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Entrance effects and high shear rate rheology of shear banding wormlike micelle fluids in a microcapillary flow

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Abstract

The viscosity of a shear-banding wormlike micelle solution at high shear rates is investigated using capillary rheology and particle streak velocimetry. Measurements of the flow profile and pressure gradient show an extended entrance region, which exceeds a length to diameter ratio of 100, to reach a fully developed flow. We characterized this entrance region for capillaries with different cross-sections and use the results to select a downstream portion of the capillary where viscosity measurements can be made on fully developed flow. Measurements from this portion of the channel show a shear-thinning power-law behavior for all channel geometries from shear rates of $1000 \ s^{-1}$ to $120000 \ s^{-1}$. Varying the surfactant concentration shows two distinct power-law behaviors that depend on both shear rate and concentration and are an indication of change in micelle length. This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

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I. INTRODUCTION

Wormlike micelle (WLM) solutions are often used in applications that produce high shear rates including drilling fluids and drag reduction agents [1]. These solutions have been extensively studied due to their characteristics as "living polymers", where the cylindrical micelles constantly grow and break [2]. These microstructural dynamics lead to interesting behavior such as single Maxwell response under small amplitude oscillatory shear (SAOS) and shear banding behavior in steady shear [3, 4]. Due to the varying dynamics exhibited in these solutions, examining their behavior across a wide range of shear conditions is of interest. The measurement of viscosity at shear rates much greater than 10^3 s^{-1} has not been performed in rotational rheometers due to instrument limits and flow instabilities. In this paper, we use capillary rheology and particle tracking to understand the flow behavior in micrometer scale capillaries and measure the rheology of wormlike micelles at high shear rates.

Millimeter scale capillaries have been used extensively to study the rheology, flow fields, and structure of wormlike micelles up to shear rates of 10^2 s^{-1} . These studies focused on the jump in flow rate in capillary flow that occurs for shear banding fluids such as WLM solutions when the wall stress exceeds a critical stress and compared this transition to shear banding behavior observed in Couette flow [5, 6]. They also showed that a fluid that shear bands in Couette flow is expected to produce a sharply blunted flow profile when the wall stress is above the plateau stress, produced by a high shear rate region near the wall and a relatively low shear rate region through the center. Some studies observed the effect of capillary length in the measurement of rheology through discrepancies between measured flow profiles and those expected from rheology; other studies directly measured different flow curves with various capillary length [5, 7]. More recent work has compared the development of the flow profile to WLM rheological models [8]. Capillary rheology has also been applied to measure concentration effects in dilute WLM solutions, where little effect of capillary length is observed [9].

Difficulties may arise in making rheological measurements of WLM solutions in pressure driven flow from various types of flow instabilities. These often arise in semi-dilute WLM solutions that exhibit shear banding. In microfluidic channels with rectangular cross sections spatio-temporal instabilities can occur, such as jetting and interfacial modulations of the shear banded interface [10–12]. In axisymmetric capillaries, large temporal flow fluctuations can occur due to the extensional flow and breakdown of micelle structure at the capillary entrance [13]. Instability

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has been predicted at the interface between the regions of low and high shear rate, giving rise either to flow profiles that differ from those predicted by the stress curve or to spatial variations [14, 15].

Despite these challenges, viscometry measurements at higher shear rates have been successfully conducted using microfluidic channels, which due to smaller dimensions increase the range of measurable shear rate. Microfluidic chips have also enabled the use of microscopic flow imaging techniques such as microparticle velocimetry in these channels along with integrated pressure sensing [16–22]. They have also enabled the measurement of structure at high shear rates through techniques such as polarization microscopy and small angle neutron scattering (SANS) [20, 23, 24].

The small dimensions of microfluidic channels also present the possibility of slip or diffusion related phenomena that can lead to errors in rheometric measurements. Masselon et al. measured velocity profiles for shear banding WLM solutions at a wall stress near the stress plateau and observed discrepancies with the velocity field expected from separate rheology measurements[25]. The measured profiles were fit to a nonlocal rheological model that describes the diffusion of material quantities, an effect that becomes significant in small channel dimensions and large changes in shear rate which occur in shear banding fluids [26, 27]. The effects of boundary conditions and wall slip were also considered on these flow profiles[28]. The results showed that surface roughness can affect wall slip magnitude and result in a nontrivial relationship between wall stress and shear rate when slip is present.

In this paper we aim to investigate the velocity profiles in capillary flow of WLM solutions at wall stresses well above the plateau stress. The large flow rates to reach this condition introduces the possibility of significant entrance effects. The strong dependence on capillary length observed in previous studies suggests that entrance effects may persist farther downstream from the channel entrance than expected for other shear thinning fluids, where a short entrance region is predicted [29]. A long entrance region is also possible in light of startup experiments in Couette flow [30, 31]. These experiments have shown that the timescale for a shear banded flow to be established is proportional and of a similar magnitude to the terminal relaxation time of the Maxwell response in small amplitude oscillatory shear. Entrance effects for pressure driven flow has been studied in more detail theoretically and numerically using viscoelastic models that produce shear banding flow and include the breaking and recombination kinetics of the micelles [32]. Similar to the startup experiments for Couette flow, these simulations investigate the response to a step increase

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of the pressure and observe a startup timescale for the plug-like flow to develop that is comparable to the terminal relaxation time.

These studies suggest that a significant entrance region may result in variations in the velocity profile and stress gradient as a function of streamwise position from the channel entrance. As noted above, some previous experimental studies do report significant entrance effects with shear banding WLM solutions. Hernandez-Acosta et al. used millimeter scale diameter capillaries and found that the measured viscosity of cetyl trimethylammonium tosylate (CTAT) solutions depended on capillary length to diameter ratio in the range of 100 to 400 [7]. Other studies using different solutions do not observe changes in flow profiles as a function of streamwise distance. For instance Nghe et al. measured velocity profiles of a WLM solution containing 0.3 mol/L cetyltrimethylammonium bromide (CTAB) in 0.405 mol/L sodium nitrate brine and did not observe changes in the profiles for different streamwise positions after a length to height ratio of 150 [19].

