Rheology of Branched Wormlike Micelles

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Abstract

The topology of self-assembled surfactant solutions includes varying degrees of micellar branching, ranging from linear wormlike micelles to a micellar network. Micellar branching acts as an effective attraction between micelles such that network condensation can lead to phase separation. Unlike chemical branching in polymers, micellar branches are labile. Movement of branches along a micelle contour has therefore been proposed as a mechanism of stress relaxation that leads to a reduction in the structural relaxation time and thus, the zero-shear viscosity. Branching is also thought to suppress flow alignment, and for lower levels of branching, may also suppress instabilities such as shear banding. The suppression of shear banding can lead to a lesser degree of shear-thinning in the apparent viscosity at higher shear rates, as well as a reduction in extensional thickening. However, for higher levels of branching, shear can induce branching for samples in proximity to such a phase transition, which can result in shear banding due to shear-induced phase separation. Recent modeling and simulations of the energetics of branching, as well as experiments on model systems, show the reduction in zero-shear viscosity is due to micelle branching. Current research includes efforts to develop a more mechanistic, quantitative understanding of micellar branching and more generally, its effects on micellar solution rheology.

Keywords: Wormlike Micelles Rheology Branching Self-Assembled Surfactant Viscoelasticity

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Preprint submitted to Current Opinion in Colloid and Interface Science – Rheology:October 28, 2014

1. Introduction

1.1. Background

Self-assembly of surfactants in solution leads to a plethora of possible microstructures with a wide-ranging array of properties [1]. Of particular scientific interest, and of significant technological value, is the formation of polymer-like or worm-like micelles (PLMs/WLMs). This results in solutions with viscoelasticity that is tunable over many orders of magnitude with variable characteristic timescale as well as a fascinatingly rich nonlinear rheological behavior. Such self-assembled microstructures are a type of "living" polymer, where breakage and reformation lead to a Poisson distribution of length scales at equilibrium for the simplest cases, and classic Maxwellian viscoelasticity in the limit where such breakage is significantly more rapid than traditional, polymer-like relaxation processes [2]. Since the seminal work of Rehage and Hoffmann [3], it has been recognized that changes in chemical composition and temperature can lead to maxima in the zero-shear viscosity as a function of salt concentration, as well as anomalous shear rheology that has become known as shear banding. Early on, it was proposed that such maxima may be associated with topological rearrangements, such as the formation of branches, which can eventually lead to network morphologies (Fig. 1). Increasing micellar length leads to an increase in zero-shear viscosity, whereas branching and network formation is proposed to lower the zero-shear viscosity.

This conceptually appealing picture of a structure-property relationship to explain the anomalous viscosity behavior has become widely accepted, but scientific validation is limited [6]. As noted in a thorough COCIS review of the use of cryo-transmission electron microscopy (cryo-TEM) to study WLMs by González and Kaler [7]: "There is not, however a universally accepted structure-property relation for these mixtures." Part of this challenge is experimental - the direct imaging of micellar branching requires cryo-TEM imaging techniques, which can be difficult due to the relatively high viscosities of concentrated surfactant solutions. Pulsed gradient spin-echo nuclear magnetic resonance (PGSE-NMR) [8] and scattering methods [9] can provide evidence for topological branching, but indeed, branching is often invoked in literature based solely on rheological observations, i.e., indirectly surmised but not proven. There is, however, no well-vetted quantitative rheological model for branched WLM solutions and so such deductions cannot, at present, be tested. A recent, comprehensive review of this field is contained

