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Linear and nonlinear rheology of an aqueous concentrated system of cethyltrimethylammonium chloride and sodium salicylate

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This work reports a rheological study on concentrated solutions of cethyltrimethylammonium chloride (CTAC) and sodium salicylate (NaSal) at a fixed molar concentration ratio [NaSal]/[CTAC]$=0.6$. While all the solutions behave as a Maxwell fluid, the measured zero-shear viscosity reveals a maximum with the surfactant concentration. The increase of the viscosity shows a power law dependence with an exponent 1.1 followed by a negative scaling law with an exponent -2.1 after the maximum. The nonlinear rheological properties identified by the reduced stress σ_p/G_0 and the Weissenberg number $\dot{\gamma}_p\tau_R$ show two different behaviors: these quantities are nearly constant for low concentrations, while they show a scaling law dependence with the surfactant concentration for the higher ones, with respectively the exponents -1.4 and -0.9. These results which do not reflect the dynamic behavior of entangled wormlike micelles are interpreted as a result of the formation of a multiconnected network structure. [S1063-651X(97)14210-6]

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INTRODUCTION

The rheology of wormlike micelles has been shown particular interest in the last few years. Many experimental works have been published on these large flexible micelles. From the initial spherical micelles to ''giant'' flexible micelles, micellar growth is favored either by increasing the surfactant concentration or by addition of an appropriate salt. For highly screened micelles the growth is characterized by a simple power-law increase, and the variation of the viscosity with the surfactant concentration is in accordance with the predictions of the mean-field theory [1,2].

The addition of salt weakens the electrostatic interactions, and allows the micellar growth. This possibility has been also explored. One of the outstanding results of these studies has been the effect of salt on the zero-shear viscosity, which reveals a maximum with the salt concentration. Experimental results showing this viscosity-maximum versus the salt concentration have been obtained for different surfactant-salt systems [3–5]. This result seems to be universal for aqueous salt-surfactant systems with regard to linear viscoelasticity. The decrease of the viscosity after the maximum has recently been explained by the apparition of connections between micelles [6–9] characterized by a new relaxation process: the sliding of the connections along the micelles. This relaxation process is faster than those of reptation and of break recombination. The model of connections [8] has predicted a decrease of the viscosity with an increase of connections, but an exact law for the variation of the viscosity with the surfactant concentration has not been established.

In this paper, we report a rheological work on a micellar system made of the surfactant cethyltrimethylammonium chloride (CTAC) and sodium salicylate (NaSal), at a fixed molar concentration ratio [NaSal]/[CTAC]$=0.6$, without adding a mineral salt. We focus our interest on the rheology when increasing the surfactant concentration, and we analyze both the linear and nonlinear rheological properties.

THEORY

Wormlike micelles are similar in behavior to polymeric chains which relax by reptation. In addition, besides the reptation mode, the micelles have the nature to break and recombine [1]. This break-recombination process generates an exponential distribution in length of micelles with a mean length $\overline{L}$ scaling with the surfactant concentration with an exponent which differs from the one (0.5) predicted by simple mean-field theory [2]:

$$\overline{L} \sim C^{0.6} \exp(E_{\mathrm{sciss}}/2k_BT), \tag{1}$$

where C is the surfactant concentration, E_{sciss} is the scission energy of the chain, k_B is the Boltzmann constant, and T the absolute temperature.

Equation (1) applies in the absence of charge effects (the case of neutral micelles or highly screened ionic micelles). With no added salt (or with very low salt content), a model calculation [10,11] has shown that electrostatic interactions modify the micellar growth law, giving an exponent for the concentration dependence of L which differs from that of the above equation.