The numerous challenges for making high shear rate measurements of WLM solutions has resulted in a limited number of measurements of WLM solutions at shear rates up to and exceeding 10⁴. The high flow rate through small dimension channels leads to high pressures in the flow system that can cause leaks in fluidic connectors and deformation or failure of measurement devices. High pressure connections have enabled capillary rheology and SANS measurements of dilute concentrations of wormlike micelle solutions at shear rates up to 10^5 s^{-1} [23]. The only observation known to the authors above 10^4 s⁻¹ of a shear banding semi-dilute concentration used a parallel plate geometry to measure a solution of 8 % mass fraction erucyl bis(hydroxymethyl)methylammonium chloride (EHAC) surfactant in potassium chloride solutions [33]. The solution exhibited a power law scaling of -2/3 for the viscosity as a function of shear rate. This scaling was replicated using course-grained simulations of the micelle solutions under shear and the scaling compared to a dilute finite extensibility Rouse model [34]. Other simulations have examined the dependence of viscosity on shear by adjusting parameters controlling micelle network strength and micelle stiffness. Varying scission energy resulted in a consistent -0.7 power law scaling for viscosity as a function of shear rate, while increasing micelle persistence length in these simulations resulted in power law scalings ranging from -0.77 to -0.66 [35].

In this study we use microcapillaries with hydraulic diameter ranging from 50 μ m to 200 μ m to measure the rheology of wormlike micelles at shear rates higher than $\dot{\gamma} = 10^3 s^{-1}$. We measure the pressure drop across different length capillaries to see how the pressure gradient varies past the channel entrance. We use capillaries with square cross-sections to visualize the flow at different

streamwise positions using particle streak velocimetry. We then compare the behavior of the pressure gradient and the flow field. After establishing an entrance length, we compare the flow profiles to the capillary rheology measurements. Finally, we use the fully developed region of the capillary, where the flow does not vary with streamwise position, to measure the high-shear viscosity of different wormlike systems by varying the surfactant concentration and surfactant type, and discuss implications concerning the structure of micelles in flow.

II. MATERIALS AND METHODS

A. Wormlike Micelle Solution Preparation

Solutions were prepared over a range of concentrations and compositions. WLM solutions containing cetylpyridinium chloride (CPCl) (Sigma-Aldrich) were prepared at concentrations ranging from 75 mmol/L to 120 mmol/L. For these solutions, sodium salicylate (NaSal) (Sigma-Aldrich) was added in concentrations such that the CPCl/NaSal concentration ratio was 1.58 to 1. In addition, a WLM solution containing 50 mmol/L of cetyltrimethylammonium bromide (CTAB) and 50 mmol/L of NaSal was also prepared. Millipore water was used as the solvent for all solutions.

Samples were mixed and stored at room temperature (approximately 23 °C). Experiments were also conducted at room temperature, typically within 6 weeks of sample preparation. The samples were stored to minimize light exposure and avoid contact with metals to reduce sample degradation. No measurable change in the sample rheology was observed over a 5 month period.

B. Standard Couette Rheometry

Couette rheometry was measured using 34 mm cup and a 32 mm bob on an ARES-G2 with (TA Instruments) for small amplitude oscillatory shear (SAOS) and a 50 mm cup and 49 mm bob on an MCR501 Anton-Paar for steady shear [36]. The bob was inserted into the cup containing sufficient fluid to cover the top of the bob even as fluid is pulled upwards by rod climbing. The steady shear rheometry was conducted in a series of steps to check for reproducibility and sample stability. Beginning at low rate and progressing to higher rates, the sample appearance was examined periodically. The results of SAOS and steady shear rheology for different surfactant concentrations are shown in Figure 1.

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The solutions in this study are known to exhibit a Maxwellian response in SAOS measurement [3]. The Maxwell model is given by,

$$G'(\omega) = \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} G_0, \tag{1}$$

$$G''(\omega) = \frac{\omega\lambda}{1 + \omega^2\lambda^2}G_0,$$
(2)

where G' is the storage modulus, G" is the loss modulus, ω is the frequency, λ is the relaxation time, and G_0 is the plateau modulus. We fit the Maxwell model, Eqs. 1 and 2, to data to obtain values for relaxation time and plateau modulus as shown in Figure 1. The surfactant concentrations of the samples and the fitted values of relaxation time and plateau modulus are shown in Table I.

The measured values for plateau modulus increase with concentration as expected from theory [2]. We note that the relaxation time does not change significantly with concentration for the CPCI/NaSal samples. This behavior might be influenced by the onset of some branching in the system, which at the surfactant cosurfactant ratio of 1.58 is close to the transition to branching for CPCI/NaSal system [37]. We expect the relaxation time of the micelles to change under shear, as has been observed using orthogonal superposition rheometry [38]. For reference, we define



FIG. 1. (a) Small amplitude oscillatory shear measurements for selected samples of the CPCl/NaSal surfactant system using a cup and bob geometry. The storage modulus, G', is shown in open circles and the loss modulus, G", is shown in closed squares. The Maxwell model fit is shown for the CPCl/NaSal (120 mmol/L /76 mmol/L) sample. (b) Steady shear rheology measurements using a stress controlled rheometer with a cup and bob geometery. The plateau stress is shown with a dashed line as a guide. A secondary axis with $Wi_0 = \dot{\gamma}\lambda$ is shown for reference with the equilbrium relaxation time of $\lambda = 3.8$ s.