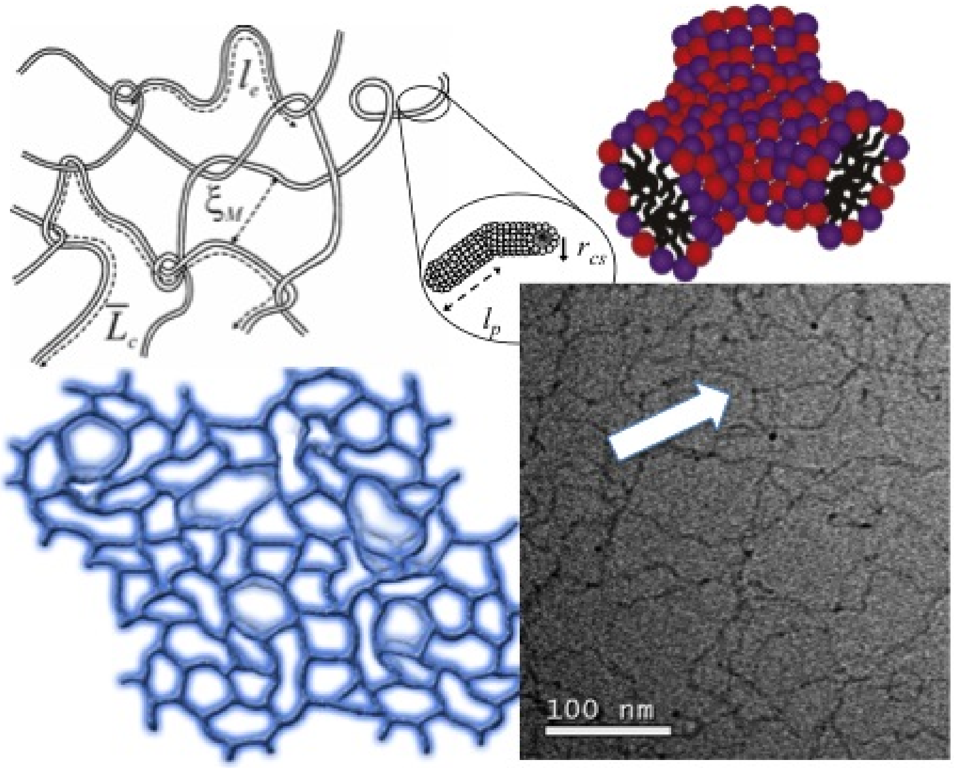

Figure 1: Topological structures associated with wormlike micelles: Clockwise from upper left: linear, entangled micelles [4]; branching junction in a mixed micellar system (note that a four fold junction is also possible); cryo-TEM of a highly branched WLM solution, arrow indicates 3-fold branch point (image courtesy of Travis Hodgdon) [5]; fully networked topology.

in volume 140 of the CRC Surfactant Science Series, entitled "Giant Micelles, Properties and Applications" edited by Zana and Kaler [10], which, along with the aforementioned COCIS reviews [7, 11], and a complementary review by Ezrahi et al. [12], provides a basis of study for those interested in this field. Consequently, the scope of this review is a summary of the recent literature reports concerning the rheology of branched wormlike micelles, with emphasis on the past half decade.

1.2. Measurements of the energetics of micellar branching

The topology of WLMs can be deduced, in part, from knowledge of the energies required to assemble end caps, linear segments, and branches. Each topological structure has a different surface curvature, and hence, the energy of packing surfactants into these structures differ. Thermal rheology measurements can be combined with neutron scattering and rheo-optical measurements along with constitutive models to determine the length scales in concentrated WLM solutions as shown by Schubert and coworkers [13, 4]. Branching occurs when the energy of scission and branching become comparable. Thus, the energetics of branch formation for ionic surfactants can be estimated from the composition corresponding to a viscosity maximum using the estimate that the scission energy is the endcap energy minus the electrostatic energy. The former can be estimated from the micellar length distribution, while the latter is expressed through system parameters such as the surfactant concentration and degree of ionization as expressed in the model by Mackintosh [14]. From literature reports of ionic surfactants, such estimates range from 18 to 25 k_bT. Using the opposing forces model, theoretical estimates of the branching energy for the mixed surfactant system of C_{12}-beta glucoside / sodium dodecyl sulfate (SDS) yields values in the range 20-22 k_bT, which decrease with increasing amount of ionic surfactant, and 14 k_bT for C_{10}-beta glucoside / SDS. Accounting for salt effects on the electrostatic energies, the opposing forces model provides estimates of topological energies around the viscosity maximum in reasonable agreement with experimental measurements, providing confidence that the rheological transition is a consequence of a change in micelle topology [4].

More recently, molecular simulations of micelle branching in self-assembled surfactants have been implemented using coarse-grained models for surfactants [15]. Results show that salt addition screens electrostatic interactions, changing the energetics of scission and branch formation, which leads to the observed zero-shear viscosity behavior. Thus, maxima in the zero-shear viscosity can be directly connected to topological branching due to changes in micelle composition.

