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Citation for published version (APA):

Janssen, J. J. M., Boon, A., & Agterof, W. G. M. (1994). Influence of dynamic interfacial properties on droplet breakup in simple shear flow. *AIChE Journal*, 40(12), 1929-1939. <https://doi.org/10.1002/aic.690401202>

DOI:

[10.1002/aic.690401202](https://doi.org/10.1002/aic.690401202)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Influence of Dynamic Interfacial Properties on Droplet Breakup in Simple Shear Flow

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The breakup of droplets in an inhomogeneous flow is the key to emulsification. Frequently, the local flow experienced by the drops is a (quasi-) simple shear flow. The breakup of droplets in a steady, simple shear flow in the absence of emulsifiers has been studied extensively. In the presence of emulsifiers, the droplet interface may acquire viscoelastic properties, which are important in the prevention of coalescence, but their influence on droplet breakup has not been established solidly. This article reports on a phenomenological approach, which links the droplet breakup dynamics to the interfacial viscoelasticity, identifying the latter with the elasticity modulus of a deforming planar interface. Over a viscosity ratio range of three decades, the results have been found to agree with the model, which uses only independently known quantities derived from equilibrium interfacial tension properties.

Introduction

The breakup of droplets in an inhomogeneous flow is a key process in emulsion manufacturing and manipulation, and has for a long time been a subject of interest in both fluid dynamics and chemical engineering. Both laminar and turbulent flows have been considered in various geometries. The breakup process depends on the local flow experienced by individual droplets. It can readily be shown that the local undisturbed flow can often be approximated as a linear shear flow, by writing the actual flow as a Taylor series in a coordinate system fixed to the droplet (Rallison, 1984). Droplet breakup in linear shear flows, especially in simple shear flow, has therefore received a lot of attention. For systems without surface-active substances, deformation and breakup in a steady, simple shear flow have been shown to depend only on the viscosity ratio λ (dispersed phase viscosity μ_D divided by continuous phase viscosity μ_C) and on the capillary number Ω , defined as:

$$\Omega = \frac{\mu_C R G}{\sigma} \quad (1)$$

where R is the initial droplet radius, G the (local) shear rate, and σ the constant and uniform interfacial tension. 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. The main conclusions (Grace, 1982; Bentley and Leal, 1986; de Bruijn, 1989) are visualized in Figure 1, in which the line represents the boundary of the stable

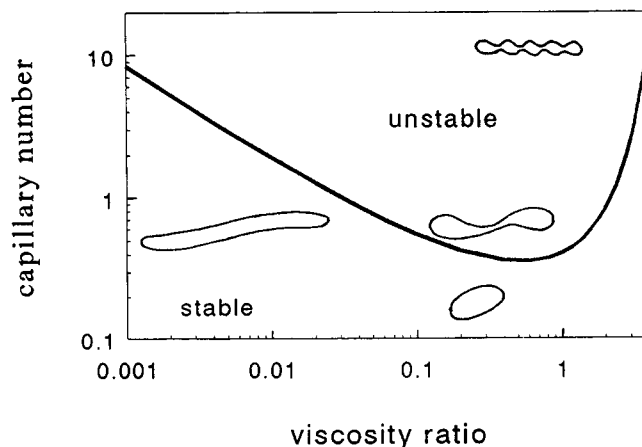


Figure 1. Droplet breakup in simple shear flow.

Drawn line: critical capillary number as a function of the viscosity ratio.

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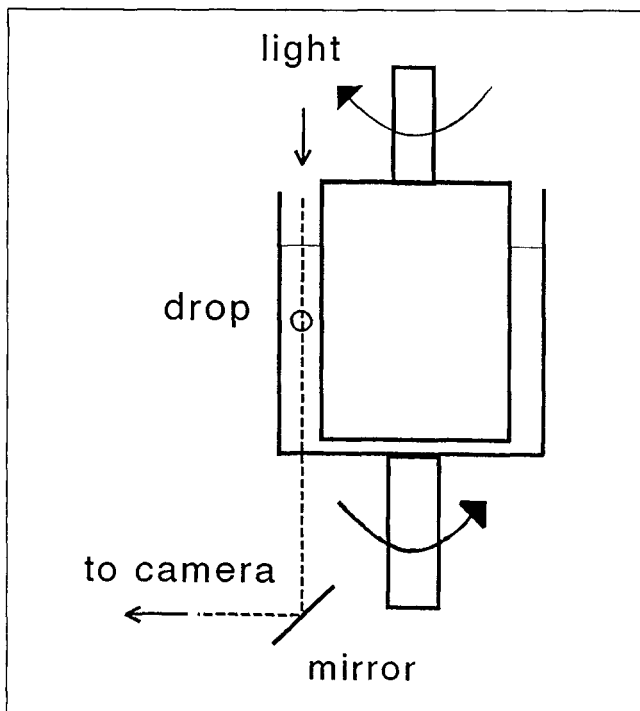


Figure 2. Couette device.

Radius outer cylinder = 50.25 mm; radius inner cylinder = 39.75 mm.

regime. When the capillary number is increased to its critical value Ω_c , the droplet breaks up into two equisized fragments and a few much smaller satellite droplets. When the capillary number is suddenly increased to a value well above Ω_c , the droplet is rapidly elongated into a long cylindrical fluid thread, which subsequently breaks into a series of fragments due to the growth of wavelike-shape distortions. As indicated in Figure 1, the deformation prior to breakup is significantly larger for low viscosity ratio than for ratios near unity. At viscosity ratios above about 4, breakup in simple shear flow is virtually impossible.

For droplet breakup in industrial emulsification processes, we have to take into account that practical emulsions almost always contain surface-active substances (surfactants, emulsifiers). Their role in emulsification is twofold (Walstra, 1993): they facilitate breakup by lowering the interfacial tension σ (which represents the elastic restoring force in droplet-breakup dynamics), and they provide a stability mechanism against coalescence. If we now want to apply the results in Figure 1 to the breakup process, the problem arises that surfactant adsorption and droplet deformation are coupled: droplet breakup implies a significant deformation of its interface, leading to an interfacial tension that will 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. The elastic restoring force thus becomes a viscoelastic one. Moreover, the deformation of a droplet interface in a breakup process will be nonuniform. The corresponding gradients in the interfacial tension will contribute to the tangential stress balance at the droplet interface and

thus will influence the deformation process. The potential importance of these effects has been recognized in such articles as those that consider correlations for the average droplet size in stirred vessels (Koshy et al., 1988; Groeneweg et al., 1993), but detailed model studies are scarce. Phenomenological approaches have been proposed by Koshy et al. (1988) (for turbulent flow), and by Lucassen-Reynders and Kuipers (1992). Numerical studies have recently been reported for the case of droplet deformation in an elongational flow (Stone and Leal, 1990; Milliken et al., 1993), albeit only for insoluble emulsifiers, which are present exclusively at the interface and not in the bulk phases.

