Distinguishing between linear and branched wormlike micelle solutions using extensional rheology measurements

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Synopsis

A filament stretching extensional rheometer and capillary breakup extensional rheometer is used to measure the effect of branching on the extensional rheology of a series of wormlike micelle solutions. The experiments are performed using a series of linear and branched wormlike micelle solutions consisting of sodium oleate (NaOA) and octyl trimethyl ammonium bromide (C_8TAB). The ratio of NaOA to C_8TAB is fixed at 70/30 while the total surfactant concentration is varied. The shear rheology of wormlike micelle solutions is found to demonstrate a maximum in shear viscosity at 4 wt% followed by a sharp decrease in viscosity with increasing surfactant concentration. It has been shown through cryo-transmission electron microscopy imaging that the maximum in the shear viscosity for these fluids corresponds to the transition from linear entangled to branched micelles. The extensional rheology measurements for all of the wormlike micelle solutions below 4 wt% demonstrated some degree of strain hardening of the extensional viscosity, however, beyond 4 wt% little strain hardening is observed. The maximum value of the Trouton ratio is found to decay rapidly with increasing micelle concentration, starting from values of nearly $Tr \approx 1000$ at a concentration of 2 wt% and approaching an asymptote close to Newtonian limit of $Tr \approx 3$ for concentrations of 4 wt% and above. These results are most likely due to the additional stress relief mechanisms available to branched micelles which appear to be extremely efficient in extensional flows. These stress relief mechanisms include the fast and fluid sliding of branch points along the length of the micelle and the increased occurrence of "ghost-like" crossing of micelles at entanglement points with increasing surfactant concentration. These observations demonstrate how sensitive the extensional rheology of wormlike micelles is to branching. © *2008 The Society of Rheology.* [DOI: 10.1122/1.2896120]

I. INTRODUCTION

Surfactants are amphiphilic molecules which have both a hydrophilic head which is often charged and a relatively short hydrophobic tail. When the surfactant molecules are dissolved in water above their critical micelle concentration (CMC), they can spontaneously self-assemble into large aggregates known as micelles [Israelachvili (1985); Larson (1999); Rehage and Hoffmann (1991)]. These large aggregates can form a number of different complex shapes depending on the size of the surfactant head group, the length

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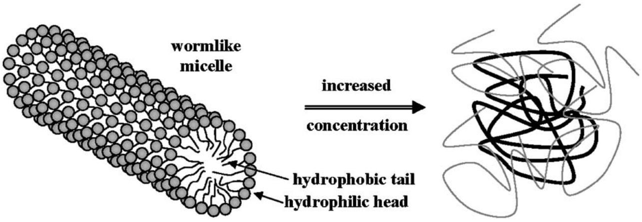

FIG. 1. Schematic diagram of wormlike micelle solutions showing various morphologies including spherical, lamellar, wormlike and long entangled wormlike micelles which can impart viscoelasticity.

and number of tails, the charge on the surfactant, the salinity of the solution, and the flow conditions [Israelachvili (1985)]. Of interest to us are surfactants which tend to form wormlike micelles as seen in Fig. 1 because at large enough surfactant concentration these wormlike micelles can grow very long, become flexible and entangle thereby making the solution viscoelastic much like polymer solutions. Viscoelastic wormlike micelle solutions are currently being used in variety of applications including many household and cosmetic products, rheological modifiers in consumer products such as paints, detergents, pharmaceuticals, lubricants and emulsifiers. Further, these micelle solutions are extensively used in agrochemical spraying, inkjet printing and enhanced oil recovery [Anderson *et al.* (2006); Kefi *et al.* (2004)]. Therefore, because of the ever-increasing commercial importance of these fluids, a better understanding of the rheological behavior of these complex fluids is needed.

Although both wormlike micelle solutions and polymer solutions can be viscoelastic, wormlike micelles are physically quite different from polymers. Whereas the backbone of a polymer is covalently bonded and rigid, wormlike micelles are held together by relatively weak physical attractions and as a result are continuously breaking and reforming with time. In an entangled network, both individual polymer chains and wormlike micelles can relieve stress through reptation driven by Brownian motion [Larson (1999)]. However, unlike polymeric fluids, wormlike micelle solutions have access to a number of stress relief mechanisms in addition to reptation. Wormlike micelles can also relieve stress and eliminate entanglement points by either breaking and reforming in a lower stress state [Rehage and Hoffmann (1991)] or alternatively by creating temporary branch point which allows two entangled micelles to pull right through each other in thereby eliminating the entanglement point and relieving stress in what has become known as a "ghost-like" crossing. A schematic diagram of a ghost-like crossing is shown schematically in Fig. 2(a) [Appell *et al.* (1992)]. The reptation and breakup relaxation mechanisms have characteristic time scales of λ_{rep} and λ_{br}, respectively. In the fast-breaking limit, where the breakup time is much shorter than the reptation time, $\lambda_{br} \ll \lambda_{rep}$, Cates [Cates *et al.* (1996)] demonstrated that the linear viscoelastic response of these wormlike micelle solutions can be described by Maxwell fluids with a single relaxation time that is the geometric mean of the reptation and breakup time, $\lambda = (\lambda_{rep}\lambda_{br})^{1/2}$ [Cates *et al.* (1996)]. However, the nonlinear viscoelastic response of these entangled micelle solutions in strong shear and extensional flows has been shown to be much more complex and is still in need of further exploration [Cates and Turner (1990); Khatory *et al.* (1993); Rothstein (2003)].

Lequeux and Candau (1997) demonstrated that the phase diagram of surfactant solutions that form wormlike micelle solutions can be quite complex. Within the semidilute regime, increasing salt concentration can drive the wormlike micelles from linear, to branched and finally to an interconnected saturated network. For a linear wormlike mi-

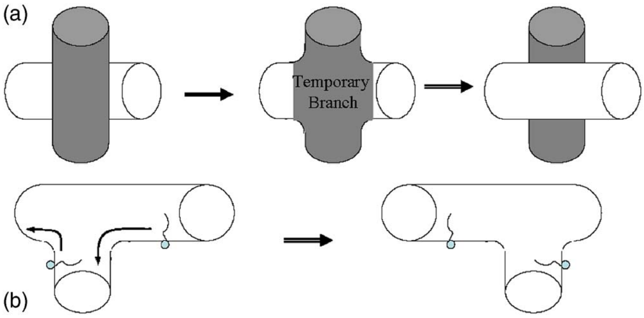

FIG. 2. Schematic diagram of stress relief mechanisms for wormlike micelle solutions. In (a) an entanglement point is eliminated as one micelle is pulled through another and in (b) stress is relieved as a branch point slides along the wormlike micelles.

celle, the shape and area per unit surfactant molecule is optimized at all positions along the backbone except at the ends [Israelachvili (1985)]. When a linear micelle breaks it must pay an energy penalty by forming two new end caps. In this regime, the electrostatic repulsion of the head groups is strong enough that the increased curvature of an end cap which spreads the head groups apart is favored over the concave curvature of a branch point which drives the charged head groups of the surfactants closer together. However, as the salt concentration is increased and the head group charges are sufficiently screened, the wormlike micelles can form three-point or four-point junctions as shown schematically in Fig. 2. Evidence of the existence of these branched micelles can be seen in the cryo-transmission electron microscopy (TEM) images [Cui *et al.* (2007); Danino *et al.* (2001)].

A number of branched wormlike micelle systems have been developed recently and their shear rheology has been well characterized [Angelescu *et al.* (2003); Appell *et al.* (1992); Hassan *et al.* (1998); Khatory *et al.* (1993); Koehler *et al.* (2000); Raghavan *et al.* (2002)]. In the experiments described in this manuscript, we have chosen to focus on the mixed anionic and cationic surfactants pioneered by Kaler and co-workers [Koehler *et al.* (2000); Raghavan *et al.* (2002)] because the systems they developed have viscosities and relaxation times suitable for extensional rheology measurements using either a filament stretching rheometer (FiSER) or a capillary breakup rheometer (CaBER). Specifically, Raghavan *et al.* (2002) used a series of mixtures of octyl trimethyl ammonium bromide (C_8TAB) and sodium oleate (NaOA) to obtain both linear and branched wormlike micelles by both varying the relative ratio of NaOA to C_8TAB or by fixing the ratio of NaOA to C_8TAB and varying the total surfactant concentration. At a fixed ratio of NaOA/C_8TAB of 70%/30%, their shear rheology measurements showed a maximum in the shear viscosity at 4 wt% while the elastic modulus of the fluids increased monotonically with increasing surfactant concentrations. Due to the presence of this maximum in these and a number of wormlike micelle solutions, solutions with very different compositions can have identical rheological properties in shear. Raghavan *et al.* (2002) hypothesized, and later demonstrated through cryo-TEM imaging, that the maximum in the shear viscosity is due to the transition from linear to branched micelles [Cui *et al.* (2007); Ziserman (2005); Ziserman *et al.* (2004)]. For these systems, branching is achieved by adequately screening the surfactant head groups either through a stoichiometric balance of the oppositely charged surfactant headgroups along the micelle or alternatively through the release of surfactant counterions which results in a reduction of the electrostatic double layer around the micelle [Raghavan *et al.* (2002)].