Sample	Surfactant	conc. (mmol/L)	NaSal (mmol/L)	λ (s)	G_0 (Pa)
CP120-S76	CPCl	120	76	3.5	44.1
CP100-S63	CPCl	100	63	3.8	30.4
CP95-S60	CPCl	95	60	3.8	27.5
CP90-S57	CPCl	90	57	3.8	23.5
CP85-S54	CPCl	85	54	3.8	20.5
CP80-S51	CPCl	80	51	3.8	17.8
CP75-S47	CPCl	75	48	3.8	14.4
CT50-S50	CTAB	50	50	7.3	13.6

TABLE I. Relaxation time and plateau modulus determined from fits to the Maxwell model Eqs. 1 and 2.

a Weissenberg number, $Wi_0 = \dot{\gamma}\lambda$, using the equilibrium relaxation time determined from the CPCI/NaSal samples.

C. Capillary Rheometry

Capillary rheometry measurements consist of driving the WLM solution through silica capillaries using a syringe pump at a flow rate, Q, and recording the pressure drop, ΔP , with pressure sensors connected to the entry and exit regions of the capillary, see Figure 2. Five capillaries are used for this study: three square capillaries with nominal width of w=50 μ m, w=100 μ m, and w=200 μ m and two round capillaries with diameters of D=100 μ m and D=200 μ m. Capillary sections of different lengths are made to make length-dependent pressure drop measurements. Round



FIG. 2. Schematic of the experimental setup. A syringe pump drives flow through a microcapillary of length *L*. Pressure sensors, connected upstream and downstream of the microcapillary, measure pressure drop across the microcapillary. The microcapillary can be mounted on a microscope to image the flow field.

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capillaries are preferred for determining wall stress because a uniform wall stress is expected. Square capillary sections are used primarily for imaging flow profiles where image distortions are reduced compared to round cross sections. Square capillary sections for imaging flow profiles are made by removing the polyimide coating with a flame and mounting the capillary onto a metal bar.

We estimate the effects of viscous heating using the energy balance between heat generated from viscous heat generation and conduction out of the capillary [39]. The energy balance yields a maximum change in temperature assuming the fluid velocity, dimensions of the capillary, and the fluid viscosity, η . We estimate that the temperature difference is $\Delta T \approx 4\eta U^2 \ln(D_{ex}/D_{in})/k_w$, where U is the mean fluid velocity, D_{ex} and D_{in} are the exterior and interior diameter of the capillary, and k_w is the thermal conductivity of the silica capillary. The most significant heating occurs at highest flow rates. For these surfactant solutions, at apparent wall shear rates $\dot{\gamma} \approx 10^5$ s⁻¹, the viscosity is $\eta \approx 10^{-2}$ Pa s, and in the 200 μ m diameter capillary the velocity is $U \approx .5$ m/s, so that the estimated temperature increase is $\Delta T \approx 0.1$ K.

The importance of elastic stresses relative to inertial stresses can be estimated by the elasticity number. $El = Wi_0/Re = \lambda \eta/(\rho D^2)$, where $Re = \rho U d/\eta$ is the Reynolds number and ρ is the fluid density. For our surfactant solutions and capillary dimensions, the elasticity number is greater than $El \approx 10^6$ using the zero shear rate relaxation time and viscosity values. Due to shear thinning, the viscosity at high shear rates can reduce to the range of 10 mPa s and the elasticity number will reduce to the range of $El \approx 10^3$. The relaxation time of the micelles may change at high shear rates and reduce the elasticity number even more at high shear rates [38]. In general, the small dimensions of the capillary reduce the influence of inertia stresses in a comparison to elastic stresses.

D. Particle Streak Velocimetry

The flow in the square test sections is imaged using particle streak velocimetry [40, 41]. The sample solution is seeded with 2 μ m red fluorescent particles, approximately 0.01 volume percent, a sufficiently low particle concentration in order to avoid overlap of particle streaks. The solution viscosity, measured with both Couette and capillary rheology measurements, of the 100 mmol/L CPCl with 63 mmol/L NaSal system is unchanged by the addition of particles. The particles in flow are imaged with a 60x (1.2NA) objective on an Olympus IX71 inverted microscope with

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a sCMOS camera (Andor Zyla), typically with frame rates of (10 to 50) frames per second. The microscope is focused in the center of the channel and the channel is illuminated by an pulsed light emitting diode (LED) with a variable duration depending on the flow velocity, typically (1 to 10) milliseconds in duration. The images are processed using standard image processing algorithms in Python to segment in-focus particle streaks above an intensity threshold. A velocity measurement is made by dividing the duration of the light pulse by length of the measured streak. Velocity profiles are constructed by sampling velocity measurements as a function of cross stream position. The velocity measurements are binned by cross stream position and the mean and spread of the velocity distribution are found by fitting a Gaussian function. Velocity profiles are measured at various distances from the entrance of the capillary at different flow rates.

III. RESULTS AND DISCUSSION

A. Entrance effects: Pressure drop

Entrance effects are separated into two different phenomena. The first is attributed to the pressure drop due to the entrance contraction and exit expansion of the capillary section. This effect can be determined measuring the pressure drop as the length of the capillary tends towards zero [42]. The second entrance effect is the change in the pressure gradient as a function of streamwise channel position, as the flow reaches full development.