We are currently performing a systematic experimental and theoretical study on the influence of surface-active agents on droplet breakup, considering individual mm-sized droplets under well-defined flow conditions. This article discusses our results for droplet breakup in a steady, simple shear flow at shear rates that are just critical. We have found that the mere use of the equilibrium interfacial tension in the established model (Figure 1) is adequate only when the surfactant concentration is very low or very high. In the former case, the surfactant has a negligible influence anyway, while in the latter the adsorption relaxation is so much faster than the deformation time scale that the interfacial tension is virtually uniform and close to its equilibrium value throughout the process. At intermediate surfactant concentrations, droplet breakup is more difficult than expected from Figure 1, when using the interfacial tension at adsorption equilibrium to calculate the capillary number. Our experiments clearly show a strong correlation between the critical capillary number and the interfacial viscoelasticity, characterizing the latter with the established relations for the elasticity modulus of a deforming planar interface. On the basis of these observations, we propose a fairly simple, phenomenological approach to describe the breakup conditions, which introduces an effective interfacial tension related to this elasticity modulus. Over a viscosity ratio range of three decades, the experimental results have been found to agree with this model, which uses only independently known quantities derived from equilibrium interfacial tension properties. Although the experimental verification has considered only mm-sized drops, the basic assumptions are estimated to be valid for micron-sized droplets also. In addition, the theoretical framework as such seems applicable to laminar flows other than simple shear.

Experimental Studies

Couette device

Simple shear flow was created in a so-called Couette device (Figure 2), which consists of two counterrotating cylinders with a small gap in-between. Due to the relatively large radius of curvature, the flow in the gap is in good approximation to a simple shear flow. The rotational speed of the cylinders was controlled by a computer, allowing a choice of various shear rate vs. time profiles. The response of the flow pattern in the gap to changes in cylinder speed has been shown to be virtually instantaneous on our experimental time scale (de Bruijn, 1989). Somewhere in the gap a stationary layer is present, the position of which depends only on the ratio of the cylinder speeds. Changing these speeds, while keeping their ratio constant, thus changes the shear rate in the stationary layer without displacing this layer. The behavior of a droplet of a second immiscible

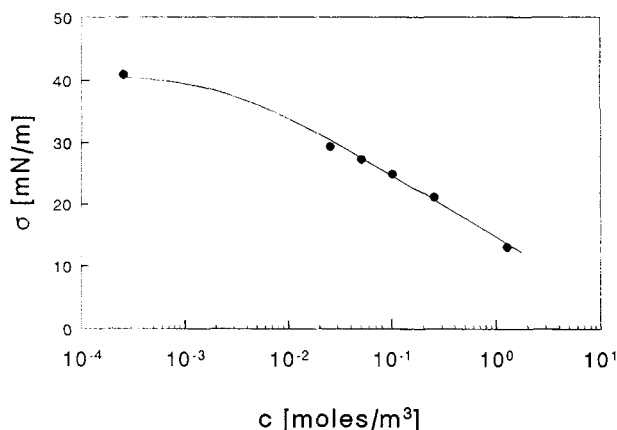


Figure 3. Measured (•) and calculated (—) equilibrium interfacial tension for the W/O/Dobanol 91-8 system with $\lambda = 0.01$.

liquid present in the stationary layer can be monitored and recorded using video equipment with magnification optics. The video camera simultaneously observes an electronic timer, which is visible in a corner of the image and enables synchronization of the droplet behavior and the shear rate vs. time profile stored by the computer. The typical droplet diameter is about 1 mm.

Materials

The continuous-phase silicon oil of viscosity 1.5 or 4.7 Pa·s (ex Rhodorsil) was purified before use by stirring in the presence of silicagel. Surface-active impurities adsorb onto the silicagel, which is removed by sedimentation after about 1 h of stirring. The dispersed phase is a water/corn-syrup mixture, in which the syrup is used to adjust the dispersed-phase viscosity. The syrup content varies from 40% w/w for the $\lambda = 0.0013$ system up to 89% w/w for the $\lambda = 1$ system. In most cases, some sodium azide (≈ 3.4 mmol/l) was added also to prevent the growth of bacteria and moulds. The azide does not show any surface activity.

In the experiments, the emulsifier was added to the dispersed phase for experimental convenience. Two emulsifiers were used. The first one is a mixture of polyoxyethylene alcohols called Dobanol 91-8 (ex Shell). The molecular formula is $\text{H}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_m-\text{H}$, where in our case $9 \leq n \leq 11$, while $m = 8$ is the average of a Poisson distribution. The properties of this type of nonionic emulsifier, frequently denoted as $\text{C}_n(\text{EO})_m$ or C_nE_m , are well established (Schick, 1966). The equilibrium

adsorption of Dobanol 91-8 at the W/O interface can be described quite well by a Langmuir isotherm, which relates the interfacial concentration Γ and the bulk concentration c as:

$$\Gamma = \Gamma_\infty \frac{c}{c+a} \quad (2)$$

The parameters Γ_∞ and a can be found by fitting the experimentally determined $\sigma - \ln(c)$ curve with the so-called Szyszkowski equation (the equation of state corresponding to Langmuir adsorption):

$$\sigma(0) - \sigma = \Gamma_\infty RT \ln \left(1 + \frac{c}{a} \right) \quad (3)$$

where $\sigma(0)$ is the interfacial tension in the absence of the emulsifier, and RT is the product of the gas constant and the temperature. The result for the $\lambda = 0.01$ system is shown in Figure 3 as an example (Γ_∞ and a : see Table 1). The σ vs. $\ln(c)$ curve at adsorption equilibrium was measured using the Wilhelmy plate technique. Dobanol 91-8 is hardly soluble in the continuous oil phase. The fact that no leakage into the continuous phase occurred was checked experimentally by monitoring the deformation of a stable droplet in time at constant subcritical shear rate and for an emulsifier concentration at which the interfacial tension is sensitive to concentration changes. No systematic changes were detected within the time scale of an experiment (30 min maximum for deformation studies, 10 min at most for breakup studies). The experiments were performed in the order of increasing emulsifier concentration.

At high corn-syrup content, where the Dobanol solubility is limited, we used a mixture of sucrose esters called Ryoto Sugar Ester L1695 (ex Mitsubishi-Kasei Food Corp.). Sucrose esters consist of a hydrophilic sucrose part and a lipophilic fatty acid group. The mixture used consists of about 80% of sucrose monolaureate (the rest being di- and trilaureates). As there are indications that this emulsifier reacts chemically with the sodium azide, the azide was omitted from these experiments. The interfacial tension was found to fit the Szyszkowski equation less well than in the previous cases. Better results were obtained for the so-called Frumkin isotherm, for which the relevant equations are (Lucassen and Lucassen-Reynders, 1967):

$$\frac{\sigma(0) - \sigma(c)}{-RT\Gamma_\infty} = \ln(1-y) + \frac{H}{RT}y^2 \quad (4)$$

$$\frac{c}{a} = \frac{y}{1-y} \exp \left(-2 \frac{H}{RT}y \right) \quad (5)$$

and $y = \Gamma/\Gamma_\infty$. The nonideality parameter H is the partial molar free energy of mixing of solvent and solute in the interface at infinite dilution. Equations 4 and 5 reduce to the Szyszkowski equation and the Langmuir isotherm, respectively, when H vanishes. When using them for a given c and known or chosen Γ_∞ , a and H/RT , the first step is to determine $y(c)$ from a numerical solution of Eq. 5. Once $y(c)$ is known, the calculation of $\sigma(c)$ is straightforward. Figure 4 shows that an acceptable fit up to the critical micelle concentration (CMC) is

