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SHORT COMMUNICATION

E. Cappelaere
R. Cressely

Rheological behavior of an elongated micellar solution at low and high salt concentrations

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E. Cappelaere · Prof. R. Cressely (✉)
Université de Metz
Institut de Physique, LPLI
Goupe Rhéophysique des Colloïdes
1, Bd Arago
F-57078 Metz cedex 3
France
E-mail: Cressely@lpli.sciences.univ-metz.fr

Abstract The aim of this experimental work is to investigate the mechanism responsible of the decrease of the zero shear viscosity at high inorganic salt content. We report the linear and some nonlinear rheological properties of aqueous worm-like micellar solutions of CTAB containing $NaNO_3$ salt. The zero-shear viscosity η_0 curve versus salt concentration exhibits a well-defined maximum. We choose two salt concentrations (low and high) having the same zero-shear viscosity, and carefully explore the rheological characteristics and their evolutions in (and around) these two situations. The experimental results presented here, without excluding the possibility of the connections, suggest the possibility that the decreasing of η_0 is a result of the reduction in size of the worm-like micelles.

Key words Rheological measurements – viscoelasticity – salt effect – CTAB – micellar solution

Introduction

Under certain conditions of concentration, salinity, temperature, presence of counterions, etc., the micelles present in aqueous solutions of surfactants tend to grow [1]. In some systems, long worm-like micelles form at higher surfactant concentrations and/or upon addition of a salt. The most extensively studied systems are alkyltrimethylammonium and alkylpyridinium halide. Entangled worm-like micellar networks were found in such systems. These systems exhibit viscoelastic behavior as a result of micellar entanglement which is analogous to that observed in solutions of flexible polymers [2]. However, unlike ordinary polymers, micellar chains can reversibly break and recombine on a time scale which is dependent on the system and the physicochemical and thermodynamical conditions.

Numerous results [3–5] have shown that the zero-shear viscosity of many surfactant solutions strongly depends on the salt concentration. Indeed, the experiments performed on systems containing no or very little salt unambiguously demonstrated the effects of electrostatic interactions. Addition of salt in excess amounts can have profound effect on the structure and rheology of worm-like micelles. Experimental results on the cetyltrimethylammonium bromide CTAB/KBr system [2, 6, 7] and other viscoelastic surfactant systems [8–10] are well accounted for in the range where the viscoelasticity increases quickly, reflecting the huge increase in micellar length. This micellar growth leads to a dramatic enhancement of the viscosity. However, Appel et al. [11] have shown that solutions of $CPClO_3$ having 1 M sodium chlorate $NaClO_3$ brine, even though form extremely long worm-like micelles [12], exhibit an amazingly high fluidity. The rhelogical properties of this system are very different from that of the CTAB/KBr system, the response to stress is Newtonian over the entire range of shear rates explored in contrast to those found in CTAB/KBr and other micellar systems. It was suggested that this behavior could be due to the formation of cross-links between micelles leading to a solution of entangled branched micelles or even to a multiconnected network [1]. The possibility of connections has been first proposed by Porte and co-workers [1]. Usually, the viscosity is first increasing with the salt concentration, passing over a maximum and is then decreasing again. The relaxation time of the system is strongly affected by the salt concentration. The salt reduces the electrostatic repulsion and attractive terms can be more dominant: the viscosity becomes larger with increasing salt concentration. It becomes easier for the micelles to collide and coalesce. The decrease of the viscosity, when the salt concentration increases further, is more difficult to explain. Several authors [1, 12–14] have proposed that this decrease of the viscosity may be due to the formation of the multiconnected network in which the stress relaxation will be made from the sliding of cross-links along the cylindrical micelles. An analogy can be drawn here with the highly fluid L_3 phase [11]. Such a mechanism can allow a very fluid solution and as well as a faster relaxation of stress rather than disentanglement or breaking of worm-like micelles. Studies conducted by Shikata et al. [15] suggested that the stress relaxation process may be due to the "ghost-like" cross-link of the micelles. Transient cross-links are formed when a micellar thread collides with another one. The two threads subsequently separate, thus allowing a flow that does not involve relaxation of entanglements. In this description of the system, there would not be permanent cross-links, but a snap shot of the system would reveal coexistence between interconnections and entanglements. Direct observation of branched micelles is rather difficult, particularly with the surfactant and salt concentrations used in this work. It is difficult to discriminate between the overlapping and the cross-linking of two micelles. A multiconnected branched micellar network cannot be distinguished from an entangled micellar network by techniques such as neutron, light scattering and microscopy. However, the rheological properties in these two situations could be considerably different. Therefore, in this paper, we study the linear and nonlinear shear rheology of worm-like micelles present in the cetyltrimethylammonium bromide (CTAB) and sodium nitrate ($NaNO_3$) system. It is well known that at low concentrations of CTAB, the addition of a simple salt like $NaNO_3$ induces the growing of the micelle, leading to a worm-like system which, particularly at rest, is analogous to semi-dilute polymer solutions [6, 10].