The decrease in the shear viscosity can be attributed to a new stress relief mechanics applicable only to branched micelles whereby the branch points are not fixed at a specific point along the backbone as is the case for branched polymers, but are free to slide along the micelle resulting in an additional stress relaxation mode not accessible in linear systems [Appell *et al.* (1992); Drye and Cates (1992)]. The branched points formed in wormlike micelles and their effect on the shear rheology are very different from branched points in polymers which, because they are fixed along the polymer backbone, make movement through reptation more difficult and can dramatically increase the relaxation time and elasticity of the polymeric fluids [Bird *et al.* (1987)].

In extensional flows of linear and long-chain-branched polyolefin melts with similar shear rheology, the branched polymers were found to exhibit significantly enhanced strain hardening in transient extensional flows [Munstedt and Laun (1981); Wagner *et al.* (2000)]. The increase in extensional viscosity is a result of increased chain stretching and reptation tube dilation resulting from the relative difficulty associated with moving a branched point in flow. For a branched micelle, the branch point may not represent a similar hindrance to flow. Appell *et al.* (1992) hypothesize that sliding of branch points represents a faster stress relief mechanism than reptation or a micelle rupture and reformation process that would allow two micelles to move through each other at an entanglement point as shown in Fig. 2. One therefore might expect that when compared to a linear system at the same surfactant concentrations, the extensional rheology of a solution of branched micelles might either exhibit significantly less strain hardening or a delay in the onset of strain hardening to larger extension rates.

Currently, there are no mechanical techniques for differentiating a branched micelle solution from a linear entangled micelle solution [Decruppe and Ponton (2003)]. To date, only cryo-TEM has been successful [Danino *et al.* (2001); Danino *et al.* (1995a, 1995b); Danino *et al.* (2000)]. Entangled linear micelles and branched micelles look identical in neutron or light scattering and are difficult to distinguish through measurements of shear rheology. In a recent paper by Decruppe and Ponton (2003), the authors chose four samples from different parts of this non-monotonic shear viscosity curve and attempted to understand the evolution of the rheological properties in terms of the structural evolution of the micelles through rheological and flow induced birefringence (FIB) measurements. The authors were unable to differentiate between the many samples. In this manuscript we will demonstrate that transient extensional rheology measurements can be used to demonstrate a quantitative difference between branched and linear micelles where shear rheology measurements could not.

The first experimental investigations of the apparent extensional rheology of linear wormlike micelle solutions used an opposed jet flow device [Lu *et al.* (1998); Prud'homme and Warr (1994); Walker *et al.* (1996)]. Prud'homme and Warr (1994) performed experiments on a series of tetradecyltrimethylammoniumsalicylate solutions and showed that these solutions strain harden at higher extensional rates similar to polymer solutions and at low extensional rates, below coil stretch transition, a plateau in the steady state extensional viscosity is observed which corresponds to Newtonian response. At higher extension rates, chain stretching within the oriented segments was observed to lead to strain hardening in the extensional rheology. More recently, Rothstein (2003) used a filament stretching rheometer to measure the extensional rheology of a series of cetyltrimethylammonium bromide (CTAB) and sodium salicylate (NaSal) wormlike micelle solutions. Bhardwaj *et al.* (2007a) later investigated the extensional rheology of a series of cetylpyridinium chloride and NaSal wormlike micelle solutions using both a filament stretching and capillary breakup extensional rheometer. These fluids were all found to demonstrate considerable strain hardening in the extensional viscosity with increasing accumulated strain [Bhardwaj *et al.* (2007a); Rothstein (2003)]. Additionally, above a critical extension rate, the filament stretching experiments were all observed to come to an abrupt end with the rupture of the fluid filament near its axial midplane [Bhardwaj *et al.* (2007a); Chen and Rothstein (2004); Rothstein (2003)]. The failure of the fluid filament likely stems from the scission of wormlike micelles resulting in a dramatic breakdown of the micelles *en masse* [Rothstein (2003)]. All of the extensional rheology measurements of the linear systems described above showed a polymer-like behavior of the extensional viscosity. Only a very limited number of studies have investigated the effect of branching on the extensional rheology of wormlike micelle solutions.

Fischer *et al.* (1997) studied a series of branched viscoelastic dodecyldimethylamineoxide-sodium laureth sulphate-sodium chloride viscoelastic surfactant solutions. They used an opposed jet device to investigate the effects of wormlike micelle branching in three different samples of an elongational flow. The first sample contains short micelles with no branches, the second sample contains completely linear, entangled micelles with slight branches, and the third sample contains only branched. The authors conducted a series experiments for extension rates from $\dot{\varepsilon}=0.1\ \mathrm{s}^{-1}$ to $20\,000\ \mathrm{s}^{-1}$. The extensional viscosity of the first sample, which only contained short, unentangled micelles, did not exhibit any extensional thickening, whereas both the linear and the branched samples demonstrated some degree of strain hardening of the extensional viscosity similar to polymer solutions. At low extension rates, both the linear and the branched samples were found to have constant extensional viscosity of roughly three times the zero shear rate viscosity, $\eta_E=3\eta_0$. The author's second sample, which contained linear, entangled micelles, showed a very weak maximum of extensional viscosity with increasing extension rate, whereas the third sample which contained branched micelles was found to reach a maximum of extensional viscosity roughly ten times the shear viscosity, $\eta_E\approx 10\eta_0$, followed by extensional thinning with further increases in extension rate. These experiments would suggest that increased branching will result in an increase in the extensional viscosity of the wormlike micelle solution. However, one should note that the strain hardening observed by the authors even in the case of the branched system is quite small considering that recent studies of linear wormlike micelle solutions have demonstrated extensional viscosities or more than one thousand times the shear viscosity [Bhardwaj *et al.* (2007a; 2007b); Rothstein (2003)]. Additionally, although the opposed jet device allows one to measure an apparent extensional viscosity for weakly viscoelastic fluids, it is plagued by an unknown pre-strain history and some degree of shearing in the flow field. We have recently shown that the extensional rheology of wormlike micelle solutions is extremely sensitive to preconditioning [Bhardwaj *et al.* (2007b)]. In addition, the opposed jet device in not able to make transient extensional rheology measurements. In the experiments described within this manuscript, we systematically investigated the effect of branching on the transient extensional rheology measurements of a series of different wormlike micelle solutions using both a filament stretching and capillary breakup extensional rheometer.

The outline of this paper is as follows. In Sec. II, we briefly describe the implementation of the filament stretching extensional rheometer and the capillary breakup extensional rheometer, the test fluids used and their shear rheology. In Sec. III A we discuss the effect of branching on the extensional rheology of the test fluids measured through capillary breakup. In Sec. III B, we discuss the effect of branching on the transient homogeneous uniaxial extensional rheology measured through filament stretching. Finally, in Sec. IV we conclude.

II. EXPERIMENTAL SETUP

A. Test fluids

A series of wormlike micelle solutions were prepared with a total surfactant concentrations ranging from 2 to 8 wt% by dissolving the surfactants octyl trimethyl ammonium bromide (C_8TAB) and sodium oleate (NaOA) in deionized water. The ratio of the two surfactants NaOA/C_8TAB was fixed at 70/30. At this concentration, the solutions were shown to transition from linear to more and more heavily branched micelles as the concentration was increased beyond 4 wt% [Cui *et al.* (2007); Ziserman (2005); Ziserman *et al.* (2004)]. To speed dissolution and insure a homogeneous mixture, the surfactant solutions were mixed with a magnetic stirring bar for up to 36 h. After the solutions were fully dissolved, they were allowed to settle at room temperature for at least 24 h before any experiments were performed to allow the air bubbles entrained during stirring to leave the sample. Due to the temperature sensitivity of these solutions, care was taken to insure that the shear and extensional rheology experiments were performed at a consistent temperature of $T=23.0\pm 0.1\ ^\circ\mathrm{C}$ so that time-temperature shifting was not required.