Table 1. Parameter Values of Dobanol Systems

Parameter	Value			
μ_D [Pa·s]	0.0062	0.05	0.235	0.228
μ_C [Pa·s]	4.7	4.7	4.7	1.5
λ	0.0013	0.0106	0.05	0.152
Γ_∞ [mol/m ²]	1.7×10^{-6}	1.8×10^{-6}	1.7×10^{-6}	1.6×10^{-6}
a [mol/m ³]	0.004	0.0025	0.002	0.001
D [m ² /s]	6.45×10^{-11}	8×10^{-12}	1.7×10^{-12}	1.7×10^{-12}

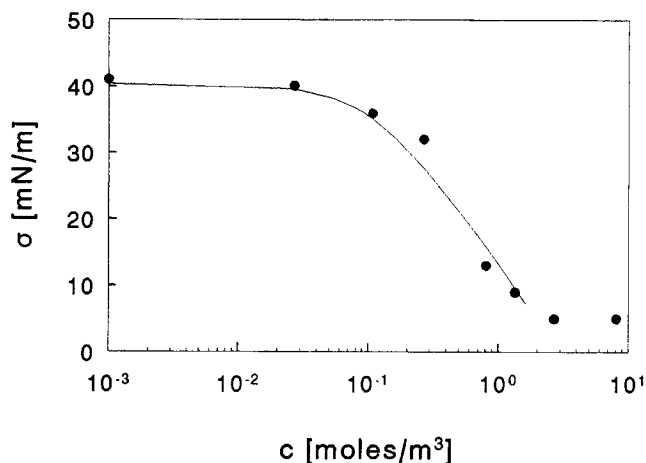


Figure 4. Measured (•) and calculated (—) equilibrium interfacial tension for the W/O/sucrose monolaureate system with $\lambda=1$, assuming a Frumkin isotherm.

found for $\Gamma_{\infty}=5 \cdot 10^{-6}$ mol/m², $a=0.25$ mol/m³, and $H/RT=0.85$.

Breakup-mode diagrams

We have studied the deformation and breakup of droplets in W/O/Dobanol and W/O/sucrose systems of various viscosity ratios, using either a suddenly applied constant shear rate or a quasi-steady shear rate increase. The breakup data were compiled in breakup-mode diagrams, in which for a series of (Ω, c) combinations the observed breakup mode (if any) is indicated. The general trends are sketched in Figure 5. The vertical axis shows the ratio of the actual critical capillary number and the value expected from Figure 1 for a uniform

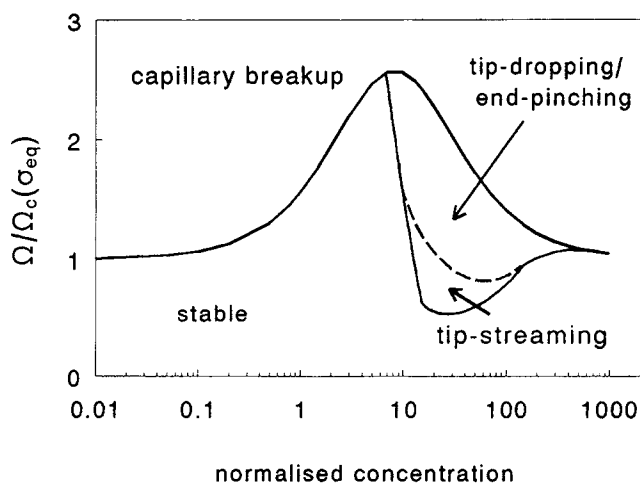


Figure 5. Typical breakup behavior of W/O/emulsifier systems as a function of the capillary number (based on σ_{EQ}) and bulk emulsifier concentration.

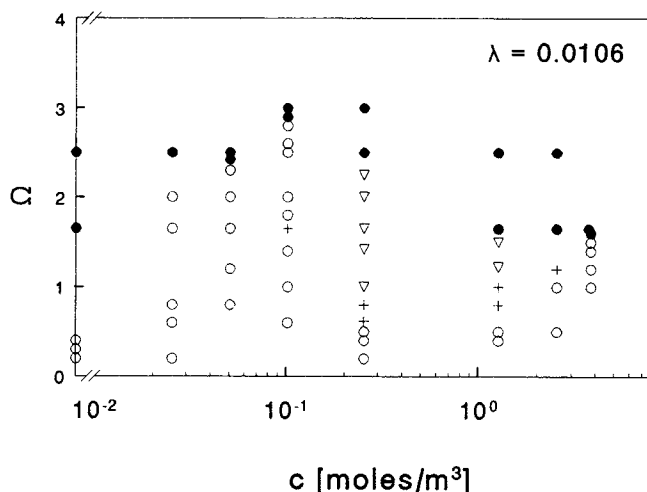


Figure 6. Breakup-mode diagram of W/O/Dobanol 91-8 with $\lambda=0.01$ in a steplike shear rate vs. time profile.

○, stable; +, tip streaming; ▽, tip dropping/end pinching; ●, binary/capillary breakup.

σ equal to σ_{EQ} . Various breakup modes have been observed, such as binary breakup for shear rates that are just critical and breakup into many fragments due to the growth of capillary waves at shear rates well above the critical value. These modes are well known for systems without emulsifiers. In the presence of emulsifiers, additional modes known as tip streaming and tip dropping are possible, which occur below Ω_C in Figure 1. Tip streaming refers to the development of pointed ends at the sigmoidal droplet, which eject a continuous stream of tiny fragments. The term tip dropping is used in the literature when tip drops are larger and are ejected more intermittently. Sometimes the mother drop seemed to retract, while leaving fairly large fragments behind. Such behavior has been observed by Stone and Leal (1989) for the breakup of elongated droplets, during their contraction after a sudden halt of the flow rate. For this case, they coined the term “end-pinching.” It should be noted, however, that in our experiments there are no sharp transitions between tip streaming, tip dropping and end pinching. The distinction made depends on the experimenter’s judgment and should be interpreted as merely indicative. As a quantitative example, experimental results for $\lambda=0.01$ are shown in Figure 6. Further results are given below in conjunction with theoretical curves. The region of tip streaming/tip dropping/end pinching was found to decrease with increasing viscosity ratios, which is in line with studies by de Bruijn (1989, 1993).

At intermediate emulsifier concentration, breakup via the modes that also occur for systems without emulsifiers is found to be more difficult than would be expected from Figure 1, for all viscosity ratios. In the absence of tip streaming/dropping (viscosity ratio larger than about 0.2), this implies an increased stability at these intermediate concentrations. Then, the boundary line between the stable regime and that of conventional breakup obviously represents the critical capillary number Ω_C (Figure 1). We will therefore refer to this boundary line as $\Omega_C(c)$, although breakup via streaming or dropping

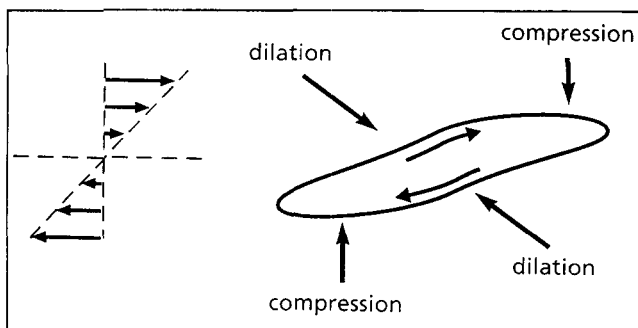


Figure 7. Droplet rotation in a simple shear flow.

may occur below it at low viscosity ratios. The rest of this article will focus on the description of this line that determines the maximum stable droplet size for flow conditions that are maintained sufficiently long compared to the time required for reducing the droplet size in a series of breakup events.

