Surfactant and Viscoelastic Effects on Drop Deformation in 2-D Extensional Flow

Derek C. Tretheway and L. Gary Leal
Dept. of Chemical Engineering, University of California, Santa Barbara, CA 93106

The deformation and breakup of polymeric drops suspended in an immiscible Newtonian fluid are examined for planar extensional flow in a computer controlled four roll mill are examined. Previous work from this lab with aqueous polymeric drops showed an increase in the degree of deformation compared to Newtonian drops, and two distinct breakup mechanisms, tip streaming, and tip streaming with stretch. This led to the conclusion that breakup for non-Newtonian drops occurred at a lower capillary number and by a distinctly different mechanism than for a Newtonian drop with a similar ratio of internal to external viscosity. This conclusion was puzzling, because numerical computations with the Chilcott-Rallison model showed that the influence of viscoelasticity for that model was to decrease the degree of deformation rather than increasing it. In this work, the results for aqueous polymer solutions are compared with results for ethylene glycol polymer solutions. The results suggest that tip streaming and tip streaming with stretch in the original experiments resulted from an undetected surfactant effect, which acts to produce a more pointed drop shape that destabilizes the drop to tip streaming. Viscoelasticity, on the other hand, acts to decrease the deformation of polymeric drops at a given capillary number and increases the critical capillary number, as predicted numerically, when compared to Newtonian drops with an equivalent viscosity ratio.

Introduction

The deformation and breakup of drops is relevant to many industrial, biological, and environmental processes. Direct applications include the formation of emulsions, the dispersion of one fluid into another to increase heat or mass transfer, and the blending of two polymeric liquids to form two-phase structures with unique thermal and mechanical properties. Drop deformation has also served as a model problem for biological phenomena such as the shear induced deformation and deactivation of biological cells, cf., Chang and Olbricht (1993) and Eggleton and Popel (1998).

Many studies of Newtonian drop deformation and breakup have been reported. In 1934 Taylor investigated drop dynamics for both shear flow and pure extensional flow. The experiments highlighted the qualitative characteristics of drop deformation and breakup, and the unique differences in the mode of breakup between flow types. These differences have also motivated experimental studies of intermediate flow types with differing degrees of vorticity and strain rate. Because of the difficulty of manually controlling a drop at the stagnation point of a general two-dimensional linear flow, many early studies were restricted to either pure extensional flow or shear flow. However, in 1986, Bentley and Leal (1986a) developed a computer controlled four roll mill capable of maintaining a drop at the stagnation point for the full range of 2-D linear flows. With computer control, Bentley and Leal (1986b) studied Newtonian drop deformation and breakup for a wide range of steady 2-D linear flows from pure extensional flow to a flow that is ''near'' to simple shear. Later, Stone et al. (1986) and Stone and Leal (1989) studied a number of transient flows.

Although the study of Newtonian drop deformation and breakup has been computationally, analytically, and experimentally thorough, the study of non-Newtonian drop deformation and breakup has been quite limited. Chin and Han (1979) and Vanoene (1972) have analytically studied non-

---

Correspondence concerning this article should be addressed to L. G. Leal.

Newtonian drop deformation, but their results were limited by the use of second-order constitutive equations to asymptotically small Deborah numbers, and they, thus, considered only cases with modest drop deformation. With the computer controlled four roll mill of Bentley and Leal (1986a), Milliken and Leal (1991) performed an experimental study of polymer drop deformation and breakup for a series of water soluble polymers in solution. When compared to Newtonian drops with equivalent viscosity ratios, they observed greater drop deformation for non-Newtonian drops at a given capillary number. They also observed two new modes of drop breakup, tip streaming and tip streaming with stretch, that differed substantially from the observed breakup of Newtonian drops. Both of these modes of breakup occurred at lower critical capillary numbers than observed for Newtonian fluids and were characterized by highly curved, cusped ends with the ejection of fluid from the cusped region. These results differ qualitatively from recent computational studies of Ramaswamy and Leal (1999), based on the Chilcott-Rallison model, which predict *smaller* drop deformations at a given capillary number than those observed for equivalent Newtonian drops, and drop shapes with *blunted* ends rather than ends with high curvature as seen in the experiments. Additional experimental studies have produced contradicting results. For shear flow, de Bruijn (1989) observed that droplet elasticity reduces deformation for a given capillary number at any viscosity ratio, while Ultracki and Shi (1992) reported that elasticity reduces drop deformation for viscosity ratios below 0.5, but increases deformation for viscosity ratios above 0.5.

Given these computational and experimental discrepancies, and the results of de Bruijn (1989) (who demonstrated experimentally that the presence of surfactants may lead to tip streaming), it was hypothesized in Milliken et al. (1993) that the results of Milliken and Leal (1991) displayed surfactant effects and that it was the water soluble polymers that were acting as a surfactant. Studies of polymers at liquid-air interfaces have shown linear flexible polymers to lay at the surface with segments of the polymer protruding into the liquid phase (Noskov, 1995). As already noted, the polymers used by Milliken and Leal (1991) were water soluble. However, because of their overall organic character, it was thought that these water soluble polymers might be attracted to the interface as a surfactant with the nonpolar organic segments protruding into the nonaqueous suspending fluid.

The suspending fluid in the experiments of Milliken and Leal (1991) was a nonpolar oil (castor oil), which when in contact with water has a relatively high interfacial tension (~ 10 dyne/cm), when compared to the Newtonian systems that had been studied originally by Bentley and Leal (1986b). At a higher interfacial tension, more significant variations in the interfacial tension can occur. During an experiment, surfactants can accumulate at the ends of the drops due to the convective action of the internal and external flow. As a result, in the presence of surfactants, a drop experiences a variation in the interfacial tension with the lowest interfacial tension occurring at the drop ends. The greater surfactant concentration at the ends may explain the higher curvature that develops. In addition, the highly polar characteristics of water increase the likelihood of a surfactant to reside at the surface by increasing the energetically favorable interactions between the drop fluid and the polar head of the surfactant.

In this article, we re-examine the aqueous polymer solutions of Milliken and Leal (1991). We show that these aqueous solutions display surfactant effects, but that these effects are *not associated with the water soluble polymer*. We further use a different polymer/solvent system to examine drop deformation and breakup of non-Newtonian drops in extensional flow when surfactant effects are negligible.

