the numerical framework in terms of interfacial elasticity parameters is suggested for future numerical work including other linear flows.

Introduction

One of the key processes in emulsification is droplet breakup in an inhomogeneous flow, which may be laminar or turbulent. The most important laminar flow types in emulsification equipment are simple shear flow (e.g., colloid mill and scraped-surface heat exchanger), and flows with a strong elongational component (e.g., extruders and homogenizers). The local flow in the vicinity of a droplet can often be approximated as a two-dimensional (2-D) linear shear flow (Rallison, 1984), which can be written as:

$$\boldsymbol{u} = \frac{1}{2} G \begin{bmatrix} 1+\alpha & 1-\alpha & 0 \\ -1+\alpha & -1-\alpha & 0 \\ 0 & 0 & 0 \end{bmatrix} \boldsymbol{x}. \tag{1}$$

Here $\boldsymbol{u}$ and $\boldsymbol{x}$ represent the velocity and position vector, respectively, in a coordinate system attached to the center of mass of the drop; G is the scalar velocity gradient; and α represents the flow type. In particular, $\alpha = 0$ for simple shear flow and $\alpha = 1$ for plane hyperbolic flow. For surfactant-free systems, many experimental studies on droplet deformation and breakup have been reported in the literature (recent review; Stone, 1994). In the absence of surface-active substances, the interfacial tension σ is constant and uniform. For that case, deformation and breakup in a steady 2-D linear flow have been shown to depend only on the viscosity ratio λ (drop-phase viscosity μ_D divided by continuous-phase viscosity μ_c), the flow parameter α, and the capillary number Ω, defined as

$$\Omega = \frac{\mu_C G}{\sigma / R}, \tag{2}$$

where R represents the radius of the undeformed drop. Physically, the capillary number measures the ratio of the deforming viscous stress exerted by the outer fluid (order $\mu_C G$) and the counteracting Laplace pressure (order σ/R), which tends to keep the droplet spherical. For each value of λ and α, a critical value Ω_C is found, above which no stable deformed drop shape exists (see Figure 1). For capillary numbers just above Ω_C, the droplet breaks into two equisized fragments and a few much smaller satellites. Clearly droplet breakup at a given viscosity ratio becomes easier when the flow type gets more elongational. For plane hyperbolic flow the critical capillary number becomes constant at large viscosity ratios. By contrast breakup in simple shear flow becomes progressively more difficult when the viscosity ratio increases beyond unity, and is virtually impossible at ratios above about 4.

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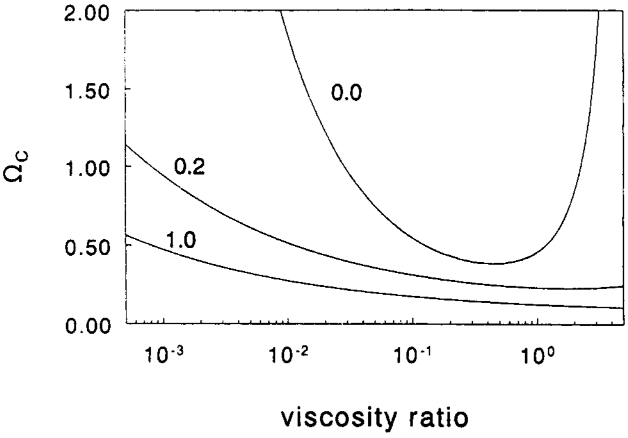

Figure 1. Critical capillary number as a function of viscosity ratio for three values of flow parameter α (after data by Bentley and Leal, 1986).

For droplet breakup in industrial emulsification processes, we have to take into account that practical emulsions almost always contain surface-active substances (surfactants, emulsifiers). These facilitate breakup by lowering the interfacial tension σ (which represents the elastic restoring force in droplet-breakup dynamics), and provide a stability mechanism against coalescence (e.g., Walstra, 1993). In the presence of surface-active substances, it is not obvious that the results in Figure 1 can be applied to find the maximum stable drop size, because droplet breakup implies a significant deformation of the droplet interface. This generally leads to an interfacial tension that will locally deviate from its value at adsorption equilibrium. The magnitude of this deviation depends on the competition between the interfacial deformation and the mechanisms that tend to restore the adsorption equilibrium: interface-bulk emulsifier exchange, and lateral emulsifier redistribution. Only when the latter mechanisms are so effective that they can keep the interfacial tension close to its value for adsorption equilibrium throughout the deformation process, can the influence of the surfactant be accounted for by merely calculating the capillary number using the equilibrium interfacial tension. This will be the case, for instance, at high surfactant concentration. In general, however, the elastic restoring force will become a viscoelastic one.

In a systematic experimental study for simple shear flow (Janssen et al., 1994) we have found that in a large range of surfactant concentrations and viscosity ratios the breakup process is affected significantly by the viscoelastic properties of the interface. In simple shear flow, the interfacial elements of a marginally stable, rotating drop are periodically deformed at twice the rotation frequency. The droplet-breakup dynamics was shown to correlate with the established elasticity modulus ϵ of a harmonically deformed planar interface, calculated at that interfacial deformation frequency. The influence of the elasticity on the breakup process was quantified by introducing an apparent interfacial tension as the sum of the value for adsorption equilibrium under quiescent conditions and a contribution proportional to $|\epsilon|$, which can be assessed theoretically for well-defined systems. The practical value of this semiphenomenological approach lies in the fact that the elasticity modulus can be in principle be measured in interfacial rheology experiments, which do not require a detailed knowledge of the adsorption behavior of the surfactant. This is particularly relevant for practical emulsifiers, like proteins and lecithines, for which the interfacial properties and adsorption isotherm are to date insufficiently quantified to allow a more fundamental theoretical analysis of the drop deformation process.

The experiments in the opposed-stream device discussed in the present article are a first step toward the extension of our approach for simple shear flow to the case of plane hyperbolic flow. As in simple shear flow, significant deviations from the uniform-σ case turned out to be possible. In plane hyperbolic flow the interfacial deformation is nonperiodic, so our previous model cannot be applied directly. We will show, however, that the same interfacial elasticity parameters can be used to characterize the influence of surface-active substances on the critical capillary number. A comparison is made between our experimental observations and some numerical studies by Milliken et al. (1993) and Milliken and Leal (1994), for droplet breakup in the presence of surfactants in an axisymmetric elongational flow. A satisfactory qualitative agreement is found, and a reformulation of the fundamental equations in terms of the interfacial parameters used in the phenomenological approach is suggested for future numerical work. Finally, we discuss the fact that our results show a striking similarity with experimental observations by Milliken and Leal (1991) for the deformation and breakup of polymeric drops in a quasi-steady-plane hyperbolic flow. This similarity suggests that the behavior of these drops is governed by the interfacial rheology related to the surface activity of the polymers, rather than by the suggested polymer-induced change in the bulk rheology of the drops.

Experimental Studies

Opposed-stream device

For our experiments, we have made use of an opposed-stream device at the Technical University of Eindhoven. Details about its construction and calibration can be found in an article by the developers (Janssen et al., 1993), who in fact use the term opposed-jets device. We prefer the term streams rather than jets to avoid the suggestion that high fluid velocities are involved. The principle of the device is sketched in Figure 2. The continuous phase is pumped into a cell that consists of four solid cylinder segments of 4 cm thickness between two parallel Perspex plates through two opposite entrances. These two entrance flows impinge, and then leave the cell via two opposite exits. The entrances and exits have a rectangular cross section of 1 × 4 cm^2. The entrances are fed by a single pump, of which the outflow is split into equal parts in a T-junction. The exit flows from the cell are combined in a special type of valve, designed such that the *ratio* of the two exit flows can be altered without changing the *total* flow rate. The outflow of the valve is lead back into the storage tank from which the pump is fed. Both computational fluid dynamics calculations and laser Doppler anemometry measurements have established that the flow in the central region is to good approximation a plane hyperbolic flow (Janssen et al., 1993).

