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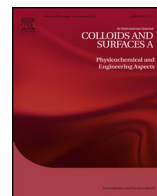35 PUBLICATIONS   401 CITATIONS

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Effects of some anions of the Hofmeister series on the rheology of cetyltrimethylammonium-salicylate wormlike micelles

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HIGHLIGHTS

- Salt complex of CTASalicylate was prepared and well characterized.
- Rheology of wormlike micelle with anions of the Hofmeister's series was determined.
- The Hofemeister's series is obeyed.
- The rheological and SAXS results are in agreement.

GRAPHICAL ABSTRACT
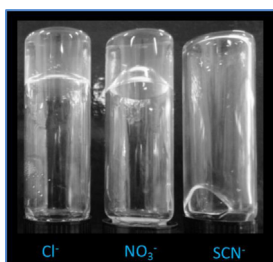
ABSTRACT

The linear viscoelasticity of systems formed with cetyltrimetylammonium salicylate (CTASal) was investigated. This system is interesting because this complex salt forms wormlike micelles (WLM), in which the aromatic ring of salicylate threads into the micelle palisade. The chains of WLM of CTASal have excess of positive charge and, in the semi-dilute regime, form systems with very long relaxation time. However, the relaxation time become short when salt is added. The effect of NaCl, NaBr, NaNO₃, NaSCN and NaSalicylate, on CTASal solutions was investigated by using rheology and SAXS. The systems in the presence of salts present shorter relaxation times due to the charge neutralization associated with the adsorption of the anions on the micelles surface. The magnitude of the effect depends on the nature of the anions, which follows the Hofmeister series.

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1. Introduction

Their remarkable tunable viscoelastic characteristics have led wormlike micelles, WLM, to be exploited to large number of applications. In the semi-dilute regime, the WLM chains entangle, forming viscoelastic systems useful to be used from cosmetic and pharmaceutical products to oil exploration fields [1–3]. In dilute regime, WLMs promote large hydrodynamic drag reduction, saving energy to pump water for long distances [4,5]. The non-covalent nature of WLMs is unique in this case, because, contrary to polymeric agents, they are immune to undergo mechanical degradation at high shear rates [6].

According to Lerouge and Berret [7], the first description of the micelle growing can be found in the pioneer work of Debye and his group [8] during the investigation of their dissymmetry by light scattering. They observed that addition of KBr to cetyltrimethylammonium bromide, CTAB, induced a transition from spherical to rod-like aggregates.

Usually, the growth of micelles takes place at high concentration of inorganic ions. This is because the screening of the electrostatic charges leads to favor decreasing in the micelle curvature, forming long cylindrical structures. However, for cationic surfactants, this

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growth can be induced in dilute regime with addition of aromatic anions, such as salicylate. The association is usually very strong due to the incorporation of the aromatic ring at the micelle palisade [9–11].

In semi-dilute regime, the entanglements of the WLM chains produce remarkable viscoelastic properties and unique rheological behavior since the micelles break and reform within a characteristic lifetime [12]. For this reason, they were referred to as 'living polymers' by Cates and Candau to describe their linear rheological behavior [13]. According to this model, two dynamic processes coexist (reptation and breaking) where each of them present a specific relaxation time, λ_{rep} and λ_{break}, respectively. When $\lambda_{break} \ll \lambda_{rep}$, the stress relaxation is described by a unique relaxation time (Eq. (1)):

$$\lambda = (\lambda_{break}\lambda_{rep})^{1/2} \tag{1}$$

The storage and loss moduli, G' and G'', respectively, are described by the Maxwell model, according to Eqs. (2) and (3), being ω the frequency of the oscillation:

$$G' = \frac{G_0\omega^2\lambda^2}{1+\omega^2\lambda^2} \tag{2}$$

$$G'' = \frac{G_0\omega\lambda}{1+\omega^2\lambda^2} \tag{3}$$

The viscoelastic properties of some WLM systems can be tuned by light [14,15], pH [16] and addition of hydrophobic solute [17]. Therefore, this is an interesting system in which macroscopic properties can be switched via simple molecular triggers [18].