As the salt concentration is increased [16], the zero shear viscosity η_0 and the stress relaxation time τ_R go through a well-defined maximum. The aim of this experimental work is to investigate the evolution of the rheological parameters in the linear and nonlinear regimes when we are on both sides of this maximum. A situation corresponding to the same value of viscosity (at low and high C_S of $NaNO_3$) has been carefully studied.

Experimental section

Products used in this work are commercially available. The surfactant system investigated here is a ternary solution consisting of cetyltrimethylammonium bromide (CTAB) and sodium nitrate ($NaNO_3$) (hereafter abbreviated as CTAB/$NaNO_3$) in distilled water. This system is known to easily form elongated worm-like micelles [16]. CTAB and $NaNO_3$ were purchased from Acros. The concentrations are given in mole per kg. The solution was left to stand at least three days in order to reach equilibrium.

The linear and nonlinear viscoelastic properties of the CTAB/$NaNO_3$ solutions were measured by on a Carrimed CSL 100 working in the constant shear stress mode and a cone plane device (4 cm, 0.5°) which operates at a wide range of shear rate (the shear rate could be varied from 1 to 6000 s^{-1} approximately). A Peltier device allows the temperature of the solution to be adjusted. To prevent errors due to evaporation, the measuring geometry was surrounded by a solvent trap containing water. The magnitude of the complex viscosity $|\eta^*(\omega)|$, the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ were measured from oscillatory measurements in an angular frequency range between $\omega = 1$ rad/s and $\omega = 250$ rad/s at 30 °C. The fresh surfactant solutions as well as the solutions which were submitted to shearing stress during an experiment, were fully transparent and free from foam and air bubbles. For each experiment we have used a new sample. By varying the scanning time for $\eta(\dot{\gamma})$, we observe differences with the curve obtained under equilibrium. Increasing the time of scanning decreases the differences with steady measurements. Results indicate that the measurements made during 30 min (or longer) give practically the same results as equilibrium values. The reported curves correspond to this scanning time which allows to limit the evaporation effect.

Results and discussion

We have measured the zero-shear viscosity sample of the system CTAB/$NaNO_3$ as a function of the salt concentration at $T = 30\,°C$. The results obtained from 0.3 M/l CTAB are shown in Fig. 1; 0.3 M of CTAB is approximately equal to the concentration at which sphere to rod transition occurs. In the domain of salt content studied here, the viscosity η_0 shows a pronounced maximum as a function of salt concentration. The growing part I of the curve corresponds to a logical evolution. It is well-known that aqueous ionic solutions of surfactants can undergo uniaxial growth upon the addition of salt. As a result, the