Correlation of Critical Capillary Number Ω_C and Interfacial Viscoelasticity

The critical capillary number is defined as the value beyond which no stable deformation exists. This analysis thus focuses on the behavior of droplets that are just stable. When a droplet is suddenly subjected to a shear flow that is just critical ($\Omega = \Omega_C$), its deformation is seen to develop as follows. Initially the droplet is rapidly elongated, while its long axis rotates toward the axis of the flow. After this initial stage, in which the major part of the increase in interfacial area takes place, the deformation rate decreases progressively. Finally, the overall droplet shape becomes stable, while the droplet interior rotates in the shear field. This means that the *total* interfacial area does not change any more, but *locally* interfacial area elements are periodically dilated and compressed during their travel around the droplet (Figure 7). In view of this deformation process there are three possible mechanisms for the observed maximum in Ω_C (based on σ_{EQ}) at intermediate emulsifier concentration.

First, the total amount of emulsifier present in the droplet is finite and may not be sufficient to restore the initial adsorption equilibrium concentration Γ at the enlarged interface. Then, the interfacial tension at breakup would be higher than that at adsorption equilibrium, leading to a higher critical shear

rate for breakup. The critical capillary number calculated using σ_{EQ} would then be larger than that expected from Figure 1. Secondly, the time scale required for restoring the initial value of Γ at the enlarged interface via surfactant transport from the bulk phase may be longer than that of an experiment. In this case, the experimenter may have decided too soon that a stable shape had been reached (the deformation near critical conditions is inherently slow) and subsequently may have applied a larger shear rate. This would again lead to higher values for the critical shear rate than those expected from Figure 1. In the Appendix it is argued, however, that neither of these possibilities will contribute significantly under our experimental conditions.

The remaining explanation then is that the ongoing *local* deformation of the interface, caused by the droplet rotation in the shear flow, leads to interfacial viscoelasticity. The interface is compressed near the droplet ends and dilated in the equatorial region. Consequently, σ will vary along the interface, being lower than σ_{EQ} near the droplet ends and higher than σ_{EQ} near the equator. For the drops in our experiments, we can identify three main effects of this nonuniformity in the interfacial coverage:

1. The interfacial tension gradients along the interface have to be accounted for in the tangential stress balance. It has frequently been found in the literature (Torza et al., 1972; Edwards et al., 1991) that even impurity levels of surface-active substances can build up an interfacial tension gradient that balances the applied stress completely, letting the drop rotate like a solid body. This reduces the stretching capability of the applied stress and stabilizes the drop against breakup.
2. The interfacial tension in the equatorial zone rises, making this zone stabler to narrowing. As a result, the conventional narrowing-waist breakup mode in Figure 1 becomes more difficult.
3. The interfacial tension at the droplet ends is lowered. As a result, a higher local curvature is required to maintain the Laplace pressure. This tends to increase the deformation, while suppressing the development of bulbous ends.

Clearly all three effects depend on the magnitude of the deviation of the local interfacial tension from its adsorption equilibrium value σ_{EQ} , this deviation being induced by the interfacial deformation and counteracted by the adsorption relaxation mechanisms. It thus seems plausible to expect a correlation between the value of Ω_C and the amplitude of the σ variation along the interface. We propose to get an estimate of this amplitude by following an individual area element on its travel around the droplet. The element is periodically dilated and compressed with a frequency that is twice the droplet rotation frequency. The response of the local interfacial tension to such a deformation can be inferred from studies, in which periodic deformation of planar surfaces in a so-called Langmuir trough was considered (Figure 8). The barrier motion is used to change the area A in a well-defined manner. The Wilhelmy plate provides an on-line measurement of the surface tension. The response of σ to various types of deformation has been studied. A case of particular interest in the present context is that of a small-amplitude sinusoidal barrier motion of angular frequency ω , in which the relaxation mechanism is provided by diffusive emulsifier transport between interface and bulk (Lucassen and van den Tempel, 1972). For this case,

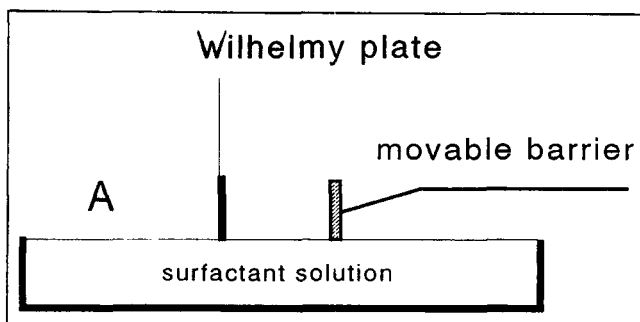


Figure 8. Langmuir trough experiment.

the surface tension was found to oscillate with the same angular frequency as the area changes, albeit with a phase shift with respect to the barrier motion. The amplitude of the deviation $\Delta\sigma(t)$ turned out to be proportional to the so-called elasticity modulus $|\epsilon(\omega)|$, which is given by:

$$|\epsilon| = \frac{\epsilon_0}{\sqrt{1 + 2\zeta + 2\zeta^2}} \quad (6)$$

where

$$\epsilon_0 = -\Gamma \frac{d\sigma}{d\Gamma}, \quad \frac{1}{\zeta^2} = \omega \frac{2}{D} \left(\frac{d\Gamma}{dc} \right)^2 \quad (7)$$

The concentration dependence of Γ and $d\Gamma/dc$ is such that at given frequency $|\epsilon|$ vanishes at both very low and very high concentration. The square of the dimensionless parameter ζ represents the ratio of the time scales $1/\omega$ for the interfacial deformation and $(2/D)(d\Gamma/dc)^2$ for the diffusional relaxation, the latter being determined by thermodynamic properties of the emulsifiers only. In a series of papers, Loglio et al. (1986, 1991, and references therein) have presented a more formal description of the viscoelasticity of deforming planar interfaces, using linear response theory. In their approach, the time-dependent, relative change in interfacial area $\Delta \ln A(t)$ is first decomposed into its Fourier components $F(i\omega)$. Next, it is assumed that the relative change in the area is small enough to apply linear response theory, which means in the present case that the deviation in interfacial tension caused by an arbitrary (but small) relative change in the area equals 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) can be used to calculate these separate terms leading to:

$$\Delta\sigma(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \epsilon(\omega) F(i\omega) \exp(i\omega t) d\omega \quad (8)$$

It should be noted that adsorption equilibrium at $t=0$ is assumed. So, the elasticity modulus for a small *harmonic* deformation as derived by Lucassen and van den Tempel suffices to calculate the interfacial tension shifts for *arbitrary* small deformation. In the case of a periodic deformation with period T , the Fourier integral reduces to a Fourier series with fundamental frequency $2\pi/T$. The fundamental term will give a major contribution, proportional to $|\epsilon(2\pi/T)|$, to the overall effect.