Nondimensional Characterization of Drop Deformation

When both the suspending fluid and the drop fluid are Newtonian and incompressible, the governing equations are the Navier-Stokes equation and the continuity equation, both inside and outside of the drop. At the drop surface with no surfactants present, the velocity field satisfies continuity of velocity and tangential stress, while the normal stress jumps by an amount proportional to the pure-fluid, interfacial tension.

By nondimensionalizing the governing equations, four nondimensional parameters appear

$\lambda = \mu'/\mu$ viscosity ratio

$\mathrm{Ca} = (\gamma\mu a)/\sigma$ capillary number

$Re = (\rho\gamma a^2)/\mu$ Reynolds number

$K = \rho'/\rho$ density ratio

where μ' is the drop viscosity, μ is the viscosity of the suspending fluid, γ is the shear rate, a is the undeformed drop radius, σ is the interfacial tension, ρ is the density of the suspending fluid, and ρ' is the drop density. In the creeping flow limit, for neutrally buoyant drops, the evolution of drop shapes depends only on the flow type, the viscosity ratio, and the capillary number. Because non-Newtonian fluids have nonlinear stress-strain relationships and finite stress relaxation time-scales, additional parameters are needed to fully describe the evolution of non-Newtonian drop shapes. The most relevant parameter is the Deborah number, the ratio of the polymer relaxation time to the inverse strain rate of the undisturbed flow (the characteristic time-scale of the external flow).

For comparison with computational and other experimental studies, the degree of drop deformation has been characterized two ways. Following Taylor's analysis (1934), the deformation parameter D_f is defined as

$$D_f = (L - B)/(L + B)$$

where L is the half length and B is the half breadth of the drop cross section. Strictly speaking, the deformation parameter is only valid for axisymmetric, ellipsoidal shapes, but is typically used for all small deformations. D_f is highly sensitive to small departures from sphericity, but asymptotically approaches unity for infinitely extended drops. For large deformations, previous studies have thus chosen the ratio of the half length of the extended drop to the radius of the undeformed drop (L/a) as an alternative measure of deformation. L/a is more sensitive than D_f to changes in large deformations and, thus, a better measure for highly extended drops.

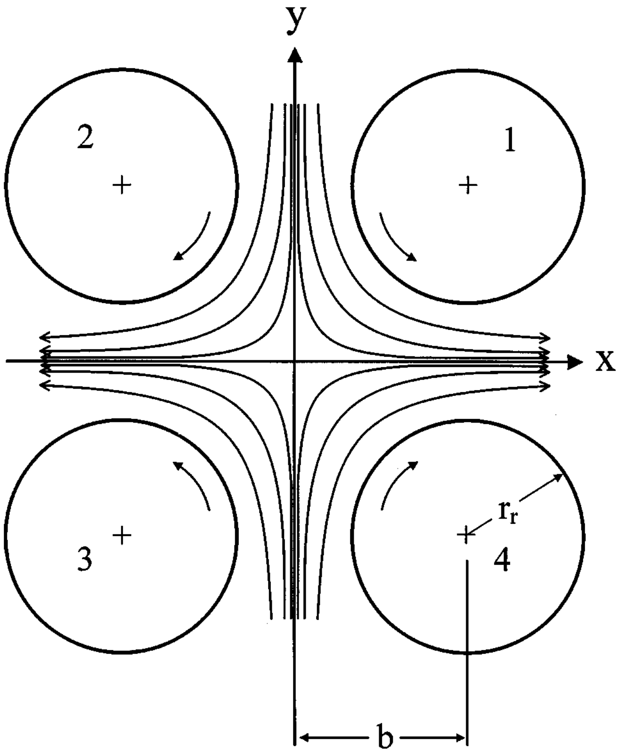

Figure 1. Four roll mill (top view).

Streamlines for pure extensional flow. b is the roller spacing, r_r is the roller radius.

Since deformations are generally small in the current study, the Taylor deformation parameter is adequate to describe drop deformation.

Experimental System

Experimental apparatus

In 1986, Bentley and Leal developed a computer controlled four roll mill capable of controlling a drop at the stagnation point for all flow types and flow strengths. After minor modifications, the four roll mill of Bentley and Leal (1986a) was employed by Milliken and Leal (1991) to study the deformation and breakup of polymeric drops and is the apparatus currently in use. Further specific details of the four roll mill and four roll mill control scheme can be found in Bentley and Leal (1986a). One of the flow fields that can be realized in the four roll mill is the purely extensional ("hyperbolic") flow in Figure 1. In terms of the Cartesian coordinates shown in Figure 1, the velocity gradient tensor near the center of the four roll mill for this flow is given by

$$\nabla u = \gamma \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

For the experiments reported here, we employ only this one type of planar flow.

During an experiment, a 1-mm to 1.5-mm radius drop is positioned at the center of the four roll mill. With the drop subjected to the extensional flow, a video camera tracks the position of the illuminated drop and the computer adjusts the rotation rates to maintain the drop at the center of the device without substantially changing the flow type or strength. Changes in the roller rotation rates shift the stagnation point from the center in the direction opposite the direction that the drops needs to be moved to return it to the center of the flow device. For subsequent analysis, 35-mm photographs of the drop are taken at recorded times to track the drop shape for either steady deformations or transient responses.

Materials

The suspending fluid and polymer used in the present experiments are the same materials studied by Milliken and Leal (1991). The suspending fluid is Pale 1000 oil, a hydrophobic polymerized castor oil (CasChem, Bayonne, NJ). On a Rheometrics model RMS 800 Rheometer, Pale 1000 oil displays a shear viscosity of 363.9 poise that is independent of shear rate and does not exhibit significant normal forces at shear rates below 10 s^{-1}. For the current experimental studies, significant deformation and/or drop breakup occurs at shear rates below 0.05 s^{-1}. Thus, at the shear rates of interest, the suspending fluid behaves as a viscous Newtonian fluid.