Particularly, we are interested on the effects of anions with different nature on the rheology of WLM. In this sense, WLM formed by cetyltrimethylammonium salycilate, CTASal, was used as a reference to investigate the effect of some anions of the Hofmeister's series. The series: $F^- \approx SO_4^{2-} > HPO_4^{2-} >$ acetate $> Cl^- > Br^- > NO_3^- > ClO_4^- > SCN^-$, was proposed by Franz Hofmeister (in 1888) according to their crescent ability to precipitate egg-white proteins [19]. Ions on the left of Cl^- reduce the solubility of proteins by inducing their crystallization and are called salting-out ions, water-structures-makers or cosmostropic ions. The opposite is observed for ions on the right of Cl^-, known as salting-in, water-structure-breakers or chaotropic ions [20,21].

WLMs of CTASal at low ionic strength present excess of positive charges at their surface. The adsorption of anions on the micelles surface reduces the electrostatic repulsion and changes the rheology of the systems. Based on this aspect, the present study describes the effects of the ions Cl^-, Br^-, NO_3^-, SCN^- and even Salicylate, Sal^-, on solutions formed by CTASal. The characteristics of these systems were investigated by using oscillatory rheology and their microstructure was probed by small-angle X-ray scattering (SAXS) measurements. The results correlate with the Hofmeister series, with important implications to tune viscoelastic properties of WLMs formulated with cationic surfactants and salicylate.

2. Experimental

2.1. Materials

CTAB and the sodium salts: bromide, chloride, nitrate, thiocyanate and salicylate were obtained from Sigma–Aldrich and used without previous purification. Ultra-pure water milli-Q (18 MΩ cm) was used in the preparation of the solutions.

2.2. Methods

2.2.1. Sample preparations

CTASal was synthesized using the protocol described by Svensson et al. [22]. Firstly, CTAOH was obtained from CTAB through an ion exchange process (by using Dowex monosphere 550A (OH) anion exchange resin – Sigma–Aldrich). Finally, CTASal was obtained by titration of CTAOH with salicylic acid (Sigma–Aldrich). Mass spectrometry (Mass Spectrometer GC/MS HP 5970A) and elemental analyses (Perkin Elmer 2400) were used to characterize CTASal. Eventual excess of bromide was verified by mixing solutions of CTASal with AgNO$_3$. Details of these experimental characterizations are available in the Supporting Information. Solutions of WLM were prepared by gravimetry (±0.0001 g).

2.3. Rheological measurements

Oscillatory experiments were conducted on a Haake RS1 rheometer equipped with a water bath and plate-plate sensor (35 mm diameter and 1 mm gap). A tension of 3 Pa was applied (within the viscoelastic linear range). The temperature was kept at $(25 \pm 1)°C$ by using a thermostatic bath.

2.4. Small angle X-ray scattering (SAXS)

SAXS experiments were performed at the Brazilian Synchrotron Light Laboratory (LNLS), Campinas, Brazil, using a detector-to-sample distance of 1.54 m and an X-ray wavelength of 1.55 Å. The samples were injected at room temperature into the sample holder and kept at $(25 \pm 1)°C$ by means of an external circulating bath.

3. Results and discussion

The results for shear oscillatory studies of pure CTASal solutions at different concentrations are shown in Fig. 1. In the concentration range between 25 and 300 mmol L^{-1}, the elastic moduli, G' (Fig. 1 – left), are always higher than the correspondent viscous moduli, G'' (Fig. 1 – right), and G' is practically constant in the studied frequency range. The solutions of CTASal behavior have very long relaxation times, which cannot be experimentally determined with the present experimental set up.

In order to interpret this result, the dynamic of WLM's was considered. The individual micellar relaxation times for reptation and breaking are given respectively by the following scaling laws [23]:

$$\lambda_{rep} \sim \bar{L}^3 C^{3/2} \tag{4}$$

$$\lambda_{break} \sim \frac{c}{L} \tag{5}$$

The combination of Eqs. (4) and (5) gives rise to $\lambda \sim \bar{L}$. Therefore, large values of λ should be explained by very long WLM (large L values). Conversely, if the micelles possess excess (positive) charge density, they maintain the chains stiffed, such as polyelectrolytes, explaining the solid-like behavior. The second supposition is more plausible because only a fraction of salicylate threads into the micelle palisade.

Fig. 2 shows the variation of G_0 as a function of the CTASal concentration, in which the values of G_0' were measured at the frequency = 1 s^{-1}.