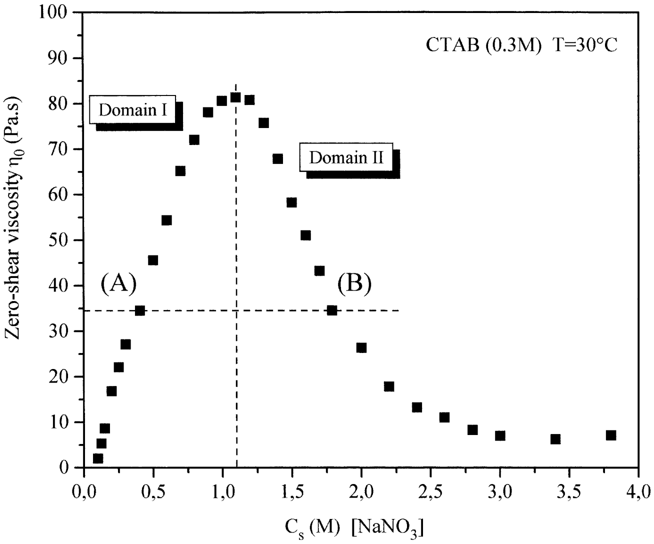


Fig. 1 Variation of the zero-shear viscosity η_0 as a function of the NaNO$_3$ concentration at fixed 0.3 M CTAB concentration at 30 °C

viscosity of the solutions increases. It is generally admitted that increasing the salt concentration amounts to an increase in the curvature energy of surfactant molecules in the end-cap relative to the one in the cylindrical body of the micelle. This leads to an increase in micellar length. The decrease of the viscosity (in the domain II) is more difficult to explain and several possible explanations have been proposed. The simplest of which is a decrease of the micellar length. One would expect that the behavior of the zero-shear viscosity (increase followed by a decrease) as a function of the salt concentration that observed here for the CTAB/NaNO$_3$ system, could be universal. Candau et al. [12] also observed for both systems (CTAB/KBr and CPClO$_3$/NaClO$_3$) a maximum of the zero-shear viscosity η_0. However, systems with salicylate or alkylbenzoate counterions show a more complex behavior. In these systems, the $\eta_0(C_S)$ curve can exhibit two maxima [10].

In this experimental work, we have studied rheological characteristics of the solutions belonging to the domains I and II of the $\eta_0(C_S)$ curve. We have chosen two solutions (A) and (B) belonging to the two different domains and having the same zero-shear viscosity: (A) CTAB (0.3 M)/NaNO$_3$ (0.405 M), and (B) CTAB (0.3 M)/NaNO$_3$ (1.79 M). In both the situations, $\eta_0 = 34.5$ Pa s. The magnitude zero-shear viscosity is given by the product of two quantities, one of which is determined by the structure and the other by the dynamic response of the system. For a quantitative understanding we must know both parameters, the one related to the structure which is the shear modulus G_0 and the other describing the dynamic behavior, the relaxation time τ_R. Appropiate modelling is necessary to quantify rheological parameters obtained by oscillatory shear measurements. In this work, we have used a simple Maxwell model to fit the rheological data obtained from our viscoelastic surfactant solutions, and as we will show later, the agreement with our experimental results is good. This simple model is constituted of a single spring connected in series to a viscous element (dashpot). In shear experiments, G' (the elastic modulus) and G'' (the loss modulus) are given by