Although in our experiments the deformation amplitude is not small in general, the above considerations suggest the possibility of a correlation between the droplet behavior and $|\epsilon(2\pi/T)|$. For a droplet in the presence of emulsifiers, the rotation period was found to be of the order of the solid body rotation period $4\pi/G$, even when it is deformed (see also Torza et al., 1972). The period of the dilation-compression cycle will then be $2\pi/G$, corresponding to an angular frequency G . The parameter values for all Dobanol-based systems are collected in Table 1. The diffusion coefficient of polyoxyethylene alcohols in water/corn-syrup mixtures is not known. An estimate, however, can be made from the known values for diffusion in pure

water [$4 \times 10^{-10} \text{ m}^2/\text{s}$ (Lucassen and Giles, 1975)], assuming that the diffusion coefficient has a reciprocal proportionality to the solvent viscosity (Lightfoot and Cussler, 1965). Using these parameters and $\omega = G$, we compared the concentration dependence of the critical capillary number and that of the elasticity modulus given by Eq. 6. The results for the W/O/Dobanol systems are shown in Figure 9. In all cases, the correlation between $|\epsilon|$ and Ω_C is found to be quite good over a wide range of parameter values used. It should be stressed that this agreement is not the result of a fit procedure: all parameters in $|\epsilon|$ have been determined from independent sources. This strongly suggests that the interfacial viscoelasticity as characterized by $|\epsilon(G)|$ is indeed the main cause of the maximum in Ω_C .

Phenomenological Model for Ω_C in the Presence of Surfactants

Our starting point for a model to map the vertical scales in Figure 9 is the hypothesis that the breakup of a droplet in the presence of an emulsifier can be calculated from the uniform- σ relations, provided that some appropriately defined, effective emulsion parameters are used. Lucassen-Reynders and Kuipers (1992) suggested that a surfactant-covered droplet would behave as if it is more viscous and proposed to introduce an effective droplet viscosity as the sum of the bulk value and a term due to interfacial viscoelasticity. Figure 1 clearly shows, however, that this would lead to a decrease in Ω_C for low λ systems. Since a surfactant only affects the interfacial properties in a significant way, we consider the introduction of an effective interfacial tension (the only parameter in the clean-system situation that is a true interfacial property) to be a more adequate choice. In view of the previous analysis, we propose the following definition:

$$\sigma_{\text{EFF}}(c) = \sigma_{\text{EQ}}(c) + \beta |\epsilon(c)| \quad (9)$$

in which the coefficient β will be used as a fit parameter. Using this effective interfacial tension in the uniform- σ breakup relation ($\Omega = \Omega_C$) we obtain:

$$\frac{\mu_c R G_C(c)}{\sigma_{\text{EFF}}(c)} = \Omega_C(\sigma_{\text{EQ}}) \quad (10)$$

where $G_C(c)$ is the actual critical shear rate in the presence of the emulsifier, and $\Omega_C(\sigma_{\text{EQ}})$ is the critical capillary number for a system with constant and uniform interfacial tension (Figure 1). Defining $\Omega_C(c) = \mu_c R G_C(c) / \sigma_{\text{EQ}}(c)$ we then find:

$$\frac{\Omega_C(c)}{\Omega_C(\sigma_{\text{EQ}})} = 1 + \beta \frac{|\epsilon(c)|}{\sigma_{\text{EQ}}(c)} \quad (11)$$

At both low and high emulsifier concentration (where $|\epsilon|$ vanishes), the relation evidently gives the correct limits, while causing a maximum in Ω_C in the correct concentration range in-between. It should be noted that $|\epsilon|$ itself depends on the applied critical shear rate G_C , as discussed before. We therefore can now write the time scale ratio $1/\zeta^2$ as:

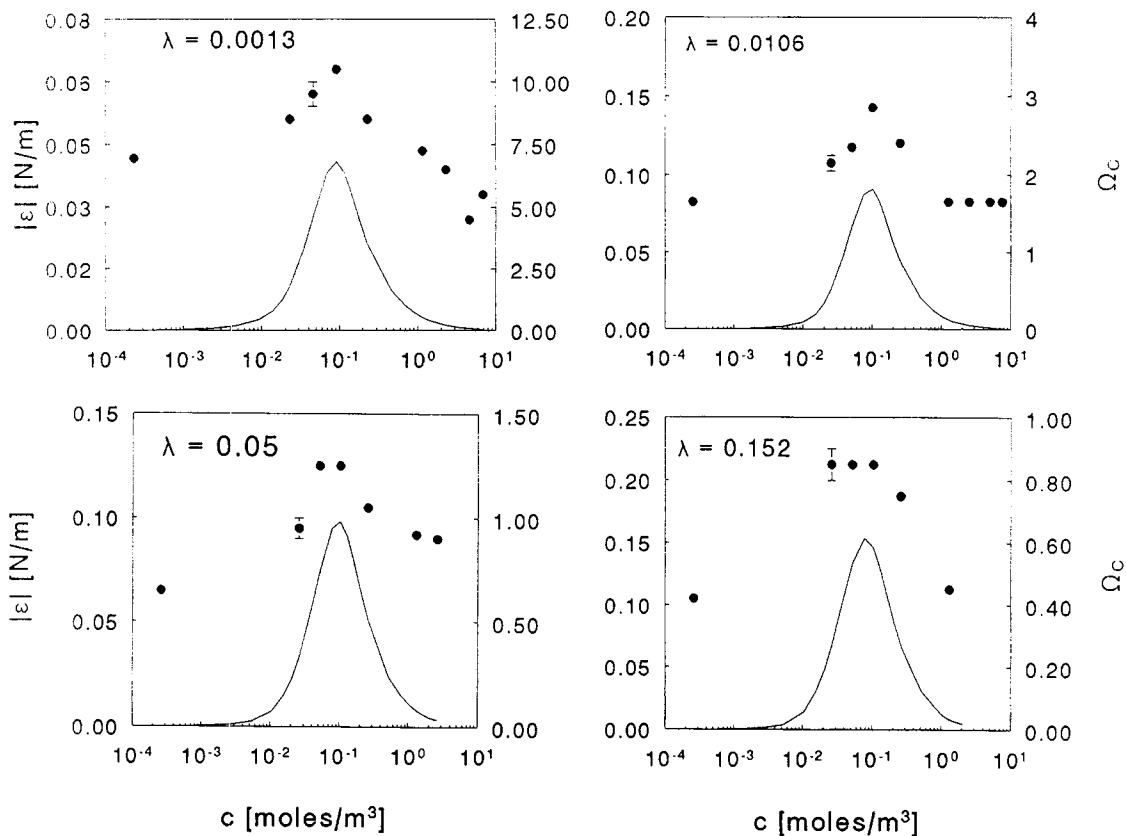


Figure 9. Correlation between the experimental critical capillary number (\dots) and calculated elasticity modulus $|\epsilon|$ (—) for W/O/Dobanol 91-8 systems.

$$\frac{1}{\xi^2} = K \frac{\Omega_c(c)}{\Omega_c(\sigma_{EQ})} \quad (12)$$

K is given by

$$K = \frac{2G_{EQ}(c)}{D} \left(\frac{d\Gamma}{dc} \right)^2 \quad (13)$$

where $G_{EQ}(c)$ is the critical shear rate for a system with uniform interfacial tension $\sigma_{EQ}(c)$. K contains only parameters that are known from independent sources (Figure 1 and surfactant properties). Equation 11 thus is an implicit equation in the ratio $\Omega_c(c)/\Omega_c(\sigma_{EQ})$, which can easily be solved for given K , β and $\sigma_{EQ}(c)$ with a simple iteration loop starting at $\Omega_c(c)/\Omega_c(\sigma_{EQ}) = 1$. Figure 10 compares Eq. 11 and the experimental results for W/O/Dobanol. $|\epsilon|$ and σ_{EQ} were calculated using the corrected concentration c in the Appendix, although the difference with c_0 decreases rapidly with increasing c_0 . The parameter β has been fitted for each curve separately, since there is no *a priori* reason to assume that it should be constant. In view of the models' simplicity, the agreement is quite satisfactory.