According to Fig. 2, there is a linear correlation between $\log G'$ and $\log [CTASal]$, in which $G_0 \propto [CTASal]^2$. This result partially agrees with the prediction of the Scaling Law, in which in the entangled regime, the properties of wormlike micelles depends only on the surfactant concentration as $G_0 \propto [surfactant]^{2.25}$ and not on their average length.
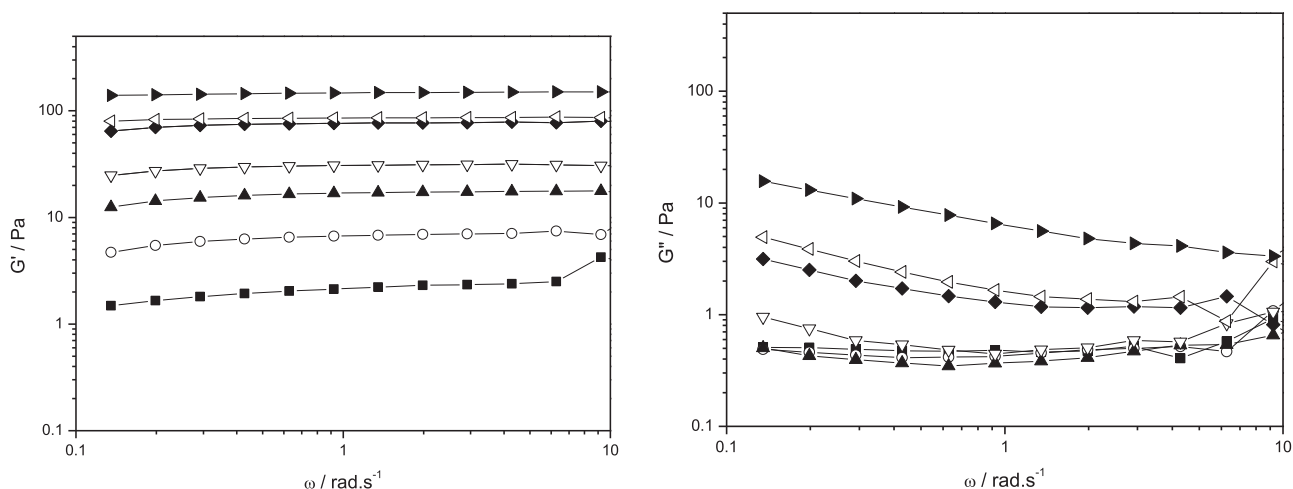
Fig. 1. Angular frequency dependence of storage, G' (at left), and loss, G'' (at right) moduli, for CTASal in different concentrations (mmol L^{-1}): ■ 25, ○ 50, ▲ 75, ▽ 100, ♦ 150, ◁ 200 and ▶ 300. The lines were used to facilitate the visualization.
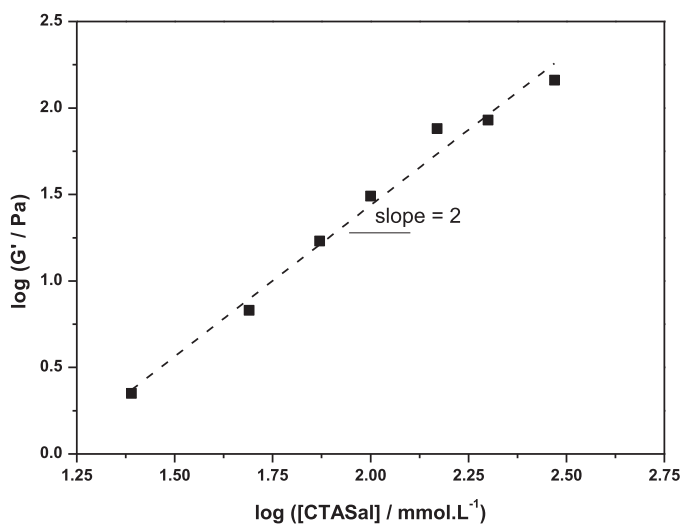

