

The influence of concentration and pH on the structure and rheology of cationic surfactant/hydrotrope structured fluids

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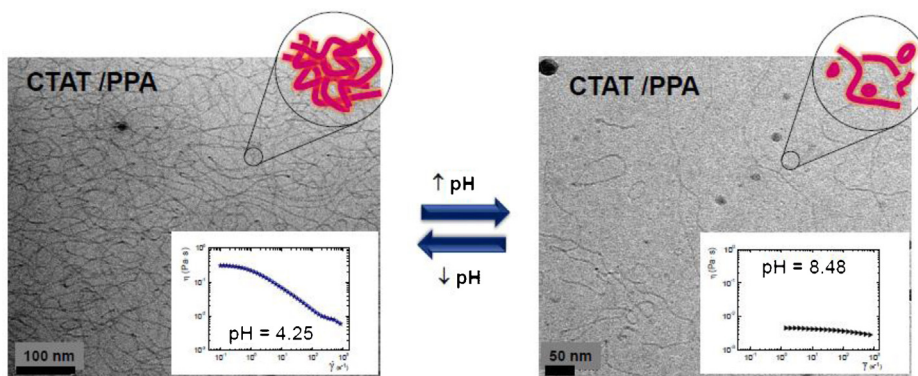
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HIGHLIGHTS

- The addition of PPA to 20 mM CTAC solutions promotes a transition from spherical micelles to cylindrical micelles, decreasing the CRC of the surfactant.
- PPA addition increases the viscosity of CTAT several orders of magnitude.
- Synergistic rheological effects are observed when pH is increased in neat CTAT solutions.
- Increasing pH of CTAT/PPA mixtures reduces viscosity as a function of the nature of the interactions between CTAT and the hydrotrope and the ionization degree of PPA.
- ¹H NMR and Cryo-TEM results correlate structure with rheology.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 September 2015

Received in revised form 28 October 2015

Accepted 29 October 2015

Available online 1 November 2015

Keywords:

Cationic surfactant/hydrotrope mixtures

Worm-like micelles

CTAT

PPA

pH responsive fluid

ABSTRACT

In this paper, we show how to tailor the structure and rheology of aqueous solutions of the cationic surfactant cetyltrimethylammonium tosylate, CTAT, by adding a hydrotrope (potassium phthalic acid, PPA) or changing pH. Aqueous solutions of neat CTAT and CTAT/PPA binary mixtures were evaluated under different hydrotrope concentrations and compared with solutions of an analogous surfactant, cetyltrimethylammonium chloride (CTAC). PPA content promotes substantial increases in micellar flexibility and inter-micellar entanglements, resulting in a higher degree of structure in the fluid. Increasing the pH in neat CTAT leads to significant increases in low shear rate viscosities in comparison with CTAT at its original pH, because the OH ions favor surfactant aggregation as well as the growth of worm-like micelles. Nevertheless, increasing the pH in CTAT/PPA mixtures produced a progressive decrease in the low shear rate viscosities. This result is due to the nature of the interactions between CTAT and PPA, as well as to the ionization degree of the functional groups present in PPA. Cryo-TEM and ¹H NMR

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measurements evidenced, respectively, the microstructural and chemical environmental changes of CTAT upon PPA addition and explain the rheological properties of the CTAT/PPA mixtures as a function of the fluid structure.

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1. Introduction

In the last few years, the interest in designing smart viscoelastic fluids has gained importance since their properties can be modified efficiently and reversibly under external stimuli, such as, pH, temperature, light, ultrasound, magnetic fields or electric fields. Of special interest are pH sensitive fluids because of their critical role on biological, chemical and physiological systems. It has been reported that certain smart fluids can be obtained by surfactants that form worm-like micelles [1–3] and their mixtures with hydrotropes [4–6].

Hydrotropes are amphiphilic molecules that are highly soluble in water. They have been studied since their discovery in 1916 [7–10]. Hydrotropes are used in separation processes and pharmaceutical applications, and they can be used as stabilizers of o/w microemulsions, as rheological modifiers or clearing agents in cloudy detergent formulations, among other applications [11–16]. These compounds can increase the solubility of organic molecules in water [17,18] and can co-solubilize high molecular weight surfactants in the same way as alcohols; however, hydrotropes have the advantage that they are not volatile and can even be less expensive.

Hydrotropes modify the behavior of surfactants in aqueous solutions and can affect their aggregation capacity, and their critical micellar concentrations (CMC). It has been reported that ionic hydrotropes decrease the CMC of oppositely charged surfactants, since the charge is screened and electrostatic repulsive forces decrease inducing micellization. For instance, an anionic hydrotrope such as sodium salicylate (NaSal) decreases the CMC of cationic cetylpyridinium chloride (CPC) while non-ionic hydrotropes such as pyrogallol and resorcinol can decrease also the CMC of CPC [19]. Nevertheless, certain non-ionic surfactants, like polyoxyethylene *t*-octylphenol (Triton X-102), are barely affected by the addition of hydrotropes [20].

Surfactant microstructure in aqueous solutions can also be affected by the addition of hydrotropes since they can modify the morphology and size of unimer aggregates. Transitions from spherical to worm-like micelles [21–23] and to vesicles [24] have been reported. Recently, Lin et al., reported the rheological response of viscoelastic fluids formed by worm-like micelles of cetyltrimethylammonium bromide (CTAB) and hydrotropes and they demonstrated that the rheological properties of these fluids can be controlled by changing the solution pH [6].

In the present work, pH responsive smart viscoelastic fluids are formulated by mixing a cationic surfactant and a pH responsive molecule, the hydrotrope potassium phthalic acid, PPA, (Fig. 1). PPA has been reported to be a hydrotrope by Lin et al. [6], since, it decreases the surface tension of water. Two surfactants were evaluated, cetyltrimethylammonium tosylate (CTAT) and cetyltrimethylammonium chloride (CTAC). The rheological properties and the microstructure of these fluids can be tailored by surfactant/PPA molar ratio and by pH changes. A detailed study was performed for CTAT/PPA system and only a few experiments were performed with CTAC/PPA for comparison purposes. As far as we are aware, this is the first report on the rheological properties and structure of this specific CTAT/PPA cationic surfactant/hydrotrope pair.

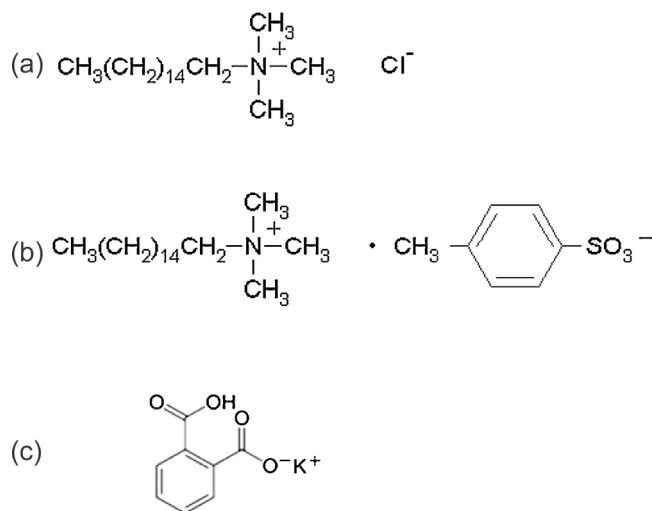


Fig. 1. Chemical structure of (a) CTAC, (b) CTAT and (c) PPA.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium chloride (CTAC, 25 wt.% in H_2O , Sigma), cetyltrimethylammonium tosylate (CTAT) (99%, Sigma) and potassium phthalic acid (PPA, 99%, Fisher Scientific) were used without any further purification.

