

Entangled versus Multiconnected Network of Wormlike Micelles

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The static and dynamic properties of solutions of cetylpyridinium chlorate micelles in 0.1 and 1 M NaClO₃ brine are studied by light scattering, rheology, and fluorescence recovery after bleaching. The static results lead to a description of the solutions of wormlike micelles as analogous to semidilute solutions of polymers in good solvent. However the dynamic properties are different from those predicted for solutions of equilibrium ("living") polymers. Comparison of the results in the two studied systems lead us to propose that, with increasing salt content, the network of wormlike micelles has an increasing proportion of connections. It is argued that the existence of a certain proportion of connections modifies the reptation mechanism for the relaxation of stress and ultimately allows new mechanisms for the relaxation of stress to become operative.

Introduction

Solutions of wormlike micelles have been found to be a handy experimental realization of solutions of equilibrium ("living") polymers. Their static and dynamic properties have been examined as such in the recent years both experimentally¹⁻¹¹ and theoretically.¹²⁻¹⁴

In "classical" polymer solutions the molecular weight distribution is quenched and their properties have been thoroughly investigated in both the dilute and semidilute regime so that they are now well understood.¹⁵⁻¹⁷ In solutions of equilibrium polymers, the linear polymers can

break and recombine and this ensures that their molecular weight distribution is in thermal equilibrium. Other examples of solutions of equilibrium polymers are end-functionalized polymers, liquid sulfur or selenium. Tentative descriptions of the properties of solutions of equilibrium polymers have recently appeared.^{12-14,18}

In solution, surfactant molecules self-assemble to form aggregates. At low concentrations the aggregates are generally globular micelles,¹⁹ but these micelles can grow upon an increase of surfactant concentration and/or upon addition of salt, alcohols, etc. In that case micelles have been shown to grow to elongated more or less flexible rodlike micelles²⁰⁻²⁶ in agreement with theoretical predictions on micellization.^{27,28} Then for sufficiently long wormlike micelles, an analogy with solutions of flexible polymers in good solvent could be expected,²⁹ as indeed was experimentally found.¹⁻⁷ However the wormlike micelles can break and recombine on a time scale which is dependent on the system and on the physicochemical conditions. We then expect the solutions of semidilute wormlike micelles to appear as identical to an entangled

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network of "classical" polymers if observations are made on a time scale shorter than the time for scission or recombination (τ_{break}) and as a solution of living polymers on a time scale larger than τ_{break} . The rheological properties of these solutions are predicted to depend on the relative magnitude of τ_{break} and of the reptation time (as defined for "classical" polymers) τ_{rept} of a micelle in the entangled network.^{15,17} In this frame, experimental results on the cetyltrimethylammonium bromide (CTAB)/KBr system are well accounted for^{1-3,8} at moderate salt content. Similarly the rheological behavior of other viscoelastic surfactant systems is well accounted for in the range where the viscoelasticity increases quickly reflecting the huge increase in micellar length,^{4,6,24} however a further increase of the triggering parameter for micellar growth often leads to a dramatic fall of the viscosity which remains to be satisfactorily explained.

We have recently reported on another system of wormlike micelles namely cetylpyridinium chlorate (CPClO₃) in 1 M sodium chlorate (NaClO₃) brine. A light scattering study of this system⁵ indicates that, over the explored concentration range, the solution is an entangled network of giant wormlike micelles. However the rheological properties do not fit in this picture,¹¹ e.g. the CPClO₃ solutions are strikingly more fluid than the CTAB/KBr solutions mentioned above. We argued in ref 11 that the possible cross-linking of the wormlike micelles leading to a multiconnected^{30,31} rather than to an entangled network could reconcile the static picture and the dynamic results. We can then figure out a very fluid system if we assume that a local stress can be relaxed by one or the other of the following mechanisms instead of disentangling through a combination of reptation and/or breakage and recombination. The first possible mechanism of relaxation is by sliding the cross-links along the micelles through the viscous flow of the surfactant molecules. This is in fact reminiscent of the highly fluid L₃ (sponge) phase,³²⁻³⁴ which consists of multiconnected fluid membranes and for which a similar explanation has been given.³⁵ The second mechanism is related to the transient character of cross-links: when a micellar thread collides with the network, it forms a transient cross-link and recombines on the other side of the encountered micelle; this can relax the stress by a "ghostlike" crossing as suggested in ref 36.