Fig. 2. Dependence of G' as a function of concentration for CTASal, at 25 °C. The G_0' values were taken at angular frequency of 1 s^{-1}.
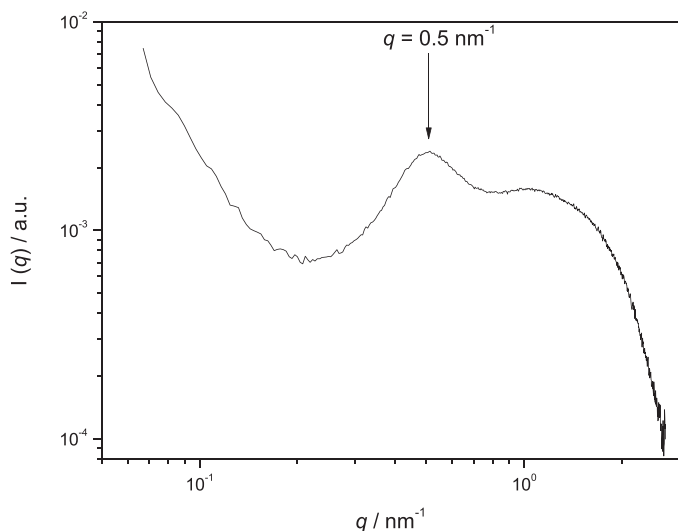

Fig. 4. Flow caused by the gravitational field for systems of CTASal 200 mmol L^{-1} and 70 mmol L^{-1} of: NaCl, NaNO$_3$ and NaSCN, respectively for the vials from left to right.

The network mesh size (ξ), can be correlated with the degree of chain entanglements, according to Eq. (6) [13]:

$$G_0 = \frac{k_B T}{\xi^3} \qquad (6)$$

Therefore, assuming $G' = G_0 \cong 90$ Pa, the system with 200 mmol L^{-1} of CTABSal presents mesh size estimated as $\xi \cong 40$ nm.

In order, to investigate the internal structure of the system containing 200 mmol L^{-1} of CTASal, SAXS experiments were carried out. The scattering patterns shown in Fig. 3, reveal a broad correlation peak at $q = 0.5$ nm^{-1}, which is associated with an inter-particle structure factor corresponding to a correlation distance of ca. 13 nm. This structure factor is common in the cases of strong repulsive interaction, as it is expected in the case of WLM of CTASal.

The CTASal solutions at this concentration are not birefringent under quiescent state. Therefore, we infer that the correlation distance of 13 nm is associated with small domains, in which the WLM
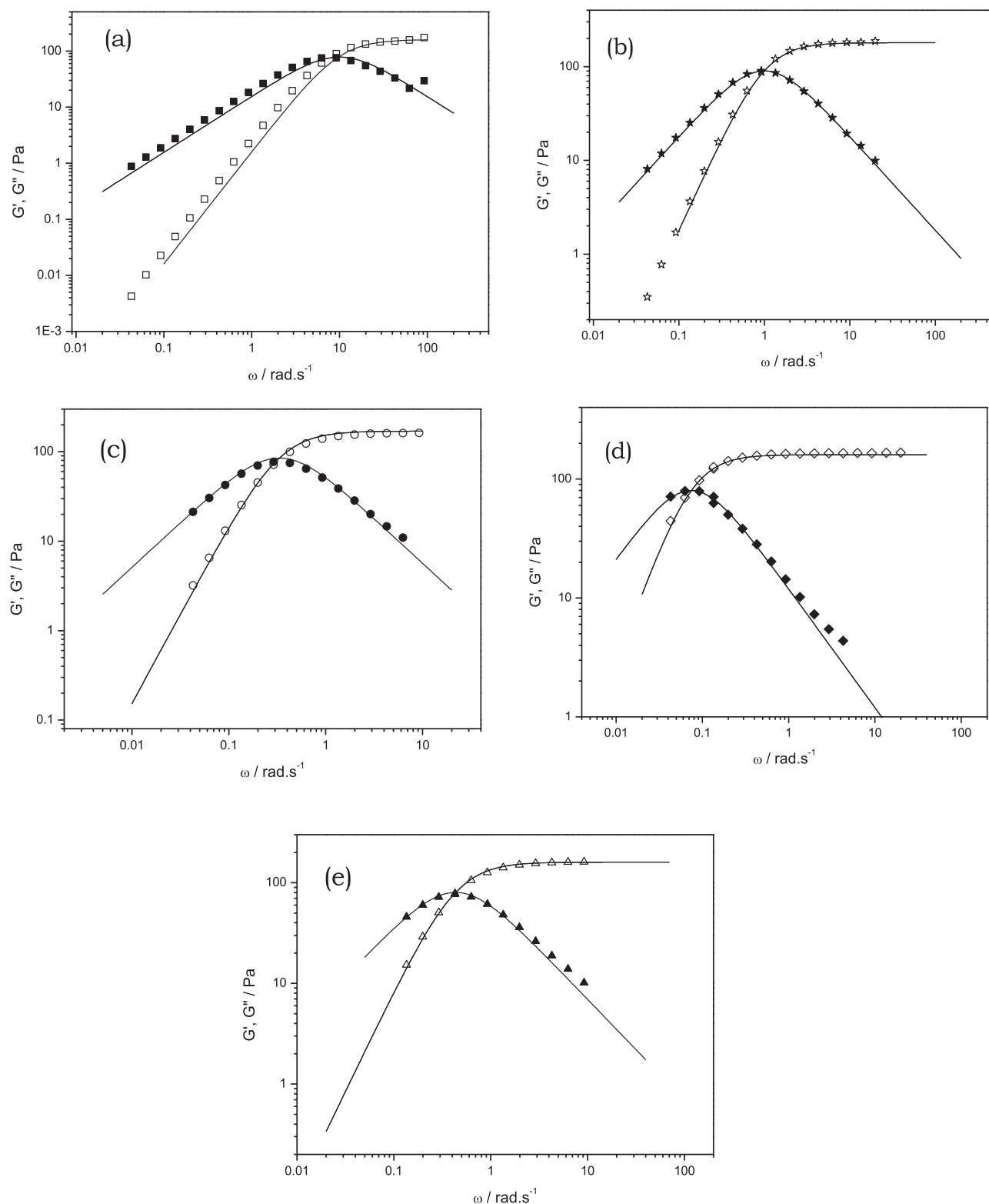