1.3. Relationship to polymer solutions and melts

The effects of long-chain branching are significant in many technologically important systems, such as poly(ethyene), so there is a significant and growing industrial and academic interest in developing quantitative and predictive constitutive models for branched polymers. Chemical branching in polymers is fundamentally different from branching in self-assembled WLMs or PLMs because the branches are permanent, and therefore, are not another source of stress relaxation. Indeed, branching in polymers hinders stress relaxation, while branching in micelles assists stress relaxation. This field of research has developed from models that extend well-defined branched polymers to industrial polymers [16, 17, 18], such that programs exist to predict the linear viscoelastic properties of branched polymers from knowledge of the synthesis conditions during industrial-scale reaction. A method for characterizing branched topologies using small amplitude oscillatory rheology is proposed by plotting the phase angle against the absolute value of the shear modulus, a so-called Van Gurp-Palmen plot [19]. However, it has been demonstrated that linear rheology alone is insufficient to unambiguously distinguish different branching topologies. Others have proposed using nonlinear oscillatory rheology and extensional rheology for this purpose [20, 21]. Although advances in the understanding of the rheology in various chemically branched polymers may aid in understanding the role of branching in WLM rheology and vice versa, the critical differences in the stress-bearing nature of the branching between these different systems must be carefully considered when making comparisons.

1.4. The importance of branched WLMs in industry

The industrial and consumer uses of wormlike micelles are broad, with some of the more common and important ranging from oil field applications in well stimulation and completion operations, consumer products such as shampoos, skin care creams, and cleaning agents, to drag reducing agents in district heating systems. As rheological control is central to many of these applications, tuning chemical composition so as to enforce known levels of branching is a possible formulation strategy. Many of the industrial applications of wormlike micelles in industrial and consumer products, and the associated formulation challenges, are reviewed in multiple chapters in the monograph by Zana and Kaler [10] and in Ezrahi et al. [12].

2. Linear Viscoelasticity

The mean-field theory describing the stress relaxation of linear wormlike micelles in the absence of rings assumes the self-assembled entities behave like chemically-bonded polymers displaying a combination of reptation, breakage, and reformation dynamics [1, 2, 22]. The basic concept is that the stress associated with a segment of a tube is relaxed when a chain end has had sufficient time to pass through it. Because the chain end has a finite lifetime, it is able to reptate a curvilinear distance l along its tube by an amount given approximately by $D_c(L)l^2 \simeq \tau_{rep}$ [1], where $D_c(L)$ is the curvilinear diffusion constant of a chain of length L in its tube. In addition to polymeric reptation providing a pathway for stress relaxation, an end can form due to chain breakage. Provided that a chain end is formed by a break within a curvilinear distance $\simeq l$ from that tube segment, then that chain end may pass through the segment, relaxing the stress. Without providing a detailed derivation, the time taken for this to occur is $\tau \simeq (\tau_{break}\tau_{rep})^{1/2}$. Stress relaxation via this mechanism involves all tube segments equally. In the so-called 'fast-breaking limit' where $\tau \gg \tau_{break}$, any given chain undergoes many breakage and recombination events before sufficient time elapses for it to reptate through its tube. Memory of the initial length or configuration of the chain is therefore erased and all tube segments are described by the same relaxation time. Linear wormlike micelles in the fast-breaking limit are therefore well described by a simple Maxwell model with a single relaxation time. Measurements of this time are often made by small-amplitude oscillatory mechanical excitations in the linear viscoelastic regime. The single relaxation time is equal to the inverse of the frequency at which the dynamic moduli are equal.

