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Effect of ionic strength on the rheological behavior of aqueous cetyltrimethylammonium *p*-toluene sulfonate solutions

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Abstract

The influence of ionic environment on the rheological properties of aqueous cetyltrimethylammonium *p*-toluene sulfonate (CTAT) solutions has been studied under three different flow fields: simple shear, opposed-jets flow and porous media flow. Emphasis was placed in the experiments on a range of CTAT concentration in which wormlike micelles were formed. It is known that these solutions exhibit shear thickening in the semi-dilute regime, which has been explained in terms of the formation of shear-induced, cooperative structures involving wormlike micelles. In simple shear flow, the zero shear viscosity exhibits first an increase with salt addition followed by a decrease, while the critical shear rate for shear thickening increases sharply at low salt contents and tends to saturate at relatively high ionic strengths. The results are explained in terms of a competition between micellar growth induced by salt addition and changes in micellar flexibility caused by ionic screening effects. Dynamic light scattering results indicate that micelles grow rapidly upon salt addition but eventually achieve a constant size under static conditions. These observations suggest that the wormlike micelles continuously grow with salt addition, but, as they become more flexible due to electrostatic screening, the wormlike coils tend to adopt a more compact conformation. The trends observed in the apparent viscosities measured in porous media flows seem to confirm these hypotheses—but viscosity increases in the shear thickening region—and are magnified by micelle deformation induced by the elongational nature of the local flow in the pores. In opposed-jets flow, the solutions have a behavior that is close to Newtonian, which suggests that the range of strain rates employed makes the flow strong enough to destroy or prevent the formation of cooperative micellar structures.

Keywords: CTAT; Shear-thickening; Extensional flow; Porous media flow

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1. Introduction

Solutions of surfactants that form long wormlike micelles have been studied for their potential applications in drag reduction, enhanced oil recovery, and as templates for material synthesis [1–5]. Wormlike micellar systems consist of long cylindrical aggregates of self-assembled surfactant molecules that potentially may behave similar to polyelectrolyte chains in solution, with the difference that they can dynamically break and recombine [6,7] which makes them stable in applications where high shear rates are encountered.

Cationic surfactants can self-assemble into long flexible wormlike micelles in the presence of salt. These micelles may entangle into transient networks, imparting viscoelastic properties to the solution [8,9]. These systems may function as thickening and rheology control agents in aqueous solutions, in a similar way to high molecular weight polymers [10–13]. Unlike polymers, however, wormlike micelles are in thermal equilibrium with their monomers. Thus, micellar self-assembly (and hence, worm length and flexibility) responds to changes in surfactant and salt concentration, nature of counterion, and temperature.

Under simple shear conditions, wormlike micellar solutions may exhibit an increase in the apparent viscosity above a critical shear rate, $\dot{\gamma}_c$ (shear-thickening transition) [10,14–25], attributed to the formation of shear-induced structures (SIS) or to

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shear-induced phase transitions (SIP) [8,9,17,20] albeit an induction time is necessary to achieve the more viscous state. This induction time increases as the applied shear rate approaches the critical value from above [14,16,22,24].

Changes of the fluid microstructure at the shear thickening transition have been studied by Rehage et al. [12], who proposed a model in which large micelles are formed when small micelles collide and fuse together. On the other hand, Berret et al. [11] suggested a shear-induced transition from rodlike to longer, more flexible entangled structures. More recently, Barentin and Liu [13] proposed that the SIS arise through the formation of micellar packages, resulting from counterion-assisted intermicellar attraction.

Gamez-Corrales et al. [8] found that $\dot{\gamma}_c$ remains constant (or varies weakly) with CTAT concentration in the range 0.26–0.75%. Moreover, Berret et al. [11,25–27] reported that the shear-thickening transition occurs continuously (in applied strain mode), and the critical value $\dot{\gamma}_c$ was independent of the surfactant concentration. However, Müller et al. [28] found that $\dot{\gamma}_c$ decreases when CTAT concentration increases in a CTAT concentration range of 0.05–0.23%, while Truong and Walker [29] found decreases in $\dot{\gamma}_c$ when CTAT concentration varies from 0.2 to 0.5%, which then remains constant when CTAT concentration varies from 0.5 to 0.75%, in concordance with previous works [8,11,25,26,30].