The stress relaxation is controlled by the competition between the reptation time τ_{rep} and the breaking recombination time τ_{break}. When scission reactions are fast during reptation i.e., $\tau_{\mathrm{break}} \ll \tau_{\mathrm{rep}}$, as for wormlike micelles, the relaxation approaches a Maxwell form [8,12–14], where the instantaneous shear modulus obeys the relation

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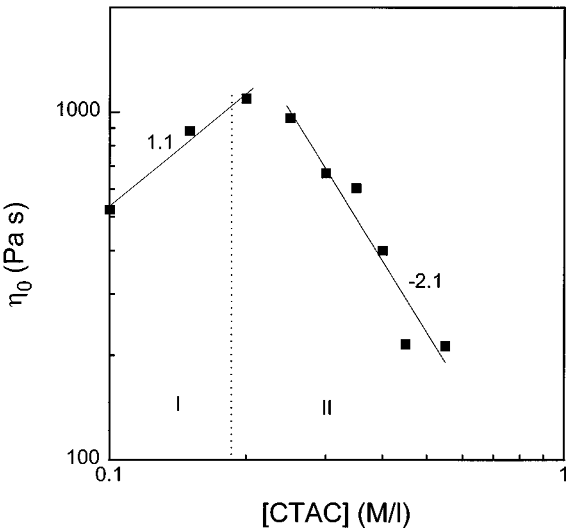

FIG. 1. Zero-shear viscosity η_0 as a function of the surfactant concentration at 30 °C.

$$G(t)=G_0e^{-t/\tau_R}. \tag{2}$$

Here G_0 is the plateau modulus and τ_R the terminal relaxation time of order:

$$\tau_R=(\tau_{\text{rep}}\tau_{\text{break}})^{1/2}, \tag{3}$$

Under the reversible scission scheme the relaxation time τ_R and the zero-shear rate viscosity are predicted to scale the surfactant concentrations as follows [15]:

$$\tau_R\sim C^{5/4}, \tag{4}$$

$$\eta_0\sim C^{3.7}. \tag{5}$$

In the case of a Maxwell fluid, the storage and the loss moduli are given by the following equations:

$$G'=G_0\omega^2\tau_R^2/(1+\omega^2\tau_R^2), \tag{6a}$$

$$G''=G_0\omega\tau_R/(1+\omega^2\tau_R^2). \tag{6b}$$

The plot of G'' versus G' on a linear scale reveals a semicircular curve (Cole-Cole) characteristic of this Maxwellian behavior.

The viscosity η_0 is related to both relaxation time τ_R and elastic modulus G_0 by

$$\eta_0=G_0\tau_R, \tag{7}$$

with

$$G_0\sim k_BTC^{2-2.3}. \tag{8}$$

Equation (8) comes from an argument that G_0 receives a contribution of k_BT per entanglement volume.

NONLINEAR RHEOLOGY

Recently Cates and co-workers [16–17] established a theoretical model for the nonlinear rheology of wormlike micelles. For the fast breaking regime ($\tau_{\text{break}}\ll\tau_{\text{rep}}$), this model reports a flow instability of a shear-banding type characterized by an asymptotic behavior of the flow curve. Beyond a certain critical value of the shear rate $\dot{\gamma}_p$, the steady-state shear stress reaches a plateau behavior σ_p and becomes independent of the shear rate. In this plateau domain high and low sheared bands coexist under the same stress. We have given experimental evidence of this behavior in a previous work [18]. The asymptotic value of the stress σ_p is related to the elastic modulus G_0 by

$$\sigma_P=\tfrac{2}{3}G_0, \tag{9}$$

and the critical shear rate $\dot{\gamma}_p$ is related to the relaxation time τ_R by

$$\dot{\gamma}_p\tau_R=2.6. \tag{10}$$

EXPERIMENT

The solutions studied in this work are made of the surfactant CTAC and NaSal in water. The NaSal acts as a cosurfactant when added to a CTAC solution: Sal$_-$ takes place in the micelles between polar head groups of the surfactants [19,20]. The ratio [NaSal]/[CTAC] is kept constant and equal to 0.6, and the surfactant concentration is varied from 0.1 to 0.55 M/l. All the experiments have been made at a constant temperature of 30 °C.

The rheological experiments have been made with a Carrimed viscosimeter working in an imposed shear stress and using a cone-plate geometry (an angle of 30° and a gap of 13 μm). The equilibrium mode was used for the steady shear measurements. For the oscillatory flow, a sinusoidal shear stress $\sigma(t)=\sigma_0\cos\omega t$ is applied at an angular frequency varying from 0.01 to 100 rad/s. The imposed stress σ_0 is chosen in the linear domain where the amplitude of the deformations are very low.