Fig. 3. SAXS curves for CTASal 200 mmol L^{-1}. The arrow indicates the correlation peak at $q = 0.5$ nm^{-1}.

Fig. 5. Angular frequency dependence of storage (G') and loss (G'') modulus for CTASal 200 mmol L^{-1} and 70 mmol L^{-1} of: (a) NaSCN; (b) NaSal; (c) NaNO$_3$, (d) NaCl and (e) NaBr. Solid lines represent fits to Maxwell's model.

chains are partially orientated. The correlation distance of 13 nm value is approximately three times lower than the mesh size estimated by Eq. (6).

If the interpretation for the structure of the CTASal system is correct, the addition of salts should promote the screening of electric charges at the micelle surface, leading to more flexible micelles. Consequently, shorter relaxation time should be observed.

The effect of addition of different salts on the rheology of CTASal is clearly demonstrated in the comparative pictures shown in Fig. 4. The vials containing 200 mmol L^{-1} CTASal with 70 mmol L^{-1} of NaCl, NaNO$_3$ or NaSCN, were inverted and the picture was taken
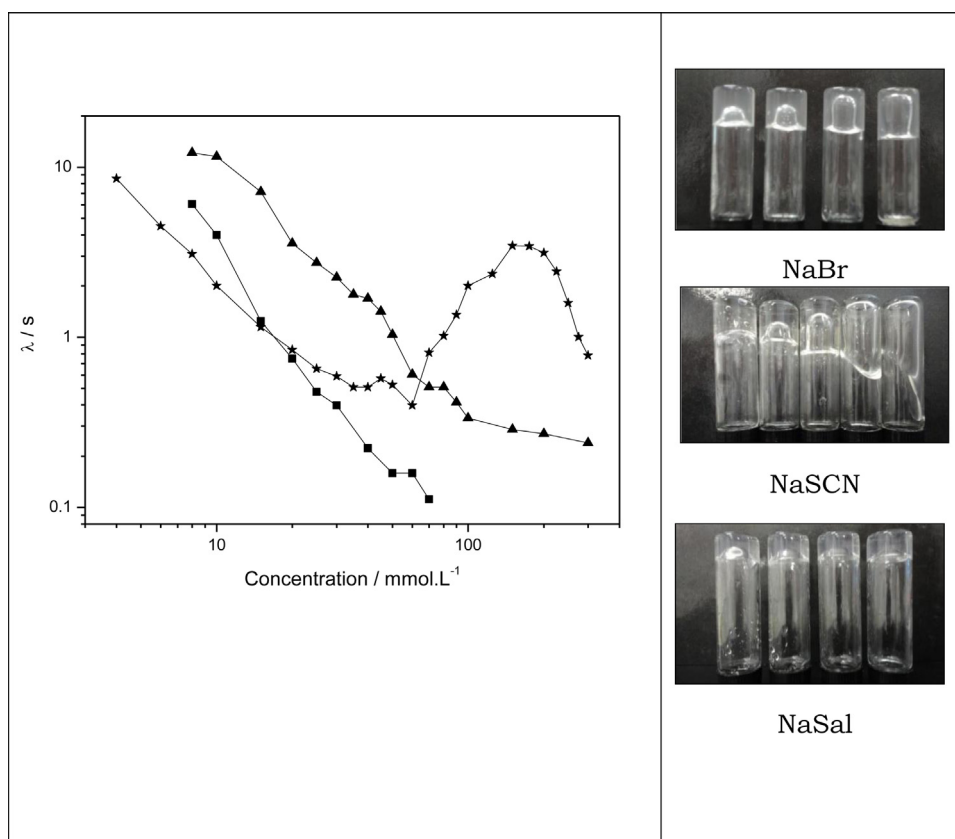
Fig. 6. The relaxation time (λ) for solutions of CTASal 200 mmol L^{-1} and with different concentration of salts: ▲ NaBr, ■ NaSCN and ★ NaSal. The lines were used as guide for the eyes. The photos at right compare the vials of the systems containing crescent amounts of: NaBr (60, 70, 80 and 90 mmol L^{-1}); NaSCN (10, 20, 30, 40 and 50 mmol L^{-1}); NaSal (60, 70, 80 and 90 mmol L^{-1}).