It should be noted that the height of the maximum is quite sensitive to β , as can be inferred from Figure 11. By contrast, the position of the maximum does not change noticeably. Figure 10 shows that β decreases somewhat with increasing viscosity ratio in the region considered. The physical meaning of

β is not clear yet. As has been argued in the previous section, the local interfacial tension at a given location on the droplet interface may be viewed as the sum of σ_{EQ} and an $|\epsilon|$ related contribution. If the effective interfacial tension is considered to be some average over the interface, β would be the result of this averaging, weighting the positive contribution from the dilated regions near the equator and the negative contributions from the compressed end-zones. The λ dependence would then be related to the droplet shape. A more detailed comment on the physical meaning of β will require a numerical study of the coupled hydrodynamic and transport equations, similar to the calculations performed by Stone and Leal (1990) and Milliken et al. (1993) for droplets in elongational flow in the presence of insoluble emulsifiers.

The results for the W/O/sucrose ester systems are shown in Figure 12, where β was fitted to be 0.23. The diffusion coefficient of the sucrose ester is chosen as $2 \times 10^{-14} \text{ m}^2/\text{s}$, which would correspond to $O(10^{-10}) \text{ m}^2/\text{s}$ in pure water. The procedure followed for the analysis of these results has been more involved than for the previous cases. As we have already mentioned, this system does not follow the simple Langmuir adsorption. When we tried to describe the $\sigma\text{-ln}(c)$ curve with the relations corresponding to the Frumkin isotherm, however, we found that a fairly wide range of parameters could produce an acceptable fit. By contrast, substitution of these values into the model equation for the critical capillary number did produce widely differing results, indicating that this model is much more sensitive to the chosen combination of Γ_∞ , a and H/RT

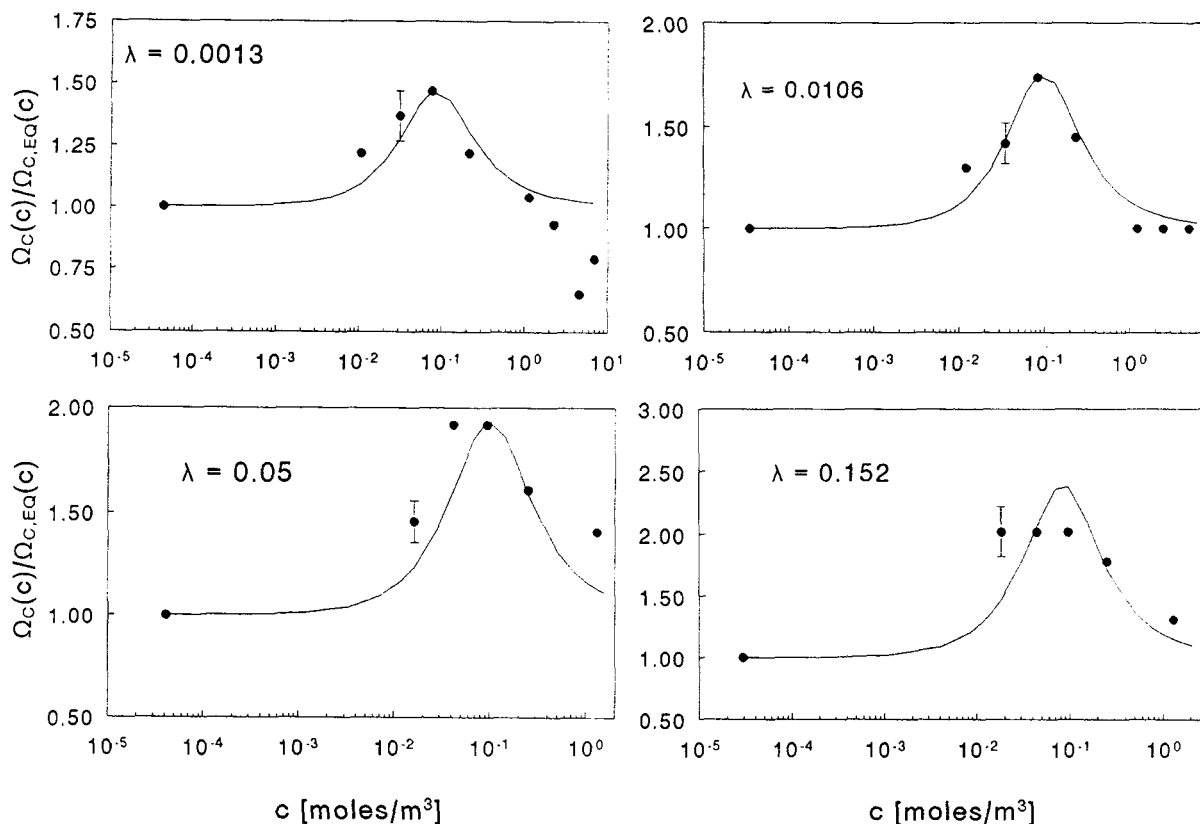


Figure 10. Model equation vs. experiments for W/O/Dobanol 91-8 systems.

β has been fitted to be 0.26, 0.23, 0.21 and 0.19 for $\lambda = 0.0013, 0.01, 0.05$ and 0.152 , respectively.

than the $\sigma\text{-ln}(c)$ curve. We, therefore, tried to find a set of adequate parameters (including β) by looking at both curves simultaneously, rather than determining the emulsifier parameters from the $\sigma\text{-ln}(c)$ curve first and then fitting β . It should be noted that the value of β is close to the values found earlier, which makes it fairly constant over three decades of viscosity ratio.

Application of the Model to Practical Circumstances in Emulsification

The model presented here is based on experiments with mm-size droplets, liquids of rather high viscosity and an emulsifier in the droplet phase. Some comments on the effects expected

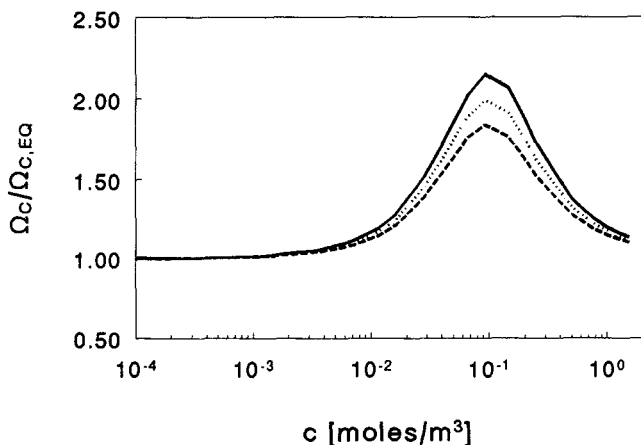


Figure 11. Typical β dependence of the calculated curves in Figure 10.