2.2. Samples preparation

Concentrated stock solutions of surfactants and hydrotropes were prepared by weighting the required amount of powder sample in distilled and deionized water. Solutions of surfactant/hydrotrope blends were prepared in a calibrated volumetric flask by mixing the required amount of each stock solution in the following order: first, the hydrotrope stock solution, then the surfactant solution was added and the desired concentration was reached by the addition of distilled/deionized water. All prepared solutions were kept under magnetic stirring at 25°C , until a homogeneous solution was obtained. Finally, samples were stored during 24 h to reach thermodynamic equilibrium prior to the measurement. Solution pH values were adjusted by adding the required amount of 0.1 M KOH.

2.3. Shear rheometry

Rheological measurements were conducted with an ARES shear rheometer by Rheometric Scientific equipped with double-wall Couette geometry. Strain sweep experiments at 1 Hz were performed to determine the linear viscoelastic range. Then, frequency sweep experiments were carried out at a constant strain of 20%, which was within the linear viscoelastic regime.

2.4. Cryogenic transmission electron microscopy (Cryo-TEM)

For cryo transmission electron microscopy studies, a sample droplet of 2 μL was put on a lacey carbon filmed copper grid (Science Services, Muenchen), which was hydrophilized by air plasma glow discharge (Solarus 950, Gatan, Muenchen, Germany) for 30 s. Subsequently, most of the liquid was removed with blotting paper leaving a thin film stretched over the lace holes. The specimens were instantly shock frozen by rapid immersion into liquid ethane cooled to approximately 90 K by liquid nitrogen in a temperature-controlled freezing unit (Zeiss Cryobox, Carl Zeiss Microscopy GmbH, Jena, Germany). The temperature was monitored and kept constant in the chamber during all the sample preparation steps. After freezing the specimens, the remaining ethane was removed using blotting paper. The specimen was inserted into a cryotransfer holder (CT3500, Gatan, Muenchen, Germany) and transferred to a Zeiss EM922 Omega EFTEM (Zeiss Microscopy GmbH, Jena, Germany). Examinations were carried out at temperatures around 90 K. The TEM was operated at an acceleration voltage of 200 kV. Zero-loss filtered images ($\Delta E = 0 \text{ eV}$) were taken under reduced dose conditions (100–1000 e/nm^2). All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 1000, Gatan, Muenchen, Germany) combined and processed with a digital imaging processing system (Digital Micrograph GMS 1.9, Gatan, Muenchen, Germany).

2.5. NMR spectroscopy

NMR spectra were recorded at Bruker Avance 300 MHz, in D_2O at 298 K. Chemical shifts are reported in ppm (δ units) downfield from 3-(trimethylsilyl)-propionic acid- d_4 .

3. Results and discussion

3.1. Simple shear behavior

The rheological behavior of cetyltrimethylammonium chloride (CTAC) has been extensively studied [24–29]. This cationic surfactant has a CMC = 1.3 mM [25,30] and at this concentration spherical micelles are formed. The critical rod-like micelles concentration (CRC) is 350 mM [25]. At this CRC concentration, the formation of rod-like micelles takes place. On the other hand, cetyltrimethylammonium tosylate (CTAT) is another widely studied cationic surfactant [31–40] and has a hydrophobic chain which is analogous to CTAC, nevertheless, the presence of the tosylate ion (also known as *p*-toluene sulfonate) gives it interesting rheological properties with potential applications in several fields [24,31,32,35,41–43]. CTAT has a CMC = 0.26 mM [32,34,35,44] and a CRC = 1.97 mM [35]. Beyond its CRC important changes on solution viscosity have been reported, including a shear thickening effect due to the formation of shear induced structures (SIS) [31,36,44].

Fig. 2 depicts the rheological profile under simple shear of CTAC and CTAT aqueous solutions at a constant concentration of 20 mM. As it can be noticed, the CTAC solution exhibits a Newtonian behavior in the whole range of evaluated shear rates with an apparent viscosity of $1 \times 10^{-3} \text{ Pa}\cdot\text{s}$, i.e., identical to that of pure water. On the contrary, CTAT shows a low-shear rate viscosity that is 1-order of magnitude higher in the low shear rate range displaying a Newtonian behavior. At shear rates higher than 10 s^{-1} , the solution exhibits a slight shear thickening effect and later a pronounced shear thinning at high shear rates.

The differences observed between CTAC and CTAT at 20 mM concentration are related to their respective concentration regimes and surfactant structure. In the case of CTAC, although the concentration exceeds its CMC (1.3 mM) it is still below the concentration at

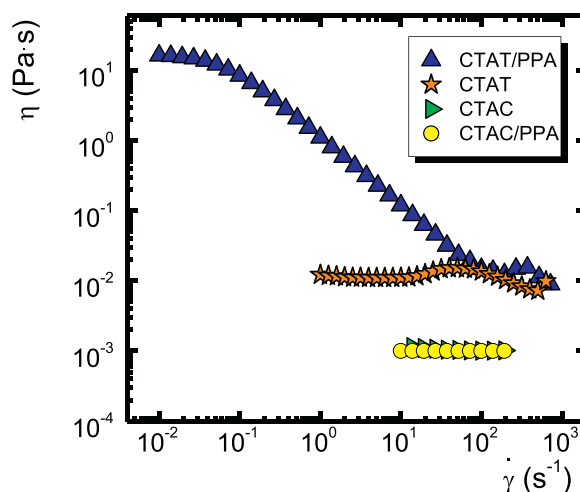


Fig. 2. Shear viscosity as a function of shear rate for pure surfactants and surfactant/PPA mixtures. [CTAC] = [CTAT] = 20 mM. [PPA] = 2 mM. $T = 25^\circ\text{C}$.

which rod-like micelles are produced (350 mM), hence, only spherical micelles are formed that do not induce any change in solvent viscosity. However, in the case of CTAT, the concentration evaluated is beyond its CRC (1.97 mM) [35] and even higher than the concentration at which worm-like micelles overlap (i.e., its semi-dilute concentration $\phi^* = 11 \text{ mM}$) [32]. Therefore, at 20 mM, the solution microstructure should be characterized by overlapping flexible worm-like micelles forming a tridimensional network. The CTAT shear thickening effect has been reported previously [34,36,44] and is attributed to shear induced structures (SIS). At high shear rates all flow induced structures are progressively destroyed and viscosity decreases.

From these results, it is evident that the presence of the tosylate ion in the CTAT favors the formation of worm-like micelles at very low surfactant concentration, provoking important changes in the rheological properties under shear flow. The ion tosylate belongs to the family of hydrotropes. In the presence of hydrotropes, surfactants show pronounced changes in their viscosity as a result of the micellar growth induced by electrostatic screening which leads to: (a) the formation of longer, more flexible and entangled micelles [22,24] or (b) a change from linear to branched micelles [45] or (c) an increase in flexibility of worm-like micelles [48].