B. Filament stretching extensional rheometry

A filament stretching extensional rheometer (FiSER) capable of imposing a homogeneous uniaxial extension on a fluid filament placed between its two endplates, was used to make simultaneously measurements of the evolution in the force and the midpoint radius. A complete description of the design and operating space of the filament stretching rheometer used in these experiments can be found in [Rothstein (2003); Rothstein and McKinley (2002a, 2002b)] and a more detailed history of the technique can be found in the following papers by the McKinley and Sridhar groups [Anna *et al.* (2001); McKinley and Sridhar (2002); Tirtaatmadja and Sridhar (1993)]. The goal of extensional rheometry is to cause a motion of the extensional rheometer's endplates such that the resulting extension rate imposed on the fluid filament, $\dot{\varepsilon}$, is constant. The deformation imposed upon the fluid filament can be described in terms of a Hencky strain, $\varepsilon=-2\ln(R_{mid}/R_0)$, where R_0 is the initial midpoint radius of the fluid filament. The strength of the extensional flow is characterized by the Weissenberg number, $Wi=\lambda\dot{\varepsilon}$, which is the ratio of the characteristic relaxation time of the fluid, λ, to the characteristic time scale of the flow, $1/\dot{\varepsilon}_0$. The elastic tensile stress difference generated within the filament can be calculated from the algebraic sum of the total force measured by the load cell, F_z, if the weight of the fluid and the surface tension are taken into account while ignoring inertial effects [see Lequeux and Candau (1997)]

$$\langle \tau_{zz}-\tau_{rr}\rangle = \frac{F_z}{\pi R_{mid}^2}+\frac{1}{2}\frac{\rho g(\pi L_0 R_0^2)}{\pi R_{mid}^2}-\frac{\sigma}{R_{mid}}, \tag{1}$$

where L_0 is the initial endplate separation, σ is the equilibrium surface tension of the fluid and ρ is the density of the fluid. The extensional viscosity may be extracted from the principle elastic tensile stress and is often non-dimensionalized as a Trouton ratio

$$Tr=\frac{\eta_E^+}{\eta_0}, \tag{2}$$

where η_E^+ is the transient extensional viscosity and η_0 is the zero shear rate viscosity of the fluid, respectively.

C. Capillary breakup extensional rheometry

In order to determine the extensional rheology of the less concentrated and less viscous fluids, capillary breakup extensional rheometry measurements were performed using the filament stretching rheometer described above [Bhardwaj *et al.* (2007a)]. In a capillary breakup extensional rheometer (CaBER), an initial nearly cylindrical fluid sample is placed between the two endplates of the filament stretching rheometer and stretched with an exponential profile, $L = L_0 \exp(\dot{\varepsilon}_0 t)$, to final length of L_f. The stretch is then stopped and the capillary thinning of the liquid bridge formed between the two endplates produces a uniaxial extensional flow that can be used to measure an apparent extensional viscosity. The final stretch length is chosen such that $L_F = 3.6 R_0$ and the stretch rate is chosen such that it is greater than the characteristic relaxation time of the fluid, $\dot{\varepsilon} \gg 1/\lambda$, and also greater than the time scale for capillary drainage of the liquid bridge, $\dot{\varepsilon} \gg \sigma/\eta_0 R_0$. It has been shown that CaBER is capable of measuring the extensional viscosity of fluids with shear viscosities as low as 70 mPa s and relaxation times as low as 10 ms [Rodd *et al.* (2005)]. In addition, CaBER can reach extremely large Hencky strains limited only by the resolution of diameter measurement transducer. In our experiments, a laser micrometer (Omron Z4LA) with a resolution of 5 μm was used to obtain final Hencky strains of up to $\varepsilon = 2 \ln(3\text{ mm}/5\ \mu\text{m}) = 12.7$ although in practice reliable measurements below 20 μm were difficult to achieve.

The breakup of the fluid filament is driven by capillary stresses and resisted by the extensional stresses developed within the flow. The extensional viscosity of the wormlike micelle solution can be determined by measuring the change in the filament diameter as a function of time. Papageorgiou (1995) showed that for a Newtonian fluid the radius of the fluid filament will decay linearly with time, $R_{mid}(t) \propto (t_b - t)$. Conversely, Entov and Hinch (1997) showed that for an Oldroyd-B fluid, the radius will decay exponentially with time, $R_{mid}(t) \propto \exp(-t/3\lambda_E)$. The extension rate of the fluid filament is given by

$$\dot{\varepsilon} = -\frac{2}{R_{mid}(t)} \frac{dR_{mid}(t)}{dt} = \frac{2}{3\lambda_E}, \tag{3}$$

and, hence, for an Oldroyd-B fluid the flow has a constant Weissenberg number of $Wi = 2/3$. This value is larger than the critical Weissenberg number of $Wi = 1/2$ needed to achieve coil-stretch transition and thus strain hardening of the extensional viscosity of the wormlike micelle solutions can be achieved. Additionally, the slope of the diameter as a function of time can be used to calculate a relaxation time in this elongational flow, λ_E. For Boger fluids, theory predictions and experiments show that $\lambda_E \approx \lambda$ [Anna and McKinley (2001); Entov and Hinch (1997)] although for wormlike micelle solutions the extensional relaxation time has been found to be quite different from the relaxation time measured in shear [Bhardwaj *et al.* (2007a); Yesilata *et al.* (2006)] An apparent extensional viscosity can be calculated by applying a force balance between capillary stresses and the elastic tensile stresses within the fluid filament [Anna *et al.* (2001)]

$$\eta_E = \frac{\sigma/R_{mid}(t)}{\dot{\varepsilon}(t)} = \frac{-\sigma}{dD_{mid}/dt}. \tag{4}$$

To calculate the extensional viscosity, the diameter measurements are fit with the functional form proposed by Anna and McKinley (2001),

$$D_{mid}(t) = Ae^{-Bt} - Ct + E \tag{5}$$

and then differentiated with respect to time. The choices of fitting parameters have their physical relevance. The decay of the fluid filament diameter at intermediate times can be related to the extensional relaxation time and the fitting parameter B such that $B = 1/3\lambda_E$. Additionally, C can be related to steady-state value of the extensional viscosity such that $C = \sigma / \eta_{E,\infty}$.

The equilibrium surface tension for each of the wormlike micelle solutions tested was assumed to be consistent with the value of $\sigma = 0.034$ N/m reported in the literature as the median value of the CTAB solutions ($\sigma = 0.036$ N/m) and the NaOA solutions ($\sigma = 0.032$ N/m) above the CMC [Cutler and Kissa (1987)]. However, in any free surface flow containing surfactants, one must also consider the role that dynamic surface tension could play. As the fluid filament is stretched and a new surface is generated, surfactant molecules diffuse from the bulk and populate the new surface. The result is a surface tension that is a function of the age of a given surface. Because the time scales of the CaBER experiments described here are slow compared to the typical time scale of the dynamic surface tension (seconds vs. milliseconds) [Cooper-White *et al.* (2002)] the equilibrium value of the surface tension was used in all of our calculations of the extensional viscosity rather than the surface tension of the solvent. Additionally, in the FiSER experiments, at the point that the fluid filament is stretching fast enough to necessitate the use of the dynamic surface tension in the force balance in Eq. (1), the elastic tensile stress typically dominates over the surface tension term and the factor of 2 change in the surface tension would make little to no difference in the final value of the extensional viscosity.

III. RESULTS AND DISCUSSIONS

A. Shear rheometry

The steady and dynamic shear rheology of the test fluids were characterized using a stress-controlled rheometer (TA instruments, Ares) with a 6 cm/2° cone-and-plate geometry. The micelle solutions were loaded and allowed to equilibrate for several minutes. In Fig. 3, the storage modulus, G', and loss modulus, G'', of the C_8TAB/NaOA wormlike micelle solutions were plotted as a function of angular frequency, ω. For many of the fluids tested, the linear viscoelastic data can be fit well with a single mode Maxwell model. The deviation of the rheological data from the predictions of the single mode Maxwell model at large frequencies in Fig. 3 corresponds to the Rouse-like behavior of the micelle between entanglement points [Fischer and Rehage (1997)].

