

# Linear Rheology of Entangled Wormlike Micelles

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We report on the statics and dynamics of long and flexible wormlike micelles made from cationic surfactants (cetylpyridinium ions) diluted in brine (0.5 M NaCl) with strongly binding counterions (salicylate ions). This survey was performed at ambient temperature by combining light scattering and rheology measurements. Varying the weight percent,  $\phi$ , of surfactants from 0.1% to 10%, both dilute and semidilute regimes were studied. Above the crossover concentration  $\phi^* \sim 0.3\%$ , the viscoelastic properties are described by an almost ideal Maxwell relaxator. The overall rheological data are found to scale with the surfactant concentration with exponents close to those predicted from a recent stress relaxation model applied to living polymers. In addition, at high angular frequency, the complex elastic modulus results are interpreted in terms of crossover between the regimes of reversible scission and of breathing of the polymer-like chains. Contrary to earlier reports, the total average length of the micellar aggregates is found to increase with surfactant concentration as:  $\bar{L}(\phi) \sim \phi^{0.25-0.4}$ .

Flexible elongated surfactant micelles can be considered as model systems for the study of reversibly breakable polymers, sometimes called "living" polymers. It is now well established that the static and quasi-static properties of these surfactant systems show strong similarities with those of polymers in solutions. In the semidilute regime, e.g., the micelles form a disordered entangled network, and one process for the flexible chains to relax external stress is reptation.

Equilibrium polymers exhibit however fundamental differences with respect to ordinary polymers: (i) The length of the flexible chains are broadly distributed, and determined by the thermodynamical equilibrium of the surfactant solution. (ii) There exists another crucial process for stress relaxation (in addition to reptation): the reversible breaking and recombination of the chain.

During the last years, the dynamical behavior of wormlike micellar solutions have attracted much attention from theoreticians<sup>1-4</sup> and experimentalists.<sup>5-13</sup> A model of stress relaxation in living polymers (essentially based on the theory of polymer dynamics<sup>14</sup>) was recently proposed by Cates and co-workers.<sup>1,3</sup> In addition to the already mentioned processes of reptation and reversible

scission, breathing and Rouse motions of the chains were taken into account to determine the overall stress relaxation function  $G(t)$ , or its dynamical counterpart, the complex elastic modulus  $G^*(\omega) = G'(\omega) + iG''(\omega)$ . The essential features of this model are the following:

In the semidilute regime of entangled network, well characterized scaling laws are predicted for the rheological properties, e.g. for the static (defined at zero shear or zero frequency) and for the dynamic shear viscosity  $\eta(\omega) = |G^*(\omega)|/\omega$ .

In the so-called Cole-Cole representation, which consists in plotting the imaginary part  $G''(\omega)$  of  $G^*(\omega)$  as a function of its real part  $G'(\omega)$ , a more or less semicircular behavior is expected, depending on the ability for the system to relax faster through unimolecular scission and/or reptation. The important parameter is then the ratio between the relaxation times of each mechanism,  $\tau_b$  and  $\tau_{rep}$ , respectively. At higher frequency, the crossover to the breathing regime manifests itself as a minimum in the Cole-Cole plot. The crucial point of the Cates model is that the height of this dip is directly related to the average number of entanglements along the chain. It allows moreover to calculate the total average length of the micelles, a quantity which cannot be derived from measurements of static properties.

In this paper, we combine light scattering and rheology measurements, so that we can investigate the connection between the static and dynamic properties of long flexible wormlike micelles. The system considered here consists of a cationic surfactant (cetylpyridinium ions) diluted in brine (0.5 M NaCl) with strongly binding counterions (salicylate ions). Measurements are performed at ambient temperature. Above the crossover concentration  $\phi^* \sim 0.3\%$ , the viscoelastic properties of the entangled micellar network vary as power laws as a function of concentration with exponents close to those predicted by the Cates model. Furthermore the total average length could be derived from complex elastic modulus data and was found to increase with surfactant concentration as  $\bar{L}(\phi) \sim \phi^{0.25-0.4}$ .

## Experimental Section

The surfactant solutions investigated here are the binary mixtures made of cetylpyridinium chloride (CPy<sup>+</sup>Cl<sup>-</sup>) and sodium salicylate (Na<sup>+</sup>Sal<sup>-</sup>), diluted in brine 0.5 M (NaCl). The weight percent  $\phi$  of surfactants range from 0.1% to 10%. This system is known to be a good candidate for forming elongated wormlike

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micelles.<sup>5</sup> The ratio  $R = [\text{Sal}]/[\text{CPy}]$  has been kept to a constant,  $R = 0.5$ . This approach is similar to that followed by Kern et al.<sup>10</sup> in a viscoelastic study of a parent compound. In order to ensure a constant electrostatic screening length while varying the surfactant concentration, we choose to work with rather concentrated brine solutions (namely, 0.5 M NaCl).