In this study, we reproduce the aqueous polymer solutions of Milliken and Leal (1991) and, in addition, examine the same polyacrylamide polymer in a second low viscosity solvent, ethylene glycol. With the same polymer, the solvents produce solutions with similar bulk rheological properties (similar viscosities, relaxation times, and normal stresses), but the interfacial tension of the ethylene glycol solutions with Pale 1000/170 oil is less than 50% that of the water solutions. The polymer solutions were prepared by dissolving granular polyacrylamide (Praestol 2530TR, Stockhausen Inc., Greensboro, NC: molecular weight of 15×10^6) in either deionized water or reagent grade ethylene glycol. The solutions were placed on a New Brunswick Scientific Rollacell mixer for three days to ensure complete dissolution of the polymer in the solvent fluid.

The polymer solutions were characterized on a Rheometrics model RMS 800 rheometer. All solutions displayed shear thinning, and an increase in the normal stress difference at higher shear rates. Figure 2 shows the viscosity as a function of shear rate, and Figure 3 provides the first normal stress difference as a function of shear rate for both the ethylene glycol and water solutions. Table 1 provides the properties of the polymer solutions. The longest relaxation times of the polymer solutions were estimated from the shear rate at which the onset of shear thinning occurred. We determine the onset of shear thinning by curve fitting the viscosity at higher shear rates (above 10^{-1} s^{-1}) and finding the shear rate at which the resulting equation equals the zero shear rate viscosity. Although this is not the best estimate of the relaxation time, it should be sufficient to approximate the range of shear rates where non-Newtonian effects should develop. We determined the zero shear rate viscosity by averaging lower shear rate viscosity data (not shown in Figure 2), and also by extrapolating the shown data to lower shear rates. Both methods produced zero shear rate viscosities that differed by only a few percent. This difference is insignificant for calculating the relaxation time or the zero shear rate viscosity ratio for

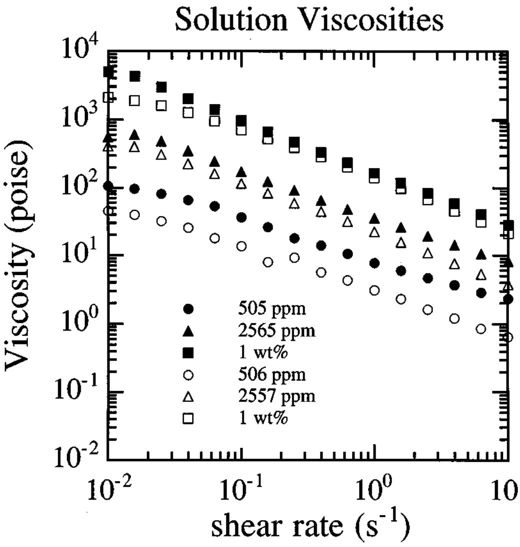

Figure 2. Viscosity vs. shear rate.

Solid symbols represent water solutions; open symbols represent ethylene glycol solutions. Legend indicates the weight fraction of polymer dissolved in each solution.

comparison with similar viscosity ratio Newtonian drops. Although it is not readily apparent from Figure 2 for all solutions, at a shear rate of 10^{-2} s^{-1} the solution viscosities are at or are nearly at the zero shear rate value.

The interfacial tension was calculated from small drop deformations by the application of Taylor's small deformation theory. As explained by Milliken and Leal (1991), Taylor's classical expression for drop deformation offers an accurate and the most reliable measure of the interfacial tension even for non-Newtonian drops. For sufficiently slow flows (small capillary numbers, small deformations, and small Deborah numbers), the viscoelastic correction to small deformation theory is small and can be neglected. Usual methods (ring tensiometer, Wilhemy Plate) of determining the interfacial tension are unreliable or difficult to conduct due to the high fluid viscosities, and the small density differences between the fluids.

Table 1. Properties of the Polymer Solutions

Solution Formulation (by wt. Polyacrylamide)	τ_R* (s)	λ	σ (dyne/cm)
158 ppm in ethylene glycol	40	0.01	3.90
505 ppm in ethylene glycol	50	0.3	3.90
2,565 ppm in ethylene glycol	70	1.6	3.90
1% in ethylene glycol	100	14.5	3.90
506 ppm in deionized water	20	0.13	10.3
2,557 ppm in deionized water	50	1.1	10.3
1% in deionized water	70	6.0	10.3

*τ_R = estimate of longest relaxation time from shear rate at the onset of shear thinning.

The high viscosity of the suspending fluid and the small density differences between the suspending and drop fluids reduce buoyancy effects sufficiently that sedimentation is insignificant.

Results

Confirmation of the results of Milliken and Leal (1991)

The steady-state deformation curves and the unsteady breakup of drops comprised of 506 ppm, 2,557 ppm, and 1% by weight solutions of polyacrylamide in water were investigated. Figure 4 shows the deformation curves (deformation vs. capillary number) for each of these water-based polymer solutions. The last data point indicates the highest capillary number with a stable drop shape. These results both quantitatively and qualitatively confirm the observations of Milliken and Leal (1991). The critical capillary numbers (the capillary number when breakup occurs) determined by Milliken and Leal (1991) were between 0.12 and 0.15, and, at these values, tip streaming or tip streaming with stretch was observed. Both modes of breakup (depending on the viscosity ratio) were also observed in this study and, as shown in Figure 4, the highest

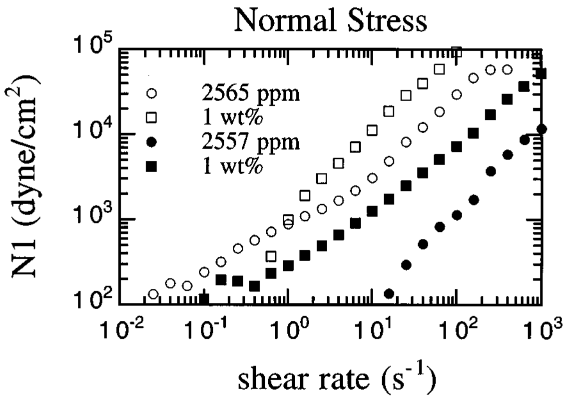

Figure 3. First normal stress difference vs. shear rate for the four highest concentration polymer solutions.

Solid symbols represent water solutions; open symbols represent ethylene glycol solutions. Legend indicates the weight fraction of polymer dissolved in each solution.