This type of response has been noted in many linear wormlike micellar solutions [23, 24], and is readily apparent when the dynamic moduli data are plotted in a Cole-Cole representation. The dynamic loss modulus, G'', is plotted against the dynamic storage modulus, G', parametrically eliminating the frequency information. In such a representation, a perfect Maxwellian response is evidenced by a semicircular arrangement of the data. Linear wormlike micelles display nearly perfectly Maxwellian responses in the fast-breaking limit. This is shown for long, linear, entangled WLMs in Fig. 2,

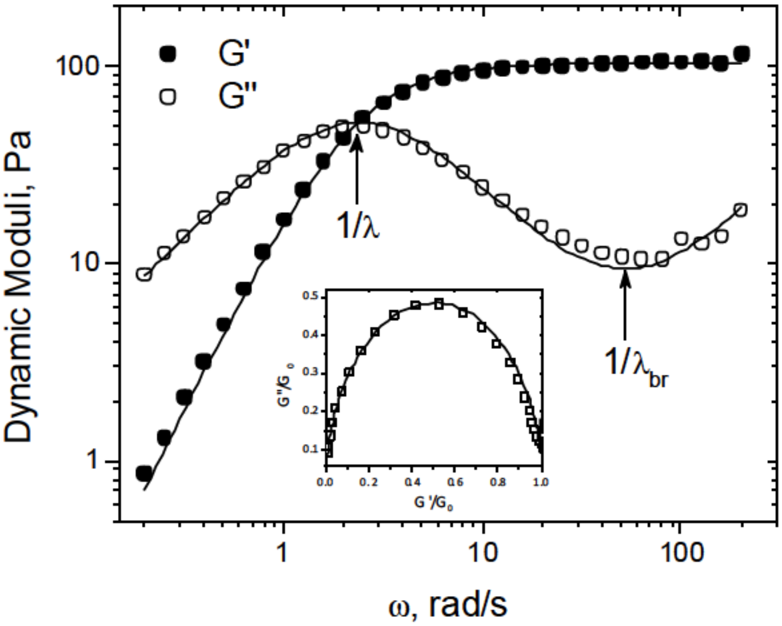

Figure 2: Cole-Cole plot for a highly entangled solution of linear micelles of CPCL/NaSal showing the primary relaxation time and the breakage time [25].

[25]. However, as the angular frequency approaches the inverse of the breaking time of the micelles, deviations from this simplistic behavior are observed. When data from the linear viscoelastic regime of polymeric systems is displayed on a Cole-Cole plot, they almost never form a semicircle due to the distribution of chain lengths leading to a dispersion of relaxation times.

Drye and Cates considered the role of branching in forming living networks that can saturate and lead to eventual phase separation [26]. Lequeux [27] also extended the models for linear micelles to account for branching, in which branch points move fluidly along a contour and act as another mechanism for stress relaxation. Many recent experimental studies of micellar solutions have invoked branching to describe their results. The method of inducing branching in each system falls into one of three categories that are summarized in Table 1: surfactants with simple inorganic salts, surfactants with penetrating salts, and mixed surfactants or emulsions. The branching

Table 1: Methods of inducing branching in WLMs

Method of Inducing Branching	**References**
Single surfactant with simple inorganic salt	[28, 29, 30, 31, 32]
Single surfactant with penetrating salt	[5, 33, 34, 35, 36, 37, 38]
Mixed surfactants or mixed emulsions	[6, 8, 13, 39, 40, 41] [42, 43, 44, 45, 46, 47, 48]

effects are more pronounced upon the addition of a hydrotropic, penetrating salt as opposed to the addition of a simple inorganic salt.

While most sources usually identify a peak in the zero-shear viscosity with respect to added salt concentration, only a few have specifically investigated the effects of branching. Some, aimed at elucidating the rheological effects of branching in reverse micellar solutions of lecithin and oil [6, 8], have confirmed the presence of branching by PGSE-NMR diffusion measurements. Importantly, these studies definitively show a viscosity reduction due to micelle branching. Further, in these studies, a deviation from the rheological Maxwellian behavior is observed at high frequencies, such that the dynamic moduli are close in value and scale with the square-root of the frequency. Koshy et al. [42] investigated cationic/anionic CTAB-NaOL mixtures, focusing on the scaling behaviors of various rheological parameters as a function of NaOL mole fraction and volume fraction of micelles. It was reported that the scaling of the plateau modulus is stronger at lower surfactant concentrations than at higher values. A distinct change in the dependence on CTAB-NaOL surfactant concentration occurs at the same value that the zero-shear viscosity peaks, which is often interpreted as the concentration above which branching begins (see Section 3). Koshy et al. [42] therefore concluded that the plateau modulus of branched systems has a weaker dependence on surfactant concentration than for purely worm-like solutions.