The addition of 2 mM of a hydrotrope, i.e., PPA, to the CTAC solution (20 mM) does not produce any change either in its viscosity or in its rheological properties (see Fig. 2). On the other hand, Fig. 2 shows that when the same amount of PPA is added to a 20 mM CTAT solution, the rheological properties change remarkably, producing an increase in the low-shear rate viscosity of 3-orders of magnitude with respect to the neat 20 mM CTAT solution. The rheological changes provoked by the presence of PPA in the CTAT solution go beyond a mere increase in the viscosity, since the rheological curve is different from that measured in the neat CTAT solution. The CTAT/PPA mixture exhibits a pseudo Newtonian behavior at low shear rates followed by shear thinning in almost the whole range of shear rates evaluated. At very high shear rates (i.e., 300 s^{-1}), a small shear thickening effect is appreciated. The behavior presented by the CTAT/PPA in Fig. 2 resembles that of a more concentrated CTAT solution (see for instance, Calderón et al. [46] and Cuggino et al. [47]).

The rheological profile of the CTAT/PPA blend suggests that worm-like micelles have considerably grown due to PPA addition. Such micellar growth produces a higher entanglement density and a significantly higher viscosity at low shear rates, as compared to neat CTAT.

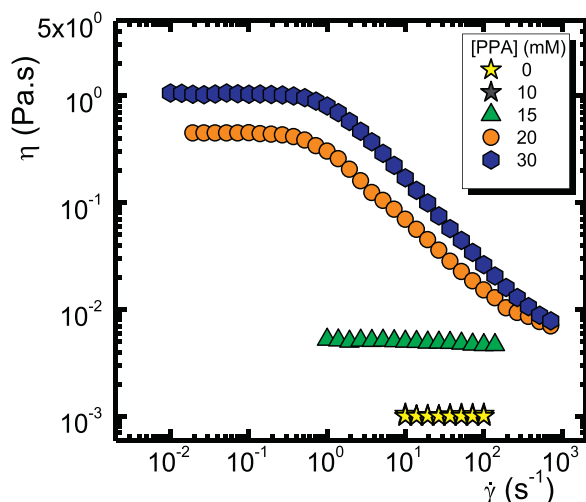


Fig. 3. Shear viscosity as a function of shear rate for CTAC/PPA system at different PPA concentrations. C_{CTAC} was kept constant at 20 mM. ($T = 25^\circ\text{C}$).

3.1.1. CTAC/PPA mixtures: effect of hydrotrope concentration

The rheological behavior of CTAC/PPA mixtures at different hydrotrope concentrations is shown in Fig. 3. It is evident that addition of PPA provides significant increases in viscosity to CTAC solutions with a constant concentration of 20 mM. It is possible to increase the viscosity up to three orders of magnitude, with respect to the pure surfactant, when a high amount of PPA is used (30 mM). This result suggests that the formation of worm-like micelles takes place and they are able to self-associate and interact with one another.

Despite the CRC for CTAC is very high (350 mM), the presence of PPA in the mixture promotes a transition from spherical micelles to rod-like micelles and, eventually, to elongated and flexible worm-like micelles at much lower surfactant concentration (C_{surf}). So that, at $C_{surf} \ll \text{CRC}$ (C_{surf} is 94% lower with respect to the CRC value), the addition of PPA increases the capacity of surfactant unimers to assemble. PPA decreases the CRC of the surfactant, and the overlap concentration ϕ^* , producing highly structured fluids with a pseudoplastic behavior at low surfactant concentration (i.e., 20 mM).

In the samples evaluated, it is important to notice that none of the CTAC/PPA mixtures exhibits the shear thickening effect observed in neat CTAT (20 mM) solution. This fact suggests that the mixed CTAC/PPA micelles formed are not sensitive to form structures induced by flow, and have a size that are not able to interact beyond their dimension in quiescent conditions. The shear thinning observed is produced by the destruction or interruption of the interactions between micelles.

Similar results have been reported for analogous systems of surfactant/hydrotrope mixtures, such as, CTAC with sodium salicylate (CTAC/NaSal) and CTAC with sodium para-halobenzoates [24,28] where the rheological changes observed were attributed to the transition from spherical to worm-like micelles. The hydrotropes can both adsorb on the micellar interface and penetrate into the micellar interior screening electrostatic repulsive forces between surfactant ionic heads in favor of micellization [48].

3.1.2. CTAT/PPA mixtures

A detailed study on the rheological properties of CTAT/PPA mixtures was also performed at different concentrations, in order to evaluate the interactions between hydrotrope and surfactant. It is well known that the rheological behavior of CTAT under shear flow depends on the surfactant concentration [47,49].

When CTAT concentration is lower than its CRC ($C_{CTAT} < 1.97 \text{ mM}$), the addition of PPA to the solutions does

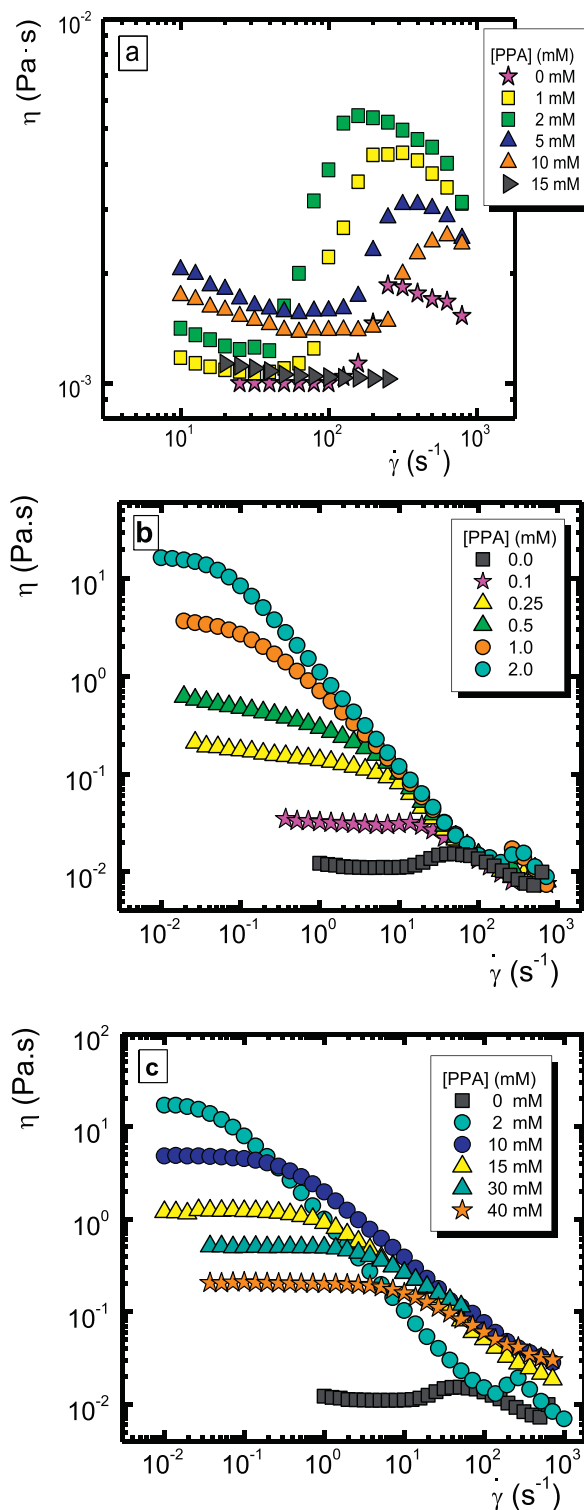


Fig. 4. Shear viscosity as a function of shear rate for CTAT/PPA mixtures at different PPA concentrations. CTAT concentration: (a) 5 mM, (b) and (c) 20 mM ($T = 25^\circ\text{C}$).

not produce any change on the rheological properties (results not shown). Nevertheless, at $C_{CTAT} \geq 2 \text{ mM}$ synergistic effects are observed. In Fig. 4a the rheological curves for CTAT/PPA are shown, for a concentration of CTAT that is slightly above its CRC, i.e., $C_{CTAT} = 2 \text{ mM}$. A complex behavior can be observed as a function of PPA concentration:

- The CTAT/PPA blends exhibit a behavior similar to neat CTAT at 2 mM. First, a Newtonian region at low-shear rates, then a shear thickening at intermediate shear rates and finally shear thinning at high shear rates.
- With increases in PPA concentration (from 0 to 2 mM), the viscosity at low-shear rates also increases and a decrease in the critical shear rate for shear thickening ($\dot{\gamma}_{c,st}$) can also be observed.
- When $C_{PPA} \geq 5$ mM, $\dot{\gamma}_{c,st}$ increases and the shear thickening effect decreases, eventually disappearing when $C_{PPA} = 15$ mM. At this PPA concentration, the solution exhibits a behavior identical to pure water.