However the study of micellar solutions of CPClO₃ in NaClO₃ brine of different salt content indicates that the situation is still more intricate. We illustrate this point here by comparing the properties observed previously for solutions of CPClO₃ in 1 M NaClO₃ brine^{5,11} to the static and dynamic properties of solutions in CPClO₃ in 0.1 M NaClO₃ brine measured recently. The static picture points in both cases to a network of wormlike micelles above a certain concentration of CPClO₃ which we identify to c^* , the threshold concentration of the semidilute regime in solutions of polymers; c^* decreases with increasing salt concentration. Similarly the dynamic properties are strongly dependent on the salt concentration; for example the solutions at low salt are more viscous than at higher

salt content and more generally the dynamic properties vary monotonically as a function of salt content. We find that these experimental results are consistent with a continuous evolution of the network where the proportion of connections increases with salt concentration. Then the dynamical results can be interpreted assuming that, at low salt content, the proportion of connections is still small: the topological constraint dominates and the relaxation of stress can be described as the reptation of branched micelles (undergoing reversible scission); the reptation then becomes faster due to the possibility for the branch points to slide along the cylindrical parts of the micelles as described in ref 37. As the salt content is increased, more and more connections exist, the topological constraint ultimately vanishes, and the mechanisms previously described (see above) for the relaxation of stress become operative. This will be discussed in light of the description of the autoassociation of surfactants in terms of a preferred local structure or equivalently a preferred curvature for the surfactant monolayer.^{28,38} We will argue that, in the present situation, the triggering parameter for the preferred curvature is the nature and concentration of the added counterion.

Experimental Section

The cetylpyridinium chlorate (CPClO₃) is obtained by recrystallization from a solution of purified²² cetylpyridinium bromide (CPBr) in concentrated sodium chlorate brine.^{23,29} The samples are prepared by weight in 0.1 M sodium chlorate brine.

For light scattering measurements the sample is filtered through a 0.22- μm Millipore filter into the cylindrical light scattering cell. Static and dynamic light scattering are performed on a standard setup (AMTEC + Brookhaven correlator). The light source is an argon ion laser ($\lambda = 4880 \text{ \AA}$). The scattering vector $q = 4\pi n/\lambda \sin(\theta/2)$ (with n the mean refractive index and θ the scattering angle) ranges from 3×10^{-4} to $3 \times 10^{-3} \text{ \AA}^{-1}$. Both the angular distribution and the time autocorrelation function (quasielastic light scattering) of the intensity of scattered light are measured at a temperature of 35 °C.

The rheological experiments are performed on a Carri-Med CSL100 apparatus (controlled stress) using a Couette geometry having an inner radius of 1.38 cm, an outer radius of 1.5 cm, and a cylinder height of 3.2 cm. The sample volume was approximately 9 cm³ and a little lid placed on the upper part of the Couette cell was used to avoid evaporation. A thermostat allowed control of temperature to $\pm 0.1 \text{ }^\circ\text{C}$.

The long time self-diffusion coefficient was measured by tracer diffusion using the technique of fluorescence recovery after fringe-pattern photobleaching (FRAP).^{39,40} Fluorescent molecules are incorporated in the micelles (i.e. insoluble in brine); the fluorescence is irreversibly destroyed upon illumination by a high intensity laser flash (bleaching). A nonuniform concentration of active tracers is created by bleaching and its relaxation is detected by a second low intensity beam and the tracer diffusion coefficient (D_s) is calculated from the recovery time τ : $D_s = 1/\tau q^2$ where $q = 2\pi/i$, where i is the fringe spacing (typically $2 < i < 100 \mu\text{m}$ so that measurable D_s are in the range 10^{-10} to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$).

Results

Light Scattering. From the angular distributions of scattered light for solutions in 0.1 M brine shown in Figure 1, we deduce a characteristic length ξ and the intensity scattered at $q \rightarrow 0$ using the classical Ornstein-Zernicke form. In Figures 2 and 3 we have plotted the evolution of ξ and $I(0)$ with c (the concentration of CPClO₃) deduced from the distributions of Figure 1 for the solutions of

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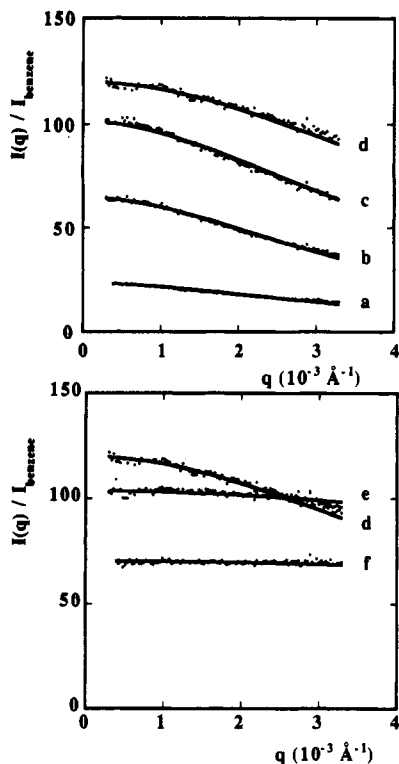


Figure 1. Angular distributions of light scattered by solutions of CPClO₃ in 0.1 M NaClO₃ brine. The lines are the best fits of the experimental distributions to the Ornstein Zernicke distribution. C_{CPClO_3} = (a) 0.001 g/g, (b) 0.0025 g/g, (c) 0.005 g/g, (d) 0.01 g/g, (e) 0.02 g/g, and (f) 0.05 g/g.