$$G'(\omega) = G_0\omega^2\tau_R^2/(1 + \omega^2\tau_R^2) \quad \text{and}$$

$$G''(\omega) = G_0\omega\tau_R/(1 + \omega^2\tau_R^2) ,$$

where ω is the frequency, G_0 is the plateau modulus and τ_R is the relaxation time. To obtain G_0 and τ_R, we fitted G' and G'' to the above expressions. In addition, the relaxation time τ_R is deduced from crossing point of $G'(\omega)$ and $G''(\omega)$ curves and G_0 from the limiting value of $G'(\omega)$ at high frequencies. The results obtained by both methods are nearly the same. Figure 2 shows the evolution of parameters τ_R and G_0 as a function of the salt concentration C_S for solutions belonging to domains I and II. These data are obtained with salt concentrations close to points A and B (Fig. 1) corresponding to domains I and II, respectively. The evolution of τ_R is very clear and differs in the two domains. τ_R increases in the domain I and it decreases in II. The increase of τ_R in the domain I is easily explained by increase in the micellar length. The decreasing part of the τ_R curve in the domain II close to (B) can be explained by a decrease in the mean size of the worm-like micelles as we have shown in a previous paper [17]. G_0 is correlated to the degree of entanglements of the network ($G_0 = \upsilon KT$, with υ the number density of the entanglement points). In contrast, the $G_0(C_S)$ curves have the same behavior in the two domains. In the both domains investigated here, G_0 is practically independent of the salt concentration. $G_0 \sim 225$ Pa in the domain I (near A) and $G_0 \sim 245$ Pa (not too different from the former value) in the domain II (near B). These values together with the corresponding relaxation times show that this system (based on the model used) has practically the same viscoelastic response at low and high salt concentrations. It is also easily conceivable that the micellar systems CTAB/NaNO$_3$ (0.405 M/l) and CTAB/NaNO$_3$ (1.79 M/l) have close similarities in their structure. The small differences observed in domains I and II can be attributed to the excess salt environment which exists in the domain II giving slighlty different slipping effects. Olsson et al. [18] suggested that the effects of ionic strength on micelle length and stiffness dominate the rheological behavior of a micellar system. They postulated that at the beginning, the effect of increase in the salt concentration is to lengthen the chains and thereby increasing their flexibility as a