Measurements of scattered light as function of wave vector  $q = 3 \times 10^{-4}$  to  $3 \times 10^{-3} \text{ \AA}^{-1}$  were performed at 25 °C on filtered solutions, using an experimental setup as described elsewhere.<sup>15</sup> The linear viscoelastic properties of the CPy/Sal mixtures were obtained on a Rheometrics fluid spectrometer (RFS II) working with controlled shear rate. Depending on the viscosity range, a cone-and-plate (for  $\eta_0 > 0.1 \text{ Pa}\cdot\text{s}$ ) or a couette (typically below 1 Pa·s) configuration was utilized. Dynamical measurements were carried out for angular frequency  $\omega = 0.1$ –100 rad/s at temperatures  $T = 20$  and 25 °C (except in the lower viscosity range where Newtonian behaviors were directly confirmed from steady-state experiments for shear rate  $\dot{\gamma}$  varying from 1 to 1000  $\text{s}^{-1}$ ).

First, it is worthwhile presenting a brief analysis of the model developed by Cates and co-workers on stress relaxation in living polymers.

As mentioned in the introduction, two dynamical regimes are usually considered, depending on the characteristic relaxation times for reptation and reversible breaking,  $\tau_{\text{rept}}$  and  $\tau_b$ :

(1)  $\tau_b \gg \tau_{\text{rept}}$ : on time scale of the order of  $\tau_b$ , the chain behaves as in strongly polydisperse "dead" polymer solutions, dominated by reptation.<sup>14</sup>

(2)  $\tau_b \ll \tau_{\text{rept}}$ : This is the case of interest. Cates et al. reported then a stress relaxation function of the form  $G(t) = G_0 \exp(-t/\tau_R)$ , where  $G_0$  denotes the plateau modulus, that is the high-frequency storage modulus and  $\tau_R$  the terminal relaxation time. It was also demonstrated that  $\tau_R \sim (\tau_b \tau_{\text{rept}})^{1/2}$ . Such a viscoelastic system (with a monoexponential decay time) is generally identified as a Maxwell element.<sup>16</sup> In terms of dynamical response,  $G^*(\omega)$ , this is equivalent to say that in the  $(G', G'')$  plane the relaxation spectrum describes a semicircle, in agreement with

$$(G' - G_0/2)^2 + G''^2 = G_0^2/4 \quad (1)$$

In the first version of the model,<sup>1</sup> the viscoelastic properties of surfactant micellar solutions as function of concentration, e.g.  $\eta_0 = G_0 \tau_R$ ,  $\tau_R$  and  $G_0$  were found to obey well-defined scaling laws. The values of the theoretical exponents are listed in Table I. In a recent extension of the theory of reversibly breakable polymers,<sup>3</sup> the same authors included the Rouse and breathing motions of the chains to determine the whole stress relaxation function. These additional modes strongly influence the basic behavior described by eq 1. At high frequency, such as  $\omega \tau_R \gg 1$ , a minimum shows up in the Cole–Cole representation, due to the crossover toward the breathing regime. The height of this dip is found to scale with the number of entanglements along the chain of average length  $\bar{L}$ , as

$$G''_{\text{min}}/G'_\infty \sim l_e/\bar{L} \quad (2)$$

where  $l_e$  denotes the length of a chain between two entanglement points and  $G'_\infty$  the "extrapolated" plateau modulus.<sup>3</sup> Equation 2 holds, however, for large number of entanglements per chain, that is for  $l_e/\bar{L} \ll 1$ . Another condition for eq 2 is that the breaking–recombination time,  $\tau_b$ , is much larger than  $\tau_e$ , the longest Rouse relaxation time for a chain of length  $l_e$ . Assuming then for the correlation length  $\xi$  good solvent conditions and mean-field approximation,  $l_e$  reads<sup>14</sup>

$$l_e \sim \xi^{5/3} b^{-2/3} \quad (3a)$$

with

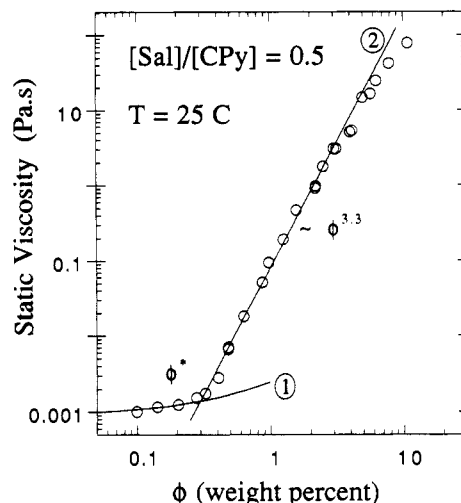
$$\xi \sim (k_B T / G'_\infty)^{1/3} \quad (3b)$$

where  $b$  is the persistence length of the micelle. Finally, the power law exponents for  $G''_{\text{min}}$  and  $G''_{\text{min}}/G'_\infty$  (see Table I) can