Gamez-Corrales et al. [8] noted that thermodynamic and physicochemical variables such as salt content, temperature, and concentration itself influence the growth of micellar aggregates. At rest and in a dilute solution, the fluid behaves as a dispersed system where the majority of the micellar aggregates are short, rodlike and unentangled. This corresponds to an average micellar length much shorter than the intermicellar distance. On the other hand, the thickened state is a viscoelastic solution of entangled wormlike micelles. They concluded that if this state could exist at rest, it would be characterized by micellar lengths much longer than the mesh size of the network.

It is well known that the low shear rate viscosity (η_0) of many surfactant solutions depends strongly on salt concentration. Usually, the viscosity first increases with increasing salt concentration, going through a maximum, and then decreases [30–33]. Wormlike micelles may undergo uniaxial growth upon the addition of salt. As a result, the viscosity of the solution increases, and the micelles form an entangled network [13,31,32]. The decrease in viscosity with further addition of salt, however, is more difficult to explain. Several works [31,34–36] have proposed that this decrease at high salt concentrations may be due to the formation of a multiconnected network in which stress relaxation can occur by the sliding of physical cross-links along the micelles. Thus, the maximum in viscosity with increasing salt concentration may indicate a shift from linear to branched micelles. On the other hand, relatively high salt contents increase the flexibility of long wormlike micelles by screening of the micelle charge and the subsequent decrease of electrostatic repulsion between micelle segments.

The effect of NaCl on the rheology and structure of CTAT micelles in the semi-dilute regimen was investigated by Truong and Walker [29]. Their shear viscosity results indicated that small amounts of electrolyte caused the growth of micelles by increasing the degree of electrostatic screening. In addition, they found that the critical shear rates for SIS formation tend to increase with NaCl concentration for these systems.

Elongational flow studies of wormlike micelle systems give further insight on the similarity between wormlike micelles and flexible polyelectrolytes. For example, in one such study [37], high ionic strength solutions exhibited shear thinning in simple shear flows and extension thickening in elongational flows, which is characteristic of high molecular weight flexible polymers [38–41]. Hu et al. [41,42] presented results that suggested that uniaxial extension might promote micellar self assembly far beyond that achieved in the quiescent state. On the other hand, Müller et al. [28] showed that a strong elongational flow field (opposed-jets flow), applied to CTAT solutions that are in the dilute regime ($C_{\text{CTAT}} < 0.5\%$) and low ionic strength, does not lead to extension thickening, since the extensional flow prevents and/or destroys micellar association. When the solutions are in the semi-dilute regime ($C_{\text{CTAT}} > 0.5\%$), they can exhibit gradual extension thickening, which resembles the opposed-jets rheology of semi-rigid polymers in solution [43].

In flow through a porous medium, CTAT solutions experience a substantial increase in apparent viscosity beyond a critical Reynolds number, which surpasses increases observed in simple shear flows. This was explained as the result of a synergistic effect of shear and relatively weak elongation on the solution microstructure [28].

In this work, we report experimental results on the influence of the type of flow field on the rheological response and the viscosity enhancement capabilities of aqueous solutions of CTAT/NaCl. Simple shear, opposed-jets flow (which approximates uniaxial extension) and porous media flows are employed. The results on porous media flow in particular could have important implications for practical applications, since this type of flow is present in tertiary oil recovery and soil remediation operations.

2. Experimental

2.1. Materials

Analytical (99% pure) CTAT was purchased from Sigma and used without any further purification. Water that has been distilled and deionized was employed as the solvent. The solutions were prepared by dispersing the solid surfactant in water at 25 °C, stirring continuously during 24 h. The solutions were maintained at that temperature at all times and throughout the experiments to keep them above the Krafft point of CTAT (22.5 °C) [8]. Solutions of NaCl and CTAT were prepared by mixing appropriate volumes of stock solutions. Every solution was allowed to stand unstirred for at least 24 h before each experiment to relax any structure formed during stirring (uncontrolled shear history). In the absence of salt, the critical micelle concentration of CTAT is 0.021% [24], whereas the critical concentration for the formation of cylindrical micelles is 0.04% [27].