The zero shear viscosity, η_0, and the plateau modulus, G_0, derived from the Maxwell model fit are plotted as a function of total surfactant concentration in Fig. 4 and tabulated in Table I. The shear rheology is in good agreement with the values of shear rheology presented in the literature by Raghavan *et al.* for identical systems [Raghavan *et al.* (2002)]. A maximum in the viscosity is observed at 4 wt% after which the viscosity begins to decrease with increasing total surfactant concentration. For these fluids, earlier cryo-TEM imaging has shown that the maximum in the shear viscosity is due to the transition from linear to branched micelles [Cui *et al.* (2007); Ziserman (2005); Ziserman *et al.* (2004)]. Conversely, no maximum is observed in the elastic modulus. The elastic modulus is observed to increase monotonically with increasing total surfactant concentration. Thus even as the viscosity passes through a plateau, the theoretical mesh size, $\zeta_m = (k_B T/G_0)^{1/3}$, is observed to monotonically decrease, meaning that the proximity of entanglement points and the density of the wormlike micelle mesh continue to increase

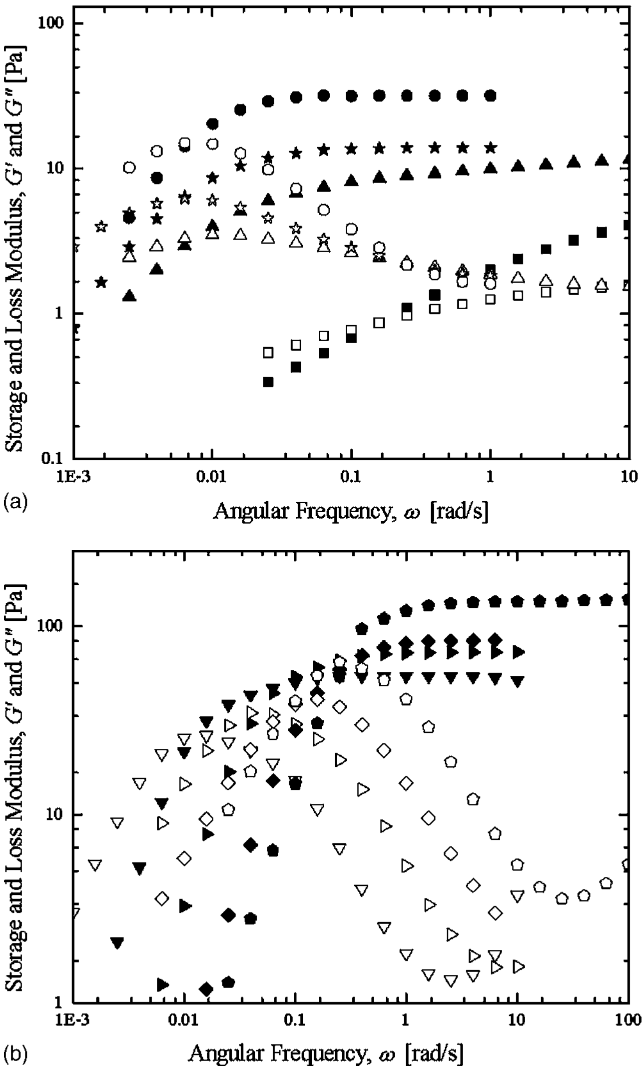

FIG. 3. Small amplitude oscillatory shear measurements of 70/30 NaOA/C_8TAB surfactant solutions at $T = 23\ ^\circ$C. The data in (a) include: storage modulus, G′ (filled symbols), and loss modulus, G″ (open symbols), for ■ 2 wt%, ▲ 2.75 wt%, ★ 3 wt% and, ● 4 wt%, while (b) includes for ▼ 5 wt%, ▶ 6 wt%, ♦ 7 wt% and open pentagon 8 wt%.

with increasing surfactant concentration [Doi and Edwards (1986); Granek and Cates (1992)]. Here k_B is the Boltzmann constant and T is the temperature. For wormlike micelles theory predicts and experiments have demonstrated that the plateau modulus for an entangled system should increase as $G_0 \propto c^{9/4}$ with increasing concentration [Cates and Candau (1990); Koehler *et al.* (2000)]. As seen in Fig. 4, our measurements match the predictions of theory quite well even with the onset of branching.

B. Capillary breakup extensional rheometry

A series of 70/30 NaOA/C_8TAB wormlike micelle solutions with increasing total surfactant concentrations were tested using a capillary breakup extensional rheometer. A

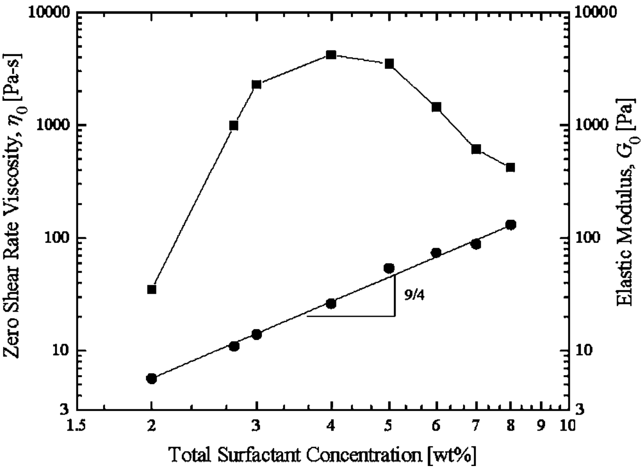

FIG. 4. Steady shear rheology measurements of 70/30 NaOA/C_8TAB mixtures as a function of total surfactant concentrations at $T=23$ °C. The data include: ■ the zero shear rate viscosity, η_0 and ● the elastic modulus, G_0.

filament stretching rheometer was used to impose an extensional step strain on an initially cylindrical sample. The fluid filament was then allowed to thin under capillary action while the decay of the diameter of the fluid thread was monitored as a function of time. As described in Sec. II C, the apparent extensional viscosity and the extensional relaxation time of the fluids can be calculated directly from the measurements of the diameter as a function of time. Because capillary breakup extensional rheology measurements can be performed on fluids with relatively low viscosities and relaxation times, it was possible to measure the extensional rheology of the wormlike micelle solutions over a broad range of concentrations. Unfortunately, as will be described in the section that follows, CaBER measurements were only possible on the less elastic samples; concentration of 5% and lower and so direct comparison between extensional rheology measurements performed in FiSER and CaBER were only possible for the concentrated solutions up to 5 wt%.

Representative plots of the fluid filament diameter as a function of time are presented in Fig. 5 for each of the 70/30 NaOA/C_8TAB wormlike micelle solutions. Superimposed over each of these data sets is a solid line corresponding to the best fit of the diameter

TABLE I. Parameters characterizing the rheology of the 70/30 NaOA/C_8TAB wormlike micelle solutions. The extensional viscosity and Trouton ratio are reported for a Weissenberg number of approximately $Wi \approx 3$.

Surfactant concentration [wt%]	η_0 [Pa s]	λ [s]	G_o [Pa]	λ_E [s]	$\eta_{E\ max}$ [Pa s] from FiSER	Tr_{max} from FiSER
2	35	6.5	5.7	6.1	9800	280
2.75	990	90	11	5.8	25 000	25.3
3	2300	164	14	3.2	38 000	16.5
4	5000	161	31	6.3	18 000	3.6
5	3500	65	54	1.1	12 000	3.4
6	1450	19.5	74		3800	2.9
7	610	7	88		2100	3.5
8	420	3.2	131		1000	2.5

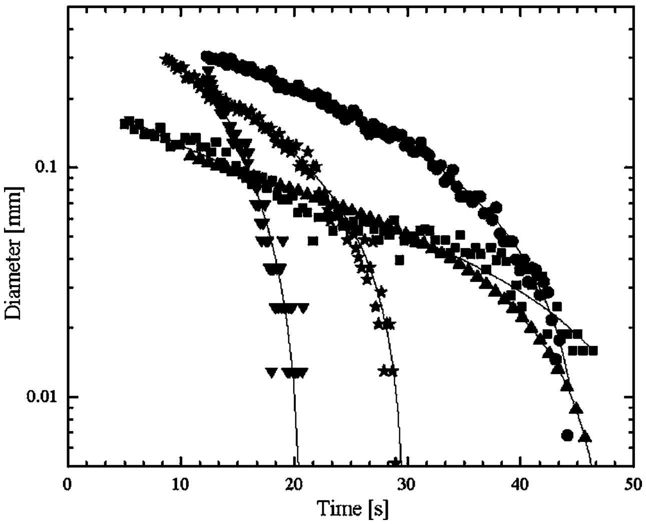

FIG. 5. Measurements of diameter as a function of time for a series of CABER experiments. Included in (a) are solutions of ■ 2 wt%, ▲ 2.75 wt%, ★ 3 wt%, ● 4 wt% and ▼ 5 wt% NaOA/C_8TAB in water.

decay to Eq. (5). The apparent transient extensional viscosity is then calculated by differentiating the diameter with respect to time as shown in Eq. (4). We denote this extensional viscosity as apparent because, unlike filament stretching experiments, the extension rate is not held fixed in these experiments, but rather it is set by the balance of extensional and surface stresses and as a result for viscoelastic fluids the extension rate will change as the effects of finite extensibility become more pronounced at larger strains. The data for concentrations of 5 wt% and below are plotted in Fig. 5. Whereas the CaBER experiments for 5 wt% below were repeated and found to be reproducible to well within a 10% error, the CaBER measurements for concentrations above 5 wt% were inconsistent and the results are difficult to interpret and were thus not included in this study. FiSER measurements for the entire range of concentrations, however, are presented in the next section. For concentrations up to 3 wt%, the micelles are linear and entangled with few if any branch points present [Raghavan *et al.* (2002)]. As the total surfactant concentration is increased and the number of branch points is increased in Fig. 5, the rate at which the fluid filament necks down increases significantly. The diameter decay thus indicates a decrease in extensional viscosity with increasing surfactant concentration and branching.