**Table I. Comparison between Predicted and Experimental Exponents for the Scaling Laws Related to the Dynamical and Static Properties of Reversibly Breakable Micelles under Dilution**

	theory	experiment
plateau modulus $G_0$	9/4	2.18
terminal time $\tau_R$	5/4	1.13
static viscosity $\eta_0$	3.5	3.3
$G''_{\text{min}}$	1/2	0.72
$G''_{\text{min}}/G_0$	-7/4	-1.44
correlation length $\xi$	-3/4	-0.65, -0.72 <sup>a</sup>
total average length $\bar{L}$	1/2	0.36, 0.24 <sup>a</sup>

<sup>a</sup> Static value, dynamic value.



**Figure 1.** Variation of the zero-shear viscosity  $\eta_0$  as function of surfactant concentration at room temperature for solutions of CPy + Sal diluted in brine (0.5 M NaCl). The continuous curves labeled 1 and 2 are explained in the text.  $\phi^* \sim 0.3\%$  denotes the crossover concentration between the dilute and semidilute regimes.

be derived considering eqs 2 and 3, and assuming for the mean chain length a  $\bar{L}(\phi) \sim \phi^{0.5}$  dependence.<sup>2</sup>

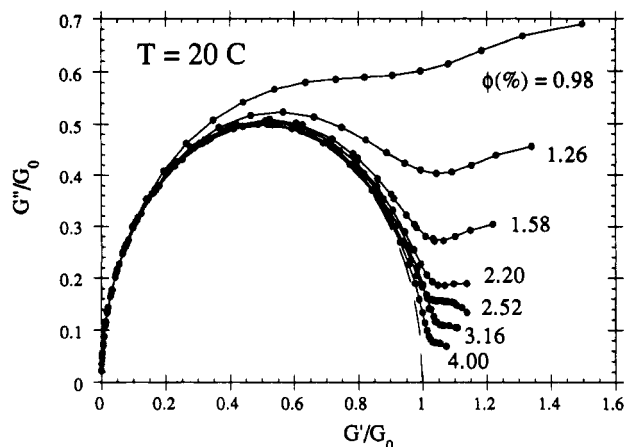
### Data Analysis and Discussion

In Figure 1, the static viscosity  $\eta_0$  is displayed as function of the surfactant concentration  $\phi$  (in weight percent). As already pointed out,  $\eta_0$  is deduced from dynamical measurement extrapolated to  $\omega = 0$ . Below the limit of 0.1 Pa·s, a Couette configuration operating in steady shear mode ( $\dot{\gamma} = 1 \text{ s}^{-1}$ ) was utilized. In this range, most of the samples exhibit a broad Newtonian plateau. Data of Figure 1 clearly evidence the crossover at  $\phi^* \approx 0.3\%$  between dilute and semidilute regimes. Below  $\phi^*$ , the zero-shear viscosity varies linearly according to the Einstein relation,  $\eta_0 = \eta_{\text{water}}(1 + c\phi)$ , where  $c$  is of the order of unity (curve labeled 1). Above,  $\eta_0$  increases drastically as  $\sim \phi^{3.3}$  on more than 1 decade. Deviations from the above power law are observed at still higher surfactant concentration.