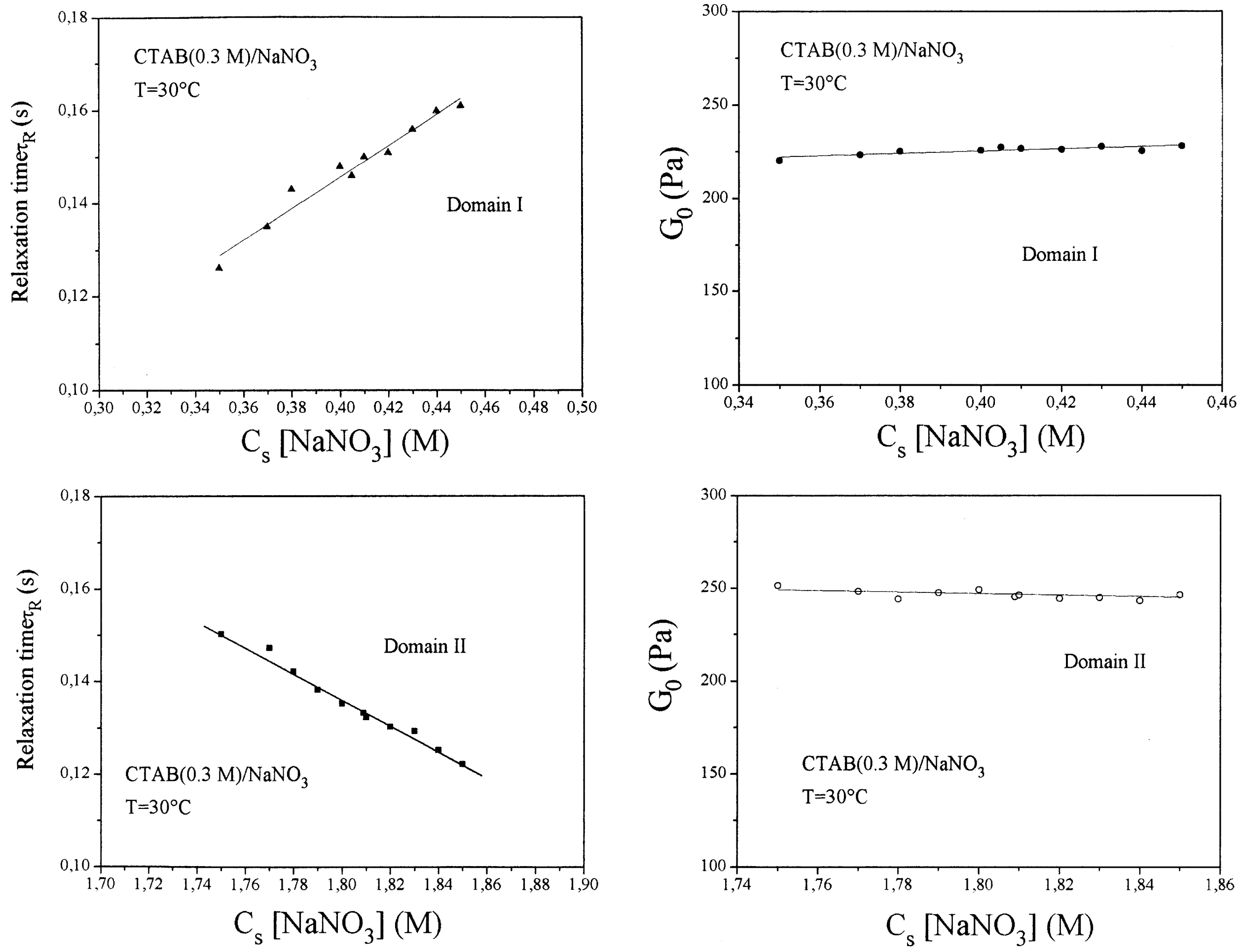


Fig. 2 Relaxation time τ_R and elastic plateau modulus G_0 versus the salt concentration for solutions of 0.3 M CTAB at 30 °C. The variations of the salt concentrations are close to 0.405 M for domain I and 1.79 M for domain II. These two salt contents give the same zero-shear viscosity η_0