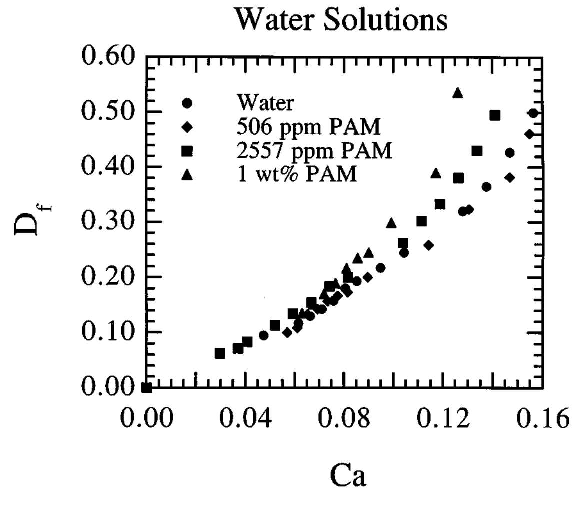

Figure 4. Deformation vs. capillary number for polyacrylamide in deionized water.

The last data point indicates the highest capillary number with a stable drop shape.

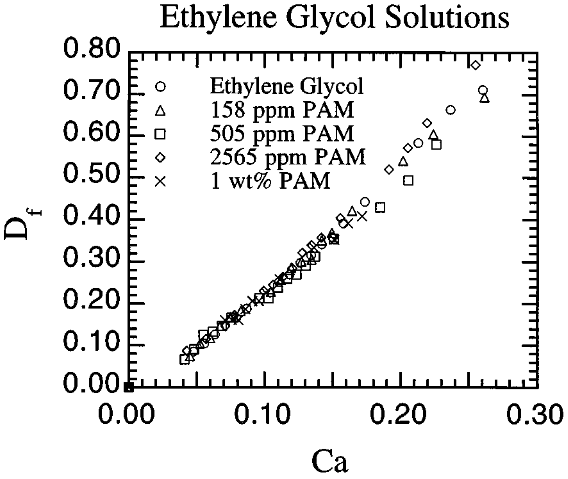

Figure 5. Deformation vs. capillary number for polyacrylamide in ethylene glycol.

1 wt. % solution has no stable shape above a critical capillary number of 0.17.

capillary number with a stable drop shape falls between 0.12 and 0.16. For convenience, we shall refer to both modes of breakup simply as "tip streaming."

Comparison between water and ethylene glycol solutions

With the results of Milliken and Leal (1991) confirmed, a series of drops consisting of polyacrylamide in ethylene glycol were examined. Figure 5 shows the steady-state deformation curves as a function of capillary number for these ethylene glycol-based solutions. The deformation curves for drops of the ethylene glycol-based polyacrylamide solutions differ significantly from the deformation curves of drops produced from water solutions of the same polymer (see Figure 4), even though the rheological properties of the two solutions are very similar. First, for fixed capillary number, the deformation is independent of the polymer concentration, including even the pure ethylene glycol with no added polymer. This result actually seems quite peculiar at first, because both the viscosity ratio and viscoelasticity increase as the polymer concentration increases. We shall return to this point later. Second, the ethylene glycol-polyacrylamide drops formed highly extended steady-state shapes similar to those observed in previous studies of low viscosity ratio ($\lambda < 0.02$) Newtonian drops even though the viscosity ratio was significantly greater than 0.02 throughout the experimental range of shear rates. The water-polyacrylamide drops with similar viscosity ratios did not deform into highly extended shapes. Third, the tip streaming mode of breakup characteristic of the water-polyacrylamide drops, which occurred at a critical capillary number between 0−12 and 0.16, was not observed for any ethylene glycol solution. In contrast, tip streaming occurred at a critical capillary number between 0.12 and 0.16 for the water solutions. For the ethylene glycol-polyacrylamide drops, an unsteady drop shape was observed for only the 1% solution (highest viscosity ratio) above a critical capillary number of approximately 0.18. The other ethylene glycol solutions exhibited steady states up to the maximum capillary number that we studied, $Ca_{\max} = 0.26$. Upon cessation of the flow, the mode of breakup of the 1% solution was qualitatively identical to the end pinching mechanism observed for Newtonian drops of similar viscosity ratio by Stone et al. (1986).

The results for deformation and breakup of the ethylene glycol-polyacrylamide drops thus show definite qualitative and quantitative differences when compared to water-polyacrylamide drops. This difference cannot be explained by a difference in the bulk rheological properties. The ethylene glycol and water-based solutions displayed similar bulk rheological properties as shown in Figures 2 and 3. The most significant difference between the water and the ethylene glycol-based solutions is the magnitude of the interfacial tension with the Pale 1000 suspending fluid. The water-based solutions (including water alone) had an average interfacial tension of 10.3 dyne/cm. Ethylene glycol and the ethylene-glycol-based solutions had an interfacial tension of 3.90 dyne/cm. As argued below, we believe that the interface for water and water-based solutions is likely contaminated with an unknown surfactant and the value of 10.3 dyne/cm is, therefore, probably reduced compared to a "clean" interface value. For ethylene glycol and the ethylene glycol-based solutions, we expect that 3.9 dyne/cm represents a "clean" value of the interfacial tension, as there is no indication of significant surfactant concentration at the interface. The deformation characteristics of ethylene glycol drops are consistent with a "clean" Newtonian drop.

The difference in interfacial tensions between the water-based and ethylene-glycol-based systems may have a significant effect if surfactants are present in the experimental system, due to the presence of Marangoni effects caused by variations in the interfacial tension as a function of position on the drop surface. The maximum interfacial tension possible is the clean interface value, while the minimum is approximately zero at points of high surfactant concentration. For the water-based solutions, the changes in interfacial tension due to nonuniform distribution of surfactant on the drop surface can thus be O(10) dyne/cm (or more, depending on the clean interface value), whereas the maximum change for the ethylene glycol solutions is only a few dyne/cm. Since the magnitude of Marangoni effects is proportional to the gradients of interfacial tension on the drop surface, we may expect these effects to be much more important for water-based drops of a particular size as compared to ethylene glycol-based drops.