A series of representative plots of the apparent extensional viscosity calculated from Eq. (4) are plotted as a function of Hencky strain and surfactant concentration in Fig. 6. One of the advantages of capillary breakup extensional rheology measurements is that large Hencky strains can be achieved making it possible, in most cases, to measure the steady-state value of the extensional viscosity. This is in contrast to filament stretching extensional rheology where the total imposed Hencky strains are limited by the travel of the endplates and the experiment often ends before a steady-state value of the extensional viscosity has been achieved. As shown by Fig. 6, the steady-state value of the apparent extensional viscosity of wormlike micelle solutions was found to decrease monotonically with increasing surfactant concentration.

In Fig. 7, the ratio of the extensional relaxation time to the Maxwell relaxation time measured in shear, λ_E/λ, is plotted as a function of total surfactant concentration. These

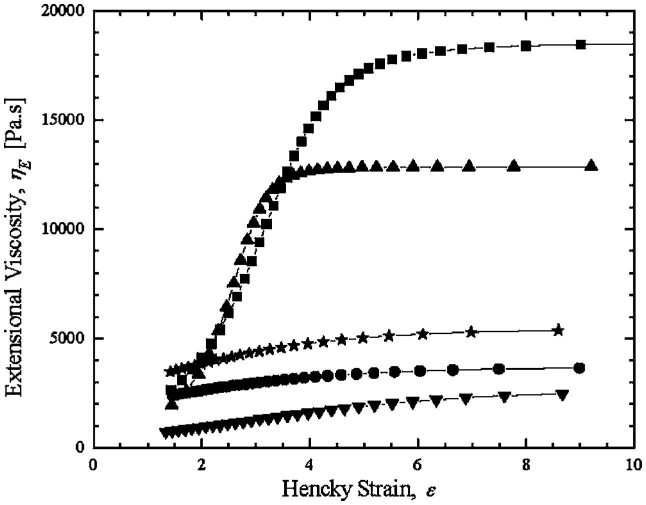

FIG. 6. CABER measurements of the extensional viscosity as a function of accumulated Hencky strain for a series of 70/30 NaOA/C_8TAB wormlike micelle solutions. Included in the figure are solutions of ■ 2 wt%, ▲ 2.75 wt%, ★ 3 wt%, ● and 4 wt% and ▼ 5 wt% with total surfactant concentrations.

values are averaged over the results from a number of experiments and error bars are superimposed over the data to demonstrate the repeatability of these measurements. For capillary break up measurements of polymer solutions, the extensional and shear relaxation times were found to be approximately equal, $\lambda_E=\lambda$ [Anna and McKinley (2001)] in accordance with the theoretical predictions of Entov and Hinch (1997). For linear wormlike micelle solutions, this has not been the case as measurements of the extensional relaxation time have been found to be as much as an order of magnitude above or below the value of the relaxation time measured in shear [Bhardwaj *et al.* (2007a, 2007b), Yesilata *et al.* (2006)]. As seen in Fig. 7, at the lowest concentration of surfactant tested

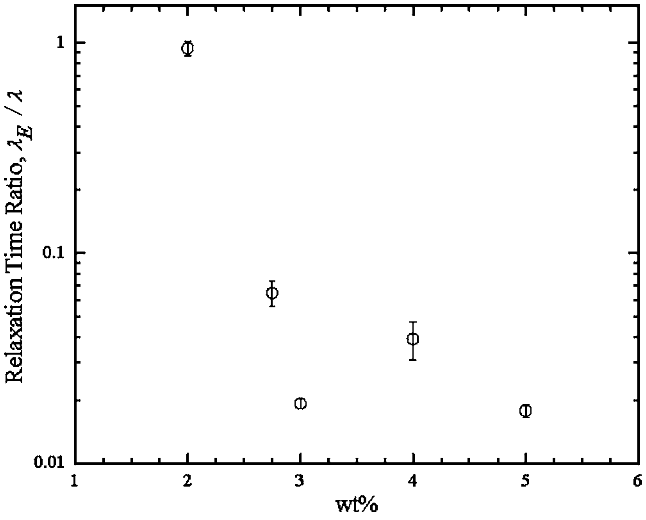

FIG. 7. Relaxation time ratio, λ_E/λ as a function of total surfactant concentration for wormlike solutions of 70/30 NaOA/C_8TAB in water.

here, 2 wt%, the normalized extensional relaxation time was found to be approximately $\lambda_E/\lambda \approx 0.94$ as one would expect for polymer solutions. However, as the concentration of surfactant is increased, the normalized extensional relaxation time was observed to decrease quickly to less than $\lambda_E/\lambda < 0.1$ for concentrations above 3 wt%. The dramatic reduction in the normalized extensional relaxation time with increasing surfactant concentration suggests that the presence of branches enhances the speed and efficiency of stress relaxation in extensional flows.

C. Filament stretching extensional rheometry

A series of transient uniaxial extensional rheology experiments were performed on a number of 70/30 NaOA/C_8TAB wormlike micelle solutions with increasing total surfactant concentrations using the filament stretching rheometer described in Sec. II B. In Fig. 8, representative plots of extensional viscosity as a function of Hencky strain are presented for a series of 70/30 NaOA/C_8TAB wormlike micelle solutions between 2 and 8 wt% at $T=23$ °C. Experiments were performed over a wide range of Weissenberg numbers varying from $Wi=1-16$, however, to facilitate comparison between solutions, the experiments in Fig. 8 are for a narrow range around $Wi \approx 3$. For each of the wormlike micelle solutions, the filament stretching experiments came to an end with an elastocapillary thinning at Weissenberg numbers close to $Wi=1$ and an abrupt rupture near the axial midplane of the fluid filament at much higher Weissenberg numbers. This is consistent with the previous observations for linear wormlike micelle solutions [Bhardwaj *et al.* (2007a); Rothstein (2003)]. As seen in Fig. 8, the extensional viscosities of all the above mentioned 70/30 NaOA/C_8TAB wormlike micelle solutions were found to increase monotonically with increasing Hencky strain. For concentrations of 4 wt% and above, the solutions exhibit a Newtonian response with little to no strain hardening, $Tr \approx 3$, at any of the extension rate tested. Although the extensional viscosity did not reach steady state in many cases, a clear trend can be observed if one compares the maximum extensional viscosity reached before filament failure. As seen in Figs. 8(a) and 8(b), the extensional viscosity initially increases with surfactant concentration, but then decreases monotonically with increasing surfactant concentration beyond a concentration of 3 wt%.

In Fig. 9, the elastic tensile stress is plotted as a function of accumulated Hencky strain for 5 wt% 70/30 NaOA/C_8TAB wormlike micelle solution at a series of large Weiessenberg number experiments, $Wi \gg 1$. The elastic tensile stresses in the fluid filaments were all observed to increase monotonically and strain harden more quickly with increasing extension rate. Each of these experiments was observed to end with a rupture of the fluid filament before the fluid reaches a steady-state value of the extensional viscosity. The value of the elastic tensile stress at rupture was found to be independent of imposed extension rate. The observations in Fig. 9 are consistent for all of the high Weissenberg number experiments of the other concentrations tested. Similar trends were observed for the rupture of linear wormlike micelle solutions in extensional flows [Bhardwaj *et al.* (2007a); Rothstein (2003)] and thus the presence of micelle branching does not seem to affect the rupture phenomena.