Oelschlaeger et al. [38] used a variety of techniques, including diffusing wave spectroscopy, optical microrheology, and macroscopic mechanical rheology, to define quantities derived from the linear viscoelastic data according to the theory laid out by Granek and Cates [22] in an investigation of the effect of added NaSal salt on solutions of CPyCl/NaSal. In describing the underlying cause of the two peaks in the relaxation time and zero-shear viscosity (see Section 3) as a function of NaSal concentration, it was concluded that the peak at low concentration was due to a transition between linear and branched morphologies. The increase in both relaxation time and zero-shear viscosity at intermediate concentrations was determined to be due to a decrease in the density of branches accompanied by an increase in the micelle length. The viscosity maximum at higher concentrations was thought to be caused by a transition to shortening micelles and an increase of branching density. These rheological transitions are interpreted as corresponding to transitions in scission energy, which were found to range between about 30 k_bT at the viscosity maximum to as low as 5 k_bT at very high salt concentrations (see Fig. 3). Micellar rings were also noted as the salt concentration was further increased beyond the second peak.

3. Steady-shear Rheology

The most often quoted rheological parameter used as indirect evidence in favor of the existence of branching in micellar solutions is the zero-shear viscosity, $\eta_0 \equiv \lim_{\dot{\gamma}\to 0} \eta\left(\dot{\gamma}\right)$. The zero-shear viscosity is a nonmonotonic function of salt concentration, surfactant concentration, or mole fraction of surfactants, with an example shown in Figure 3. At low concentrations or mole fractions, the zero-shear viscosity is an increasing function of the argument, while at higher values of the argument, the zero-shear viscosity is a decreasing function. This behavior is accounted for by noting that increasing the concentration or mole fraction at small values leads to an increase in the micellar length. As longer micelles are more entangled, and take more time to reptate through their respective tubes, the stress they carry is relaxed more slowly than shorter micelles. At some intermediate concentration or mole fraction, further increases lead to a tipping in the energy balance away from end-cap formation and toward branch point formation. Unlike polymeric systems, branches in micellar systems are able to move fluidly along the stress-bearing backbone of the micelle, thus providing another mechanism for stress relaxation. The number of branch points is increased upon further addition of salt or surfactant resulting in a continued decrease in the zero-shear viscosity.

Koshy et al. [42] observed that at a fixed total surfactant concentration, CTAB-NaOL solutions behave Newtonian across a wide range of shear rates when the mole fraction of NaOL was low. With increasing mole fraction, shear-thinning was observed in the experimentally-accessible shear rate range. The shear rate at which shear-thinning begins is related to the inverse

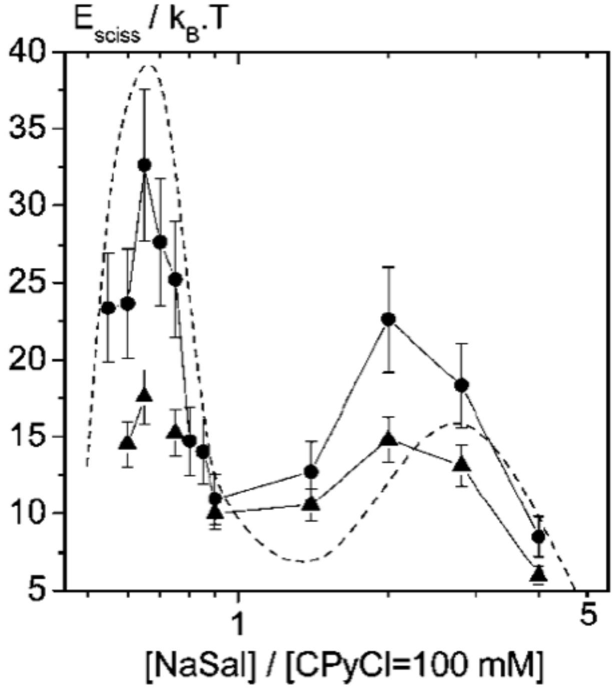

Figure 3: Variation in scission energy E_{sciss} as a function of surfactant composition obtained from DWS (circles) and oscillatory squeeze flow (triangles) measurements. The dashed line represents the variation of the zero-shear viscosity in arbitrary units [38] (used with permission).