A droplet of a second, immiscible phase can be introduced into the cell with a syringe via a narrow channel (at the inlet

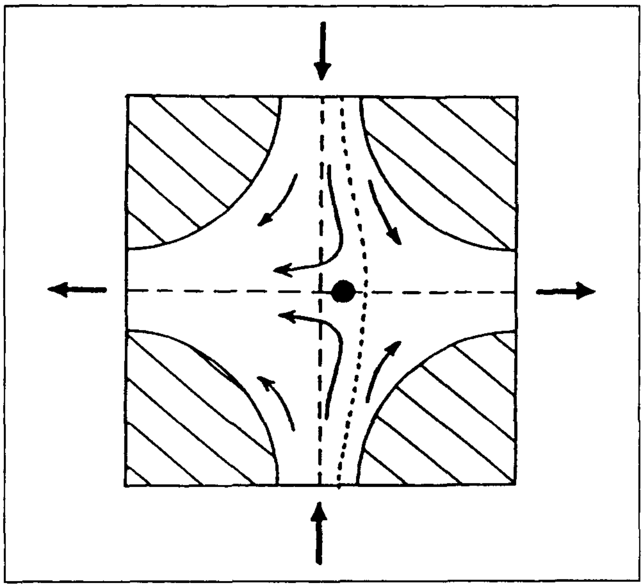

Figure 2. Principle of the opposed-stream device.

side) in one of the circular spacers. This drop is observed using a video camera with magnification optics. The position of the drop can be centered via the exit-flow ratio: when the drop starts to move toward a particular exit, the flow through this exit is decreased, which, by the construction of the outlet valve, automatically gives a stronger flow toward the opposite exit. This flow carries the drop back to the center, provided that it has not moved too far away. At higher flow rates a human operator will have difficulties in keeping the drop centered by manual control of the outlet valve, as the flow velocity increases exponentially with the "out-of-center" distance. This problem was solved following Bentley and Leal (1985), who faced the same problem with their four-roll mill. These authors digitized the video image of the droplet, and used this information to let a computer operate the rotation speeds of the rolls. This sophisticated control system, which checks and corrects the droplet position many times per second, enabled a stable droplet positioning for long periods of time and allowed an accurate determination of the critical capillary number over a wide range of viscosity ratios. A similar control system is used for the opposed-stream device: a special-purpose tracking system receives and digitizes the video image, and uses this information to adapt the control valve at a rate of 25 times per second. Meanwhile the elongation rate can be changed via the total flow rate either manually or by the computer, which can use a previously specified elongation rate vs. time profile to operate the pump.

In a typical experiment the droplet was inserted and centered by manual operation of the pump and exit valve. Then the control of the valve was turned to the automatic droplet tracking system. The droplets were kept centered at a low flow rate for about 3 min, for allowing surfactant adsorption to equilibrate. After that period, the flow rate was slowly increased in small steps until a *steady* droplet deformation no longer existed. The critical pump speed was taken to lie between the last two levels. Indeed, the last pump speed recorded was obviously too large. Whether the previous level was too small is not fully clear, however, as the deformation inherently slow, close to Ω_C, and it is not possible to wait very long for breakup to occur. This is caused by the fact that the tracking system can get confused by passing fragments of earlier experiments, and by air bubbles that were inevitably introduced during the filling of the device and the injection of droplets. This would lead to droplet loss before the transient deformation has set in, particularly at higher flow rates. The critical deformation, D_C, was calculated from the length L and width B of the most deformed, stable drop shape on the video screen ($D=(L-B)/(L+B)$). As for Ω_C, there is some uncertainty about whether the drop shape taken indeed corresponds to the stability limit.

Materials

In all the experiments we have used silicon oil (Rhodorsil) as the continuous phase, and water/corn-syrup mixtures as the droplet phase. Unfortunately the aforementioned problems with the tracking system limited the possible range of viscosities and viscosity ratios. For instance, a very viscous oil would lead to finely dispersed air, which hardly escaped via buoyancy in the storage tank. On the other hand, a low oil viscosity would imply the use of high flow rates to obtain breakup and to prevent the drop from settling. The need to limit the flow rate also prevented the study of very low viscosity ratios (high Ω_C). It may be noted in passing that the tracking problems were much less severe in the experiments by the developers of the setup (Janssen et al., 1993). In their case, the density differences were much smaller (Castor oil in silicon oil). Also they often focused on the behavior of drops that were stretched into long filaments using flow pulses, at which point prolonged tracking is irrelevant.

For low viscosity ratio systems, we used a mixture of polyoxyethylene alcohols with the trade name Dobanol 91-8 (Shell) as surfactant. In the other cases, a mixture of sucrose esters, with the trade name Ryoto Sugar Ester L1695 (Mitsubishi-Kasei Food Corporation) was used. Sucrose esters consist of a hydrophylic sucrose part and a lipophilic fatty acid group; the mixture consisted of sucrose monolaureate for about 80% (the rest being di- and trilaureates). Both the sucrose ester and the Dobanol are water-soluble, and are thus present in the droplet phase.

The equilibrium adsorption of Dobanol 91-8 at the oil–water interface in our systems can be described by the so-called Langmuir isotherm, which relates the interfacial concentration Γ and the bulk concentration c as

$$\Gamma(c)=\Gamma_\infty\frac{c}{c+a}. \tag{3}$$

Here Γ_∞ is the value for a fully saturated interface and a is the half-saturation concentration. The equation of state corresponding to the Langmuir isotherm is the so-called Szyszkowski equation:

$$\sigma(0)-\sigma(c)=\Gamma_\infty RT\ln\left(1+\frac{c}{a}\right). \tag{4}$$

Here $\sigma(0)$ is the interfacial tension of a clean interface, and RT is the product of the gas constant and the temperature. Γ_∞ and a can be determined by fitting the Szyszkowski equa-

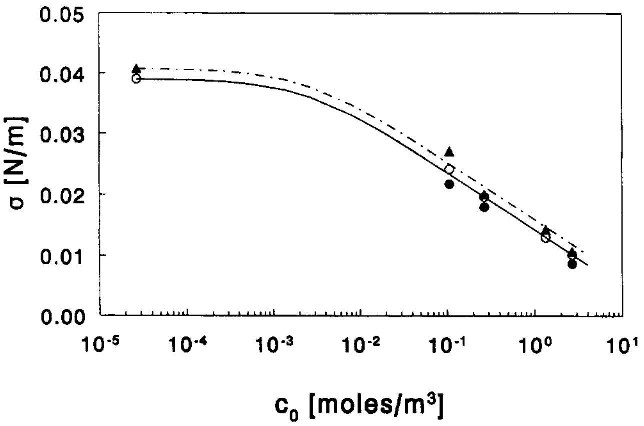

Figure 3. Measured (symbols) and calculated (lines) interfacial tension of W/O/Dobanol 91-8 as a function of the Dobanol concentration, for viscosity ratios 0.12 (▲, —·—) and 0.2 (○, ●, —).

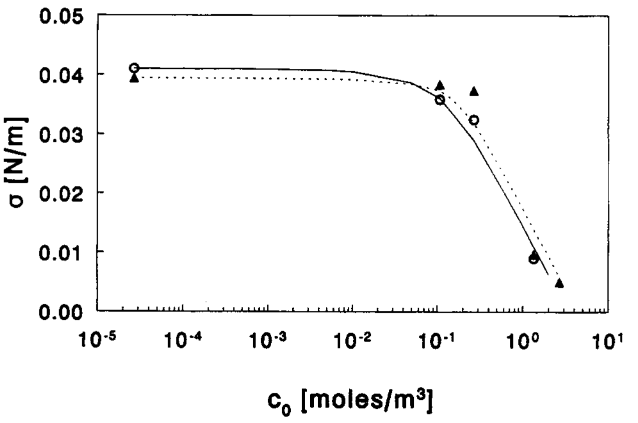

Figure 4. Measured (symbols) and calculated (lines) interfacial tension of W/O/sucrose ester as a function of sucrose ester concentration, for viscosity ratios 0.96 (▲, ----) and 1.36 (○, —).

tion to an experimental σ vs. ln(c) curve, measured (in our case) with the Wilhelmy plate technique. The results are shown in Figure 3, and lead to $\Gamma_\infty \approx 1.7\times10^{-6}$ mol/m^2 and $a = 2.5\times10^{-3}$ mol/m^3.