In Fig. 10, the maximum values of the extensional viscosity and the Trouton ratio for each of the FiSER measurements in Fig. 8 are plotted as a function of the total surfactant concentration. These values represent an average over a number of separate experiments with error bars superimposed over the data to demonstrate the repeatability of these measurements. In some cases this value also corresponds to a steady-state value, however, some experiments ended before steady state could be obtained. The Trouton ratio

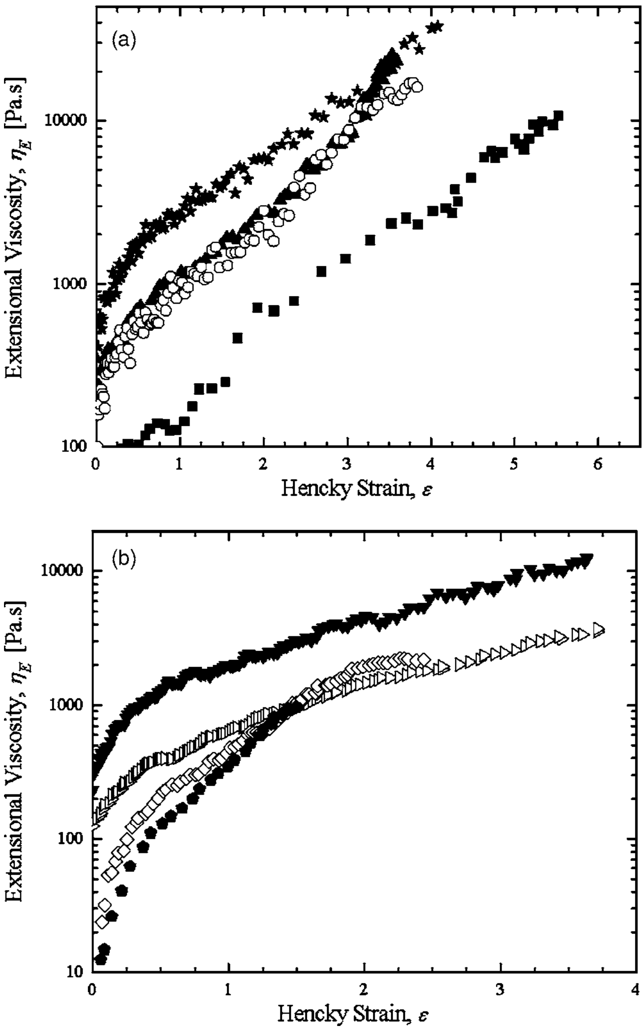

FIG. 8. FiSER measurements of the transient extensional viscosity as a function of accumulated Hencky strain for a series of 70/30 NaOA/C_8TAB wormlike micelle solutions at $T=23$ °C. Included in (a) are solutions with total surfactant concentrations of ■ 2 wt% ($Wi=3.2$), ▲ 2.75 wt% ($Wi=3.6$), ★ 3 wt% ($Wi=3.2$) and ○ −4 wt% ($Wi=3.2$) while in (b) are solutions of ▼ 5 wt% ($Wi=3.2$), ▷ 6 wt% ($Wi=3.9$), ◇ 7 wt% ($Wi=2.1$) and closed pentagon 8 wt% ($Wi=3.2$).

was found to initially decrease quite rapidly before approaching a plateau close to the Newtonian limit of $Tr\approx 3$ for concentrations above 3 wt%. The initial decrease in the Trouton ratio with increasing concentration for concentrations below 4 wt% is consistent with the previous literature which showed that for both entangled linear wormlike micelle solutions and entangled polymer solutions, that the degree of strain hardening decreases with increasing concentrations [Rothstein (2003); Rothstein and McKinley (2002a)]. Physically, this can be explained by considering that for a linear wormlike micelle as the total surfactant concentration is increased, the number of entanglement points along a wormlike chain increases and the molecular weight of the micelle stretched between the entanglement points decreases. This reduces the finite extensibility of the chain between entanglement points and therefore the steady state extensional viscosity [Rothstein and McKinley (2002a)].

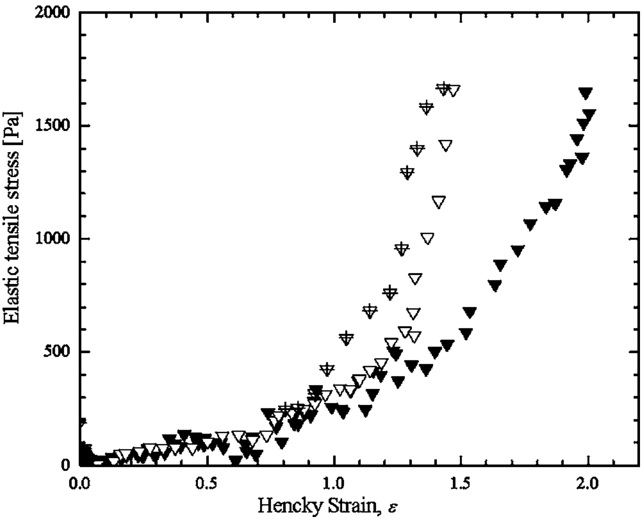

FIG. 9. FiSER measurements of elastic tensile stress growth as a function of accumulated Hencky strain for the 5 wt% 70/30 NaOA/C_8TAB wormlike micelle solution at $T=23$ °C and Weissenberg numbers of $Wi=19.5$ ▼, $Wi=65$ ▽ and $Wi=130$ triangle with plus sign. All experiments are observed to end with a rupture of the fluid filament before the fluid reaches a steady-state value of the extensional viscosity.

The expected decrease in the Trouton ratio with increasing concentration can be seen more clearly if we think about the asymptotic analysis of the FENE-P model that the steady-state extensional viscosity can be written in the form [Doyle *et al.* (1998)]

$$\eta_{E,\infty} - 3\eta_s = 2nk_BT\lambda L^2(1 - 1/(2\lambda\dot{\varepsilon}) + \cdots). \tag{6}$$

In the limit of large Weissenberg numbers, Eq. (6) reduces to $\eta_{E,\infty}=2nk_BT\lambda L^2$ or equivalently a Trouton ratio of $Tr_\infty=2L^2$. Of course this analysis is not quite right because Eq. (6) is derived from the FENE-P model which was developed to describe the rheology of

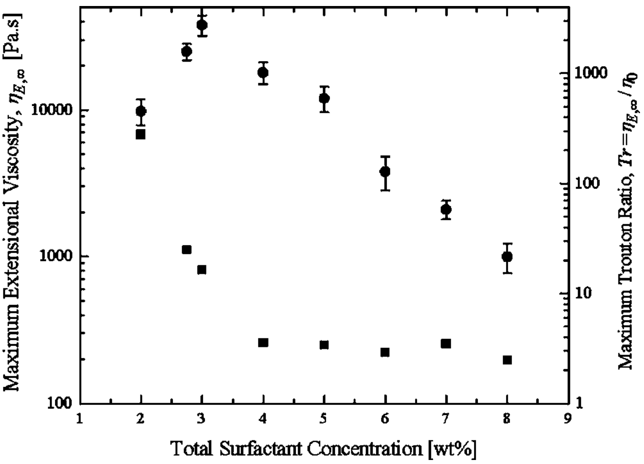

FIG. 10. FiSER measurements of the maximum value of extensional viscosity obtained before filament failure, ● and the corresponding Trouton Ratio, ■, as a function of total surfactant concentration for wormlike solutions of 70/30 NaOA/C_8TAB in water.