20 s after inversion. It can be noticed that under gravitational force, the flow of the systems increases, but it clearly depends on the nature of the added anion.

Shear oscillatory behaviors of the samples present in Fig. 4 and also for NaSal and NaBr, were obtained and the results are shown in Fig. 5. The effect of the salts is notable in all cases. The systems shown short relaxation time and their rheological behavior can be precisely described by the Maxwell model (Eq. (2) and (3)). Table 1 presents the characteristic parameters G_0 and λ, obtained from the fitting to the Maxwell's model, which were used to compare the effect of each salt.

According to Fig. 5, the relaxation times are quite sensitive to the nature of the anion. However, as expected, the values for G_0 are practically the same for all CTASal systems (with or without salt). This is because, for a fixed concentration of CTA$^+$ (200 mmol L^{-1}), G_0 depends only on the surfactant concentration ($G_0 \propto [surfactant]^{2.25}$). The following decreasing trend for λ is observed: Cl$^-$ > NO$_3$$^-$ > Br$^-$ > Sal$^-$ > SCN$^-$, which is interpreted as the crescent order for anion adsorption at the WLM surface. This order practically agrees with the one predicted in the Hofmeister

series, which is: Cl$^-$ < Br$^-$ < NO$_3$$^-$ < Sal$^-$ < SCN$^-$ [19,20,24]. However, Sal$^-$ is a special case, due to the threading of the aromatic ring into the micelle.

The understanding of the correlation between the effects of the Hofmeister anions on WLM of CTASal and the breaking-reptation mechanism is an interesting point to be investigated.

The study was extended for different concentrations of NaSal, NaBr and NaSCN by fixing the concentration of CTASal at 200 mmol L^{-1}. The relaxation times for the correspondent solutions were obtained and the values were plotted as a function of the respective salt concentration (Fig. 6). The pictures of the vials, in addition the plot, highlight comparative flows of the systems driven by the gravity.

The concentrations of the salts were chosen based in some regions of interest. For solutions containing NaBr and NaSCN, λ decreases abruptly when the salt concentration is increased and become almost constant at higher salt concentrations. However, the effect is clearly more intense for NaSCN. For this salt, the study is limited to the concentrations around 70 mmol L^{-1}. Above this concentration, some phase separation is observed, which is attributed to the charge neutralization of the WLM chains. For the systems containing NaSal, a more complex result is observed. A sharp decreasing of λ followed by a minimum at 60 mmol L^{-1} is obtained. However, above this concentration, λ increases, reaching maximum value around 170 mmol L^{-1}, and finally, decreasing again.

The rheological trend can be clearly observed in the pictures for the system containing the three salts in selected concentration ranges. It can be highlighted that for the vials containing NaSal, the gravitational flow becomes slower again when the salt concentration ranges from 60 to 90 mmol L^{-1} (pictures

Table 1
Comparative values for G_0 and λ obtained from the fitting of rheology data to Maxwell's model for solutions of CTASal 200 mmol L^{-1} and 70 mmol L^{-1} of different salts.