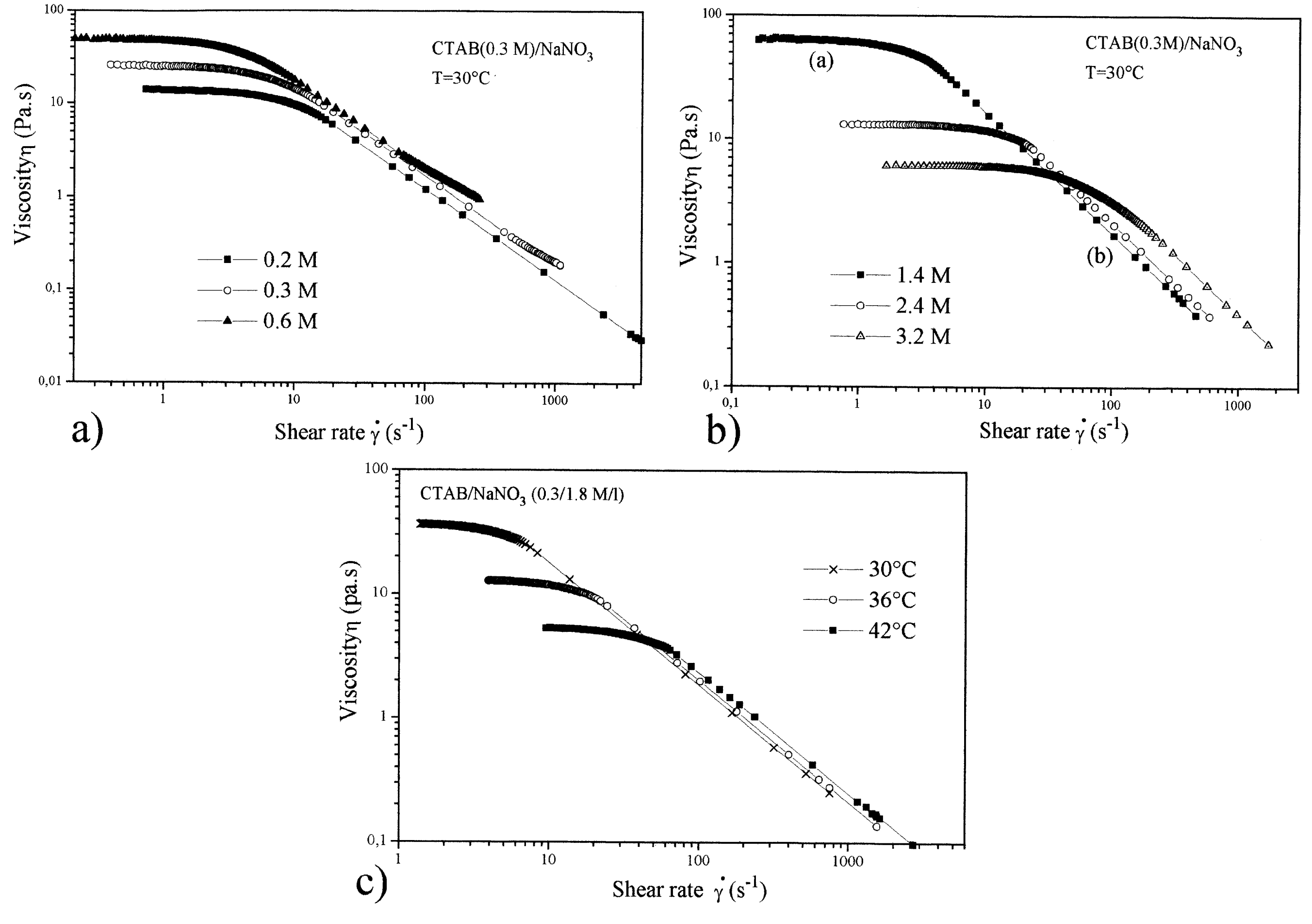
result of the lower surface charge density. This increase in length and flexibility stops when the counterion binding exceeds 100% and the surface charge changes sign. Further addition of salt increases the surface charge density, which stiffens the micelle and promotes a change in morphology from worm-like to spherical. Drye and Cates [19] investigated theoretically the formation of cross-links between worm-like micelles. They concluded that the free energy cost for the formation of cross-links is much higher than that for forming end-caps. Also, the formation of smaller cylindrical micelles is easier than the formation of a multiconnected network. Imae and Kohsaka [20, 21] have studied the effect of added salt [NaSal] in the cationic surfactant system of the alkyltrimethylammonium. These authors have also shown that the micellar length reaches a maximum. At this point, the viscosity of the system is also maximum. As the concentration of added salicylate is further increased, excess adsorption and penetration of salicylate ions allow micelles to become negatively charged and break into smaller sizes, e.g. spherical because of the electrostatic repulsion in a micelle. Hu et al. [22] have also suggested that an excess of salt [NaSal] can tend to shorten the micellar lifetime and size. Light scattering data [23, 24] indicate that, as the salt [NaSal] concentration increases, the micelle size increases first, reaches a maximum at a certain salt concentration and then decreases again. Furthermore, the decrease of micellar length in the presence of large amount of counterions has been verified by light scattering on CTASal/NaSal system [20]. A similar electrostatic effect can be used to explain the behavior at high $NaNO_3$ concentrations in the system studied here.