All of these factors, as well as the modes of deformation observed, lead us to conclude that the qualitative and quantitative differences between the ethylene glycol and water-based solutions are most likely the result of surfactant contamination. The main question is what the source of surfactant could be in our systems, which consist of pure chemical components (polyacrylamide and Pale oil) and deionized water? To elucidate the surfactant source, the deformation and breakup of deionized water drops (without any polymer) was studied.

Deformation and breakup of deionized water and ethylene glycol

As shown in Bentley and Leal (1986b), a Newtonian drop with a low viscosity ratio ($\lambda < 0.02$) forms at higher capillary numbers a highly extended steady shape with pointed ends.

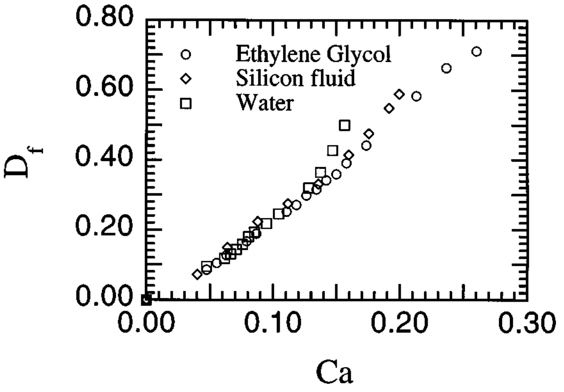

Figure 6. Deformation vs. capillary number for ethylene glycol ($\lambda = 0.0005$), water ($\lambda = 2 \times 10^{-5}$), and a silicon fluid ($\lambda = 0.0113$) investigated by Bentley and Leal (1986b).

The deformation characteristics of pure ethylene glycol drops agree with these earlier results. Because the viscosity ratio of ethylene glycol ($\lambda = 0.0005$) and water ($\lambda = 0.0003$) are similar and both fluids are Newtonian, we would expect drops of pure ethylene glycol and water to have similar deformation characteristics (that is, nearly identical deformation curves, the same drop shapes, and similar breakup mechanisms). Figure 6 provides a comparison between the deformation curves of ethylene glycol, deionized water, and a slightly higher viscosity ratio silicon drop from Bentley and Leal (1986b). From Figure 6, it is apparent that the deformation characteristics of deionized water and ethylene glycol drops differ significantly. Ethylene glycol drops produce highly extended steady shapes up to a capillary number of 0.27, which is consistent with previous Newtonian results. Water drops, on the other hand, never became highly extended or exhibited the shape characteristic of previously studied low viscosity ratio Newtonian drops. This is primarily because the deionized water drops exhibited tip streaming at a critical capillary number of approximately 0.16. Neither the tip streaming mechanism, nor the critical capillary number of 0.16 is consistent with the previously observed behavior of other low viscosity ratio Newtonian drops. The discrepancy between water and ethylene glycol drops (as well as earlier data for silicon drops) provides strong circumstantial evidence that the behavior of the water drops is strongly affected by surfactant effects. Furthermore, comparison with the data for water-based polyacrylamide drops (refer to the first part of this section) suggests that it is either the water or the suspending Pale 1000 oil that is the surfactant source and not the water soluble polymer (polyacrylamide) as (incorrectly) hypothesized in an earlier study (Milliken et al., 1993).

Discussion

Possible surfactants

The obvious question is what surfactant is present, and how did it enter the experimental system? We can only speculate at this time. Possible sources may include the following. First, when the four roll mill was constructed, it was designed to have the upper surface of the suspending fluid exposed to the surroundings. As a result, small amounts of contaminants have settled into the suspending fluid and these contaminants may include surfactants. However, these contaminants are unlikely to be the source of the surfactants, because the original experiments by Milliken and Leal (1991), which showed tip streaming, were conducted in clean (new and contaminant free) Pale 1000 oil. The second and most likely source is the "pure" Pale 1000 suspending fluid itself. The suspending fluid is a derivative of castor oil, a triglyceride of fatty acids. The suspending fluid is produced by cross linking and oxidizing the castor oil molecule. It may be possible that these reactions produce byproducts, which behave as surfactants. This speculation is corroborated, in part, by the fact that Langmuir trough results for the deionized water and the water soluble polymer solutions show no measurable surface active contaminants (that is, the surface pressure remains constant at the value of pure water even at extremely fast compression rates).

Deformation curves of ethylene glycol and ethylene glycol polymer solutions

We have noted earlier the apparently puzzling result that drops of pure ethylene glycol and of ethylene glycol-polyacrylamide solutions at various polymer concentrations all displayed nearly identical values for the drop deformation as a function of capillary number. Indeed, within error, the results are barely distinguishable. These nearly identical results elicit the question as to why there seem to be no bulk rheological effects. As shown in Figures 2 and 3, all of the polymer solutions display shear thinning and an increase in the first normal stress difference at higher shear rates. Even though the changes in the solution properties (that is, the reduction in viscosity) are relatively small for the experimental range of shear rates (0.005 to 0.03 s^{-1}), it is believed (and will be shown) that the results should be affected significantly by bulk rheological effects. We shall see shortly that the direct comparison between pure ethylene glycol and ethylene glycol-based polymer solutions can be, in fact, misleading.

Figure 7 shows the deformation characteristics of Newtonian fluids with a surfactant-free interface at different viscos-

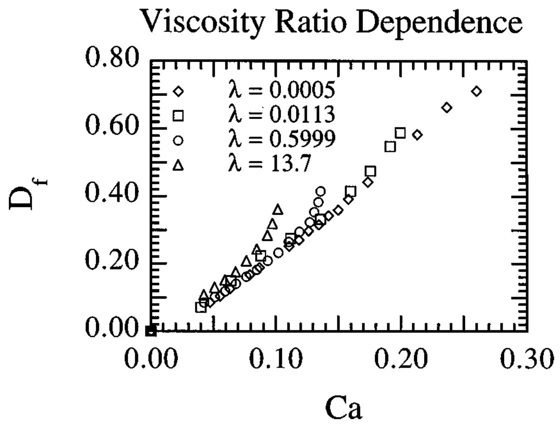

Figure 7. Deformation characteristics of Newtonian fluids with different viscosity ratios.

ity ratios. These viscosity ratios span the range of viscosity ratios of the ethylene glycol and water-based polyacrylamide solutions. The results are from both the current study and the experimental data of Bentley and Leal (1986b). These Newtonian results show that, with an increase in viscosity ratio, both the critical capillary number and the critical deformation at breakup decrease, and the deformation at a given capillary number increases. If bulk rheological effects were negligible for the ethylene glycol-based polyacrylamide solutions, the deformation characteristics of the pure ethylene glycol drops and the ethylene glycol-polyacrylamide drops (shown in Figure 5) should follow the Newtonian trend, as displayed in Figure 7, of increased deformation with increased viscosity ratio (that is, with increased polymer concentration), which they do not.