When the CTAT concentration is increased to 5 mM or 10 mM, the effects of adding PPA are more pronounced. The information regarding CTAT/PPA mixtures with 5 mM and 10 mM can be found in the supplementary material (see Fig. S-1 and -2).

Increasing CTAT concentration in the CTAT/PPA aqueous solutions to values above the overlap concentration, i.e., $\phi^* = 11$ mM, causes even more significant synergistic effects. ϕ^* represents the crossover concentration between dilute and semi-dilute regime, above this concentration worm-like micelles entangle and form a transient network that breaks and re-forms constantly under shear [1,4,42]. Fig. 4b shows how the shear thickening effect disappears by the addition of only 0.25 mM PPA to a 20 mM CTAT solution. Samples exhibit a highly pseudoplastic behavior. The increase in the viscosity is about 3-orders of magnitude with the addition of just 2 mM of PPA, and the viscosity at low shear rates is higher than that of CTAT at a concentration of 30 mM (see Supplementary material, Fig. S-3). Similar results have been reported for CTAC/Sodium Salicylate [24], tetradecyltrimethylammonium bromide in the presence of sodium *p*-toluene sulfonate, sodium xylene sulfonate and sodium chlorobenzene sulfonate [19]. Hassan et al. observed a viscosity increase in sodium dodecyl sulfate/*p*-toluidine hydrochloride (SDS/PTHCl) system and attributed this behavior to the exponential growth of surfactant micelles promoted by the hydrotrope [22]. Nevertheless, the changes observed on the viscosity for the systems mentioned in the literature above are not very pronounced at the surfactant and hydrotrope concentrations used in this work. Although the literature reports an increase in the viscosity up to five orders of magnitude, the surfactant concentrations oscillate between 50 and 75 mM and the hydrotrope concentrations reach 100 mM, i.e. 50 times higher than in our CTAT/PPA system.

It is clear that PPA is able to promote important changes in the CTAT viscosity due to micelles growth and increases in aggregation number. The interaction between both species is maximum at a determined PPA concentration, after which a gradual reduction in viscosity and in shear thinning is produced. These results suggest the existence of a saturation effect on the interaction sites between hydrotrope and surfactant. In the case of the (20 mM/2 mM) CTAT/PPA mixture (Fig. 4b), the fluid is highly structured and the capacity of association between PPA and CTAT seems to be saturated and no further association can be produced when PPA is increased (Fig. 4c). In fact, increasing PPA reduces the viscosity of the mixtures (Fig. 4c).

The existence of an optimum CTAT/PPA ratio at which the interactions saturate may be attributed to a steric hindrance effect, one that would lead to the interaction of only a fraction of PPA with a specific amount of surfactant. Then further hydrotrope addition should not produce further viscosity increases.

Analogous drops in the viscosity of worm-like micelle forming structured surfactants, after a maximum viscosity value has been achieved, has been attributed to the formation of branched micelles which produces slip points between them allowing a faster structural relaxation [22,27,50,51]. Other scientific works suggest that this viscosity decrease may be due to a reduction in the size

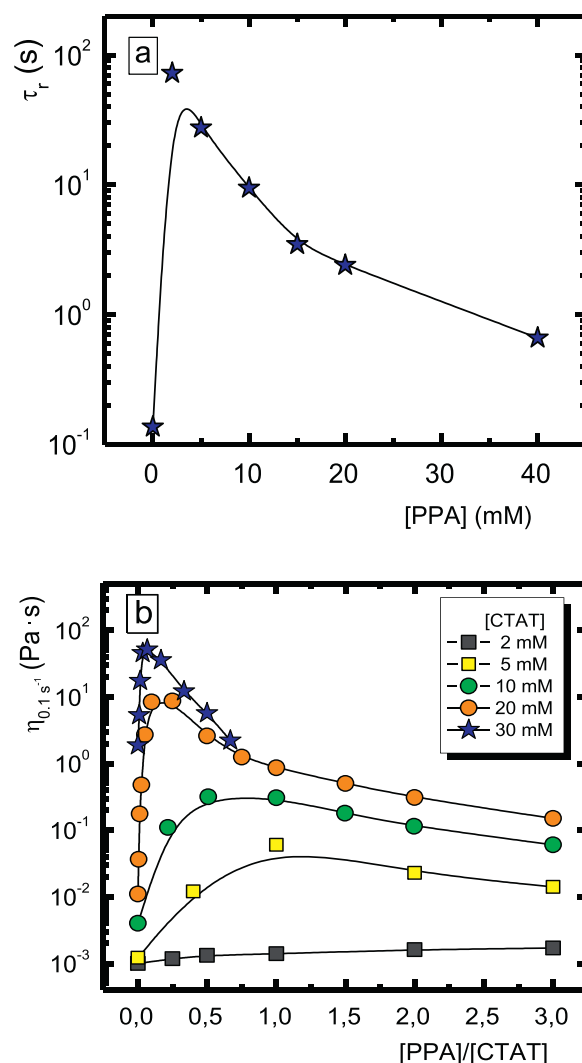


Fig. 5. (a) Relaxation time as a function of PPA concentration for CTAT/PPA mixtures. C_{CTAT} is fixed at 20 mM (b) Low-shear rate viscosity as a function of PPA/CTAT molar concentration ratio. C_{CTAT} fixed at: 2, 5, 10, 20 and 30 mM ($T = 25^\circ\text{C}$).

of the micelles [36,37] while others justify it by the increase in micelle flexibility and the poly-ionic nature of worm-like micelles in cationic systems [28,42].

From the data obtained in Fig. 4b and c, it is possible to calculate the longest relaxation time associated with the destruction of the worm-like micelles network. As observed previously, CTAT/PPA mixtures exhibit a Newtonian behavior at low shear rates followed by a shear thinning region. The onset of shear thinning occurs at a critical shear rate, $\dot{\gamma}_c$. The inverse of $\dot{\gamma}_c$ gives an estimate of the longest relaxation time of the micelles, τ_r , similar to that obtained in oscillatory shear.

Fig. 5a shows the variation of the relaxation time, τ_r , versus PPA concentration at a constant CTAT concentration of 20 mM. Notice that τ_r increases quickly up to 3-orders of magnitude at very low PPA concentration (2 mM) and then, decreases progressively in the whole concentration range evaluated. This result is very interesting since it shows how the addition of only 2 mM of hydrotrope is able to modify dramatically the dynamics of micellar association in this system and suggests the existence of a micro-structural change induced by PPA on CTAT micelles.