Non-Newtonian viscosity measurements also seem to be in agreement with the hypothesis of a diminution of the micellar length when the salt concentration is greater than that corresponding to the maximum of the $\eta_0(C_S)$ curve. The steady-state shear viscosity as a function of shear rate is shown in Fig. 3 for the salt concentrations, belonging to the domains I and II of the $\eta_0 = f(C_s)$ curve. The viscosity of the viscoelastic solutions shows shear thinning with a power law over the entire range of shear rates investigated. In both cases, one observes that the $\eta(\dot{\gamma})$ curves were sensitive to the variation of the salt concentration. Futhermore, in domain I (Fig. 3a), η_0 increases as a function of C_S whereas the critical shear rate $\dot{\gamma}_{1c}$ at which the shear thinning occurs, decreases. The evolution of these two rheological parameters is correlated to the growing size of the micelles in domain I. It is well-known that $\tau_R \sim 1/\dot{\gamma}_{1c}$, so a decrease of $\dot{\gamma}_{1c}$ gives a greater value of τ_R corresponding to a greater particle size. Physically, the longer the micelles, the easier is their alignment in the shear flow. So, logically $\dot{\gamma}_{1c}$ is, a decreasing function of the salt concentration in this domain as we have found. The observed increase of the $\dot{\gamma}_{1c}$ and diminution of η_0 as C_S varies from 1.4 to 3.2 M in the domain II (Fig. 3b) is in agreement with the hypothesis of a diminution of the length of the micelles at high salt concentrations (due to same reasons as given before). The rheological behavior of the solutions for increasing salt concentrations (Fig. 3b) is very similar to the one observed, at fixed concentrations, by increasing the temperature (Fig. 3c). Indeed, It is well-known that the apparent average micellar length $\bar{L}$ decreases when the temperature increases:

$$\bar{L} = \phi^{1/2} \exp(E_A/kT) , \qquad (1)$$

where E_A is the activation energy and ϕ is the surfactant volume fraction. These comparisons are in agreement with a possible decrease in size of the micelles with increase in

Fig. 3 (a–c) Apparent viscosity η as a function of shear rate $\dot{\gamma}$ at 30 °C for a solution of 0.3 M CTAB and three different salt concentrations belonging to the domain I (a) and to the domain II (b). Influence of the temperature for a solution of 0.3 M CTAB and 1.8 M $NaNO_3$ (c)



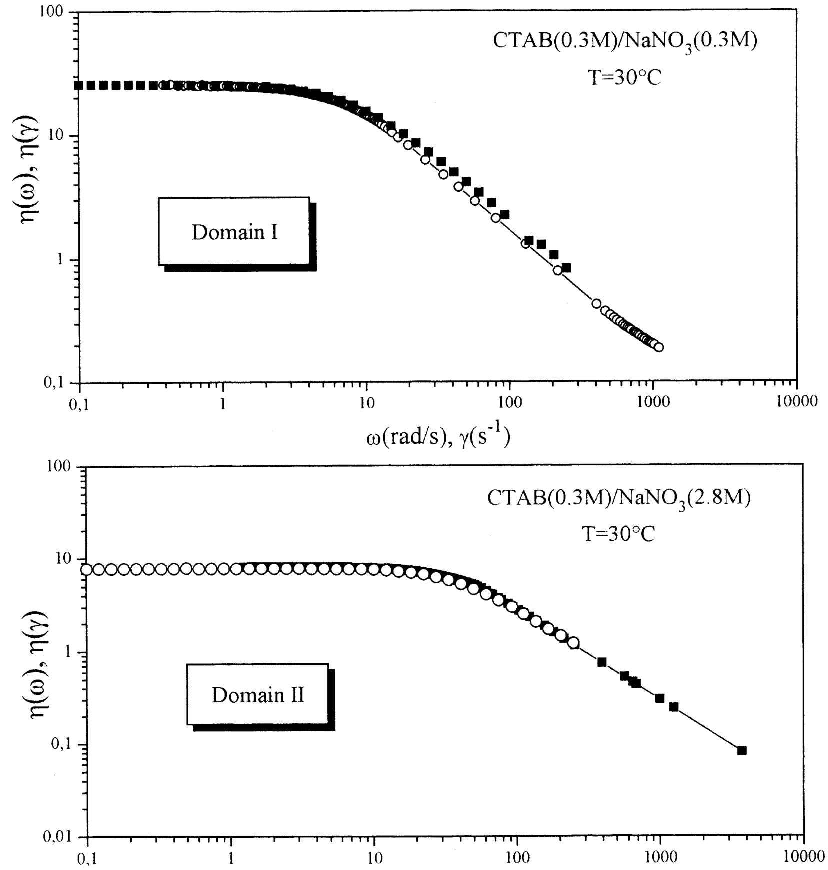


Fig. 4 Comparison between the dynamical $|\eta^*(\omega)|$ and the steady shear $\eta(\dot{\gamma})$ viscosities, respectively plotted against ω and $\dot{\gamma}$ at 30 °C for two concentrations of the salt belonging to the two domains I and II