of the relaxation time (see Section 2), which depends on the concentration with a minimum transition rate occurring at the same concentration that as a maximum zero-shear viscosity. Similar dependencies on the onset rate of shear-thinning were shown by: Ahmed and Aramaki [39] by controlling the temperature of $ChEO_m$ ($m = 15$ and 30); by Aramaki et al. [40] by varying the weight fraction of alcohol in water/$C_{16}SE$/monohydroxy alcohol systems; by Chu et al. [28] by altering the total surfactant concentration in EDAS and NaCl mixtures; by Ge et al. [37] by altering the ratio of mixed aromatic counterions of NaSal and NaEBS in CTAC cationic surfactant solutions; by Li et al. [35] by controlling the temperature in CTAB and AZONa mixtures; by Lu et al. [30] by altering the mass fraction of HN in HN/CTAB systems at a fixed temperature; by Sakai et al. [44] by varying the HTAB concentration in mixtures of gemini surfactants; by Shrestha et al. [45] by varying the $C_{12}EO_4$ concentration in 5% $ChEO_{20}/H_2O$ mixtures; and by Shrestha et al. [49] by varying the $C_{16}EO_3$ concentration for 15 wt% LAD-TEA/water/$C_{16}EO_3$ systems with fixed KBr content.

4. Extensional Rheology

The extensional viscosity of WLMs has been explored using filament stretching methods that are typically performed at low to moderate extensional rates. Highly entangled solutions are known to exhibit strain hardening and relatively large ($\sim$100) Trouton ratios (ratio of extensional to shear viscosities) [50]. Introducing branching has been shown to reduce, and eventually eliminate strain hardening, leading to a significant reduction in the Trouton ratio to a value characteristic of Newtonian fluids (Tr=3) [51]. The mechanism for this reduction is proposed to be the same branch-sliding mechanism proposed for the reduction in the shear viscosity. Using similar methods, Sachsenheimer et al. [52] also determined that extensive micellar branching greatly reduced the Trouton ratio to a value similar to that for Newtonian fluids. The authors highlight additional, significant differences between branched and unbranched, entangled WLM solutions in extensional flow. For branched WLM solutions, the constitutive parameters determined under shear flow quantitatively describe the extensional flow; there is no evidence of flow-induced change of recombination or breakage rates, such that the elongational relaxation time is essentially equal to the longest shear relaxation time. Finally, elongational flow is found to induce structures at low surfactant concentrations whether the micelles are branched or linear.

These studies demonstrate that extensional flow can discriminate between branched and linear, entangled micellar solutions, but not unambiguously due to the possiblity of extensional-induced structures [52]. The nature of these extensional-induced structures and their relationship to branching topology is at present, unresolved.

5. Rheo-Scattering Experiments

Advances in our understanding of the role of branching on the nonlinear rheology requires direct measurement of the nanoscale structure of WLM solutions under shear flow. Such measurements are now possible using small angle neutron scattering performed using sample geometries consisting of flow cells and rheometers [53]. An extensive study of a highly branched WLM solution of a cationic surfactans (erucyl bis(hydroxyethyl)methylammonium chloride) mixed with a hydrotropic salt (sodium salicylate) by Liberatore and co-workers using rheology, cryo-TEM (see fig. 1), rheo-optics, and flow SANS in the 1-2 plane of flow, and constitutive equation modeling demonstrates how branching can significantly suppress flow alignment relative to unbranched WLMs [5, 54]. However, the high degree of branching leads to phase separation near the equimolar compositions, and shear flow near to this composition results in shear-induced phase separation (SIPS). SIPS, which is visually evident as turbidity, can further induce shear banding [55], but of a different type than observed in highly entangled, linear wormlike micelles [56]. The strong coupling between branching-induced phase separation, flow-induced branch formation, and flow kinematics leads to a rich and highly nonlinear flow behavior for these network-like solutions.