RESULTS AND DISCUSSION

Linear rheology

In Fig. 1, the zero-shear rate viscosity η_0 is given versus the surfactant CTAC concentration. This behavior shows a

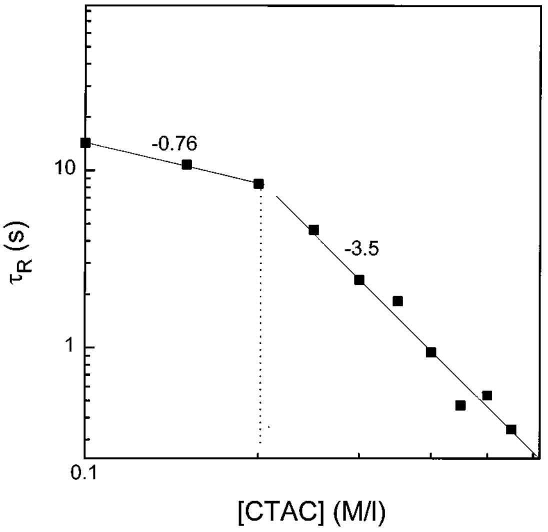

FIG. 2. Relaxation time τ_R as a function of the surfactant concentration at 30 °C.

maximum which is not expected. Usually, the viscosity is an increasing function of the surfactant concentration. In the domain I, η_0 increases until a surfactant concentration around 0.2 M/l showing a power-law dependence with the exponent of 1.1. This exponent is very low compared to the theoretical value, predicted to be equal to 3.7 in the case of entangled wormlike micelles undergoing a reversible scission scheme. In domain II, after the maximum, the viscosity decreases strongly, showing a negative scaling law with an exponent of -2.1. This behavior (a viscosity maximum with the surfactant concentration) reminds us of the viscosity maximum with the a concentration, which is explained by the formation of a multiconnected network structure.

The evolution of the corresponding relaxation time τ_R reported in Fig. 2 [τ_R is measured from the intersection of the curves $G''(\omega)$ and $G'(\omega)$] is also nonmonotonous. It shows two negative power laws with the exponents of -0.76 and -3.5 in domains I and II, respectively. The relaxation appears to occur faster as the system becomes more and more concentrated. This result is also opposite to what is usually observed for wormlike micelles or classical polymers.

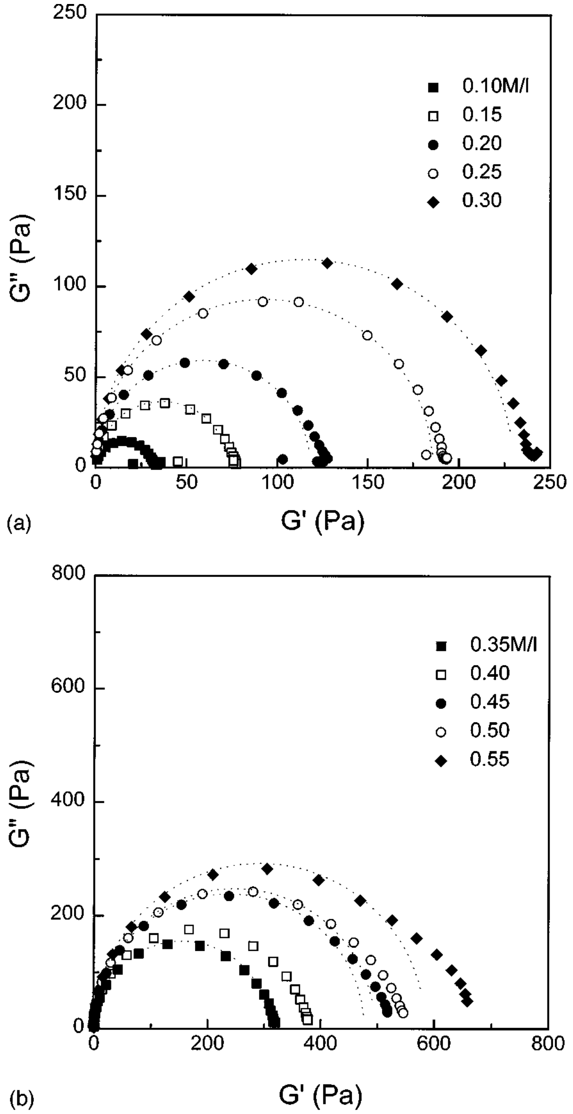

FIG. 3. (a) Cole-Cole plots of different surfactant concentrations varying from 0.1 to 0.3 M/l at 30 °C. (b) Cole-Cole plots of different surfactant concentrations varying from 0.35 M/l to 0.55 M/l at 30 °C.