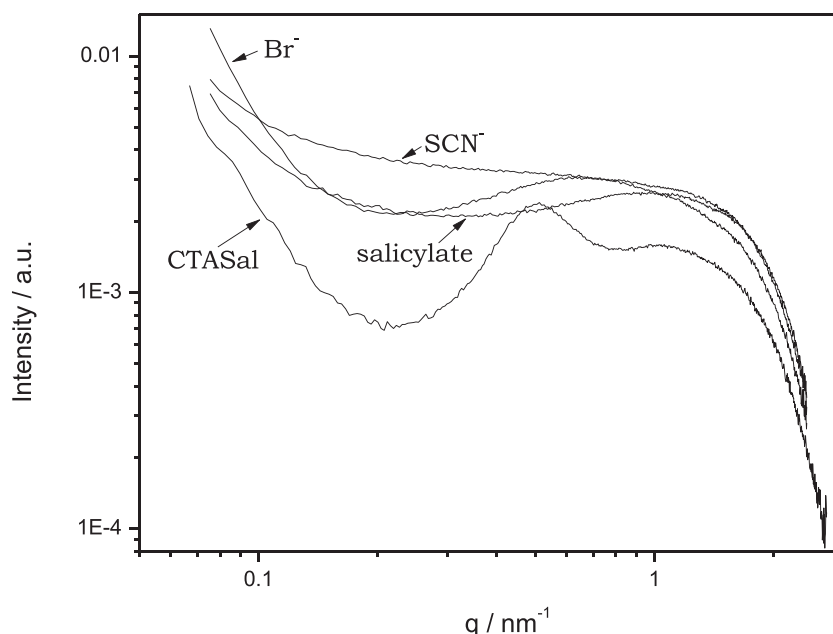| Salt	G_0 (Pa)	λ (s)
NaSCN	161	0.1
NaSal	184	1.0
NaBr	159	2.3
NaNO$_3$	160	3.0
NaCl	164	13.3

Fig. 7. SAXS curves for: 200 mmol L^{-1} CTASal and with: 50 mmol L^{-1} of NaSal, NaBr or NaSCN.

for CTASal with NaSal for all concentration ranges are available in Supplementary Information). A similar rheological trend was observed by Hoffmann et al. [25,26] for systems containing cetylpyridinium and salicylate. Additionally, Olsson et al. [27] have determined in NMR experiments, changes on the correlation time for the motions of CTASal chains when concentration of NaSal is increased. We infer that the interpretations of these previous authors are useful to explain the rheological results for the relaxation time of CTASal with NaSal. The threading of salicylate into the micelle palisade leads to the screening of the positive charge. At the minimum value of λ, when the extra NaSal concentration is 60 mmol L^{-1}, the surface charge is neutralized. At this stage, even with the charge neutralization, the surfactant cannot be salted out due to the specific binding behavior of salicylate. Beyond this concentration, more aromatic anions are incorporated into the micelle palisade and the micelle surface become negative leading to a new increase of λ.

The adsorption of the anions (commonly referred to as ions condensation) [28] around the WLMs of CTASal was investigated by SAXS and the results are shown in Fig. 7. The SAXS curves for CTASal 200 mmol L^{-1} with 50 mol L^{-1} of NaBr, NaSal or NaSCN were obtained at this specific concentration since, according to Fig. 6, this is the situation around the minimum for the relaxation times for the solutions containing the salts. The peak observed at 0.5 nm^{-1} for the CTASal is indeed, no longer observed for the systems containing NaSal and NaSCN. However, for CTASal with NaBr, a small shoulder at $q = 0.5$ nm^{-1} is still present. The disappearance of the peak is associated with the decreasing of the Debye screening length, because the charge screening reduces the extension of the short-range order between the micelles [28,29]. This microscopic result presents good correlation with the rheological observations.

4. Conclusions

The present study demonstrates that the rheological behavior of CTASal solutions is strongly affected by addition of salts (NaCl, NaBr, NaSal and NaSCN) leading to a transition from long to short relaxation time. Therefore, the rheological properties of the WLM of CTASal can be tuned by using salts with different anions and at different concentrations. It was demonstrated that the Hofmeister series is obeyed. However, salicylate is a special case due to the threading of the aromatic ring into the micelle palisade. Its effect on the rheology is explained by the condensation of the anions on the positively charged micelle surface. The chains of CTASal stretched due to the repulsion between the positive head groups and become flexible after the addition of the salts. The SAXS results allow us to investigate the structural changes of the WLMs providing a microscopic view of the anionic effect.

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.2015.01.052.

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