These entrance effects are quantified by measuring the total pressure drop across capillary sections of different lengths. For the characterization of the entrance effects we use the 100 mmol/L CPCl with 63 mmol/L NaSal system for all experiments. An example of the pressure drop measurement in a $w = 200 \ \mu m$ square capillary as a function of channel length is shown in Figure 3 for different volumetric flow rates. A nonzero pressure drop is observed as the capillary length approaches zero, as is expected for capillary flows, due the additional pressure drop contribution at the entrance and exit. For many viscoelastic fluids tested previously, a linear trend is observed as a function of length [42], but here the pressure drop for the CPCl/NaSal micelles clearly shows a nonlinear dependence. In Figure 3, we show a linear fit of the last three points. The pressure gradient decreases along the flow direction for all flow rates. The intercept at channel length L = 0 cm shows the excess pressure drop contribution from both the end effects and the changing pressure gradient past the entrance. ACCEPTED MANUSCRIP

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We analyze the mean pressure gradient for subsections of the capillary by subtracting the total pressure drop for different channel lengths. This procedure assumes that the pressure drop at a given flow rate in the upstream section of a longer capillary is the the same as that of a shorter capillary, including the contraction and expansion effects, i.e. the pressure drop contributions from the contraction and expansion are not length dependent. The resulting pressure gradient from the subtracted data is normalized by the pressure drop from the shortest capillary section and the mean position of the subsection is used as the streamwise position (Figure 4).

The results of such analysis for the w=100 μ m capillary are shown in Figure 4 for different wall shear rates. The data for different flow rates are all well represented by an exponential decay, $dP/dx = p_2 + p_1 \exp(-x/L_p)$, where x is the streamwise channel position from the capillary entrance. This function has a characteristic entrance length scale L_p for the pressure gradient to reach a constant value. The fitted entrance length scale for different capillaries are plotted in Figure 5 as a function of apparent shear rate, defined as $\dot{\gamma}_A = 4Q/\pi R^3$ for round capillaries and $\dot{\gamma}_A = 14.2Q/w^3$ for square capillaries. We observe a fairly constant L_p as a function of apparent shear rate, yet an



FIG. 3. Pressure drop versus capillary length for CPCl/NaSal (100 mmol/L /63 mmol/L) system in w=200 μ m square channel for various apparent shear rates. As the capillary length approaches zero, a finite pressure drop is observed from entrance/exit effects. A change in the pressure gradient is observed for different channel lengths. Dashed lines are linear fits to the last three points to show the approach to a constant gradient. Uncertainty from pressure sensors and channel lengths is smaller than the symbol sizes.

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increase in entrance length with capillary dimension. The mean entrance length scaled by the characteristic capillary dimension, hydraulic diameter d, is in the range of about $L_p/d \approx (90 \text{ to } 130)$ for the different cross sections, see Table II. There is a lack of dependence of the entrance length on channel dimension and our results demonstrate that the flow of wormlike micelles has an entrance length that can exceed $L_p/d \approx 100$.

Since the structural change of the wormlike micelles at high stress and its equilibration takes a finite amount of time, we would expect the entrance length to scale as $L_p \sim \langle U \rangle \tau$, where τ is a characteristic timescale for stress relaxation, and $\langle U \rangle$ is the mean velocity. In terms of shear rate this scales to $L_p/d \sim \dot{\gamma}\tau$. However, the constant entrance length with changing flow rate implies that the timescale for stress relaxation is inversely proportional to the flow rate. From the constant entrance length, we see a magnitude of the relaxation timescale that is approximately $\tau \approx 1000\dot{\gamma}^{-1}$ For our experiments this is in the range of (0.01 to 1) *s*. Both the trend of decreasing timescale with increasing shear rate and the order of magnitude agrees with previous measurements of semidilute CPyCl/NaSal micelles in Couette flow just above the plateau stress [43, 44].

The data show that the pressure gradient will reach a few percent of its asymptotic value after



FIG. 4. Normalized pressure gradient for CPCl/NaSal (100 mmol/L /63 mmol/L) system in 100 μ m diameter round channel for different apparent shear rates. The mean streamwise position is the calculated pressure gradient between two capillaries of different length. The pressure gradient is normalized by smallest mean position used for this capillary, (x= 0.6 cm).





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FIG. 5. Characteristic entrance length for the pressure gradient as a function of shear rate for different hydraulic diameter for CPCI/NaSal (100 mmol/L /63 mmol/L) system. Square symbols denote data from square cross section capillaries and round symbols denote data from round cross section capillaries. Error bars are defined as one standard deviation uncertainty from least squares curve fitting.

 $L_p/d \approx 400$. As a result of this relatively long entrance region, the pressure drop from the entrance effects can be a large percentage of the total pressure drop. A capillary section longer than this entrance region is therefore needed for an accurate measurement of the equilibrated pressure gradient. The pressure drop of multiple capillaries, the shortest being slightly longer than the entrance region $L_p/d \approx 400$, can be subtracted and used to obtain the pressure gradient from the fully developed flow, as shown in the linear fits of Figures 4. Again, this procedure assumes that the entrance and exit effects do not change with the total capillary length.

The pressure drop from the fully developed flow region, ΔP , of length, ΔL , is used to determine the wall stress, σ_w . These values in addition to the channel dimensions and the flow rate Q are used to determine the wall shear rate $\dot{\gamma}_w$. In square capillaries, the capillary rheology equations for wall shear rate and wall shear stress are [45],

$$\dot{\gamma}_{w} = \frac{14.2Q}{w^{3}} \frac{1}{3} \left(2 + \frac{d \log Q}{d \log \Delta P} \right), \ \boldsymbol{\sigma}_{w} = \frac{\Delta P w}{4\Delta L}.$$
(3)

In round capillaries, the wall shear rate and wall shear stress are given by, [45],

$$\dot{\gamma}_{w} = \frac{4Q}{\pi R^{3}} \frac{1}{4} \left(3 + \frac{d \log Q}{d \log \Delta P} \right), \ \boldsymbol{\sigma}_{w} = \frac{\Delta P R}{2\Delta L}.$$
(4)

Capillary geometry	L_p/d		
w=50 μm square	105 ± 18		
w=100 μm square	123 ± 33		
D=100 μm round	118 ± 32		
w=200 μm square	$91\pm\!15$		
D=200 μm round	74 ± 30		

TABLE II. Characteristic (flow development) entrance length, L_p , scaled by hydraulic diameter, d, for different capillary geometries. The characteristic entrance length is determined from the fits to an exponential decay of the pressure gradient shown in Figure 5. The uncertainty is determined from a weighted average standard deviation of the measured entrance lengths at different applied flow rates.