The adsorption behavior of the W/O/sucrose ester system was found to correspond poorly to the Szyszkowski equation. We therefore tried to describe these results with a so-called Frumkin isotherm, for which the relevant equations are (e.g., Lucassen and Lucassen-Reynders, 1967):

$$\frac{\sigma(0)-\sigma(c)}{-RT\Gamma_\infty} = \ln(1-y) + \frac{H}{RT}y^2 \tag{5}$$

$$\frac{c}{a} = \frac{y}{1-y}\exp\left(-2\frac{H}{RT}y\right), \tag{6}$$

where $y = \Gamma/\Gamma_\infty$. The nonideality parameter H is the partial molar free energy from mixing the solvent and solute in the interface at infinite dilution. These equations reduce to the Szyszkowski equation and the Langmuir isotherm, respectively, when the additional parameter H vanishes. When using them for a given c and known or chosen Γ_∞, a, and H/RT, the first step is the determination of $y(c)$ from a numerical solution of Eq. 6. Once $y(c)$ is known, the calculation of $\sigma(c)$ is straightforward. In our previous article (Janssen et al, 1994), we noted that the calculated equilibrium interfacial tension is much less sensitive to changes in Γ_∞, a, and H/RT than our model equations for describing the breakup behavior in simple shear flow. The same insensitivity of the calculated σ-ln(c) curve for parameter changes was found in the present cases. This implies that the fit values obtained are not too accurate. For Γ_∞ we assumed that the value of 5 10^{-6} moles/m^2 found in our earlier work remains valid, as this is essentially a molecule-related property (reciprocal of the area of the molecule's polar head group). For a and H/RT we tried to stay close to the earlier values ($a = 0.25$ mol/m^3, $H/RT = 0.85$, for $\lambda = 1$), since the systems used are in fact quite similar to those in our earlier work. For the system with $\mu_d = 5.65$ Pa·s and $\lambda = 1.36$, we finally decided on $a = 0.28$ mol/m^3 and $H/RT = 0.85$. For the $\mu_d = 1.91$ Pa·s ($\lambda = 0.96$) system, the best fit was found for $a = 0.7$ mol/m^3 and $H/RT = 1.4$. The results are shown in Figure 4. It should be noted that numerical work on droplet deformation in the presence of a surfactant by Milliken et al. (1993) has shown that the qualitative trends are essentially independent of the details of the isotherm. We therefore expect that the Frumkin approximation used here will be adequate for our purposes.

Qualitative features of the drop deformation process

An important common feature in all droplet deformation experiments is the almost complete absence of internal motion in the droplets. For droplets in elongational flow, such behavior has been observed frequently in the literature, and has been attributed to the influence of surface-active substances. Rumscheidt and Mason (1961), for instance, have studied the surfactant influence on the internal circulation in nearly spherical droplets in a plane hyperbolic flow. They found that even trace amounts of surface-active contamination are sufficient to prevent internal circulation almost completely. Only when both fluids were rigorously purified was internal circulation as calculated theoretically observed. The effect is also well known from studies of rising or settling drops and bubbles in a liquid, in the presence of surfactants or surface-active contamination (Edwards et al., 1991). Also in these cases the interfacial tension gradients immobilize the interface, letting the drop or bubble rise almost like a solid sphere. This shielding of the droplet interior has severe consequences for deformation and breakup in a quasi-steady-plane hyperbolic flow: as long as the droplet interior is quasi stationary, its rheology does not play a role! Indeed, we found the critical capillary number in the absence of added surfactant to be essentially independent of the viscosity ratio, as will be discussed below. Apparently surface-active impurities were still present in these experiments, despite purification of the fluids.

For the systems with viscosity ratio of order unity, the typical breakup process in the absence of added surfactant was found to be of the familiar "narrowing-waist" type (Bentley and Leal, 1986), as is shown in Figure 5a for the $\lambda = 1.37$ system. For breakup in the presence of surfactants a one-sided

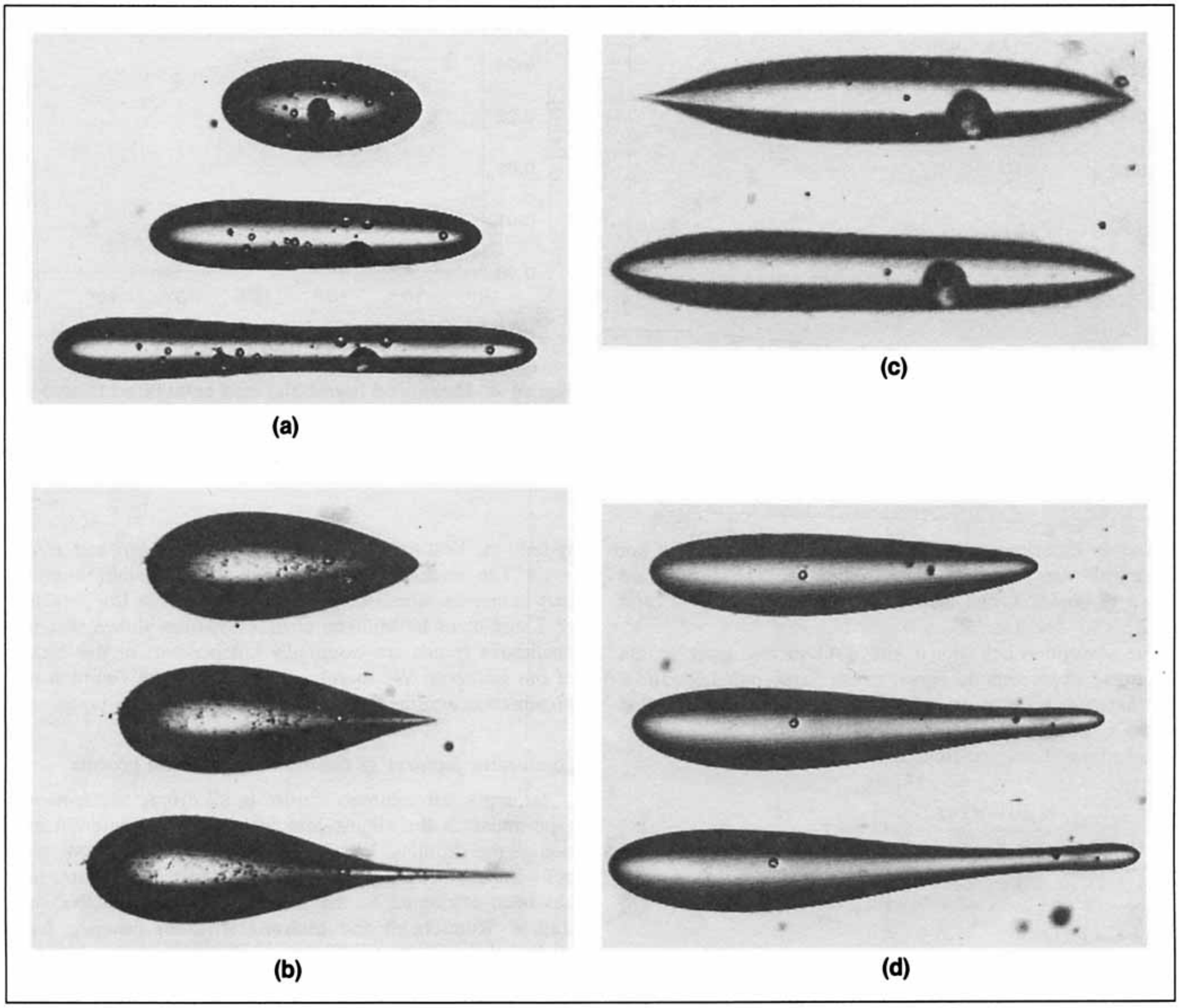

Figure 5. Typical breakup modes: (a) narrowing-waist breakup (no added surfactant, λ, of order unity); (b) one-sided elongation (low and moderate surfactant concentration); (c) narrowing-waist plus tipstreaming (low viscosity ratio, low surfactant concentration); and (d) highly asymmetric narrowing-waist breakup (low viscosity ratio, high surfactant concentration).

elongation was observed, as is illustrated in Figure 5b. The droplet develops a strongly curved end, from which a thread is drawn. This elongates into the fluid, and breaks up due to the development of Rayleigh instabilities. Frequently the one-sided elongation was preceded by the development of cusped ends.

The typical breakup process of the low-λ systems without added surfactant is shown in Figure 5c. First we note that tipstreaming occurs, which confirms the presence of surface-active contamination assumed above to explain the absence of internal circulation in these cases. The breakup mode as such is basically consistent with the narrowing-waist mode. In the presence of surfactant we again found the one-sided elongation. For high surfactant concentration the narrowing waist seemed to reappear in some cases, albeit in a highly asymmetric form (Figure 5d).