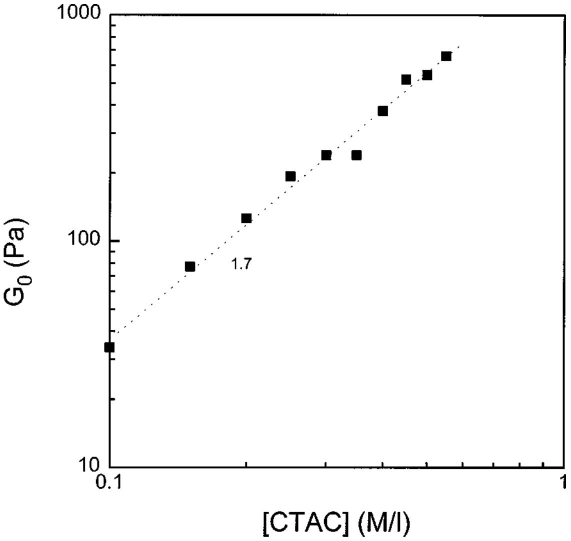

FIG. 4. Elastic modulus G_0 as a function of the surfactant concentration at 30 °C.

The Cole-Cole plots of these different solutions are displayed with their respective fits in Fig. 3. The curves ranging from 0.1 to 0.35 M/l [Fig. 3(a)] appear very semicircular in practically the whole pulsation domain of the experiment. This form is characteristic of a Maxwell fluid. This is a well-known result which predicts the obtaining of a single relaxation function when the ratio [NaSal]/[surfactant] is equal or higher than 0.6 [4]. For higher concentrations [Fig. 3(b)], the curves show an upturn in the Cole-Cole plots at high frequencies. In systems of entangled linear chains, Rouse modes are conventionally invoked to show this effect. For transient networks, which are of interest here, this effect could be due to the motion of the entanglements across the network.

The plateau modulus G_0 of these samples (measured for high pulsation values where G' reaches a plateau independent of the pulsation) is represented in Fig. 4 versus the

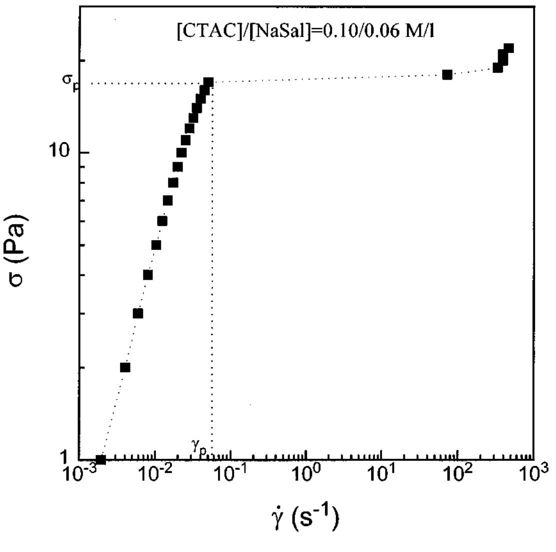

FIG. 5. Flow curve $\sigma = f(\dot{\gamma})$ for a 0.1 M/l CTAC solution at 30 °C.

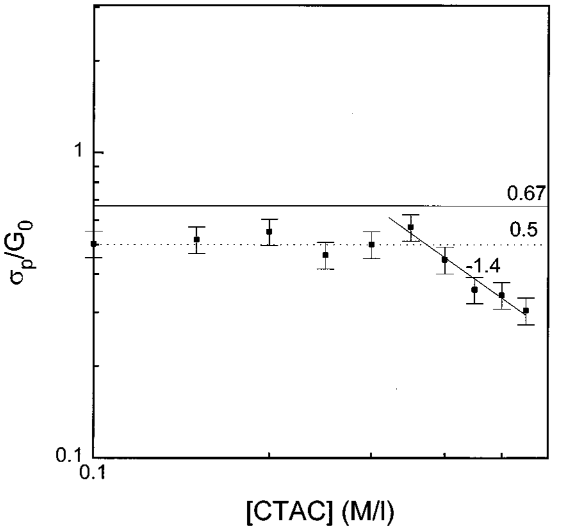

FIG. 6. Variation of σ_p/G_0 with the surfactant concentration at 30 °C.