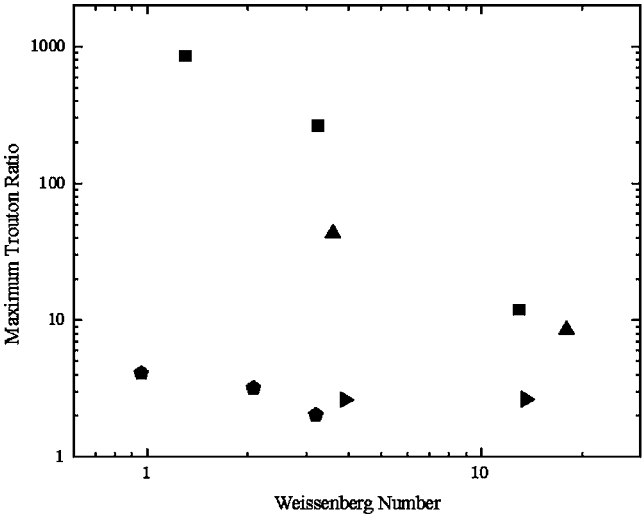

FIG. 11. FiSER measurements of the maximum Trouton ratio as a function of Weissenberg number for a series of 70/30 NaOA/C_8TAB wormlike micelle solutions at $T=23$ °C. Included are solutions with total surfactant concentrations of ■ 2 wt%, ▲ 2.75 wt%, ▶ 6 wt% and closed pentagon 8 wt%.

dilute polymer solutions not entangled wormlike micelle solutions, however, for an entangled system we expect the finite extensibility of each entangled segment, L_{seg}^2, to be reduced by a factor of $Z=M_w/M_e$ such that $L_{seg}^2=L^2/Z$ [Bhattacharjee *et al.* (2002); Doi and Edwards (1986); Mead *et al.* (1998); Rothstein and McKinley (2002a)]. The molecular weight between entanglements can be expressed as $M_e=cN_Ak_BT/G_0$ where c is the concentration of surfactant and N_A is Avogadro's number [Ferry (1980)]. Thus the finite extensibility of an entangled segment and therefore the equilibrium value of the Trouton ratio for an entangled wormlike micelle system can be directly related to the mesh size of the wormlike micelle solution; $L_{seg}^2 \propto \xi^3$, and thus the Trouton ratio varies as $Tr_\infty \propto \xi^3$ or equivalently $Tr_\infty \propto G_0^{-1} \propto c^{-9/4}$. This scaling of the finite extensibility and the steady-state value of the Trouton ratio was followed by a number of linear wormlike micelle solutions in the past [Rothstein (2003)]. However, for the micelle solutions tested here, the decay in the Trouton ratio is much faster dropping by two orders of magnitude for an increase in surfactant concentration from 2 to 4 wt%. In addition, for concentrations for 4 wt% and above, Trouton ratios of $Tr \approx 3$ were achieved such that for concentrations where micelle branching has been observed the wormlike micelle solutions do not strain harden but instead behave like a Newtonian fluid in extensional flows. These observations of the extensional viscosity of branched systems are consistent with the measurements of Fischer *et al.* (1997), however, due to the dramatic strain hardening we have observed for the low concentration linear micelles, our interpretation of the results is quite different.

From Fig. 10, it is clear that the branching has a significant effect on extensional viscosity measured in CaBER and FiSER. Additionally, it appears that the extensional rheology of wormlike micelles may be a bulk measurement technique capable of discriminating between linear and branched wormlike micelles solutions. To emphasize this point, it is possible to compare any two samples with approximately the same shear viscosity, but taken from either side of the maximum in the shear viscosity. This is done in Fig. 11 by comparing the maximum Trouton ratio as a function of Weissenberg number for four wormlike micelle solutions with different total surfactant concentrations. The consistent observation over all Weissenberg numbers tested is that linear wormlike micelles strain harden and branched systems do not. For the lower concentration solutions the maximum Trouton ratio is found to decrease monotonically with increasing Weissenberg number while for the higher concentration solutions, the Trouton ratio is found to remain fixed at approximately $Tr \approx 3$ independent of Weissenberg number. These observations are in stark contrast to extensional rheology measurements of linear and branched polymer melts where the presence of branching dramatically increases strain hardening of the extensional viscosity by reducing polymer mobility at a branched point which results in increased chain stretching and reptation tube dilation. For branched micelles, our measurements clearly demonstrate that the branch points do not represent a similar hindrance to flow. In fact, the observed trend in the extensional viscosity demonstrates just how effective ghost-like crossings and sliding branch points are at relieving tensile stress in extensional flows. Even in a system without stable branch points, ghost-like crossings become more likely as the concentration of surfactant is increased and electrostatic screening reduces the energy barrier for producing a temporary branch point. Additionally, in a system which contains micelles with stable branch points, the branch points are not fixed, but are quite fluid and move along the micelle with little to no energy penalty. It was hypothesized by Appell *et al.* (1992) that sliding of branch points represents a faster stress relief mechanism than reptation or a micelle rupture and reformation process that would allow two micelles to move through each other at an entanglement point. The data appear to agree with this hypothesis.

IV. CONCLUSIONS

The effects of branching on the shear and the extensional rheology of a series of wormlike micelle solutions was studied using both a filament stretching rheometer and capillary breakup rheometer. A series of NaOA/C_8TAB wormlike micelle solutions were tested with a fixed ratio of NaOA to C_8TAB of 70/30 and increasing total surfactant concentrations. The shear rheology of the wormlike micelle solution demonstrated a maximum in shear viscosity at 4 wt% followed by a sharp decrease in viscosity with increasing surfactant concentration. Conversely, no maximum is observed in the plateau modulus. The plateau modulus was found to increases monotonically with increasing total surfactant concentration. It has been long hypothesized and recently demonstrated through cryo-TEM imaging that the maximum in shear viscosity for these fluids can be explained as a transition from an entangled linear micelle solution to a branched micelle solution [Cui *et al.* (2007); Ziserman (2005); Ziserman *et al.* (2004)]. These branched points are quite fluid and can move easily along the wormlike micelle [Drye and Cates (1992)] resulting in an additional stress relaxation mode not accessible in linear systems [Appell *et al.* (1992)].

A series of transient uniaxial extensional rheology experiments were performed on a number of 70/30 NaOA/C_8TAB wormlike micelle solutions with increasing total surfactant concentrations between 2 and 8 wt% using both a filament stretching and a capillary breakup rheometer. The extensional viscosity measurements of the filament stretching rheometer are in agreement with those of the capillary breakup rheometer. All of the wormlike micelle solutions below 4 wt% demonstrated some degree of strain hardening, however, beyond 4 wt% little strain hardening is observed. For the lowest concentration surfactant solutions tested, the fluids are known to contain only linear wormlike micelles. For these linear micelle solutions dramatic strain hardening of the extensional viscosity and Trouton ratios of close to $Tr \approx 1000$ were observed. It should be noted that these are not steady-state values of the extensional viscosity, but are instead the maximum value of the extensional viscosity obtained before the fluid filament failed. The maximum value of the Trouton ratio was initially found to decrease very rapidly with increasing surfactant concentration and micelle branching, reducing by two orders of magnitude as the concentration was increased by two weight percent and eventually approaching an asymptote close to the Newtonian limit, $Tr=3$, for concentrations of for 4 wt% and above. This decrease of Trouton ratio and the sharp reduction in the extensional relaxation time ratio with increased surfactant concentration and branching are likely due to the new stress relief mechanisms available to branched micelles which appear to be extremely efficient in extensional flows. These new stress relief mechanisms include sliding of branch points along the length of the micelle and the increased occurrence of ghost-like crossing with increasing surfactant concentration. These results suggest that extensional rheology may be a bulk measurement technique capable of identifying branching in wormlike micelle solutions when one considers that the extensional viscosity of branched micelles shows little or no strain hardening even as the solutions continue to demonstrate significant elasticity.

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References

Anderson, V. J., J. R. A. Pearson, and E. S. Boek, “The rheology of worm-like micellar fluids,” edited by D. M. Binding and K. Walters, *Rheology Reviews* (The British Society of Rheology, Aberystwyth, UK, 2006).

Angelescu, D., A. Khan, and H. Caldararu, “Viscoelastic properties of sodium dodecyl sulfate with aluminum salt in aqueous solution,” Langmuir **19**, 9155–9161 (2003).

Anna, S. L., and G. H. McKinley, “Elasto-capillary thinning and breakup of model elastic liquids,” J. Rheol. **45**, 115–138 (2001).

Anna, S. L., G. H. McKinley, D. A. Nguyen, T. Sridhar, S. J. Muller, J. Huang, and D. F. James, “An inter-laboratory comparison of measurements from filament stretching rheometers using common test fluids,” J. Rheol. **45**, 83–114 (2001).

Appell, J., G. Porte, A. Khatory, F. Kern, and S. J. Candau, “Static and dynamic properties of a network of wormlike surfactant micelles (etylpyridinium chlorate in sodium chlorate brine),” J. Phys. II **2**, 1045–1052 (1992).

Bhardwaj, A., E. Miller, and J. P. Rothstein, “Filament stretching and capillary breakup extensional rheometry measurements of viscoelastic wormlike micelle solutions,” J. Rheol. **51**, 693–719 (2007a).

Bhardwaj, A., D. Richter, M. Chellamuthu, and J. P. Rothstein, “The effect of preshear on the extensional rheology of wormlike micelle solutions,” Rheol. Acta **46**, 861–875 (2007b).

Bhattacharjee, P. K., J. Oberhauser, G. H. McKinley, L. G. Leal, and T. Sridhar, “Extensional rheometry of entangled solutions,” Macromolecules **35**, 10131–10148 (2002).

Bird, R. B., R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids: Volume 1 Fluid Mechanics* (Wiley, New York, 1987).