The capillary rheology measurements are compared to rotational rheometer measurements using a Couette geometry with a 50 mm cup and a 49 mm bob on an Anton-Paar MCR501 rheometer. The viscosity is measured from $\dot{\gamma}$ =0.02 s⁻¹ to $\dot{\gamma}$ =6300 s⁻¹ in steady shear with the rotational rheometer.

The stress curve obtained from capillary rheology for different channels is plotted in the range of shear rates $10^3 s^{-1} < \dot{\gamma} < 10^6 s^{-1}$. Capillary rheology measurements below $\dot{\gamma} = 10^3 s^{-1}$ are excluded because significant wall slip causes a decrease in stress. This slip-induced decrease in stress is most noticeable for the smallest capillary dimension, w=50 μ m, near $\dot{\gamma} \approx 10^3 s^{-1}$. The onset of wall slip below $\dot{\gamma} = 10^3 \text{ s}^{-1}$ is confirmed using particle streak velocimetry where we observe plug-like velocity profiles in this shear rate regime. We attribute the decrease in wall slip as shear rate increases to the shear induced breakage of micelles that can occur when the shear rate exceeds the inverse micelle breakage timescale. The decrease in wall slip effects at higher shear rates is confirmed by the agreement with Couette rheometry above $\dot{\gamma} = 10^3 s^{-1}$ and for the large capillary dimensions where slip effects are less significant. The reduction of wall slip at higher shear rates leads to a good agreement for capillary and velocity profile measurements across channels of different dimensions and geometries, which will be discussed further in the following section. With the exception of the smallest capillary in the range of $\dot{\gamma} \approx 10^3 s^{-1}$, the various capillary cross sections produce similar viscosity measurements. Effects that may scale with size and shape that are detrimental to a viscometric measurement, such as viscoelastic instabilities, do not appear to affect the measurement significantly. We conclude that the pressure gradient from

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the fully developed flow can produce a reliable viscosity measurement at high shear rates.

The results of the combined Couette and capillary rheology show a power law behavior with a slope of approximately 1/3 in the range of $\dot{\gamma} \approx 500 \ s^{-1}$ to $\dot{\gamma} \approx 10^5 \ s^{-1}$, above which an increase in the slope of the power law is observed. The increase in the slope above $\dot{\gamma} = 10^5 \ s^{-1}$ follows a power law close to a 2/3 slope. The viscosity of the system approaches the solvent viscosity limit, shown as a solid line in Figure 6 for reference. We investigate these power laws further by changing surfactant concentration in Section III C.

B. Entrance effects: Flow field

In stress controlled rotational rheometry, the equilibration time for the flow field in shear banding fluids can be over 10 to 100 times the relaxation time [44]. The timescale for flow development can be related to transition to a high shear micelle phase [46]. In our capillary experiments, the flow rate is held constant, but the velocity field can change shape as the micelle structure changes.



FIG. 6. Shear stress as a function of shear rate for Couette measurements and capillary rheology measurements of the CPCI/NaSal (100 mmol/L /63 mmol/L) system for different capillary cross sections. The capillary rheology measurements are in terms of wall shear rate and account for entrance effects. A similar stress curve is obtained for different capillary cross sections. A power law of 1/3 is shown in a dashed line for comparison. The viscosity of water at 23 C is shown in a calculated solid line for reference.

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Both the pressure gradient and velocity field will change with this structural transition, but an independent measurement of the flow field is needed to observe when the flow field is fully developed. Additionally, we compare the fully developed flow field to the measured capillary rheology to see if nonlocal effects are present. We note that we do not observe cross stream particle trajectories resulting from a secondary flow that may be indicative of an elastic or inertial flow instability.

The velocity profile is measured using particle streak velocimetry as a function of streamwise position and at different flow rates in each of the square cross section capillaries. A representative set of measurements is shown in Figure 7 for the $w = 200 \ \mu$ m channel. We plot the absolute value of the cross stream y-position to emphasize the change in velocity profile shape. We did not observe any asymmetric velocity profiles for any measurement.

The velocity profiles near the capillary entrance have a nearly uniform pluglike velocity profile. Farther downstream the profile is smoother, the local shear rate increases gradually upon approaching the wall and little or no wall slip is observed. The transition from pluglike to a smooth profile appears gradually, rather than a shear band drifting from the wall towards the centerline. We note that at these high shear rates, the position corresponding to the plateau stress is located at approximately 10 μ m from the centerline.

To quantify the development of flow, we calculate the centerline velocity from an average of the measurements in the center third of the channel. The center third has negligible variation in velocity magnitude as function of cross-stream position because the shear rates are relatively small in this region. The relative centerline velocity magnitude quantifies the shape of the entire profile, because it increases in magnitude when the velocity profile has a more gradual decrease in shear rate from the wall. This measure is preferred to a direct measurement of the near wall region, which as a result of higher velocity gradients is more sensitive to errors from finite tracer particle size and imaging obscured by the channel wall. A characteristic entrance length for the velocity field is determined from this measurement, denoted L_v , by fitting an exponential decay function, $U_m(x) = U_0(1 - \exp(-x/L_v))$, to the change in centerline velocity magnitude as a function of streamwise distance.