Critical capillary number and critical deformation

When a droplet of radius R is divided into two fragments with radii R_1 and R_2, respectively, the increase in interfacial area (and thus the increase in interfacial energy) will be maximal for $R_1 = R_2$. Nambiar et al. (1992) concluded from this fact that breakup into unequal parts should be easier than breakup into equal parts, thus requiring (in our case) a smaller elongation rate. We have studied this suggestion experimentally, by deliberately shifting the focus point of the droplet control system gradually to one side. This shift of the focus point visibly influenced both the equilibrium position of the droplet in the flow field and the "extent of asymmetry" of the breakup. Nevertheless, no systematic shift in the values found for Ω_C was observed. Another test was provided by the fact that the asymmetry was more pronounced for larger droplets, which would lead to the expectation that shifts in Ω_C due to asymmetry should be larger for larger droplets. However, no systematic correlation between the initial droplet radius and the measured value of Ω_C was found. We thus conclude that the extent of asymmetry in the actual breakup process does not influence Ω_C appreciably, and we believe that this can be understood by recalling that the drops remain almost symmetrical during their *steady* deformation. The balance between the shear stress exerted by the outer fluid and the interfacial stress resisting deformation will thus be almost symmetrical for the two halves of the droplet as long as a steady shape exists, but due to a slight asymmetry in the flow, one side may reach the critical condition just before the other side would. Once the least stable side starts to stretch, causing internal flow toward it, the asymmetry in the situation will be amplified rapidly and a distinctly asymmetric breakup is observed. The details of the breakup process can thus be strongly dependent on the droplet rheology, while the value of the critical capillary number for the quasi-steady increase of the elongation rate does not.

The results for Ω_C as a function of the surfactant concentration are plotted in Figure 6. For the W/O/Dobanol systems (low viscosity ratio), the critical capillary number at low surfactant concentrations is found to be considerably smaller than expected from Figure 1. At higher concentrations the difference with Figure 1 is smaller. For the high-λ W/O/sucrose systems, the behavior of Ω_C vs. surfactant concentration is similar to that found in simple shear (Janssen et al, 1994): Ω_C passes through a maximum at intermediate concentrations. At low concentration, Ω_C is consistently somewhat smaller than expected from Figure 1.

The critical deformation is given in Figure 7. Clearly these figures show no significant trend as a function of surfactant concentration. In fact, it seems fair to say that D_C is constant within experimental accuracy. Also there is hardly a systematic difference between the W/O/Dobanol systems and the W/O/sucrose systems. It should be noted, however, that even for surfactant-free drops D_C in plane hyperbolic flow hardly depends on the viscosity ratio for λ larger than about 0.1 (Bentley and Leal, 1986).

Depletion effects and adsorption kinetics

The occurrence of a maximum in Ω_C as a function of emulsifier concentration could be a consequence of emulsi-

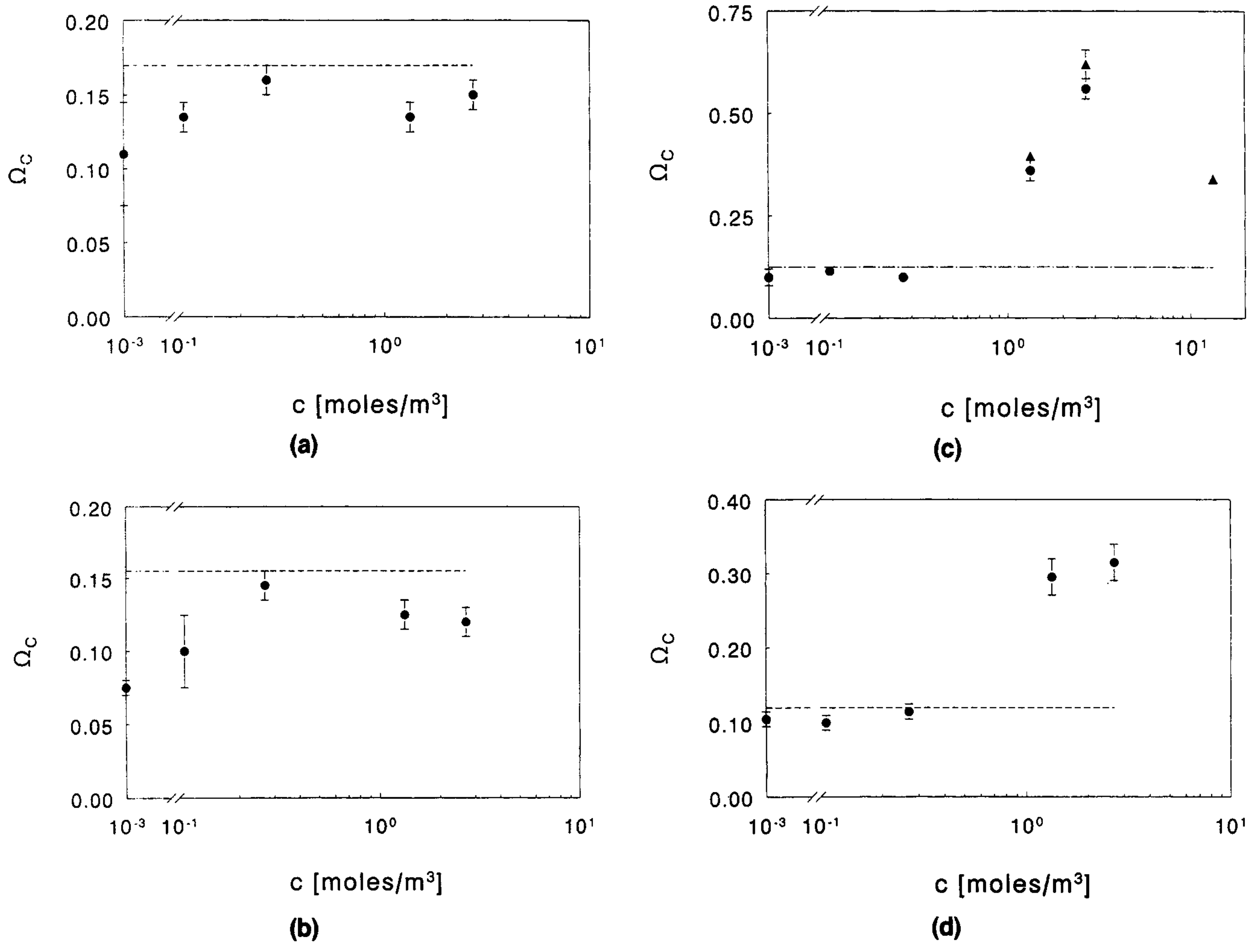

Figure 6. Critical capillary number vs. surfactant concentration: (a) W/O/Dobanol system of $\lambda = 0.12$; (b) W/O/Dobanol system of $\lambda = 0.2$; (c) W/O/sucrose ester system of $\lambda = 0.96$; (d) W/O/sucrose ester system of $\lambda = 1.36$ (the dashed line is the value expected for a uniform interfacial tension (Figure 1)).

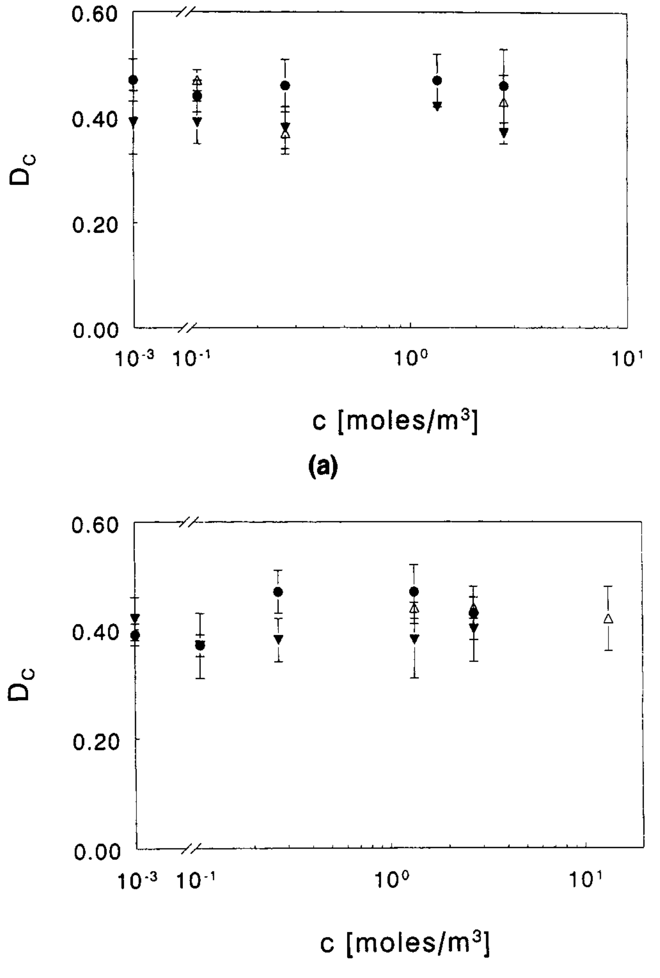

Figure 7. Critical deformation vs. surfactant concentration: (a) W/O/Dobanol systems of $\lambda = 0.12$ (● and Δ) and $\lambda = 0.2$ (▼); (b) W/O/sucrose ester systems of $\lambda = 0.96$ (● and Δ) and $\lambda = 1.36$ (▼).

