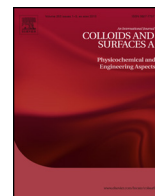




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On the shear thickening behavior of micellar aqueous solutions of cetyltrimethylammonium fluorobenzoates: Effect of the fluor position



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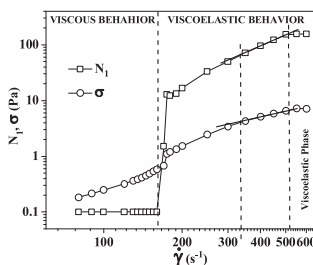
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HIGHLIGHTS

- The rheological properties of aqueous diluted solutions of CTAnFB were studied.
- The counterion position was tested as a function of concentration and temperature.
- The shear thickening behavior is strongly affected by the counterion position.
- Only the aqueous solutions of CTA3FB and CTA4FB exhibit shear thickening behavior.
- The counterions studied here follow a Hofmeister-like sequence.

GRAPHICAL ABSTRACT

After a critical shear, a viscoelastic phase is formed due to structure induction by shear (SIS).



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ABSTRACT

The shear thickening behavior of micellar solutions made with homologous cetyltrimethylammonium (CTA) fluorobenzoate (FB) surfactants, in which the fluor is located in the 2-(CTA2FB), 3-(CTA3FB) or 4-position (CTA4FB) of the counterion aromatic ring, is studied here. In the temperature and range studied, the aqueous solutions made with CTA2FB do not exhibit shear thickening because 2FB is more kosmotropic than the 3FB and 4FB counterions, and larger shear rates than the ones covered here are needed to observed shear thickening in the CTA2FB system. CTA3FB and CTA4FB aqueous solutions undergo the shear thickening transition due to the formation of shear induced structures (SIS) in the shear range studied. The shear thickening transition in CTA3FB micellar solutions is stronger and appears at lower shear rates than that detected in CTA4FB ones; in addition, the intensity of shear thickening in both systems augments as the parallel-plates gap is increased. These discrepancies detected between the three surfactants studied are related to the differences among the counterion hydrophobicity i.e., $3FB^- > 4FB^- > 2FB^-$. Moreover, the penetration of the counterions into the core and charge neutralization of the surface of the surfactant aggregates induces micellar growth according to the Hofmeister-like anion series.

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1. Introduction

Hydrotropes are organic molecules that have an amphiphilic structure and the ability to increase the solubility in water of scarcely soluble organic molecules up to several orders of magnitude [1,2]. Hydrotropes cannot form organized self-associated structures, such as micelles, because their hydrophobicity is lower than that of surfactants; however, they decrease substantially the *critical micellar concentration* (cmc) and induce the transition from spherical to rod micelles (cmc_2) as well as wormlike micelles formation at lower surfactant concentrations. This ability typically increases when the hydrotrope molecules have aromatic structures [3–15]. For instance, the addition of hydrotrope salts such as 2-hydroxybenzoate to cetyltrimethylammonium bromide (CTAB) solutions induces the formation of wormlike micelles at very low concentration whereas the addition of 3- and 4-hydroxybenzoate counterions does not. In contrast, the addition of 4- and 3-chlorobenzoate counterions to CTAB solutions produce the formation of rodlike micelles at concentrations slightly larger than the onset of the cmc , whereas micelles remain roughly spherical with 2-chlorobenzoate, even at high surfactant concentrations [16–19].

These results indicate that the nature of both counterion and surfactant tail affect micelle size and shape. In the case of the counterion, the preferred localization and orientation within or at the micellar interface are determined by its substitution pattern and the nature of its substituent [12,13,17–19], its size [12], its hydrophobicity [5,12,20], and its degree of hydration [13]. In fact, the aggregate growth is influenced by the localization and orientation of the substituent in aromatic counterions [17–19,21]. Furthermore, changes in surfactant concentration [18,19], headgroup area [11,21], charge density [17] and/or electrostatic interactions among the headgroups [4,21–24] also affect micelle morphology. Moreover, Berlot et al. [25] reported that there is a specificity following the Hofmeister series for various monovalent counterions. Such hydrophobic counterions bind very strongly and induce the formation of very long cylindrical micelles.

Vermathen et al. [15] studied the factors that promote micellar growth and induce the sphere-to-rod transition in three micellar aqueous systems formed by tetradecyltrimethylammonium (TTA^+) as cation and 2-, 3-, or 4-fluorobenzoate as counterion. They reported that the principal factor that promotes the sphere-to-rod transition is the reduction of the headgroup repulsion among the counterions at the micellar surface and found that the 3- and 4-fluorobenzoate are more effective to induce this transition due to their correct hydrophobic-hydrophilic balance (HLB) to insert themselves among the TTA^+ headgroups, forming tight ion pairs. However, these authors did not study the rheological behavior of these surfactant systems.