Recent experiments have used rheo-SANS to distinguish levels of branching in mixed cationic/anionic WLMs composed of cetyltrimethylammonium tosylate and sodium dodecyl benzene sulfonate (CTAT/SDBS), a system that has been studied previously [13]. Sodium tosylate (NaTos) is added as a screening salt that adds flexibility to the micelles and thereby induces branching. In rheo-SANS, a shear field is applied while simultaneous small angle neutron scattering (SANS) and shear rheology measurements are recorded. A detailed description can be found in a recent review by Eberle and Porcar [53]. Under shear flow, segmental alignment of WLMs is often observed in the flow direction [53, 56]. These microstructural rearrangements are quantified by a scalar alignment factor, calculated from the 1-3 flow-vorticity plane SANS. The resulting anisotropy is quantified by the degree of increased intensity in the vorticity direction, in the q^{-1} (rod-like segment) scattering regime:

$$A_{f,1-3plane} = \frac{\int_0^{2\pi} I(q,\phi)\cos 2\phi d\phi}{\int_0^{2\pi} I(q,\phi) d\phi} \tag{1}$$

where $I(q)$ is the intensity at a fixed q-value and ϕ is the azimuthal angle. Rheo-SANS measurements were performed on samples with mild levels (0.05 %wt NaTos) and high levels (0.15 %wt NaTos) of branching to compare the stress and alignment factor at equivalent shear rates. Figure 4 (top) shows the steady shear flow curve for both samples. The mildly branched system exhibits a stress plateau, suggestive of shear banding, and linear stress behavior beyond the plateau. The highly branched sample shows shear-thinning behavior only and anomalous, non-linear behavior beyond the shear-thinning regime ($\dot{\gamma} > 420$ s^{-1}). While the mildly branched sample generally exhibits larger stresses, two locations on the flow curve show approximately the same measured stress for both samples (green, $\dot{\gamma} = 45$ s^{-1} ; blue, $\dot{\gamma} =$ 1000 s^{-1}). The corresponding rheo-SANS alignment factor at each shear rate is shown in Figure 4 (bottom). At low shear rate, $\dot{\gamma} = 45$ s^{-1} (green), the alignment factor for the mildly branched system (rheo-$A_f = 0.25$) is four times larger than the alignment factor for the highly branched system (rheo-$A_f = 0.06$). With increasing shear rate, the alignment factor for the highly branched system surpasses that of the mildly branched system by over 30%, despite a lower measured stress. At $\dot{\gamma} = 1000$ s^{-1}, the alignment factor of the highly branched system exceeds that of the mildly branched system, with $A_f = 0.55$ and $A_f = 0.37$, respectively. The crossover in alignment between the two samples, which is attributed to branch breakage, is observed at $\dot{\gamma} = 420$ s^{-1}. The underlying intensity distribution I(q, ϕ) measured from the scattering widens as branching level increases, as branches sterically hinder alignment. However, the intensity distribution of the highly branched system significantly sharpens at the crossover point, indicating alignment of linear, broken chains as opposed to branched chains. The additional salt in the highly branched sample allows the system to achieve a higher degree of alignment, as the salt screens electrostatic repulsions and adds flexibility to the micelles.