Addition of small amount of PPA to a 30 mM CTAT solution (see Supplementary material, Fig. S-3) leads to a synergy similar to the observed in Fig. 4b and c. Since, a CTAT solution with 30 mM con-

centration already presents a relatively high viscosity at low shear rates, viscosity increment is less pronounced compared to a starting solution of 20 mM CTAT. In this case, the increase on CTAT concentration implies a remarkably high level of interconnection of the formed network, so that, at higher surfactant concentration the fluid reaches the maximum entanglement density possible or the maximum level of interpenetration between the CTAT worm-like micelles therefore, PPA is not able to induce noticeable changes in the viscosity or in the rheological properties.

Fig. 5b shows a summary of the synergistic rheological effects observed for the CTAT/PPA system obtained by plotting the low-shear viscosity, in our case fixed at 0.1 s^{-1} ($\eta_{0.1\text{s}^{-1}}$), as a function of CTAT/PPA molar ratio, for the following CTAT concentrations: 2, 5, 10, 20 and 30 mM. Significant changes in viscosity are not only due to the addition of PPA but also to the effect of CTAT concentration on the synergy achieved. A balance between the initial entanglement density, or degree of structuration, provided by the CTAT concentration in the solution, and the amount of added PPA determines the final viscosity. Upon increasing the CTAT base concentration in the mixtures, the maximum in viscosity is reached at increasingly lower molar CTAT/PPA ratio. In other words, the amount of PPA needed to reach a maximum viscosity decreases as the initial entanglement density of the fluid is higher.

Oscillatory shear experiments were also performed and the results are shown in the Supplementary material (Fig. S-4). PPA addition causes an increment in the magnitude of elastic and viscous moduli, G' and G'' respectively. This result indicates that strong inter-molecular interactions between surfactant and hydrotrope are present, a fact that agrees with the results obtained under simple shear. The elastic modulus dependence with frequency is less pronounced and is closer to a gel-like behavior, where G' not only dominates but also is independent of the frequency applied.

3.2. Effect of pH on rheological behavior of CTAT/PPA mixtures

The interesting effects of changing the pH on the rheological properties of fluids based on worm-like micelles and other colloidal structures formed by cationic surfactants have been reported [1,2,52,53]. Fluids that vary their rheological behavior by changing pH have potential applications in different fields such as in sensors or microfluidic devices, among others [54]. Recently, Lin et al. [6] reported the effect of pH on CTAB/PPA mixtures and demonstrated that the low-shear rate viscosities of the solutions decrease sharply when pH increases. These effects are fully reversible by changing pH.

The rheological response of neat CTAT solutions at three different concentrations, i.e., 5, 10 and 20 mM as a function of pH variations was first studied (see Fig. S-5 in the Supplementary material and Fig. 6a). In fact, no prior reports in the literature were found in this respect.

Initial pH values for all CTAT solutions evaluated ranged between 6.9 and 7.4 depending on surfactant concentration. In all cases, low shear rate viscosities increase with pH (see Fig. S-5 in the Supplementary material). When $C_{\text{CTAT}} = 20 \text{ mM}$, the changes in the rheological properties of CTAT with increasing pH are very significant, as shown in Fig. 6a. At pH 9.1 the shear thickening effect that is characteristic of these CTAT 20 mM solutions disappears. Furthermore, at pH 10.4 a pronounced shear thinning behavior is observed in the entire range of shear rates evaluated, and the low shear rate viscosity is 2-orders of magnitude higher with respect to the original CTAT solution (i.e., at pH 7.0).

The pH in Fig. 6a is changed by adding KOH to the original CTAT/deionized water solution that has a pH 7. Therefore, it is envisaged that a high concentration of OH ions locate near the micelles surface reducing the repulsive forces between the charged hydrophilic groups of the surfactant (see Fig. 1). As a consequence

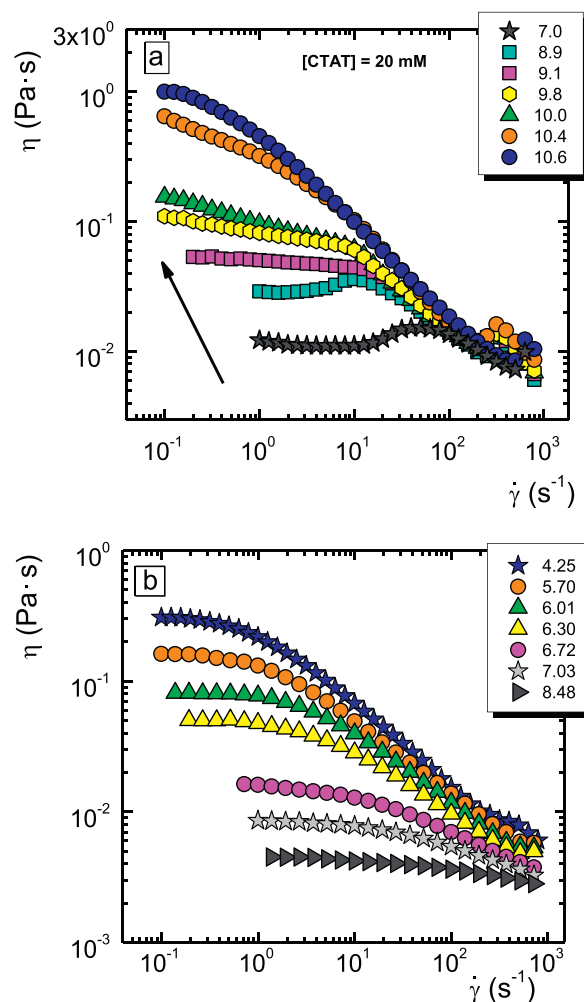


Fig. 6. (a) Effect of pH value on shear viscosity as a function of shear rate for 20 mM CTAT solutions. (b) Shear viscosity as a function of shear rate for CTAT/PPA (10 mM/10 mM) mixtures at different pH values (legend). $T = 25^\circ \text{C}$.

of this, surfactant aggregation is favored as well as the growth of worm-like micelles, inducing intermicellar interactions and the formation of a tridimensional network of interconnected long-range micelles, that leads to such significant increases in viscosity of the solutions. Mendoza et al., evaluated the viscoelastic behavior of 5 wt% CTAT solution at different NaOH concentrations and reported a deviation from Maxwell model at high frequencies, attributed to the electrostatic screening by OH ions that modifies the micelles curvature promoting their growth and increasing the entanglement density [55].

CTAT/PPA mixtures were evaluated at different pH values, surfactant concentrations and molar ratios. The most representative results are shown in Fig. 6b for 10 mM/10 mM CTAT/PPA mixtures at different pH values. Initially, the solution has a pH 4.25, and it exhibits a pseudoplastic behavior in the entire shear rate range evaluated. Increasing the pH leads to a progressive decrease in the low shear rate viscosities. This result is the opposite to the one observed for neat CTAT solutions, although encompassing a different pH range, and it is related to the nature of the interactions between CTAT and PPA, and to the ionization degree of the functional groups presents in the chemical structure of PPA (see Fig. 1). This hydrotrope has two carboxylic acid groups that can be ionized, depending on the pH. The $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ are 2.90 and 5.40, respectively [6]. When the $\text{pH} > \text{pK}_{\text{a}2}$ the carboxylic acid is deprotonated and the PPA hydrophilic character increases. As a result,

the association capacity between the CTAT and the PPA through electrostatic and hydrophobic interactions is disfavored. Presumably, as pH increases, PPA is gradually pushed by the ionic repulsion outside the CTAT micelles, thus preventing the electrostatic screening, perturbing micelles growth and their interaction. This change in micellar morphology can be observed by cryo-TEM experiments, as shown in the next section of the present work.