The fitted entrance length for the velocity field normalized by the channel width is plotted in Figure 8 for different capillary sizes. Unlike the pressure gradient, the entrance length for the velocity field varies as a function of both wall shear rate and channel widths. We note that the entrance length for the velocity field is also always larger than the entrance length for the pressure gradient. This seems to indicate that the wall region reaches near equilibrium somewhat before



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the intermediate portions.

Both velocimetry measurements and the increase in entrance length with decreasing channel dimension suggests a transient wall slip just past the entrance. Similar to the increase in shear rate experienced by the fluid at the wall, recent experiments of wormlike micelles in Couette geometries have observed a transient slip after imposing a step shear increase which were attributed to the dynamic microstructure of the micelles [47]. Due to the resolution limits of particle streak velocimetry, it is difficult to differentiate between wall slip and a narrow near wall region of high shear rate. The gradual transition of the entire flow profile suggests that the entrance effects are not entirely a result of wall slip, although the effect of channel size and flow rate on the entrance length suggests that it is a factor.

The high shear rates near the wall may also indicate an overshoot of the structural change of the micelles, which would cause a rapid breakdown of micelles at the entrance. In this scenario, the length of micelles near the wall would recover downstream as the inner region becomes flow aligned or breaks down. Measurements of micelle structure as a function of streamwise position and changes in surface chemistry to reduce wall slip would be needed to better understand the



FIG. 7. Measured velocity field normalized by the mean velocity, $\langle U \rangle$, of CPCl/NaSal (100 mmol/L /63 mmol/L) system at different streamwise x-positions in 200 μ m channel at $\dot{\gamma}_A = 4000 \text{ s}^{-1}$. The velocity profile changes from a plug-like profile just after the capillary entrance to a smooth flow profile far downstream. Error bars indicate one standard deviation of the data collected at each cross-stream position.

effects of slip on the entrance region.

Having determined when the flow is fully developed, we now investigate the properties of this fully developed flow. To assess whether the capillary rheology and the flow profiles agree, we approximate the stress-shear rate relationship observed in Figure 6 by fitting a smoothing spline that fits both the Couette and capillary rheology. The velocity profile, U(y), is determined using the equation,

$$U(y) = \int_{w/2}^{y} \dot{\gamma}(\sigma_w y') dy', \qquad (5)$$

where σ_w is the wall stress. This equation assumes that the shear stress, σ_{yx} , varies linearly as a function of cross stream position, $\sigma_{yx} = \sigma_w y/(w/2)$. We assume no slip boundary conditions and zero velocity gradient at the channel centerline.

The flow profile predicted in this way from the capillary rheology is compared to velocity profiles for the different sized channels at a position that shows fully developed flow and at similar values of wall stress, see Figure 9. The cross stream dimension y is normalized by channel half height, w/2, in order to compare different channel widths. The similar magnitude of wall



FIG. 8. (a) Normalized centerline velocity as a function of streamwise position for the CPCl/NaSal (100 mmol/L /63 mmol/L) system at different flow rates in the w=200 μm channel. Fits to an exponential decay function are shown with dashed lines. (b) Characteristic entrance length of the measured velocity field as a function of wall shear rate for the CPCl/NaSal (100 mmol/L /63 mmol/L) system. Entrance length is determined by fitting an exponential decay function to the centerline velocity. Error bars are defined as one standard deviation uncertainty from least squares curve fitting.

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stress results in a nearly identical flow profile from the integrated rheology. The prediction shows good agreement with the measured profile with a slight underestimation in the neighborhood of 0.6y/(w/2). The velocity fields near the wall trends towards zero, which suggests that there is not appreciable slip at this flow rate and channel position. The lack of slip at this flow rate is also supported by the agreement in the capillary rheology obtained from different channel cross-sections.

The flow profile data shown in Figure 9 are at similar wall stress values, $\sigma_w \approx 10^2$ Pa, which correspond to wall shear rates of $\dot{\gamma}_w \approx 10^4 \,\mathrm{s}^{-1}$. From the capillary rheology measurements, shown in Figure 6, the stress versus shear rate relationship in this range of stresses is approximately follows a n=1/3 power law. The stress curve deviates from power law behavior for stress close to the plateau stress, $\sigma \approx 18$ Pa for the CPCl/NaSal (100 mmol/L /63 mmol/L) system. The flow profile is well approximated by a power law because the location corresponding to the plateau stress is close to the center of the capillary where shear rates are relatively small. We fit the combined profiles to a power law $\sigma = K \dot{\gamma}^n$ and find n=0.31, in reasonable good agreement with



FIG. 9. Flow field normalized by the mean velocity for different channel cross sections of the CPCI/NaSal (100 mmol/L /63 mmol/L) system. The velocity profile data has wall stress values of $\sigma_w = 128$ Pa, $\sigma_w = 118$ Pa, and $\sigma_w = 118$ Pa for w=50 μm , w=100 μm , and w=200 μm channels respectively. The data is compared to an integrated stress curve with a n=1/3 power law and a wall stress of 155 Pa shown in a solid line. The data are also fit to a power law viscosity model and exponent of n=0.31 is found. The position in the channel that corresponds to plateau stress $\sigma = 18$ Pa is shown for reference.

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the rheology data.

The agreement we observe between profiles and capillary rheology measurements suggests that nonlocal effects do not significantly affect the flow at high shear rates, i.e. even when the stress gradient is large. Any nonlocal effects that might arise from material diffusion would also result in a profile shape that changed with channel dimension [25]. The lack of nonlocal behavior is likely due to the location of the plateau stress close to the center-line of the capillary when the wall stress is much greater than the plateau stress. This differs from previous velocity profile observations at lower flow rates when wall shear stresses were close to the plateau stress [25, 28]. As a result, the transition from high shear rate branch to a low shear branch occurs closer to the wall. Further measurements at the lower shear rate regime, just above the plateau region, would help determine the applicability of nonlocal behavior, particularly if the effects of wall slip were reduced through surface modification.