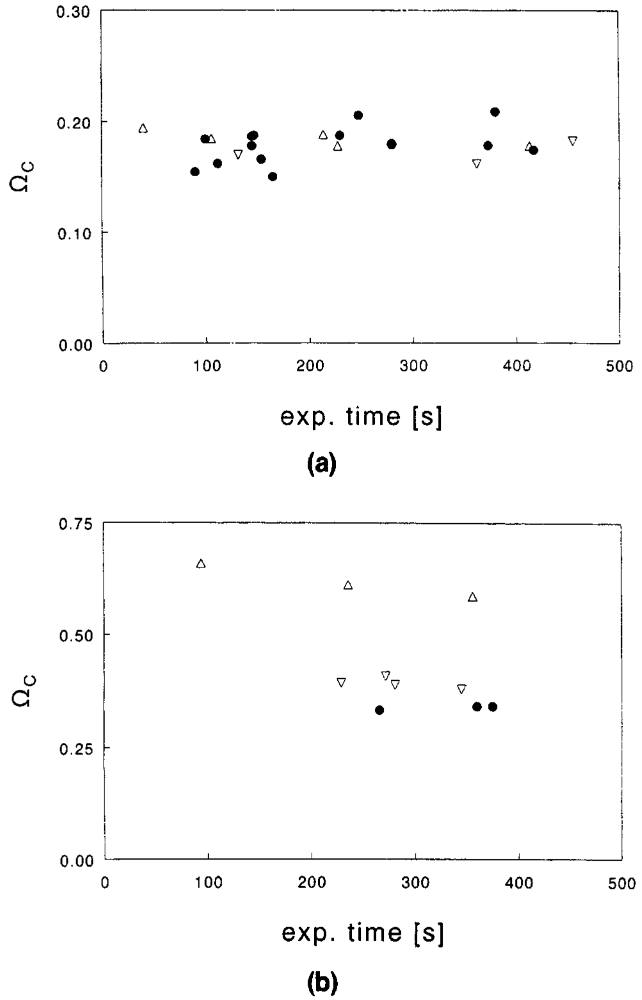

Figure 8. Critical capillary number vs. duration of elongation rate increase, for several surfactant concentrations: (a) $\lambda = 0.2$, and Dobanol concentration is 0.11 (∇), 0.27 (Δ), and 2.7 (●) mol/m^3, respectively; (b) $\lambda = 0.96$, and Sucrose ester concentration is 1.33 (∇), 2.67(Δ), and 13.3 (●) mol/m^3, respectively.

fier depletion from the bulk droplet phase: the total amount of surfactant available in the drop is finite, and may be too small to restore the initial interfacial concentration Γ at the enlarged interface. This would lead to an increase in the interfacial tension, and consequently to a higher critical elongation rate for breakup. However, in our article on droplet breakup in simple shear flow (Janssen et al., 1994) we have shown that such depletion effects are of minor importance in those experiments. The same analysis can be applied to our current systems, leading to the conclusion that these effects cannot be relevant in our present experiments either.

After a droplet has been formed at the tip of the syringe, the surfactant will need some time to reach adsorption equilibrium at the newly formed interface. Similarly, a certain relaxation time is required to reach a steady state after an interface has been deformed. In our experiments, we intended to assess the influence of interfacial tension gradients on a marginally stable drop, due to the ongoing *local* deformation of the droplet interface. This implies that the elongation rate increase in the experiments had to be performed sufficiently slowly to allow the adsorption relaxation processes to keep up with the *overall* enlargement of the interface. In Figure 8 the critical capillary number is shown for different lapses of time between the moment at which the position control is transferred to the tracking system and the moment of breakup (or loss) of the droplet. Clearly there is no systematic dependence of Ω_C on time, which indicates that there is no residual influence of the total enlargement of the interface.

Comparison with the Literature

Milliken et al. (1993) and Milliken and Leal (1994) have performed numerical studies of drop deformation in an axisymmetric elongational flow, in the presence of both insoluble and soluble surfactants. Although our experiments concern plane hyperbolic flow, it is interesting to make a comparison with our observations. Milliken et al. described the evolution of the drop shape, and the surfactant distribution along the interface. They also presented graphs of the deformation D vs. the capillary number Ω (based on the interfacial tension for adsorption equilibrium, as in the present article) for various combinations of the other parameters. D is defined as $(L - B)/(L + B)$, where L and B are the droplet length and width, respectively. These graphs end in the appropriate critical point (D_C, Ω_C), beyond which no stable dropshape exists. Because the influence of a surfactant is taken into account only via its effect on the local interfacial tension, the sign and magnitude of the deviation of the actual D vs. Ω curve from the curve for drops with a constant and uniform interfacial tension basically depends on two issues: (1) how much the local interfacial concentration Γ can deviate from its value for adsorption equilibrium under given conditions, and (2) how sensitive the local interfacial tension is to these changes in local interfacial coverage. For insoluble surfactants the former issue is determined by the competition between the interfacial deformation and the diffusive surfactant redistribution along the interface, characterized in the numerical work by the parameter $\gamma = R\sigma(0)/\mu_C D_I$, where D_I is the interfacial diffusion coefficient. For soluble surfactants, the competition between interfacial deformation and interface-bulk surfactant exchange provides an additional relaxation mechanism. This process was characterized by the Damköhler number Da, which is defined as the ratio of the rate of adsorption/desorption and the rate of diffusive mass transfer in the bulk Rk_a/D (Milliken and Leal, 1994). Here k_a is the adsorption coefficient and D is the bulk diffusion coefficient. It is important to note that the most effective of these relaxation mechanisms will basically determine the magnitude of the deviation from uniform interfacial coverage. The influence of a nonuniform interfacial concentration Γ on the droplet behavior depends on the sensitivity of the interfacial tension σ to changes in Γ. This can be characterized by the slope of the σ vs. Γ curve in $\Gamma = \Gamma_{EQ}$. In fact Milliken et al. defined the dimensionless form β of this slope from a linear equation of state, which is strictly valid only at low surfactant concentration. However, as we will argue further on, it is more general to interpret this equation as the linearization of an arbitrary equation of state about the point $\Gamma = \Gamma_{\text{EQ}}$. Then the appropriate definition of the dimensionless slope β is $d(\sigma/\sigma_{EQ})/d(\Gamma/\Gamma_{EQ})$.