Lin et al. [6] have reported similar decreases in the viscosity of surfactant/hydrotrope solutions induced by increasing pH, for mixtures of cationic CTAB worm-like micelles and PPA. However, to the best of our knowledge, the interactions between CTAT and PPA and the effect of pH on this surfactant/hydrotrope pair have not been reported in the scientific literature. Since a small change on the pH or on the CTAT/PPA molar ratio is enough to modify dramatically the rheological properties of the solutions, a broad range of technological applications may be conceived.

3.3. Morphological study

Cryo-TEM studies were performed to correlate the rheological changes observed with the morphology of the surfactant and surfactant/hydrotrope micellar aggregates. Fig. 7 shows the morphologies for neat surfactant solutions at three different concentrations: 2, 10 and 20 mM. For CTAT = 2 mM, Fig. 7A and B, spherical micelles (pointed by short black arrows in A) coexist with stiff rod-like long micelles and some flexible micelles, loops, short micelles and in some cases it is possible to observe the end-capped micelles (long black arrows in B). Large spherical particles pointed by white arrows are contaminations with ice crystals.

Micelles radii (r_{mic}) determined by small angle neutron scattering (SANS) have been reported in the literature. Gámez-Corralles et al. [34] and Berret et al. [44] reported values of $r_{\text{mic}} = 20.6 \pm 0.5 \text{ \AA}$ for both 3.5 and 9 mM neat surfactant solutions (below ϕ^*) and Truong et al. [35] reported $r_{\text{mic}} = 21 \pm 0.4 \text{ \AA}$ for 11 mM. As it can be noticed, cross-sectional radii remain constant upon increasing surfactant concentration. Micellar length (L), on the other hand, changes with surfactant concentration, for example, $L = 155 \pm 5 \text{ \AA}$ for 3.5 mM and $L = 580 \pm 30 \text{ \AA}$ for 9 mM [41].

From our cryo-TEM measurements of the 2 mM CTAT sample (the solution is slightly above its CRC), the average micellar radius is $29 \pm 6 \text{ \AA}$ ($2.9 \pm 0.6 \text{ nm}$). Our cryo-TEM measurements are therefore in very good agreement with values determined by SANS [34,44]. Nevertheless, the micellar length observed by cryo-TEM is in the order of microns and some of them appear to be very stiff. We speculate that at $c = 2 \text{ mM}$ some micelles are very long and stiff for one of two possible reasons: (1) the system is highly diluted, and this allows micelles to grow without becoming flexible. A similar behavior has been reported by Liu et al. [56] when they observed the formation of rigid and long cylindrical micelles by cryo-TEM upon dilution for the system methacryloyloxyundecyltrimethylammonium bromide (MUTB) and the hydrotropic salt sodium tosylate (TSNa); or (2) during sample preparation, micelles are submitted to large deformation rates during the blotting process, and this may cause micellar growth.

When $C_{\text{CTAT}} = 10 \text{ mM}$, Fig. 7C, micelles become more flexible with an increase in number. At $C_{\text{CTAT}} = 20 \text{ mM}$, Fig. 7C depicts highly interpenetrated worm-like micelles which form a very dense network. Patel et al. [57] reported for a $C_{\text{CTAT}} = 20 \text{ mM}$ solution some cryo-TEM results where short micelles, loops and flexible micelles can be seen. Similar morphology was observed in some regions of our micrographs (results not shown). However, the most representative structures seen at this CTAT concentration are those depicted in Fig. 7D, where the flexible worm-like micelles form a dense network. In fact, such a dense network is expected on the basis of the rheological behavior depicted in Fig. 2.

The transition observed in these micellar aggregates from stiff micelles (rod-like micelles) to elongated and flexible ones (worm-like micelles), which eventually overlap and form an interconnected network, is consistent with the synergy and changes observed in the rheological properties under simple shear. Additionally, the microstructural changes in CTAT solutions correspond with the increase in viscosity with surfactant concentration reported above.

The effect of PPA on CTAT micellar morphology was also investigated. Fig. 8A and B depicts micrographs for CTAT/PPA at two different molar ratios, with $C_{\text{CTAT}} = 2 \text{ mM}$. As it can be seen, the addition of only 1 mM of PPA to a CTAT solution of 2 mM promotes a substantial increase in micellar flexibility and greater interconnection between them, resulting in a higher degree of structure in the fluid. The results shown in Fig. 8A evidence that the formation of structures induced by flow can take place at lower shear rates, as observed in the rheological measurements (see Fig. 4a).

When the PPA content is increased to 10 mM in the CTAT/PPA mixture ($C_{\text{CTAT}} = 2 \text{ mM}$), Fig. 8B shows the formation of smaller structures that could explain the changes observed in the rheological profile for this solution, i.e., a decrease of the shear thickening effect and the low-shear rate viscosities (see Fig. 4a).

For CTAT/PPA, 10 mM/ 10 mM at the original pH value of 4.25, an increase in micellar size and in their flexibility is observed as compared to the neat surfactant solution at the same concentration; see Fig. 8C. For the sample CTAT/PPA (10 mM/10 mM) at pH 8.11 cryo-TEM results show structures with smaller size, Fig. 8D, that could be related with the decrease in viscosity (see Fig. 6b).

3.4. NMR results

^1H NMR spectra were recorded in D_2O for neat CTAT and PPA and for the mixture CTAT/PPA, 10 mM/10 mM (it corresponds to the solutions evaluated in Figs. 6a, 7C and S-2). Fig. 9 depicts the spectra at three different pH values. All protons were assigned. Signals at 4.86 and 0.0 ppm correspond to the solvent (D_2O) and to the internal standard, 3-(trimethylsilyl)-propionic acid- d_4 (TSP), respectively.

No significant changes were observed in the chemical shift for CTAT protons under pH variation. For pure PPA there is a chemical shift upfield of protons H1 and H2 when increasing pH values. If $\text{pH} > \text{pK}_{\text{a}2}$, i.e., >5.4 , both carboxylic groups are deprotonated and H1 protons are more protected.

Under the mixture of both CTAT and PPA, in the sample CTAT/PPA (10 mM/10 mM), three scenarios are displayed:

- pH 2: Protons H2 are shifted upfield as compared to the chemical shift of neat PPA at the same pH. According to the literature [29,58], this might indicate that they are located within the micelle interior. On the contrary, protons H4 displaced downfield indicating that tosylate ions are moving away from the micelle interface, i.e., headgroups, to allow the incorporation of PPA inside the micelle.
- pH 4 (and at original pH 5.5): Protons H1 shifted downfield, in a similar way to H4. This suggests that tosylate ions continue moving away from the micelle head group but now the hydrotrope is moving out of the micelle, at a distance of the counterion. The evidence that hydrotrope is inside the micelles or is interacting with the tosylate group, by electrostatic and/or hydrophobic associations, explains the high viscosity observed at low pH values (see Fig. 6b).
- pH 8: protons H3 and H_d are shifted downfield. It indicates that they are more exposed to the solvent since they changed from an apolar to polar environment, interacting with the surfactant headgroups. Also protons from the headgroups, H_e , presented a chemical shift downfield. PPA signals practically remained