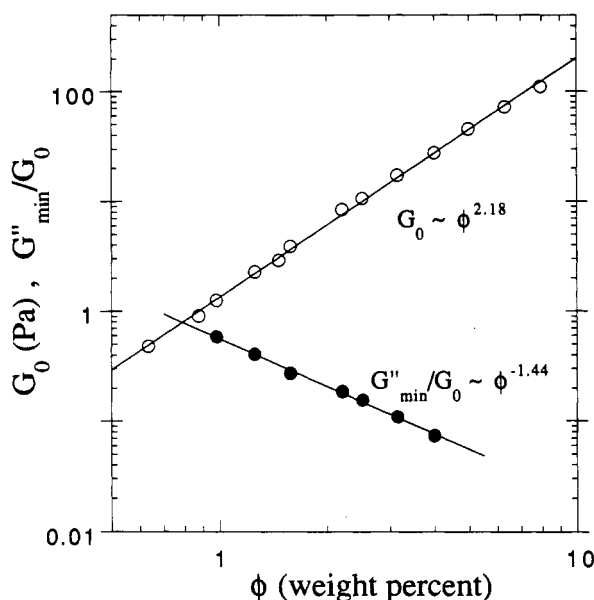
In the semidilute range, the frequency dependence of the viscoelastic modulus  $G^*(\omega)$  is illustrated using Cole–Cole representations. In Figure 2, the imaginary part  $G''(\omega)$  is plotted versus  $G'(\omega)$  for  $\phi = 1$  to 4%, both quantities being normalized to  $G_0$ . At low angular frequency, such as  $\omega \tau_R \ll 1$ , all data sets of Figure 2 agree with the Maxwellian asymptotic limit  $G''/G_0 \approx (G'/G_0)^{1/2}$  (see eq 1). Contrary to this, in the elastic regime (for  $\omega \tau_R \gg 1$ ) two different Cole–Cole behaviors are evident: (i) At concentrations high enough ( $\phi > 5\%$ ), nearly perfect semicircles are obtained, indicating a monoexponential stress relaxation decay. In these conditions, the "extrap-

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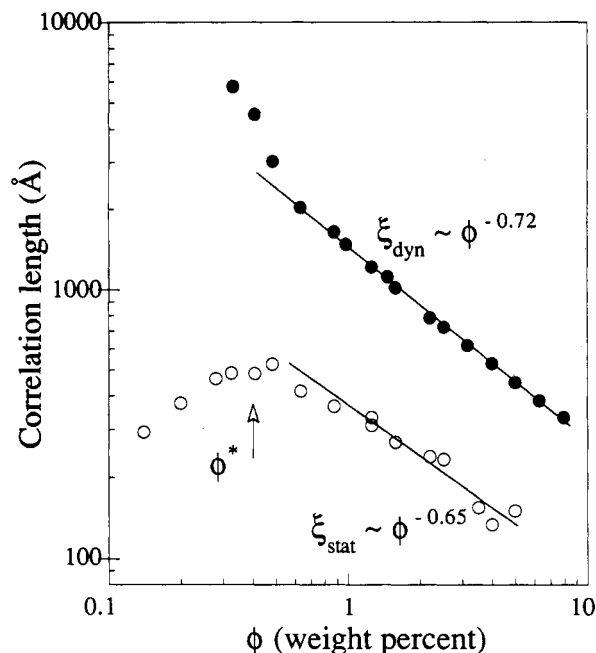
**Figure 2.** Cole-Cole plot for CPy + Sal micellar solutions at various surfactant concentrations,  $\phi = 0.98\text{--}4.0\%$  ( $T = 20\text{ }^{\circ}\text{C}$ ).  $G'$  and  $G''$  data have been normalized to  $G_0$ , the plateau modulus. The half-circle (dashed curve, eq 1) corresponds to an ideal Maxwell element with a unique relaxation time.



**Figure 3.** Surfactant concentration dependence of the plateau modulus  $G_0$  and of the ratio  $G''_{\min}/G_0$  as determined from Figure 2. The power-law variations with exponents 2.18 and -1.44, respectively, are in agreement with the theoretical predictions (see Table I).

olated" and the exact plateau modulus  $G'_\infty$  and  $G_0$ , respectively, are approximately identical. (ii) Below that concentration,  $G''$  is found to pass through a minimum at large  $G'$ . As expected from the model and directly illustrated in Figure 2,  $G''_{\min}/G_0$  increases with decreasing surfactant concentration. For the  $\phi = 0.98\%$  sample, the minimum disappears, due to the collapse of both low and high frequency relaxation mechanisms.

The plateau modulus  $G_0$  is determined from the osculating half-circles fitted to the data (the dashed line in Figure 2 corresponds to eq 1). Problems arise for the lowest concentrated samples ( $\phi \sim 1\%$ ): for these data, only the low-frequency part of the relaxation spectrum is considered for  $G_0$  best fit calculations. The equality  $G'_\infty \approx G_0$  is still assumed, yielding probably an underestimation of the plateau modulus of eq 2. The variations of the plateau modulus as well as the dip normalized to  $G_0$  are shown in Figure 3. As function of surfactant concentration, results are  $G_0 \sim \phi^{2.18}$  and  $G''_{\min}/G_0 \sim \phi^{-1.44}$ , in relative agreement with theoretical predictions, (cf. Table I). This



**Figure 4.** Correlation length  $\xi$  for CPy + sal micellar solution as determined from rheological  $\xi$  data (i.e. using eq 3b and the  $G_0$  data of Figure 3) and from elastic light scattering measurements. In the entangled regime ( $\phi > \phi^*$ ) both sets of data, labeled  $\xi_{\text{dyn}}$  and  $\xi_{\text{stat}}$ , respectively, exhibit scaling laws as a function of surfactant concentration.

agreement for the ratio  $G''_{\min}/G_0$  should not be overestimated however; especially on the low-concentrated side where  $l_0/L$  approach unity, the previous model is not appropriate.

