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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 that 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.

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 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

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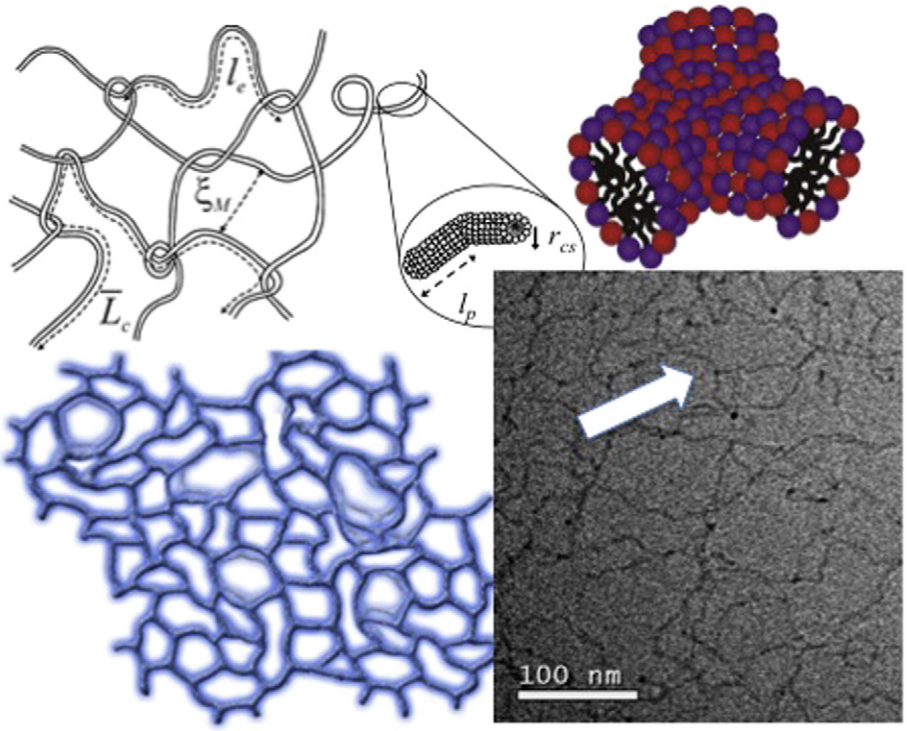

Fig. 1. Topological structures associated with wormlike micelles: Clockwise from upper left: linear, entangled micelles [4]; branching junction in a mixed micellar system (note that a four fold junction is also possible); cryo-TEM of a highly branched WLM solution, arrow indicates 3-fold branch point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

branches. Each topological structure has a different surface curvature, and hence, the energy of packing surfactants into these structures differs. 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_b T. 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) yield 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(ethylene), 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 [16–18], 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