Figure 8 compares the deformation of the ethylene glycol-based polymer drops to Newtonian drops with similar viscosity ratios based on the zero shear rate viscosity of the polymer solutions. Figure 8 shows that the polymer drops exhibit greater critical capillary numbers, larger critical deformations, and smaller deformations at a given capillary number, when compared directly to Newtonian drops with a nearly identical viscosity ratio. This is *qualitatively* consistent with the recent computational results of Ramaswamy and Leal (1999). In addition, the Newtonian and non-Newtonian curves deviate from each other at a capillary number (nondimensional shear rate), which corresponds to a Deborah number equal to approximately one (longest relaxation time estimated from the onset of shear thinning). Near this capillary number shear thinning begins and non-Newtonian effects develop.

Thus, the observation that drops of pure ethylene glycol and of ethylene glycol-based polymer solutions show nearly identical results for drop deformation vs. capillary number is quite interesting. It implies that, for this particular fluid system, the increased deformation expected due to the increased viscosity ratio that occurs with an increase in polymer concentration must be balanced quite precisely by the viscoelastic effect of decreased deformation, as illustrated above. In other words, the viscoelastic contribution to drop deformation (shown in Figure 8) acts equally and opposite the effect of an increase in the viscosity ratio (shown in Figure 7).

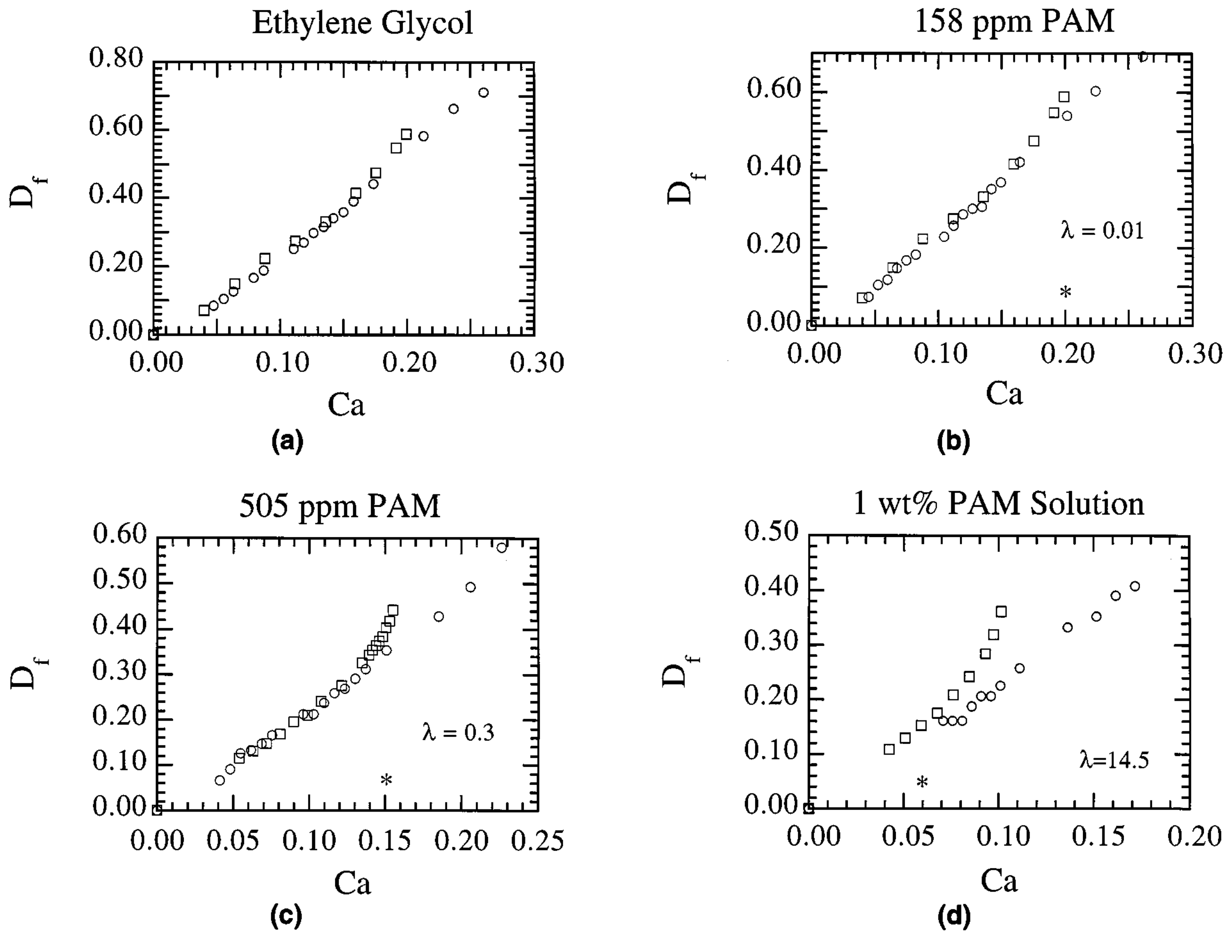

Figure 8. Comparison of ethylene glycol solutions (circle) to Newtonian fluids (square) with an equivalent viscosity ratio.

(a) Ethylene glycol ($\lambda = 0.0005$) and a Newtonian silicon fluid ($\lambda = 0.0113$); (b) 158 ppm PAM solution; (c) 505 ppm PAM solution; (d) 1 wt. % PAM solution. Asterisk indicates the capillary number at which the $De = 1$.