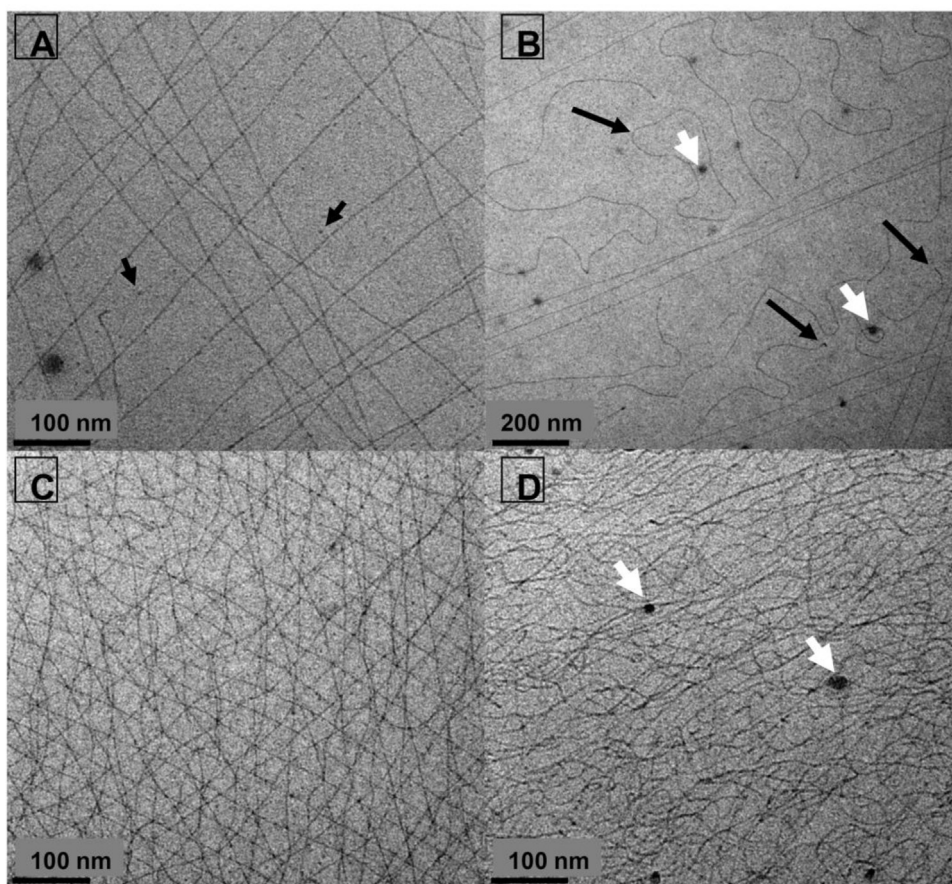


Fig. 7. Cryo-TEM for neat surfactant, CTAT; aqueous solutions at (A, B) 2 mM; (C) 10 mM and (D) 20 mM. White arrows indicate contaminations with ice crystals.

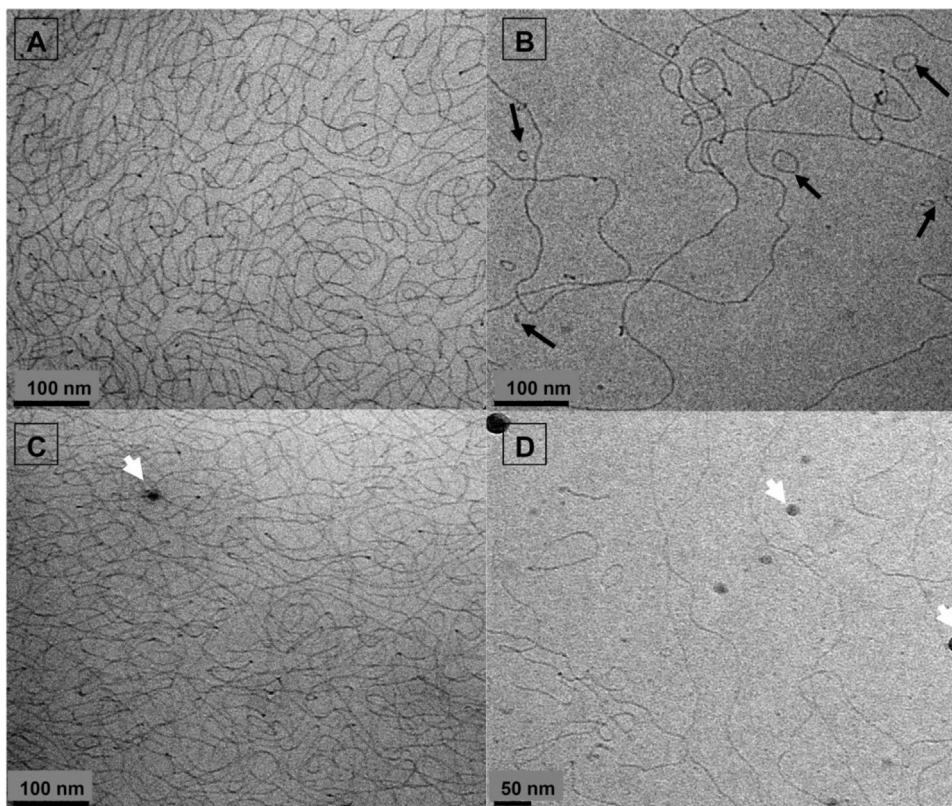


Fig. 8. Cryo-TEM for CTAT/PPA mixtures (A) CTAT/PPA (2 mM/1 mM); (B) (2 mM/10 mM); (C) CTAT/PPA (10 mM/10 mM, pH 4.25); and (D) CTAT/PPA (10 mM/10 mM, pH 8.11). White arrows indicate contaminations with ice crystals.