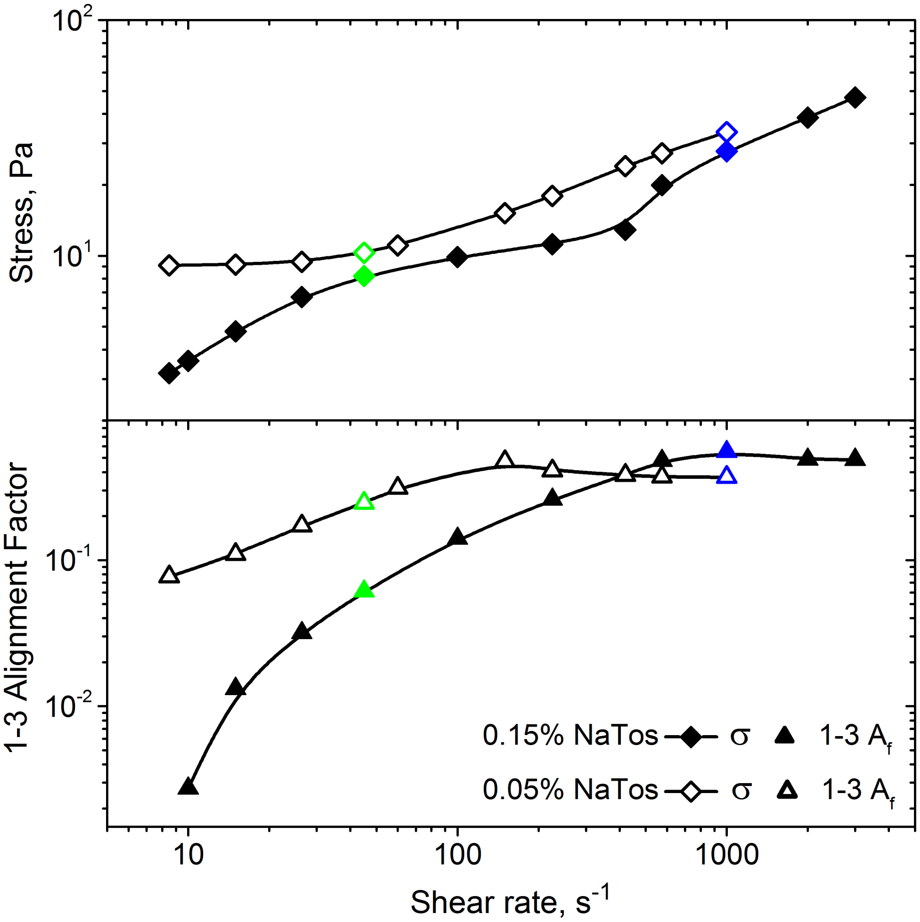

Figure 4: Steady shear stress (top) and associated rheo-SANS alignment factor (bottom) for a mildly branched (0.05% NaTos) and highly branched WLM sample (0.15% NaTos). At approximately equal stresses at low shear rates (green), the alignment factor is significantly higher in the mildly branched system. At higher shear rates and approximately equal stress (blue), the alignment factor of the highly branched system surpasses that of the mildly branched system, indicative of branch breakage.

6. Inducing Branching by Nanoparticle Addition

Nettesheim and coworkers were able to induce branching and develop viscoelasticity in cationic surfactant solutions by the addition of nanoparticles [57]. Surfactant was observed to adsorb onto the nanoparticles and measurements of the energetics combined with models for polymer bridging provide a method for understanding how nanoparticle-directed network formation builds viscoelasticity [58]. Subsequent measurements show that branching induced by nanoparticle addition can suppress shear banding instabilities as the branching reduces flow-alignment of the micelles [59]. Note that nanoparticle addition, and the associated branching, results in non-Maxwellian behavior in linear viscoelasticity, presumably due to the broadening of the spectrum of relaxation times. Practical, industrial applications of the introduction of branching in WLMs by addition of nanoparticles include building viscosity by nanoparticle addition at reduced surfactant concentration [60].

7. Summary and Outlook

Branching in “living” micellar systems reduces the viscosity by reducing the relaxation time. Specifically, the reptation time scales with the distance between branch points rather than the contour length as for linear micelles. The effect of micelle branching on the high frequency viscoelasticity as well as the nonlinear shear and extensional rheology continues to be an active area of research, and measurements of branching are generally independently determined from NMR and/or cryo-TEM measurements. Some level of branching suppresses flow alignment in strong flows, thereby suppressing nonlinear instabilities such as shear banding. Increased branching leads to saturation of the network and phase separation. Shear-induced phase separation that can lead to shear banding may be observed as network saturation is approached. Calculation of the energies of endcap, scission, and branching are possible from the opposing forces mode such that estimates of compositions corresponding to the viscosity maximum are possible. Alternatively, measurements of the viscoelasticity, complemented by measurements of the persistence and micelle contour length, which may be determined by scattering, provide a method to estimate branching energies and micellar topology. Branching can be induced and controlled by chemical additives as well as by nanoparticle addition. Molecular simulations of branching in self-assembled aggregates are now feasible using coarse-grained models for surfactants, such that *ab initio* calculations of micelle topology are possible. Finally, explorations to determine the role of micellar branching on the flow of WLM solutions in flow types other than shear flows and uniaxial extension are needed.

8. Acknowledgement

This manuscript was prepared under cooperative agreements 70NANB7H6178 and 70NANB10H256 from the National Institute of Standards and Technology (NIST), U.S. Department of Commerce. The statements, findings, conclusions and recommendations are those of the author(s) and do not necessarily refect the view of NIST or the U.S. Department of Commerce. Beamtime from the NCNR is gratefully acknowledged.

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