To understand the complex rheological behavior of micellar solutions, it is convenient to distinguish three surfactant concentration regimes: dilute, semi-dilute and concentrated. The dilute regime ends at the *overlapping or entanglement concentration* (c^*), and the semi-dilute concentration range covers from c^* up to the concentration where the entanglement network presents a mesh size larger than the persistent length [26]. At concentrations above the cmc_2 but below c^* , in start-up experiments at a constant shear rate above a critical shear rate, $\dot{\gamma}_c$ (or stress, σ_c) and after an induction time, t_{ind} , the viscosity increases up to a steady value, which is reached after a saturation time (t_{sat}) [26,27]. Both the induction and the saturation times may range from seconds to several minutes and become shorter as the shear rate departs from $\dot{\gamma}_c$ with a power law dependence, $t_{ind} \dot{\gamma}^{-m}$ [27].

The shear thickening phenomena observed in rodlike micellar solutions is caused by shear-induced structures (SIS), the morphology of which is still in debate, inasmuch as rod micelles orientation

to form wormlike micelles, strings of micellar beads or gel formation has been proposed [27].

In this work the effect of the organic hydrotropic counterions, 2-fluorobenzoate (2FB, *ortho*), 3-fluorobenzoate (3FB⁻, *meta*) or 4-fluorobenzoate (4FB⁻, *para*), on the shear thickening behavior of rod-like micellar aqueous solutions of cetyltrimethylammonium (CTA^+) surfactants is studied. The steady and transient nonlinear rheological behaviors as a function of concentration and temperature are reported. These results are compared with those of surfactants with similar organic counterions such as 4-methylbenzenesulfonate (CTAT) and 4-vinylbenzoate (CTAVB), previously published [28–30].

2. Experimental

Cetyltrimethylammonium hydroxide (10 wt.% CTAOH solution in water), 2-fluorobenzoic acid (2FBH), 3-fluorobenzoic acid (3FBH) and 4-fluorobenzoic acid (4FBH), with purities of 99 wt.%, were all purchased from Fluka-Aldrich, and used as received. Cetyltrimethylammonium 2-fluorobenzoate (CTA2FB), 3-fluorobenzoate (CTA3FB) and 4-fluorobenzoate (CTA4FB) were synthesized at 10 °C by neutralization of a 1 wt.% CTAOH aqueous solution with a concentrated solution of 2FBH, 3FBH and 4FBH, respectively, in acetone (analytical grade from Ferment). Each surfactant was precipitated by adding absolute ethanol (Aldrich) to the solution and dried with phosphorus pentoxide for a week. The structure of these surfactants was confirmed by NMR spectroscopy (Advance DMX500 Bruker spectrometer).

Kraft temperatures were obtained in a TA Instruments Q2000 differential scanning calorimeter (DSC) calibrated with indium, water and n-octane standards. All scans were done with heating and cooling rates of 1.0 °C/min. Aluminum pans for volatile samples (TA Instruments) were employed to minimize water loss by evaporation. Samples in the sealed pans were weighted before and after each test. Results from samples that lost weight were discarded.

For rheological measurements, samples were prepared by weighing appropriate amounts of CTA2FB, CTA3FB or CTA4FB and water in glass vials; for these measurements, samples in a range of 0.1–10 wt.% were prepared, placed in a water bath at 60 °C for a week where they were frequently shaken, and allowed to reach equilibrium at the temperature of analysis or measurement. All samples were centrifuged to remove suspended air bubbles before being tested. Steady and transitory rheological measurements were carried out in a strain-controlled ARES22 and a stress-controlled ARG2 rheometers from TA Instruments with parallel plate geometry of 60-mm in diameter. To obtain the optimum gap for measuring the shear thickening behavior, shear rate sweeps at different gaps for 1.5 wt.% CTA3FB solutions were performed (see SM1 in supporting material). Results indicated that for gaps smaller than 0.1 mm, shear thickening was not detected. At larger gaps, shear thickening behavior appeared and the thickening intensity augmented as the gap increased (see SM1 in supporting material). Wunderlich and Brunn [31] in Couette geometry and Herle et al. [32] in parallel-plate geometry reported that shear thickening diminishes as the geometry gap is decreased and suggested there is a critical gap dimension below which the SIS cannot develop. Since it is difficult to maintain the sample between the plates at gaps higher than 1.8 mm, measurements were performed at this gap. Because the long transients in the kinetics of the SIS formation, the shear rate as a function of shear stress was determined by transient experiments, until the steady state value was detected. With these values, the steady state flow curves were constructed point by point. Here, the reported shear rate is the one at the edge of the moving plate. An environmental control unit was placed around the parallel plate fixture to prevent water evaporation. Temperature was controlled within

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