Cates, M. E., and S. J. Candau, “Statics and dynamics of worm-like surfactant micelles,” J. Phys.: Condens. Matter **2**, 6869–6892 (1990).

Cates, M. E., and M. S. Turner, “Flow-induced gelation of rodlike micelles,” Europhys. Lett. **11**, 681–686 (1990).

Chen, S., and J. P. Rothstein, “Flow of a wormlike micelle solution past a falling sphere,” J. Non-Newtonian

Fluid Mech. **116**, 205–234 (2004).

Cooper-White, J. J., R. C. Crooks, and D. V. Boger, "A drop impact study of worm-like viscoelastic surfactant solutions," Colloids Surf., A **210**, 105–123 (2002).

Cui, H., T. K. Hodgdon, E. W. Kaler, L. Abezgauz, D. Danino, M. Lubovsky, Y. Talmon, and D. J. Pochan, "Elucidating the assembled structure of amphiphiles in solution via cryogenic transmission electron microscopy," Soft Mater. **3**, 945–955 (2007).

Cutler, W. G., and E. Kissa, *Detergency: Theory and Technology* (CRC, New York, 1987).

Danino, D., A. Bernheim-Groswasser, and Y. Talmon, "Digital cryogenic transmission electron microscopy: An advanced tool for direct imaging of complex fluids," Colloids Surf., A **183**, 113–122 (2001).

Danino, D., Y. Talmon, H. Levy, G. Beinert, and R. Zana, "Branched threadlike micelles in an aqueous solution of a trimeric surfactant," Science **269**, 1420–1421 (1995a).

Danino, D., Y. Talmon, and R. Zana, "Alkanediyl-alpha,omega-bis(dimethylalkylammonium bromide) surfactants (dimeric surfactants). 5. Aggregation and microstructure in aqueous solutions," Langmuir **11**, 1448–1456 (1995b).

Danino, D., Y. Talmon, and R. Zana, "Cryo-tem of thread-like micelles: On-the-grid microstructural transformations induced during specimen preparation," Colloids Surf., A **169**, 67–73 (2000).

Decruppe, J. P., and A. Ponton, "Flow birefringence, stress optical rule and rheology of four micellar solutions with the same low shear viscosity," Eur. Phys. J. E **10**, 201–207 (2003).

Doi, M., and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).

Doyle, P. S., E. S. G. Shaqfeh, G. H. McKinley, and S. H. Spiegelberg, "Relaxation of dilute polymer solutions following extensional flow," J. Non-Newtonian Fluid Mech. **76**, 79–110 (1998).

Drye, T. J., and M. E. Cates, "Living netwoks: The role of cross-links in entangled surfactant solutions," J. Chem. Phys. **96**, 1367–1375 (1992).

Entov, V. M., and E. J. Hinch, "Effect of a spectrum of relaxation times on the capillary thinning of a filament of elastic liquid," J. Non-Newtonian Fluid Mech. **72**, 31–53 (1997).

Ferry, J. D., *Viscoelastic Properties of Polymers* (Wiley-Interscience, New York, 1980).

Fischer, P., G. G. Fuller, and Z. Lin, "Branched viscoelastic surfactant solutions and their responses to elongational flow," Rheol. Acta **36**, 632–638 (1997).

Fischer, P., and H. Rehage, "Rheological master curves of viscoelastic surfactant solutions by varying the solvent viscosity and temperature," Langmuir **13**, 7012–7020 (1997).

Granek, R., and M. E. Cates, "Stress relaxation in living polymers: Results from a Poisson renewal model," J. Chem. Phys. **96**, 4758–4767 (1992).

Hassan, P. A., S. J. Candau, F. Kern, and C. Manohar, "Rheology of wormlike micelles with varying hydrophobicity of the counterion," Langmuir **14**, 6025–6029 (1998).

Israelachvili, J. N., *Intermolecular and Surface Forces: With Applications to Colloidal and Biological Systems* (Academic, London, 1985).

Kefi, S., J. Lee, T. Pope, P. Sullivan, E. Nelson, A. Hernandez, T. Olsen, M. Parlar, B. Powers, A. Roy, A. Wilson, and A. Twynam, "Expanding applications for viscoelastic surfactants," Oilfield Rev. Serv. **16**, 10–16 (2004).

Khatory, A., F. Lequeux, F. Kern, and S. J. Candau, "Linear and nonlinear viscoelasticity of semidilute solutions of wormlike micelles at high salt concentration," Langmuir **9**, 1456–1464 (1993).

Koehler, R. D., S. R. Raghavan, and E. W. Kaler, "Microstructure and dynamics of wormlike micellar solutions formed by mixing cationic and anionic surfactants," J. Phys. Chem. B **104**, 11035–11044 (2000).

Larson, R. G., *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999).

Lequeux, F., and S. J. Candau, "Structural properties of wormlike micelles," *Theoretical Challenges in the Dynamics of Complex Fluids*, edited by T. McLeish (Kluwer, Dordrecht, 1997).

Lu, B., X. Li, L. E. Scriven, H. T. Davis, Y. Talmon, and J. L. Zakin, "Effect of chemical structure on viscoelasticity and extensional viscosity of drag-reducing cationic surfactant solutions," Langmuir **14**, 8–16 (1998).

McKinley, G. H., and T. Sridhar, "Filament stretching rheometry," Annu. Rev. Fluid Mech. **34**, 375–415 (2002).

Mead, D. W., R. G. Larson, and M. Doi, "A molecular theory for fast flows of entangled polymers," Macromolecules **31**, 7895–7914 (1998).

Munstedt, H., and H. M. Laun, "Elongational properties and molecular structure of pollyethylene melts," Rheol. Acta **20**, 211–221 (1981).

Papageorgiou, D. T., "On the breakup of viscous liquid threads," Phys. Fluids **7**, 1529–1544 (1995).

Prud'homme, R. K., and G. G. Warr, "Elongational flow of solutions of rodlike micelles," Langmuir **10**, 3419–3426 (1994).

Raghavan, S. R., G. Fritz, and E. W. Kaler, "Wormlike micelles formed by synergistic self-assembly in mixtures of anionic and cationic surfactants," Langmuir **18**, 3797–3803 (2002).

Rehage, H., and H. Hoffmann, "Viscoelastic surfactant solutions: Model systems for rheological research," Mol. Phys. **74**, 933–973 (1991).

Rodd, L. E., T. P. Scott, J. J. Cooper-White, and G. H. McKinley, "Capillary break-up rheometry of low-viscosity elastic fluids," Appl. Rheol. **15**, 12–27 (2005).

Rothstein, J. P., "Transient extensional rheology of wormlike micelle solutions," J. Rheol. **47**, 1227–1247 (2003).

Rothstein, J. P., and G. H. McKinley, "A comparison of the stress and birefringence growth of dilute, semi-dilute and concentrated polymer solutions in uniaxial extensional flows," J. Non-Newtonian Fluid Mech. **108**, 275–290 (2002a).

Rothstein, J. P., and G. H. McKinley, "Inhomogeneous transient uniaxial extensional rheometry," J. Rheol. **46**, 1419–1443 (2002b).

Spenley, N. A., X. F. Yuan, and M. E. Cates, "Nonmonotonic constitutive laws and the formation of shear-banded flows," J. Phys. II **6**, 551–571 (1996).

Tirtaatmadja, V., and T. Sridhar, "A filament stretching device for measurement of extensional viscosity," J. Rheol. **37**, 1133–1160 (1993).

Wagner, M. H., H. Bastian, P. Hachmann, J. S. K. Meissner, H. Munstedt, and F. Langouche, "The strain-hardening behavior of linear and long-chain-branched polyolefin melts in extensional flows," Rheol. Acta **39**, 97–109 (2000).

Walker, L. M., P. Moldenaers, and J.-F. Berret, "Macroscopic response of wormlike micelles to elongational flow," Langmuir **12**, 6309–6314 (1996).

Yesilata, B., C. Clasen, and G. H. McKinley, "Nonlinear shear and extensional flow dynamics of wormlike surfactant solutions," J. Non-Newtonian Fluid Mech. **133**, 73–90 (2006).

Ziserman, L., "Relationship between rheological properties and nanostructure in mixed micellar surfactant," Thesis, Technion Israel Institute of Technology, 2005.

Ziserman, L., S. R. Raghavan, B. Baser, E. W. Kaler, and D. Danino, "Micellar structure and rheological behavior in mixed surfactant systems," in *Annual Scientific Meeting of the Israel Society of Microscopy*, Jerusalem, 2004.