C. Rheology of various surfactant systems

The investigation of the entrance effects demonstrates that a steady rheometric flow is obtained far downstream of the entrance. We use round capillaries with diameter d=200 μ m due to the reduction of slip effects we observed in larger capillaries. The smaller hydrodynamic resistance per unit length allows for the use of longer capillaries without exceeding pressure limitations of the syringe pump and pressure sensors. We use three lengths of L = 29 cm, L = 20 cm, and L = 10 cm. The pressure drop across the longer capillary is subtracted from the shorter capillary to give the pressure drop across the downstream portion of the longer capillary. The subtraction of these three measurements verifies that the entrance effects are negligible through the later portion of the capillary, i.e. the pressure gradient is constant.

We use this subtraction procedure to measure the viscosity of different concentrations of CPCI/NaSal wormlike micelles. The ratio of 1.58 parts CPCl to 1 part NaSal by mass is maintained while the total CPCl concentration is varied from 75 mmol/L CPCl to 120 mmol/L. We note that all of these surfactant concentrations produce a stress plateau indicating shear banding (Figure 1b). We also measure a surfactant system with a different chemistry and a similar high shear rate viscosity, 50 mmol/L cetyltrimethylammonium bromide (CTAB) with 50 mmol/L NaSal co-surfactant. The results of the capillary rheology measurements are shown in Figure 10 along with Couette measurements at lower shear rates. We show results from the capillary

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rheology measurements above $\dot{\gamma} = 10^3 \text{ s}^{-1}$; below this value wall slip results in a reduction in stress compared to Couette measurements.

The surfactant concentration changes not only the viscosity but also power law scaling. We use a power law function in terms of viscosity, $\eta = A_i \dot{\gamma}^{n-1}$, where *n* is the power law index, and A_i is



FIG. 10. Flow curves of various solutions. (a) Shear stress and (b) viscosity as a function of shear rate from capillary rheology and Couette rheology for different surfactant systems. The shear rate for the capillary rheology measurements are in terms of wall shear rate. The two distinct power laws of -2/3 and -1/3 are shown for reference. The dotted line shows the critical viscosity, $\eta_c \approx \dot{\gamma}^{-.19}$, defined the by intersection between the two power law behaviors.

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the viscosity coefficient. We observe a power law index $n \approx 2/3$ mainly for the lower concentration systems while a $n \approx 1/3$ power law index mainly is observed for the higher concentration systems. These power laws for viscosity vs shear rate, n - 1, are shown for reference on Figure 10. The behavior depends also on shear rate. We also note a modest shear thickening transition at shear rates generally below 10^3 s^{-1} . This thickening transition for the lower concentrations is abrupt and occurs at a higher shear rates, while a more gradual transition is observed in higher concentrations at lower shear rates. At the higher shear rates, a transition in power law from $n \sim 1/3$ to $n \sim 2/3$ is observed as elaborated below.

We fit the curves therefore using a power law relationship, $\eta = A_i \dot{\gamma}^{n-1}$, with exponent n = 1/3and n = 2/3 for low and high shear rates respectively. The value A_i determines how the viscosity coefficient changes with CPCl concentration. A critical viscosity is defined as where the slope changes from -2/3 to -1/3. This will be defined more rigorously after determining the concentration dependence on A_i . Data above the critical viscosity are fit for the value A_0 with n = 1/3 while the data below the critical value are fit for A_1 with n = 2/3. The uncertainty is defined as one standard deviation uncertainty from linear least squares fitting. The increase in the viscosity coefficient A_0 with concentration shows a scaling with concentration, $A_0 \sim c^{m_0}$, with fitted $m_0 = 3.13 \pm 0.23$, see Figure 11. This scaling is similar in magnitude with the scaling observed for the zero shear rate



FIG. 11. Viscosity coefficients determined from fits to power law (a) above the critical viscosity to a power law index of n = 1/3 and (b) below the critical viscosity to a power law index of n = 2/3. The lines shows fits of $A_0 \sim c^{3.13}$ above the critical viscosity and $A_1 \sim c^{0.93}$ below the critical viscosity. Error bars are defined as one standard deviation uncertainty from least squares curve fitting to the power law viscosity models.

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viscosity in the semi-dilute regime and suggests that interactions between micelles remain relevant in this regime [48]. The fit for the parameter A_1 gives a scaling of concentration, $A_1 \sim c^{m_1}$, with a fitted $m = 0.93 \pm 0.08$, see Figure 11. This scaling is close to 1 which suggests that the solutions have transitioned to a dilute-like behavior. A decrease in mean micelle length with shear rate likely leads the solution to transition from semi-dilute to a dilute scaling even though the surfactant concentration is constant [49].

This crossover from the $n \approx 1/3$ slope to the $n \approx 2/3$ slope is observed for the CPCI/NaSal system with concentrations above 80 mmol/L CPCl and 51 mmol/L NaSal. The critical viscosity for this transition is found from concentration scaling. The crossover between the power laws occurs at a critical stress, $\sigma_c \sim c^{m_0}\dot{\gamma}^{1/3} \sim c^{m_1}\dot{\gamma}^{2/3}$. Solving for the critical viscosity yields $\eta_c \sim \dot{\gamma}^{\left(\frac{m_0/3}{m_0-m_1}-2/3\right)}$, which is found to be $\eta_c \sim \dot{\gamma}^{-.19}$. This line separating the two power law behaviors is plotted on Figure 10. To emphasize the two power law behaviors, we divide each data set by the critical viscosity and shear rate at which each system crosses critical viscosity and plot the data with scaled axes in Figure 12. The higher initial viscosity of the high concentration systems results in a wider shear rate range of $n \approx 1/3$ slope, while the lower initial viscosity of the low concentration solutions causes the transition to the $n \approx 2/3$ slope to occur at lower shear rates.