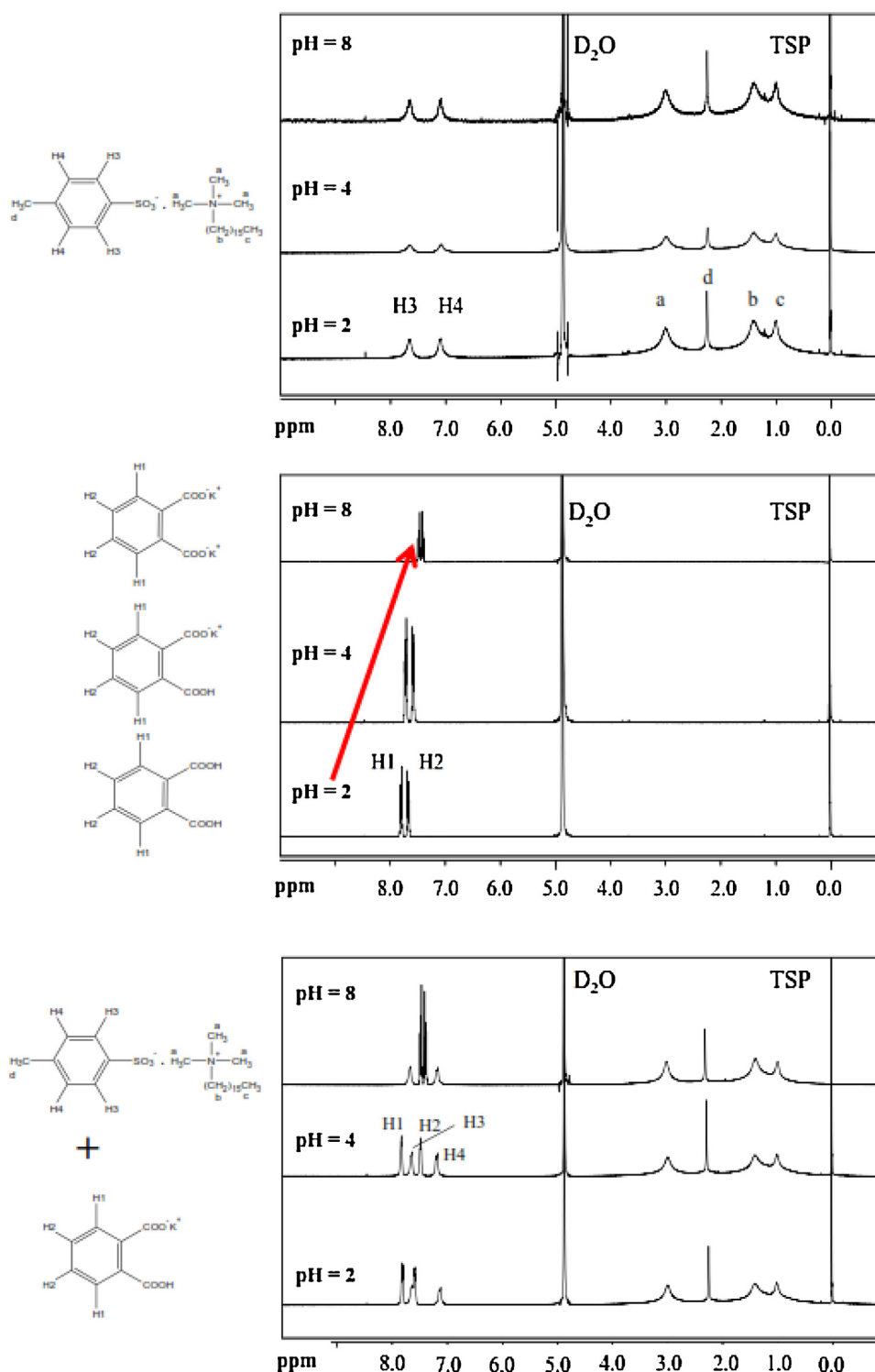
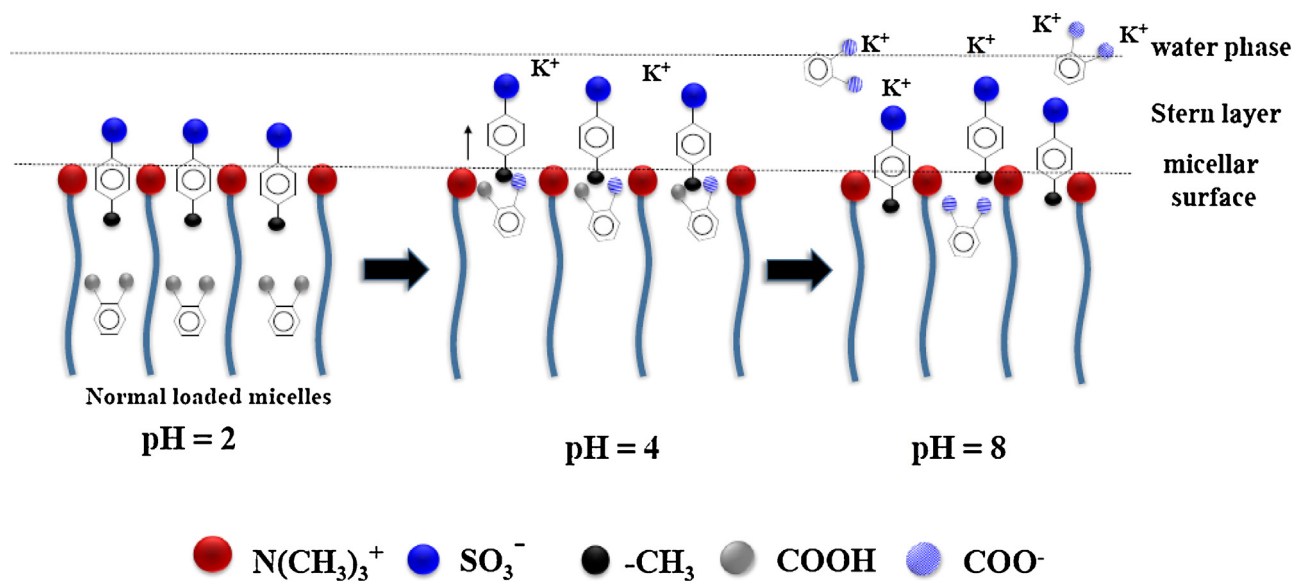


Fig. 9. ^1H NMR spectra for neat CTAT and PPA and for the mixture CTAT/PPA, 10 mM/10 mM at three different pH values.

unchanged in presence of CTAT with respect to the neat PPA sample at the same pH value. These results indicate that PPA is not interacting with surfactant micelles since both carboxylic groups are deprotonated and the molecule becomes more hydrophilic, as proposed by Lin et al. [6] and might justify why viscosity drops for CTAT/PPA systems when pH increases (Fig. 6b). This is also in agreement with the morphological behavior observed in cryo-TEM micrographs (Fig. 8C and D).

NMR observations are summarized in Scheme 1. At pH 2 CTAT micelles contain PPA molecules within them and they are labeled “normal PPA-loaded micelles” in the scheme. The tosylate ions are located at the micelle surface in this case (pH 2). When pH 4, one of the PPA carboxylic acid groups is ionized and as a consequence, the hydrotropes are now at the interface and the tosylate ions move away from the surfactant headgroups. Increasing the pH even more leads to complete ionization of PPA (both COOH groups are now



Scheme 1. Schematic representation of micelle-PPA interactions.

COO^-) and they move out of the micelles locating either in the Stern layer or in water phase.

4. Conclusions

In the present work, interactions between CTAT and PPA have been investigated. PPA addition leads to a remarkable increase in low-shear rate viscosity since it promotes a higher entanglement density of the worm-like micelles of CTAT.

The rheological response of neat CTAT solutions depends strongly on pH variations. As pH increases with KOH addition, low shear viscosity increases, shear thickening disappears and the solution becomes shear thinning. This is a result of OH ions locating near the micelles surface reducing the repulsive forces between the charged hydrophilic groups of the surfactant. Thus, surfactant aggregation is favored, as well as the growth of worm-like micelles, leading to the formation of a tridimensional network.

Increasing the pH of CTAT/PPA mixtures leads to a progressive decrease in the low-shear rate viscosities. This result is opposite to the one observed for neat CTAT solutions and it is related to the nature of the interactions between CTAT and PPA, and to the ionization degree of the functional groups presents in the chemical structure of PPA.

The microstructural changes experienced by CTAT upon PPA addition were monitored by cryo-TEM and ^1H NMR. The results are in good agreement with the rheological measurements, evidencing that microstructural changes are induced by either surfactant, PPA concentration and/or pH changes. The results presented here show that pH responsive viscoelastic fluids can be easily formulated by mixing CTAT and PPA, and it opens up the possibility of designing stimuli responsive smart materials for specific applications.

Acknowledgements

The USB team would like to acknowledge funding by “Decanato de Investigación y Desarrollo” of Simon Bolívar University, DID, through its research groups funding scheme (DID-G-02, Grupo de Polímeros 1) and research assistant scholarship for Miss Karolaine Silva.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2015.10.054>.

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