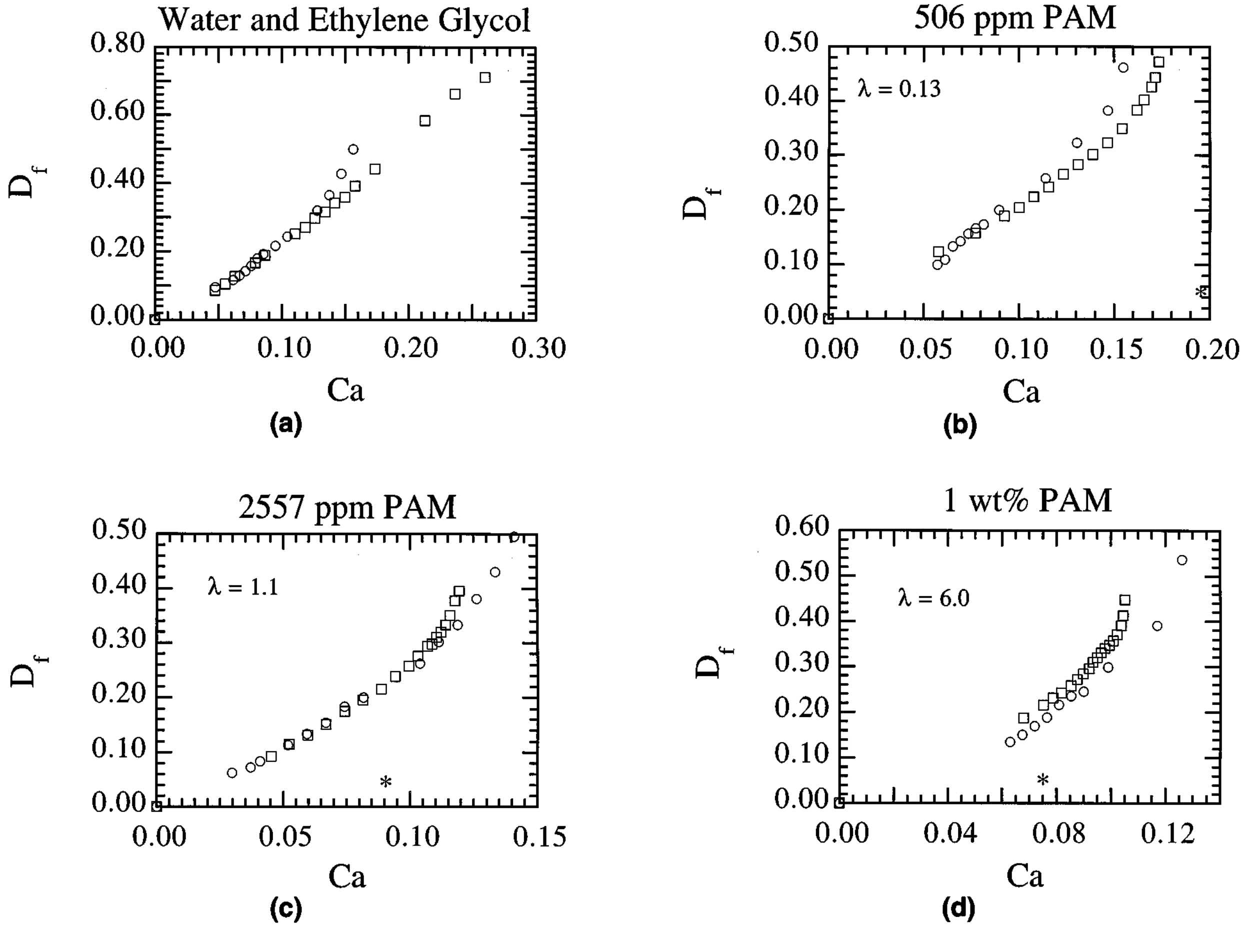

Figure 9. Comparison of water solutions (circle) to Newtonian fluids (square) with an equivalent viscosity ratio.

(a) Water and ethylene glycol; (b) 506 ppm PAM solution; (c) 2,557 ppm PAM solution; (d) 1 wt. % PAM solution. Asterisk indicates the capillary number at which the $De = 1$.

Of course, the precise balance with increased polymer concentration is almost certainly a coincidence for this particular system.

Surfactant and non-Newtonian effects on water polymer solutions

While it has been shown earlier that the deionized water drops and the water-based polymer drops display surfactant effects, the water-based polymer drops display non-Newtonian effects as well. Figure 9 compares the deformation curves for the water and water-based polymer drops with results for Newtonian drops with equivalent viscosity ratios. The surfactant effect on the pure water drops is pronounced. In addition to displaying tip streaming, water has a greater deformation at a given capillary number, a lower critical capillary number, and a smaller critical deformation at breakup than expected for Newtonian drops without surfactants. This is qualitatively consistent with the theoretical and computational surfactant analysis of Milliken et al. (1993), and with the more recent computational work of Pawar and Stebe (1996) for drops with a dilute, fixed quantity of insoluble surfactant, and for drops with an insoluble surfactant undergoing a 2-D phase transformation. As the concentration of polymer dissolved in water increases, however, non-Newtonian effects increase and tend to counteract these surfactant effects. As shown in Figure 9, the non-Newtonian deformation curves shift, as the polymer concentration increases, from the surfactant dominated features of the pure water to the non-Newtonian dominated features of the ethylene glycol solutions. We interpret this shift as resulting from the increased magnitude of non-Newtonian effects, which ultimately overcome the surfactant effect. For the 506 ppm solution, the Deborah number remains relatively small (less than one) for the range of capillary numbers with a stable drop shape. Thus, non-Newtonian effects should be relatively weak. We would expect and Figure 9 shows that the deformation curve of the 506 ppm solution primarily exhibits surfactant effects. However, because of the weak non-Newtonian effects, the surfactant effect on the 506 ppm solution drops is not as pronounced as the surfactant effect on pure water drops. The differences in the critical deformation at breakup, the critical capillary number, and the deformation at a given capillary between the 506 ppm solution and its equivalent viscosity ratio Newtonian fluid are significantly smaller than those differences between pure water and pure ethylene glycol. However, as expected, for the 506 ppm solution, the non-Newtonian effects remain relatively weak. For the 2,557 ppm and 1% solutions, the Deborah number reaches a value of one at capillary numbers with stable drop shapes. Thus, we expect stronger non-Newtonian effects on the deformation characteristics and a stronger tendency to counteract surfactant effects on drop deformation. This is observed with the deformation characteristics of the 2,557 ppm and 1% solution drops being qualitatively similar to drops of the ethylene glycol-based polyacrylamide solutions (higher critical capillary numbers, larger critical deformations, and lower deformations at a given capillary number for the polymer drop when compared to its equivalent viscosity ratio Newtonian drop). However, unlike the deformation curves for the ethylene glycol-based polymer drops, the water-based drops (2,557 ppm and 1%) only show significant deviation from the Newtonian deformation curves for Deborah numbers that are greater than (instead of equal to) one and this deviation from the Newtonian curve is not as pronounced. This is due to the continued presence of surfactant effects, which ultimately lead to tip streaming even for the relatively concentrated water-based polymer solutions.