Parameter values of $\lambda = 0.05$. $\beta = 0.25$ (—); $\beta = 0.22$ (····); $\beta = 0.19$ (---).

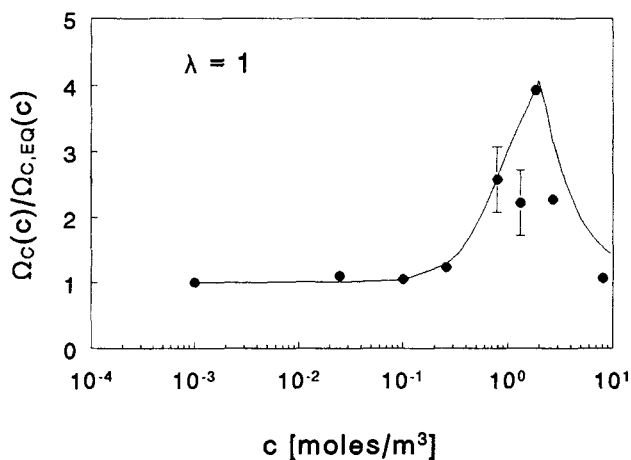


Figure 12. Model equation vs. experiment for W/O/sucrose mono laurate at slowly increasing shear rate.

$\beta = 0.23$.

for the more practical situation of low-viscosity liquids, micron-sized droplets and emulsifier in the continuous phase are therefore in order.

The model considers a droplet which has just reached its critical deformation and exhibits a rotation in the shear flow. The interfacial area elements that travel around the droplet are periodically dilated and compressed. In the model, the droplet behavior is correlated with the elasticity modulus of such an element, assuming that it is similar to a planar surface subjected to a small-amplitude harmonic deformation. The emulsifier exchange between interface and bulk is assumed to be predominantly diffusive. The neglect of lateral emulsifier redistribution in our experiments can be justified from the large value of the interfacial Peclet number (Stone and Leal, 1990):

$$Pe_I = \frac{G_c R^2}{D_I} \quad (14)$$

For our experimental conditions, $G \geq O(1) \text{ 1/s}$, $R \approx 0.5 \text{ mm}$ and $D_I = O(D) \leq O(6 \times 10^{-11}) \text{ m}^2/\text{s}$, so $Pe_I \geq O(4,000)$. The emulsifier redistribution is thus dominated by the exchange between the interfacial elements and the adjacent layers of the bulk. Close to the interface convective transport will be very small, since the continuity of the fluid velocity requires the relative velocity of bulk and interface to vanish when the interface is approached. If the exchange is confined to a layer in which the relative velocity between interface and bulk is low, the transport will be predominantly diffusive (as is assumed in the Lucassen-van den Tempel analysis). A sufficient condition seems to be that the exchange layer thickness $d\Gamma/dc$ (Lucassen and van den Tempel, 1972) is much smaller than the smallest local radius of curvature R_1 . In our experiments, $d\Gamma/dc$ is of the order $30 \text{ }\mu\text{m}$ at most, and the condition is estimated to be valid (except possibly near the droplet ends for the lowest concentrations). It may be noted that $d\Gamma/dc \ll R_1$ also seems to be a sufficient condition for the assumed flatness of the interfacial elements.

For micron-sized droplets the critical shear rate will be of the order 10^4 1/s at least, and Pe_I is again found to be large. The neglect of lateral emulsifier redistribution is thus expected to be satisfied here also. For an estimate of the exchange layer thickness we note that in practice usually values of $a = O(0.1) \text{ mol/m}^3$ and $c = O(1) \text{ mol/m}^3$ are found. Then, $d\Gamma/dc$ often decreases to submicron values [$O(0.2) \text{ }\mu\text{m}$ here]. Under such conditions, $d\Gamma/dc$ may be small compared to the local radius of curvature for drops of sizes down to a few tens of microns. For droplets that are much smaller, the convective contribution (emulsifier in outer phase) will enhance the adsorption relaxation, and the model will probably overestimate the consequences of the inhomogeneous interfacial coverage.

The value of G_{EQ} in Eq. 13 is inversely proportional to the continuous-phase viscosity. The diffusion coefficient is inversely proportional to the viscosity of the phase containing the surfactant, which in addition influences the half-saturation concentration a . So, if we reduce the viscosities while keeping their ratio λ constant, the ratio G_{EQ}/D remains constant. For a given λ the absolute values of the viscosities thus only enter via parameter a , which means that the maximum will shift to another concentration. In other words, the relaxation that becomes faster at lower viscosities is compensated by the fact

that higher shear rates are required for breakup. A smaller droplet size also increases the value of the critical shear rate (G inversely proportional to R at given Ω). This will shift the maximum to higher concentrations.

In our experiments, the critical capillary number increased by a factor of 4. To check whether significant effects may be expected under more practical circumstances, we also performed some calculations using $\Gamma_\infty = 3 \times 10^{-6} \text{ mol/m}^2$, $a = 0.2 \text{ mol/m}^3$, $\sigma(0) = 30 \text{ mN/m}$, $\sigma(\text{CMC}) = 4 \text{ mN/m}$, $\mu_d = 1 \text{ mPa}\cdot\text{s}$, $\mu_c = 50 \text{ mPa}\cdot\text{s}$, $D = 10^{-11} \text{ m}^2/\text{s}$, and $R = 5 \text{ to } 10 \text{ }\mu\text{m}$. These values correspond to a water in sunflower oil emulsion with glycerol monooleate as an emulsifier in the oil phase. The emulsifier parameters have been determined by fitting a Langmuir isotherm to interfacial tension data, while $G_c(\sigma_{EQ})$ follows from $\Omega_c(\sigma_{EQ})$ in Figure 1. For $\beta = 0.22$ we then find an increase of Ω_c by a factor of 10 for $c \approx 6 \text{ mol/m}^3$ ($\approx 0.23\%$ w/w). In this case, the decrease of σ_{EQ} caused by the surfactant is thus compensated by the stabilizing effect of the interfacial viscoelasticity, giving an effective interfacial tension close to that of the surfactant-free system.

It may be noted that the approach taken should be applicable also to other laminar flows in which a significant vorticity is present, since the physical view is the same: a droplet exhibiting a stable solid body rotation with some period T_{SB} and interfacial area elements that are periodically dilated and compressed. For these flows results similar to those in Figure 1 are available for the surfactant-free case (Bentley and Leal, 1986). When the vorticity decreases the fundamental frequency will become less dominant in the Fourier spectrum of the interfacial deformation, and a weaker correlation between Ω_c and $|\epsilon(4\pi/T_{SB})|$ is expected. These hypotheses can be investigated in a four-roll mill as used by Bentley and Leal (1986).

Conclusions

Droplet formation leads to dynamic interfacial tension and interfacial rheology. As a result, the deformation and breakup process may deviate from the behavior expected on the basis of models that assume a constant and uniform interfacial tension.