In our experiments with mm-sized drops and $\sigma(0) \approx 40$ mN/m, $\mu_C \geq 2$ Pa·s and $D_I \leq O(10^{-11})$ m^2/s, we are in the limit $\gamma \gg 1$. The Damköhler number Da is difficult to estimate, but for our large drops the transport distances typical for interface-bulk surfactant exchange are likely to be much smaller than the drop size (which is the typical transport distance for the interfacial diffusive relaxation). We thus assume that Da is the most relevant parameter for the relaxation, and that Da decreases with increasing surfactant concentration. The slope β will be a few tenths at low surfactant concentration (Henry regime), but will increase significantly when the concentration rises beyond the half-saturation value a. Keeping these estimates and trends in mind, several points of agreement between the numerical analyses and our experimental results can be noticed:

- In the absence of added surfactant, we only have surface-active impurities. Then β is a few tenths, while Da and γ will be high enough to give basically the insoluble surfactant limit. For that case the numerical results (Figure 7 in Milliken and Leal, 1994) show that the critical capillary number is about 0.12, independent of the viscosity ratio. This agrees quite well with our results.
- For $c < a$, the slope β will remain a few tenths (Henry regime). The numerical results show that the actual Ω_C will be smaller than the value corresponding to the uniform σ limit, but the magnitude of the deviation will decrease with decreasing Da (increasing c). This is the behavior observed in our experiments in the range $0 < c < a$, particularly for low λ.
- For $c > a$, the slope β will increase significantly. For β above about 0.5, the numerical analysis demonstrated the possibility that the critical capillary number in the presence of a surfactant becomes larger than the equilibrium value (Figures 2b and 6 in Milliken and Leal, 1994). This is evident also in our results for λ of order unity. For very high concentration the increasing relaxation will reduce the amplitude of the nonuniformity in Γ, and Ω_C will decrease again. In our experiments for the low-λ systems, the critical capillary number does not rise above its equilibrium value. It is not clear if this is inconsistent with the numerics, as Milliken et al. do not mention if a critical capillary number above the value for adsorption equilibrium is a necessity or merely a possibility (depending on other parameters) for high β.
- For λ larger than about 0.5, droplets in surfactant-free systems were experimentally found to break by developing bulbous ends connected by a narrowing waist. Despite some asymmetry, however, we concluded from the video images that there is hardly any bulbing in our experiments in the presence of surfactant, except at high concentration. This is in line with the numerical work, which showed that bulbous ends do not develop for the slow relaxation limit (large γ and Da). The reason is the fact that the surfactant accumulation at the droplet ends lowers the interfacial tension near the ends substantially, requiring a high degree of interfacial curvature (pointed ends rather than bulbs) to maintain the Laplace pressure.

Physically, the dependence of Ω_C on the surfactant concentration is determined by the interplay of several effects. The interfacial velocity is strongly reduced by the counteracting interfacial tension gradients. This also makes the interface more susceptible to tangential stresses, which thus become more effective for droplet deformation. Milliken and coworkers (1993) alternatively describe this effect as an apparent increased droplet viscosity. Obviously this Marangoni retardation of the interfacial velocity will be most pronounced at low λ, where the interfacial velocity in the absence of surfactants would have been substantial. At high λ, where the interfacial velocity is small anyway, the effect is only marginal. Since impurity levels of surface-active substances can already cause a considerable Marangoni retardation (e.g., Edwards et al., 1993), this mechanism prevails down to low concentrations, and explains why the droplet breakup in the low concentration limit of our results is more effective than expected from equilibrium adsorption.

A second effect is the relative depletion of the equatorial region of the interface. There the actual value of the local interfacial tension will be higher than the adsorption-equilibrium value σ_{EQ} used to calculate Ω. This increase in local Laplace pressure will counteract the narrowing-waist breakup. Whether or not this can give a substantial contribution will depend on the efficiency of the bulk-interface surfactant exchange and the lateral surfactant diffusion. If these mechanisms provide a rapid resupply of surfactant, the actual interfacial tension near the drop equator will not differ much from σ_{EQ}. However, if the resupply is slow, the difference can become substantial, particularly at higher concentrations (see Figures 3 and 4, realizing that $\sigma(0)-\sigma_{EQ}$ is the maximum deviation that can be obtained). In our experiments the viscosity ratio λ was changed via the droplet phase viscosity. Since the surfactant resided in the droplet, this implies a much more effective adsorption relaxation at low λ (low droplet viscosity) than at high λ. For the low-λ systems the Marangoni retardation apparently remains predominant, as the Ω_C vs. c curve remains below the value expected from Figure 1. For the cases with viscosity ratio 0.96 and 1.37, however, the stabilizing effect of equator depletion becomes predominant at higher concentrations.

It is also interesting to note that our observations show a striking similarity to results of an experimental study by Milliken and Leal (1991) on the deformation and breakup of viscoelastic drops in a quasi-steady-plane hyperbolic flow. These authors used two Newtonian oils as the continuous phase, and various polymeric solutions as the droplet phase. These droplet phases can be classified as shear-thinning, purely elastic (so-called Boger fluids), and fully viscoelastic fluids. In the experiments, however, this distinction turned out to be of no importance for the critical capillary number and the critical deformation under quasi-steady conditions. Both were found to be almost independent of both the fluid properties and the zero-shear viscosity ratio (Figures 8 and 9 in the original paper). Initially the authors claimed that the polymers used to prepare the viscoelastic droplet phases are not surface active, but in a more recent article (Milliken et al., 1993) they have withdrawn this remark: additional measurements of the equilibrium interfacial tension did show a small but significant deviation from the values found without the polymers, thus suggesting that some surface activity was likely to be present. The authors made no mention of the internal circulation behavior of the droplets, but since the polymers have been found to be somewhat surface active it is likely that internal circulation was virtually absent. This would explain the independence of Ω_C and D_C from the droplet-phase rheology. Milliken and Leal also observed asymmetric breakup modes that are very similar to those described earlier, and do depend on the droplet-phase rheology. They pointed out that their four-roll mill was carefully designed to reduce asymmetries in the flow as far as possible, and that no asymmetry was ever observed for purely Newtonian systems. They therefore suggested that the nonlinear stress–strain relation of the polymeric drops might render them more sensitive to the remaining slight asymmetries in the flow than Newtonian drops. Milliken and Leal (1993) explicitly note the qualitative similarity between the breakup of polymeric drops and drops covered with surfactant, and speculated that several aspects of the behavior of polymeric drops in elongational flow may well be dominated by the surface activity of the polymer, rather than by its influence on the bulk rheology. Our results clearly corroborate this hypothesis.

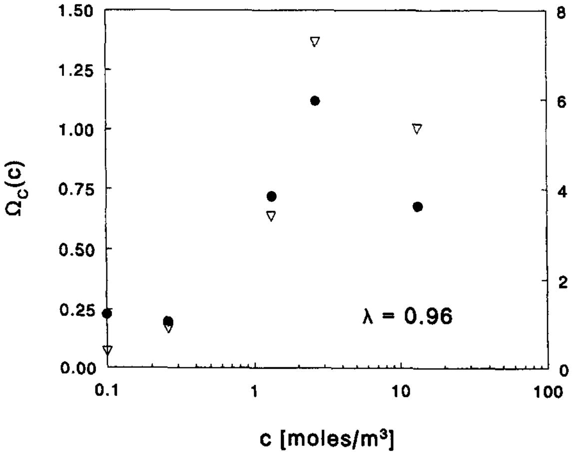

Figure 9. Critical capillary number (lefthand scale, ●) and the group $F(c)=\epsilon_0/\sigma_{EQ}\ [De/(1+De)]^{0.3}$ (righthand scale, ∇) against the surfactant concentration, for the W/O/sucrose ester system of $\lambda = 0.96$.

The figure is intended to illustrate similar qualitative trends rather than a quantitative agreement.

Formulation of Practical Correlations

For droplet breakup in simple shear flow (Janssen et al., 1994), we proposed to correlate the critical capillary number with the amplitude of the σ variation along the interface. The variation of the interfacial tension of a planar interface during deformation has been analyzed using linear response theory (Loglio et al., 1986): first the time-dependent, relative change in interfacial area Δ ln $A(t)$ is decomposed into its Fourier components $F(i\omega)$. Next it is assumed that the relative change in area is small enough to allow the use of linear response theory, which means in the present case that the deviation in interfacial tension caused by an arbitrary (but small) relative change in area is equal to the sum of the deviations caused by each Fourier component separately. Since these components represent purely harmonic small-amplitude deformations, the elasticity modulus as given by Lucassen and van den Tempel (1972) for sinusoidal deformations can be used to calculate these separate terms, leading to

$$\frac{\Delta\sigma(t)}{\sigma_{EQ}}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{\epsilon(\omega)}{\sigma_{EQ}}F(i\omega)\exp(i\omega t)\,d\omega, \qquad (7)$$

where adsorption equilibrium at $t=0$ is assumed. The elasticity modulus $\epsilon(\omega)$ is defined as

$$\frac{\epsilon}{\sigma_{EQ}}=\frac{\epsilon_0}{\sigma_{EQ}}\,\frac{1+\zeta+i\zeta}{1+2\zeta+2\zeta^2}, \qquad (8)$$

where

$$\frac{\epsilon_0}{\sigma_{EQ}}=-\frac{\Gamma_{EQ}d\sigma}{\sigma_{EQ}d\Gamma},\qquad \frac{1}{\zeta^2}=\omega\frac{2}{D}\left(\frac{d\Gamma}{dc}\right)^2. \qquad (9)$$

The first group, which can also be written as $d(\sigma/\sigma_{EQ})/d(\Gamma/\Gamma_{EQ})$, characterizes the sensitivity of the interfacial tension to changes in the interfacial concentration. As has been mentioned earlier, the parameter β introduced by Milliken et al. (1993) is, in fact, the low concentration limit of this group. The group $1/\zeta^2$ is a so-called Deborah number, and gives the ratio of the most important relaxation time of the system (here the typical timescale of diffusion-driven adsorption relaxation) and a typical experimental timescale, here $1/G$.