FIG. 12. Viscosity normalized by the critical viscosity as a function of shear rate normalized by the critical shear rate for different concentration CPCI/NaSal surfactant systems. The rescaled data show more clearly the transition between power law behaviors.

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Shear stress here is expected to affect micelle length, since shear rates are comparable to or exceeding the inverse of the micelle breakage timescale, $\tau_b \approx 1$ ms [50]. This limit is relevant because the applied shear will induce breakdown of micelles at a faster rate than the thermodynamic micelle breakage, thus the micelles will begin to break and become extended. Below $\dot{\gamma} = 10^3 s^{-1}$ the micelles may still be entangled (not extended) and therefore may not follow the 1/3 power law. This is especially evident for higher concentration systems that have longer micelles at equilibrium. A similar power law with slope of $n \sim 1/3$ has been observed in simulations of micelles at shear rates above a disentanglement transition [51]. The $n \approx 1/3$ power law also appears to occur for other surfactant types. We observe a similar scaling for the CTAB system above $\dot{\gamma} = 10^3 \text{ s}^{-1}$, although we do not observe a transition to the $n \approx 2/3$ slope. The lack of transition to the $n \approx 2/3$ scaling for the CTAB is likely due to a different persistence length and binding energies, so that the critical shear rate may be above conditions accessed here.

The $n \approx 1/3$ power law behavior has also been observed in simulations of wormlike chains comprising self-associating rod particles that include bending potentials and model scission and recombination kinetics under shear [34, 35]. In addition, different surfactant types, including CPCl, CTAB and with EHAC micelles, have exhibited the same power law behavior, suggesting it is not a surfactant-specific scaling. The disentanglement (or micelle extension) due to shear induced breaking changes the applicable modeling for micelles. A n = 1/3 slope is predicted for unentangled polymers with finite extensibility where it is assumed polymers interact through hydrodynamic interactions [52, 53]. This scaling is also length independent, which may explain why the power law persists even when a change in average micelle length likely occurs with shear rate. This point however merits more careful investigation of micelle length and rheology.

The observation of the $n \approx 1/3$ slope also suggests that the micelles are sufficiently long to act as flexible chains. As the micelles decrease in length with shear rate, a critical length will be reached where the micelle length will be comparable with the persistence length and begin to act like rigid rods. A power law exponent of n = 2/3 is predicted for a rigid dumbells and multi-bead rod models [52]. The transition to a $n \approx 2/3$ slope has been observed in simulations at a sufficiently high shear rate to leave only a population of short micellar rods and in other simulations that result in micelles with rodlike behavior [35, 54]. The shear viscosity predicted by the rigid rod models do include a dependence on length, making it somewhat surprising that dependence follows this power law [52]. SANS or X-ray scattering measurements may shed light on the length and orientation of the micelles in this high shear rate limit.

The methodology used here to examine the scaling of viscosity with shear rate, up to very high rates, will be useful for measuring various types of wormlike micelle solutions or other self-associating fluids. For example, we anticipate that non-shear banding wormlike micelle fluids may exhibit behavior at very high shear rates that is similar to observations here. However at lower rates, closer to the onset of shear thinning where physics based on Pincus blobs is relevant, there may be different power law regimes [55, 56].

IV. CONCLUSION

In this paper, we measure the entrance effects and high shear rate viscosity of shear banding wormlike micelle solutions in capillary flow. We show that a pressure gradient is higher in capillaries immediately after the entrance and decays exponentially with a characteristic length scale of $L_p/d \approx 100$. This characteristic decay length does not change significantly with shear rate or capillary size. In contrast, the flow field takes longer to reach a fully developed flow and varies with flow rate and channel size. We observe that larger channels and higher flow rates yield a velocity field entrance length similar to entrance lengths for the pressure gradient. Above wall shear rates of $\dot{\gamma}_w \approx 10^3 s^{-1}$ we do not observe the effects of wall slip in fully developed velocity profiles, which are consistent with prediction by integrating the shear rate as a function of stress observed from rotational and capillary rheology.

The characterization of entrance effects provides a distance from the entrance where the flow can be considered fully developed. We use the pressure drop subtracted from two channels of different length to obtain the pressure gradient from this fully developed section. The viscosity results show good agreement between channels with different hydraulic diameter. This approach is used to investigate the dependence of surfactant concentration on the stress versus shear rate relationship. A power law $n \approx 1/3$ is observed for higher concentration systems at lower shear rates that transitions to a power law with an exponent close to $n \approx 2/3$ at high shear rates. The $n \approx 1/3$ slope is observed over a wider range of shear rates for high concentration systems (longer micelles) and a $n \approx 2/3$ slope is more prevalent in lower concentration systems (shorter micelles). The scaling for the viscosity coefficient with concentration in the $n \approx 1/3$ regime is similar to the zero shear rate viscosity for semi-dilute solutions, while the $n \approx 2/3$ shows dilute-like concentration scaling. These results suggest that the wormlike micelles undergo a reduction in mean length with increasing shear rate. This change in length results in a transition from a behavior similar to

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finite extensible spring models at low shear rates until they reach a critical size and then transition to another, perhaps rodlike, behavior.

The observed agreement between velocity profiles and capillary rheology in the fully developed flow indicate that nonlocal effects resulting from material diffusion are negligible and the recent scattering data analysis from capillary flows is valid when the flow is fully developed [23]. Scattering experiments, particularly X-ray and small angle neutron scattering, will be important for understanding the microstructural transitions that correspond to the different power laws observed at high shear rates.

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