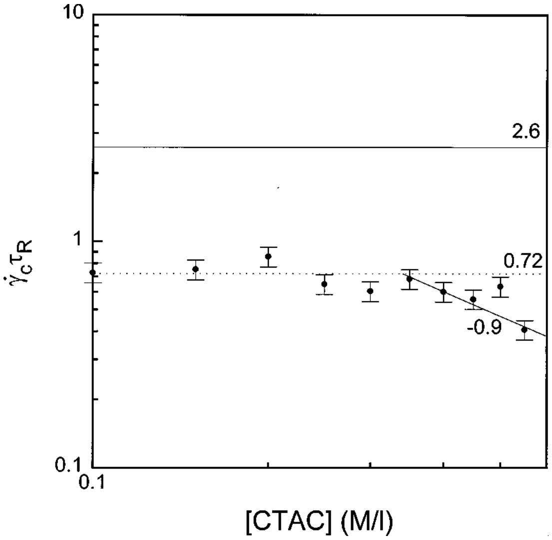

FIG. 7. Variation of $\dot{\gamma}_p\tau_R$ with the surfactant concentration at 30 °C.

CTAC concentration. It follows a continuous evolution showing a scaling law dependence with the surfactant concentration with an exponent 1.7 below the theoretical value which is of order of 2–2.3.

Nonlinear rheology

The nonlinear measurements of the steady-shear flow σ for the different concentrations studied reveal an analogous behavior for all the concentrations. On a log-log scale, versus the shear rate $\dot{\gamma}$, σ increases linearly at low $\dot{\gamma}$ (an evolution which corresponds to the Newtonian domain), and reaches a plateau σ_p beyond a certain critical value of the shear rate $\dot{\gamma}_p$. At high shear rates, the stress again increases in a disordered way, and the sample is expelled as bubbles from the cone-plate surface. A typical flow curve showing this behavior is reported in Fig. 5 for the concentration of 0.1 M/l of CTAC. One can remark that there is no data points in the plateau domain as has already been observed for nonlinear measurements at equilibrium.

The quantities σ_p/G_0 for different CTAC concentrations studied are reported in Fig. 6. Two distinct behaviors are observed. For low concentrations below, 0.3 M/l, σ_p/G_0 seems to be constant, with an experimental value around 0.5, not much lower than the theoretical one. Such result is analogous to the one obtained in our previous work [5] in the presence of a mineral salt at high salt concentrations. For higher surfactant concentrations, this quantity decreases linearly (in a log-log representation) showing a quasi-power-law dependence with the surfactant concentration with an exponent -1.4. The Weissenberg numbers $\dot{\gamma}_p\tau_R$ are reported in Fig. 7 versus the CTAC concentration. The same result is obtained: two domains can be distinguished. One domain for concentrations below 0.3 M/l, where $\dot{\gamma}_p\tau_R$ is constant and equal to 0.7, and another domain where $\dot{\gamma}_p\tau_R$ decreases with a power law characterized by an exponent -0.9. A similar power-law behavior with an exponent of -1.5 has been reported in the literature [21] in the presence of a higher amount of a mineral salt. At these higher salt concentrations, the accepted interpretation is the formation of a multiconnected network structure.

CONCLUSION

The exponents of the power law of η_0 in domain I, which is very low, and those of τ_R, which are negative, do not reflect the dynamic behavior of wormlike micelles. Values of exponents as small as these cannot match pure reptation or reptation-break-recombination processes. They are inconsistent with all three reaction schemes (reversible scission, end-interchange, and bond-interchange) considered in Ref. [15].

Furthermore, when varying the surfactant concentration, the ratio [NaSal]/[CTAC] is maintained constant. Consequently, this behavior cannot be explained by counterion effects. It is, however, compatible with the formation of a multiconnected network picture, where the relaxation occurs more and more quickly due to a sliding of the connections, and leads to a weak increase of the viscosity in domain I and a strong decrease in domain II.

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