The magnitude of the deviations from the uniform- σ case depends on the ratio of the time scale of the interfacial deformation and that of its relaxation toward adsorption equilibrium. In particular, the use of the equilibrium interfacial tension in the uniform- σ relations will be adequate only when the relaxation is very effective.

The behavior of the critical capillary number as a function of emulsifier concentration cannot be explained from too slow a relaxation during the enlargement of the interface as a whole. Instead the *local* interfacial deformation due to the droplet rotation in the shear field is found to be the most likely mechanism causing interfacial viscoelasticity. In particular, the critical capillary number correlates with the established viscoelastic behavior of a harmonically deforming planar interface over a wide range of parameter values. Via the hypothesis of an effective interfacial tension related to the interfacial elasticity modulus, a phenomenological relation between the critical capillary number and this elasticity modulus has been formulated. Although the model was developed and verified for mm-sized drops, its basic assumptions are estimated to be valid for droplets down to the range of a few tens of microns. The theoretical

framework also seems to be applicable to other laminar flows with a significant vorticity.

Acknowledgment

This work is part of a BRITE/EURAM project (project number BE-4098). The partial funding by the EC is gratefully acknowledged.

Notation

- a = half-saturation concentration, mol/m³
 A = total area and area element, m²
 c = surfactant concentration in bulk, mol/m³
 d = droplet/bubble diameter, m
 D = diffusion coefficient, m²/s
 G = shear rate, 1/s
 $O(\cdot)$ = order of magnitude
 R = droplet/bubble radius, m; gas constant = 8.314 J·mol⁻¹·K⁻¹
 R_1 = smallest local radius of curvature
 T = period time and temperature
 V = volume, m³

Greek letters

- β = model (fit) parameter
 Γ = interfacial concentration, mol/m²
 Γ_∞ = saturation interfacial concentration, mol/m²
 ϵ = elasticity modulus, N/m
 ζ = square of time scale ratio
 λ = viscosity ratio
 μ = viscosity, Pa·s
 σ = interfacial tension, N/m
 ϕ = phase shift
 ω = angular frequency, rad/s
 Ω = capillary number, based on σ_{EQ} throughout this article

Subscripts

- D = droplet phase
 C = continuous phase and critical
 0 = initial value
 EQ = equilibrium value
 EFF = effective value

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Appendix

Depletion effects

As the emulsifier is dissolved in the dispersed phase, the total amount available for adsorption at the interface is finite. We, thus, have to check whether this amount is sufficient to restore the initial interfacial concentration Γ at the enlarged interface. Let us consider an experiment starting with an emulsifier solution of concentration c_0 , from which a small volume V is taken and placed in the gap of the Couette device. Let us denote the interfacial area as A . After (re-) establishment of adsorption equilibrium, the new bulk concentration is c , and the interfacial concentration is Γ . Mass conservation then gives:

$$\Gamma A + cV = c_0V \quad (A1)$$

In the case of Langmuir adsorption, this can be combined with Eq. 2 to yield:

$$Vc^2 - (Vc_0 - Va - \Gamma_\infty A)c - Vac_0 = 0 \quad (A2)$$

The physically relevant solution is:

$$c = \frac{1}{2} \left(c_0 - a - \frac{\Gamma_\infty A}{V} \right) + \frac{1}{2} \sqrt{\left(c_0 - a - \frac{\Gamma_\infty A}{V} \right)^2 + 4ac_0} \quad (A3)$$

For other isotherms, the relation between c and c_0 can be determined numerically. In our experiments, the ratio A/V for the deformed droplets at breakup can be estimated from the video images. Using these estimates and the parameter values in Table 1, the ratios c/c_0 and $\sigma(c)/\sigma(c_0)$ were calculated from Eq. A3 and the Szyszkowski equation. For very low c_0 the difference between c and c_0 can be large, but in that range the interfacial tension is close to its clean system value anyway.

For higher concentration the difference between c and c_0 decreases rapidly. For the c_0 values of our experiments the difference between $\sigma(c)$ and $\sigma(c_0)$ is about 2% at most for $\lambda = 0.0013$ and smaller (because of smaller elongation) for the higher viscosity ratios.

Adsorption time scale

In our experiments the shear rate is kept constant until the droplet has either broken up or has reached a stable deformation. Strictly this means that the critical capillary number found has to correspond to a steady state, since Ω will be subcritical ($\sigma > \sigma_{EQ}$) until this steady state is established. In practice, however, the droplet deformation near the critical conditions is inherently very slow, and the experimenter could decide prematurely that a stable deformation has been reached. In this case, a higher value of Ω_C than that corresponding to $\sigma_{EQ}(c)$ will be determined experimentally. For this explanation of our results to be possible, the emulsifier transport should be slow on the experimental time scale (minutes in the case of quasi-steady shear rate increase). This emulsifier transport will be driven by both convection and diffusion. The convective contribution will have a major effect, but unfortunately it is difficult to estimate. Walstra (Becher, 1983) gives the following estimate for the adsorption time scale at the interface of a small droplet of radius R in a laminar flow at shear rate G :

$$t_{ADS} \approx \frac{3\pi\Gamma}{RGc} \quad (A4)$$

For the W/O/Dobanol systems we have $\Gamma \approx 1.7 \times 10^{-6}$ mol/m², $R \approx 0.6$ mm, $G_C \geq O(1)$ L/s and $c \geq 0.025$ mol/m³, leading to $t_{ADS} \leq O(1)$ s. This is in line with our experimental observation that a suddenly applied shear rate (breakup, a few

seconds) and a slowly increased shear rate lead to the same critical capillary number within experimental accuracy (provided no tip-streaming occurs during quasi-steady increase of G , since this implies surfactant loss).

The above estimate suggests that the enlargement of the interface can be compensated for by interface-bulk emulsifier exchange before breakup occurs. Nevertheless, it is instructive to show that even the diffusive transport alone would be fast enough to resupply the interfacial coverage in most of our experiments. Consider, for instance, the case of $\lambda = 0.01$ and $c_0 = 0.1$ mol/m³ (corresponding to the maximum increase in Ω_C for this system). From the video images it is estimated that the increase in interfacial area is such that the interfacial concentration is about halved at breakup, while the bulk concentration reduces to $c \approx 0.08$ mol/m³ (Eq. A3). For the diffusion time scale a first-order estimate can be obtained by recognizing that the emulsifier amount required for restoring the interfacial coverage is present in a layer of thickness $(\Gamma/2)/c$. The time needed to travel this distance by diffusion is of the order of $(1/D)(\Gamma/2c)^2$. For $\Gamma \approx \Gamma_\infty = 1.8 \times 10^{-6}$ mol/m² and $D = O(6 \times 10^{-12})$ m²/s, the diffusion time is about 21 s. This is small compared to the duration of the slow shear rate increase in the quasi-steady experiments (which took several minutes). Another example is provided by the sucrose ester at $c_0 = 2.69$ mol/m³, where D is taken as $O(2 \times 10^{-14})$ m²/s, while the area increase is such that Γ decreases to about 70% of its initial value. Now the estimated diffusion time is found to be about 15 s, which is small compared to the duration of the quasi-steady area increase. Thus, the increase in Ω_C cannot be explained from too slow a relaxation after enlargement of the interface as a whole.

Manuscript received Mar. 25, 1994.