Conclusions

This article examines the viscoelastic and surfactant effects on the deformation and breakup of drops. We consider both ethylene glycol-based and water-based solutions of polyacrylamide. The results for the ethylene glycol-based drops show little influence of surfactants, but illustrate the competing effects between increased viscoelasticity and increased viscosity ratio, which both increase with the polymer concentration. Surfactant effects, which appear when the drops are water or water-based polymer solutions, increase the deformation at a given capillary number, decrease the critical capillary number and critical deformation for breakup, and produce the tip streaming breakup mechanisms observed in this study and in the previous work by Milliken and Leal (1991). Viscoelasticity, on the other hand, decreases the deformation at a given capillary number, and increases the critical capillary number and critical deformation for breakup when compared to equivalent viscosity ratio Newtonian drops. This observed viscoelastic effect is qualitatively consistent with the recent computational work of Ramaswamy and Leal (1999). Interestingly, for the ethylene glycol solutions examined in this study, the results show almost an exact balance on drop deformation between the increasing viscoelasticity and the increasing viscosity ratio that occurs as the polymer concentration increases. Although the non-Newtonian effects are modest in these experiments, the effects are significant enough to collapse the deformation curves for the ethylene glycol-polyacrylamide drops onto the deformation curve of pure ethylene glycol drops. While the ethylene glycol-polyacrylamide drops display only viscoelastic and viscosity ratio effects, additional surfactant effects are observed in the deformation characteristics of the water-polyacrylamide drops. The discrepancies between the deformation characteristics of drops of pure water and pure ethylene glycol, and between the water-based and ethylene glycol-based polymer solutions clearly show the effect of surfactants, even though we have not been able to unambiguously isolate the source of surfactant in our experimental system.

Acknowledgments

This research was supported by a grant from the Fluid Mechanics program of the National Science Foundation.

Literature Cited

Bentley, B. J., and L. G. Leal, "A Computer-Controlled Four-Roll Mill for Investigations of Particle and Drop Dynamics in Two Dimensional Linear Shear Flows," *J. Fluid Mech.*, **167**, 219 (1986a).

Bentley, B. J., and L. G. Leal, "An Experimental Investigation of Drop Deformation and Break-up of Viscous Drops," *J. Fluid Mech.*, **167**, 241 (1986b).

Chang, K. S., and W. L. Olbricht, "Experimental Studies of the Deformation and Breakup of a Synthetic Capsule in Steady and Unsteady Simple Shear Flow," *J. Fluid Mech.*, **250**, 609 (1993a).

Chang, K. S., and W. L. Olbricht, "Experimental Studies of the Deformation of a Synthetic Capsule in Extensional Flow," *J. Fluid Mech.*, **250**, 587 (1993b).

Chin, H. B., and C. D. Han, "Studies on Droplet Deformation and Breakup. I. Droplet Deformation in Extensional Flow," *J. Rheol.*, **23**, 557 (1979).

de Bruijn, R. A., "Deformation and Breakup of Drops in Simple Shear Flow," PhD Thesis, Technische Univ., Eindhoven (1989).

Eggleton, C. D., and A. S. Popel, "Large Deformation of Red Blood Cells Ghosts in a Simple Shear Flow," *Phys. Fluids*, **10**, 1834 (1998).

Milliken, W. J., and L. G. Leal, "Deformation and Breakup of Viscoelastic Drops in Planar Extensional Flows," *J. Non-Newt. Fluid Mech.*, **40**, 355 (1991).

Milliken, W. J., H. A. Stone, and L. G. Leal, "The Effects of Surfactants on the Transient Motion of Newtonian Drops," *Phys. Fluids*, **5**, 69 (1993).

Noskov, B. A., "Dynamic Surface Elasticity of Polymer Solutions," *Colloid Poly. Sci.*, **273**, 263 (1995).

Pawar, Y., and K. J. Stebe, "Marangoni Effects on Drop Deformation in an Extensional Flow: The Role of Surfactant Physical Chemistry. I. Insoluble Surfactants," *Phys. Fluids*, **8**, 1738 (1996).

Ramaswamy, S., and L. G. Leal, "The Deformation of a Viscoelastic Drop Subjected to a Steady Uniaxial Extensional Flow," *J. Non-Newt. Fluid Mech.*, in press (1999).

Stone, H. A., B. J. Bentley, and L. G. Leal, "An Experimental Study of Transient Effects in the Breakup of a Viscous Drop," *J. Fluid Mech.*, **173**, 131 (1986).

Stone, H. A., and L. G. Leal, "The Influence of Initial Deformation on Drop Breakup in Subcritical Time-Dependent Flows at Low Reynolds Numbers," *J. Fluid Mech.*, **206**, 223 (1989).

Taylor, G. I., "The Formation of Emulsions in Definable Fields of Flow," *Proc. Roy. Soc. A*, **146**, 501 (1934).

Ultracki, L. A., and Z. H. Shi, "Development of Polymer Blend Morphology During Compounding Twin-Screw Extruder. Part I. Droplet Dispersion and Coalescence—A Review," *Poly. Eng. Sci.*, **32**, 1824 (1992).

Vanoene, H., "Modes of Dispersion of Viscoelastic Fluids in Flow," *J. Coll. and Interf. Sci.*, **40**, 448 (1972).

Manuscript received Oct. 13, 1998, and revision received Mar. 15, 1999.