In simple shear flow the deformation is periodic, and the integral reduces to a Fourier series with a fundamental frequency of twice the droplet rotation frequency $G/2$. This frequency was found to give a major contribution to the overall effect, proportional to $|\epsilon(G)|$ (Janssen et al., 1994). In plane hyperbolic flow, the righthand side of Eq. 8 will also be proportional to ϵ_0/σ_{EQ}. However, the deformation is not periodic. As a result there is no single, typical deformation frequency that will give a dominant contribution to the Fourier integral. Nevertheless, one would expect the range $\omega \approx G$ to be particularly relevant. We therefore tried to find a dimensionless group defined as the product of ϵ_0/σ_{EQ} and some simple, analytical function of the Deborah number $De = (G/2D)(d\Gamma/dc)^2$, which has the same qualitative dependence on the surfactant concentration as Ω_C for all four viscosity ratios. This group should vanish when De vanishes, since this implies a very rapid relaxation. In addition, it should become independent of De when De gets large, since this represents the insoluble surfactant limit, in which bulk-interface surfactant exchange is irrelevant. The best correlation by far was found for the group ϵ_0/σ_{EQ} $[De/(1+De)]^{0.3}$ The result for the $\lambda = 0.96$ system is shown in Figure 9 as an example. For the low-λ systems the group ϵ_0/σ_{EQ} $[De/(1+De)]^{0.3}$ depends only weakly on the surfactant concentration, while it increases without passing through a maximum in the relevant concentration range for $\lambda = 1.37$. It turned out that the correlation is quite sensitive to the exponent: a deviation from 0.3 of only a few hundredths makes the agreement significantly worse. Figure 10, Ω_C is plotted against ϵ_0/σ_{EQ} $[De/(1+D_e)]^{0.3}$ for all four systems. It should be mentioned that we have also used the Lucassen–van den Tempel expressions for an experiment with bulk surfactant concentration well above the CMC. Although the corresponding point falls on the curve, the applicability of these expressions in this concentration range is strictly not permitted. Figure 10 suggests that all points fall approximately on a single curve. We thus conclude that the critical capillary number can be correlated with the same characteristic dimensionless groups as in the simple shear case, although their combination into a single parameter is different.

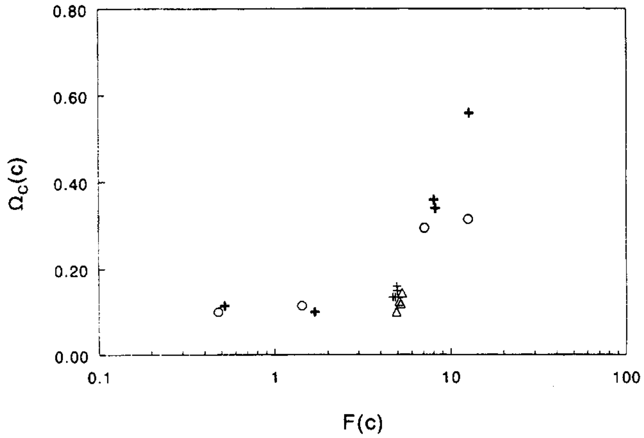

Figure 10. Critical capillary number vs. the group $F(c) = \epsilon_0/\sigma_{EQ}$ $[De/(1+De)]^{0.3}$ for all systems: W/O/Dobanol of $\lambda = 0.12$ (+), W/O/Dobanol of $\lambda = 0.2$ (Δ), W/O/sucrose ester of $\lambda = 0.96$ (+), W/O/sucrose ester of $\lambda = 1.36$ (○).

Although the phenomenological framework just described does seem to provide a way of extracting practically useful correlations from experimental data, it would require many, carefully performed breakup and interfacial rheology studies, covering a range of surfactant types and viscosity ratios, to formulate such correlations with confidence. Moreover, such an exercise will probably add little to our physical understanding of the relevant subprocesses and their interaction. By contrast, numerical studies like those quoted in the previous section do provide physical insight, and allow an assessment of the relative importance of various subprocesses by switching them off selectively. Also they can be readily extended to other linear flows. However, the formulation introduced by Milliken et al. (1993) and Milliken and Leal (1994) requires that the surfactant parameters describing the adsorption isotherm and the bulk transport are known. As mentioned earlier, this information is often not available, for example, for practical emulsifiers such as proteins and lecithines. We therefore propose a reformulation of the surfactant-related part of the equations, given below. The equations for the hydrodynamical part (Navier–Stokes, continuity, boundary conditions for stress and velocity) remain the same as in the original analysis by Milliken et al. (1993), and are quoted in the Appendix. In order to make them dimensionless, the radius R of the undeformed drop is used as a length scale, and the reciprocal velocity gradient $1/G$ is introduced as the timescale. The scales for the fluid velocity and the pressure then become RG and σ_{EQ}/R, respectively.

Consider a drop in an unbounded 2-D linear flow, in the presence of a surfactant for which the basic assumptions of the Lucassen–van den Tempel theory are valid. These are instantaneous (local) adsorption equilibrium between interface and the adjacent bulk layer, and diffusion-dominated transport of surfactant in the bulk layer that is relevant for the interface-bulk surfactant exchange. The latter assumption requires that the typical thickness $d\Gamma/dc$ of the exchange layer (see Lucassen and van den Tempel, 1972) is small compared to the drop dimensions. Also the surfactant is assumed to influence only the interfacial tension: there are no "intrinsic" interfacial elasticities or viscosities, as induced, for instance, by the formation of an interfacial network. Finally, the deviations from adsorption equilibrium are assumed to be small enough to allow linearization of the adsorption isotherm and the equation of state (variables with an asterisk are dimensionless: $\Gamma = \Gamma^* \Gamma_{EQ}$ and $\sigma = \sigma^* \sigma_{EQ}$):

$$\Gamma^* = 1 + \frac{d\Gamma}{dc} \frac{c - c_{EQ}}{\Gamma_{EQ}} \tag{10}$$

$$\sigma^* = 1 - \frac{\epsilon_0}{\sigma_{EQ}} (\Gamma^* - 1), \tag{11}$$

where we have introduced the first of the interfacial rheology parameters, ϵ_0/σ_{EQ}. Note that Eq. 11 is different from the linear equation of state proposed by Milliken et al. (1993), and Milliken and Leal (1994). These authors use a low concentration approximation for the Szyszkowski equation