salt concentration (domain II). Finally, in Fig. 4, we have compared the dynamical $\eta(\omega)$ and the steady shear $\eta(\dot{\gamma})$ viscosities, for the two samples belonging to the domains I and II of the $\eta_0(C_S)$ curves. Figure 4 is a typical plot of results obtained for these two solutions. The linear viscoelastic regime is denoted by a constant viscosity as a function of applied shear rate. At high shear rates, the entangled network of worm-like micelles is deformed and aligned under the orienting forces of the applied shear rate. As a consequence, the solution develops an anisotropy that becomes more pronounced with increasing shear rate. In this nonlinear regime, the sample exhibits shear thinning behavior. According to the Cox–Merz rule, the shear viscosity $\eta(\dot{\gamma})$ and the magnitude of the complex viscosity $|\eta(\omega)^*|$ are equal when the shear rate $\dot{\gamma}$ and the frequency of oscillation ω are equal. This relationship between linear and nonlinear viscoelastic properties seems to hold in solutions of entangled macromolecules. Rehage et al. [25] showed in a micellar system CPCl/NaClO$_3$ that a significant departure from the Cox–Merz rule occurs in the region of high shear rates. This deviation is thought to be a consequence of shear-induced structural transitions, leading to the formation of large scale anisotropic structures. Recent experimental studies (with small-angle light scattering under shear) conducted by Kadoma et al. [23] allowed to probe the regime where the Cox–Merz rule fails. They suggest the formation of large-scale structure at high shear rate as well as the formation of a multiconnected network at high salt [NaSal] concentrations. These two structural transitions account for the departure from the Cox–Merz rule. With the CTAB/NaNO$_3$ system, no departure occurs. Indeed, we have shown in Fig. 4 that dynamic and steady shear viscosities of the solution CTAB (0.3 M)/NaNO$_3$ (0.3 M) do not deviate significantly from each other. At high salt concentration (2.8 M), the result is identical. The Cox-Merz rule is applicable and no deviation between $|\eta(\omega)^*|$ and $\eta(\dot{\gamma})$ appears. This result is important because it allows us to demonstrate that, the formation of a multiconnected network is not necessary to explain our experimental results at high salt concentrations in the CTAB/NaNO$_3$ system, in contrast to that shown, i.e. in ref. [26].

Conclusion

The results presented in this paper show that the dynamical and structural properties of a solution of worm-like micelles is very sensitive to the salt concentration [$NaNO_3$]. To explain the decrease of η_0 at high salt content there are schematically two current interpretations: branching of the micelle (with sliding connection [26]) or shortening of the micelle. The first hypothesis is not excluded from our presented rheological measurements in this work, but the lack of theory in predicting the evolution of parameters other than η_0 in the high salt concentration domain cannot impose this mechanism. Although no clear theory exists to explain the mechanism for the diminution of the mean micellar length for concentrations of simple inorganic salt high enough to induce a decrease of the zero-shear viscosity, all the rheological results presented in this experimental work in the linear and nonlinear regime, are in agreement with this simple hypothesis. It is nevertheless possible that, in addition, connections are induced, but in a quantity too small to explain the observed evolution of the rheological behavior. Direct observations of connections for concentrations used in this work are very difficult and artefacts are possible. The transmission electron microscopy (Cryo-TEM) observations realized at very small concentration and showing connections, correspond to an added organic salt (such as NaSal) [23] or more complicated surfactant systems [3, 27]. To our knowledge, no direct observations of the connections exist with a simple (inorganic) salt. Scattering methods are unable to distinguish between entanglements and connections. Flow birefringence measurements are now conducted in our laboratory to obtain new informations about the evolution of the micellar system in the domain of high salt concentration.

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