To proceed further, we have now to estimate the correlation length  $\xi$  appearing in eq 3a. It has been derived according to two techniques: first using eq 3b from rheological data, second by direct measurements through elastic light scattering experiments. This approach allows us a double determination of  $\xi(\phi)$ , the former being labeled  $\xi_{\text{dyn}}$  and the latter  $\xi_{\text{stat}}$ . The angular distribution of the scattered intensity in the range  $\phi = 0.1\text{--}6\%$  exhibits clear Ornstein-Zernicke dependences as function of wave vector  $q$ . This is a typical behavior for long flexible surfactant micelles well above the critical micelle concentration (cmc) (more details are given in ref 15). The  $\xi_{\text{stat}}$  data extracted from the light spectra present a rounded maximum at  $\phi^* \approx 0.4\%$  (Figure 4), i.e. at the dilute/semidilute transition. Below  $\phi^*$ , the correlation length represents the radius of gyration of the nonoverlapping polymer-like micelles. For  $\phi \geq \phi^*$ , it provides the mean size of the "blobs" modeling the entangled network. The value of  $\phi^*$  is in accordance with that established from the static viscosity data of Figure 1. Above the maximum, the correlation length varies as  $\xi_{\text{stat}} \sim \phi^{-0.65 \pm 0.05}$ , a dependence which is close to that expected from mean-field predictions for an entangled network ( $\xi \sim \phi^{-0.75}$ ). Also shown in Figure 4 are the  $\xi_{\text{dyn}}$  data computed through eq 3b and using the  $G_0$  data of Figure 3. The exponent is now -0.72 in the  $\phi$  range of interest, in good agreement with the theoretical value. The strong discrepancy in the absolute values between  $\xi_{\text{stat}}$  and  $\xi_{\text{dyn}}$  is essentially due to the fact that the prefactor in eq 3b is not known.

We are hence able to calculate the  $\phi$  dependence for the average chain length  $\bar{L}$ . Putting together eqs 2 and 3 and the results of Figures 3 and 4

$$\bar{L}(\phi) \sim \xi^{5/3} b^{-2/3} \{G''_{\min}/G_0\}^{-1} \sim \phi^{5\alpha/3+1.44}$$

with  $\alpha = -0.65$  or  $-0.72$  depending on how  $\xi$  was determined.

One gets finally in both cases an *increase* of the average chain length with *increasing* surfactant concentration,  $\bar{L}(\phi) \sim \phi^{0.36}$  from light scattering experiments and  $\bar{L}(\phi) \sim \phi^{0.24}$  from rheological data. The whole set of exponents is again summarized in Table I and compared to the theoretical ones.

Moreover, assuming for the persistence length of CPy/Sal micelles the value usually admitted of 150 Å, the mean length  $\bar{L}$  ranges between 1000 and 2000 Å using the light scattering  $\xi_{\text{stat}}$  data. This is roughly one-tenth of what can be calculated from the relationship  $\xi \sim G_0^{-1/3}$  or what was previously reported in the literature<sup>3,13</sup> (typically of the order of few micrometers). The absolute value of  $\bar{L}$  falls probably between both extremes.

In conclusion, we have studied the viscoelastic properties of aqueous surfactant solutions forming long and flexible micelles (CPy/Sal diluted in brine 0.5 M). Our results

confirm the predictions of a new model of stress relaxation recently developed for living polymers.<sup>1-3</sup> In particular, the micellar mean length is found to increase with surfactant concentration, as expected from statistical equilibrium. This last finding contradicts recent reports, however, one by Granek and Cates<sup>3</sup> analyzing rheological data on CTAC/NaSal (in brine 0.25 M)<sup>7</sup> and one by Khatory et al.<sup>13</sup> on CTAB aqueous solutions in the presence of KBr. Both systems were analyzed in a similar way, as for the present one. In order to explain the anomalous decrease of the average chain lengths with increasing surfactant concentrations, the formation of a cross-linked network resulting from intermicellar branching was proposed. Contrary to this, the present data suggest that CPy/Sal aqueous solutions (in brine 0.5 M NaCl) are prototypes for entangled but not branched wormlike micellar systems.