(Henry isotherm), while Eq. 11 is valid for all concentrations, provided the deviation from equilibrium conditions is small. If the interface would have rheological properties that cannot be explained from the local interfacial tension only (e.g., interfacial elasticity or viscosity due to network or skin formation), the equation of state could be extended. The dimensionless transport equation for the interfacial surfactant transport reads (Milliken et al., 1993):

$$\frac{\partial \Gamma^*}{\partial t^*} + \Gamma^* \boldsymbol{\nabla}_t^* \cdot \boldsymbol{u}_{l,t}^* + (\boldsymbol{u}_{l,t} \cdot \nabla_{l,t})\Gamma^* - \frac{1}{Pe_I} \nabla_t^{*2} \Gamma^* + \Gamma^* (\boldsymbol{\nabla}_t^* \cdot \boldsymbol{n})(\boldsymbol{u}_l \cdot \boldsymbol{n}) = j_n^*, \quad (12)$$

introducing the interfacial Peclet number $Pe_I = RG/D_I$ and the dimensionless flux $j_n^* = j_n/\Gamma_{EQ}G)$, which represents the source/sink term for surfactant exchange with the adjacent bulk phase. Within the assumptions made about the surfactant properties and the relaxation mechanism, the flux toward the interface is given by

$$j_n^* = -\frac{D}{G\Gamma_{EQ}} \boldsymbol{n} \cdot (\nabla c)_I, \quad (13)$$

where $\boldsymbol{n} \cdot (\nabla c)_I$ denotes the normal component of the bulk concentration gradient at the interface. We now recall from the Lucassen-van den Tempel analysis (1972), that $d\Gamma/dc$ is the typical thickness of the bulk layer that is involved in the surtactant exchange. We may then approximate the normal gradient as

$$\boldsymbol{n} \cdot (\nabla c)_I \approx \frac{c_{EQ} - c}{d\Gamma/dc}, \quad (14)$$

which should at least give the correct order of magnitude. Using the linearization of the isotherm, the source term may then be rewritten as

$$j_n^* \approx -\frac{D}{G\Gamma_{EQ}} \frac{-(dc/d\Gamma)(\Gamma - \Gamma_{EQ})}{d\Gamma/dc} = \frac{2}{De}(1 - \Gamma^*), \quad (15)$$

introducing the second interfacial parameter from the phenomenological framework, the Deborah number $De = (G/2D)(d\Gamma/dc)^2$. Equation 15 clearly has the required physical properties: it gives rise to adsorption when $\Gamma^* < 1$, and to desorption for $\Gamma^* > 1$. Also the interface-bulk surfactant exchange is large for small De, and negligible for large De, in line with the physical interpretation given to these limits in the phenomenological framework.

In this approximation the relevant equations (also see the Appendix) thus depend on Ω, λ, α, ϵ_0/σ_{EQ}, Pe_I, and De. It should be noted, however, that usually the interfacial diffusion coefficient D_I will be of the same order as the bulk diffusion coefficient D, while the drop radius R is assumed to be large compared to the exchange layer thickness $d\Gamma/dc$. So $De \ll Pe_I$, which implies that the interface-bulk exchange is a much more powerful relaxation mechanism than lateral diffusion. This term for lateral diffusion in Eq. 12 can thus be omitted in the context of our present assumptions, and consequently Pe_I is irrelevant. In a sense, the preceding derivation thus also gives a more fundamental support for our phenomenology-based proposal to use ϵ_0/σ_{EQ} and De for characterizing the surfactant influence on the droplet behavior under steady-state conditions.

Since no explicit assumptions about the adsorption isotherm and the equation of state are needed, the results will also apply to complex emulsifiers, for which these equations are not known to date. The condition of small deviation from adsorption equilibrium will probably not be satisfied in practice, but the trends may nevertheless be valid. If so, empirical parameters might be introduced to fit the numerical curves more closely to experimental data, for example, by writing $j_n^* = k(2/De)(1 - \Gamma^*)$, with k an empirical proportionality constant.

Conclusions

The influence of surfactants on droplet deformation and breakup in a plane hyperbolic flow has been studied experimentally in an opposed-stream device. As in the case of simple shear flow, described in an earlier article, the inhomogeneity of the surfactant distribution along the droplet interface has been found to have a pronounced effect.

Under quasi-steady conditions, the interfacial tension gradients make the droplet interface rigid with respect to tangential stresses, leading to an almost stationary droplet interior. This effect already exists for trace amounts of surfactant (impurities), and dominates the droplet behavior at low surfactant concentration. In particular, the critical deformation and critical capillary number do not depend on the bulk rheology of the drop in this range, as was also found in the literature for drops that were made viscoelastic with slightly surface-active polymers. At higher concentrations, an increase of the critical capillary number up to a factor of 4.5 compared to the uniform-σ-based value was found for the highly viscous droplet phases. In those cases the drops are more stable than expected from the interfacial tension at adsorption equilibrium σ_{EQ}, because the flow tends to deplete the equatorial region of the interface. This raises the local interfacial tension to values well above σ_{EQ}, which has a stabilizing effect on the narrowing-waist breakup.

In the presence of surfactants stable droplets are only slightly asymmetric, but as soon as the transient deformation leading to breakup sets in the asymmetry is strongly amplified. The breakup as such follows the familiar narrowing-waist mode at low surfactant concentration, but for higher values the instability starts near one of the droplet ends. Again this behavior has also been observed for polymeric drops in the literature. The most probable explanation for the asymmetry seems to be that the nonlinear stress–strain characteristics of the interface make the droplet more sensitive to slight asymmetries in the flow.

Our data suggest that the surfactant effects can be characterized by two dimensionless groups. The first one is proportional to the slope of the interfacial tension vs. interfacial concentration curve, and indicates how sensitive the interfacial tension is to changes in interfacial concentration. The other one is a Deborah number, defined as the ratio of the timescale of the most important adsorption relaxation mechanism and the timescale of the interfacial deformation. This number indicates whether or not deviations in the interfacial coverage from the uniform coverage at adsorption equilibrium will be effectively counteracted by the dominant adsorption relaxation mechanism. For further study, a numerical analysis supported by a limited number of dedicated experiments seems to be the most promising and most general approach. Indeed our results were found to be qualitatively in line with numerical studies in the literature. A (re)formulation of the relevant equations in terms of the aforementioned dimensionless parameters is proposed.

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Notation

G = shear rate, L/s
t = time [s]
ω = angular frequency [rad/s]

Subscripts

EQ = equilibrium value

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Appendix

Consider a drop in an unbounded 2-D linear flow, in the presence of a surfactant. The steady-state drop deformation is then described by the following set of equations, made dimensionless using the radius R of the initial undeformed drop as a length scale. Several possibilities exist for the timescale (Rallison, 1984). Here we choose the reciprocal velocity gradient $1/G$. The scales for the fluid velocity and the pressure then become RG and σ_{EQ}/R, respectively. For the hydrodynamical part of the problem the dimensionless equations then are:

- The Navier–Stokes equation, which can be used in its low Reynolds number limit (creeping flow):

$$-\boldsymbol{\nabla}^* p_c^* + \Omega \nabla^{*2} \boldsymbol{u}_c^* = \boldsymbol{0} \tag{A1}$$

$$-\boldsymbol{\nabla}^* p_D^* + \lambda \Omega \nabla^{*2} \boldsymbol{u}_D^* = \boldsymbol{0}, \tag{A2}$$

where $\lambda = \mu_D/\mu_C$ is the viscosity ratio and $\Omega = \mu_C RG/\sigma_{EQ}$ is the capillary number.

- The continuity equation (conservation of mass):

$$\boldsymbol{\nabla}^* \cdot \boldsymbol{u}_D^* = \boldsymbol{\nabla}^* \cdot \boldsymbol{u}_D^* = 0. \tag{A3}$$

- The velocity boundary condition at large distance from the drop, which states that far from the drop the undisturbed linear flow is regained:

$$\boldsymbol{u}_c^* = \frac{1}{2} \begin{bmatrix} 1+\alpha & 1-\alpha & 0 \\ -1+\alpha & -1-\alpha & 0 \\ 0 & 0 & 0 \end{bmatrix} \boldsymbol{x}^*. \tag{A4}$$

- The velocity boundary condition at the interface:

$$\boldsymbol{u}_D^* = \boldsymbol{u}_C^* = \boldsymbol{u}_I^*. \tag{A5}$$

- The stress boundary conditions at the interface:

$$T_{t,C}^* - T_{t,D}^* = \boldsymbol{\nabla}_t^* \cdot (\sigma^* I_I) \tag{A6}$$

$$T_{n,C}^* - T_{n,D}^* = \sigma^* \left(\frac{1}{R_1^*} + \frac{1}{R_2^*} \right), \tag{A7}$$

where I_I is the metric tensor of the interface, and T the stress tensor. The subscripts n and t refer to normal and tangential components respectively.

For surfactant-free systems, $\sigma^* = 1$ by definition, and we end up with three relevant dimensionless parameters, the capillary number Ω, the viscosity ratio λ, and the flow parameter α. These parameters also emerge for the other timescale choices (Rallison, 1984), the difference being that some of them occur at different places in the equations. In the presence of a surfactant, we also need to specify the equation of state, which describes σ^*, and equations for the surfactant transport. This is discussed in the main text, and in Milliken et al. (1993, 1994).

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