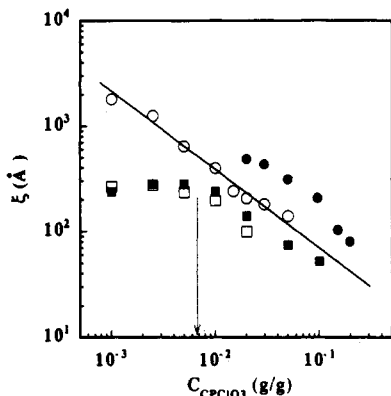


Figure 2. Evolution of the characteristic lengths with the concentration of CPClO₃: the open signs are the static lengths and the black signs are the hydrodynamic lengths; (O, ●) 1 M NaClO₃ brine, (□, ■) in 0.1 M NaClO₃ brine. The arrow indicates the corresponding approximate value of c^* for the solutions in 0.1 M NaClO₃ brine. The straight line has a slope of -0.75 .

CPClO₃ in 0.1 M brine. Both ξ and $I(0)$ are found to increase first then to decrease with increasing concentration. This behavior contrasts with the results for solutions in 1 M brine,^{5,11} also plotted in Figures 2 and 3, where ξ and $I(0)$ decrease over the whole range of concentration.

In dilute solutions the micelles are far apart, the characteristic length proportional to the radius of gyration R_g ; from models of micellar growth,^{20-23,27} the micelles (and thus R_g) are expected to grow with increasing concentration. In semidilute solutions, above the concentration c^* where the micelles begin to overlap, the characteristic length is the correlation length ξ which will decrease with increasing concentration. Similarly the osmotic compressibility, and thus $I(0)$, is expected to increase with the micellar concentration in the dilute regime and to decrease

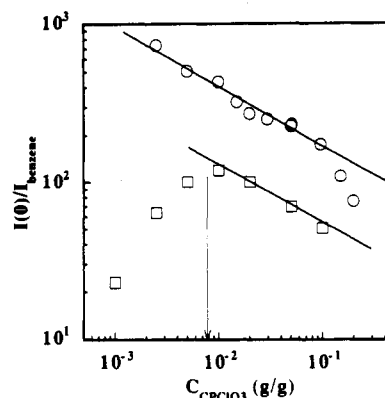


Figure 3. Evolution of the scattered intensity $I(q=0)$ with the concentration of CPClO₃ (O) in 1 M NaClO₃ brine and (□) in 0.1 M NaClO₃ brine. The arrow indicates the corresponding approximate value of c^* for the solutions in 0.1 M NaClO₃ brine. The straight lines have slopes of -0.35 .

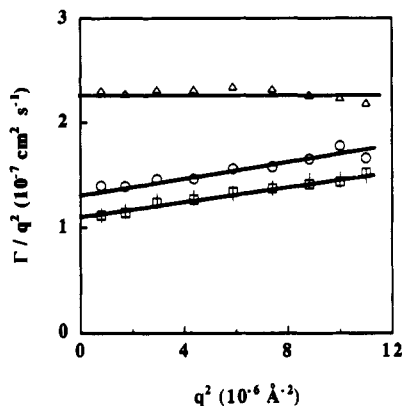


Figure 4. Evolution of Γ/q^2 with q^2 . Γ is the relaxation rate measured in QELS on solutions of CPClO₃ in 0.1 M NaClO₃ brine: C_{CPClO_3} = (∇) 0.0025 g/g, (□) 0.005 g/g, (O) 0.01 g/g, and (Δ) 0.02 g/g.

in the semidilute regime. The maximum in the ξ and $I(0)$ curves for the 0.1 M solutions corresponds to the crossover from the dilute to the semidilute regime, and we can deduce $c^* \sim 8 \times 10^{-3}$ g/g. For the 1 M solutions c^* is below the lowest accessible concentration $c^* \leq 1 \times 10^{-3}$ g/g.

The passage from the dilute to the semidilute regime in the 0.1 M system is further evidenced by the quasielastic light scattering results. In QELS one probes the relaxation of the local concentration fluctuations which relax through diffusion of individual micelles in the dilute regime or through the diffusion of "blobs" in the semidilute regime. In the first case, the large size distribution of the large wormlike micelles leads to a dependency of the apparent mean diffusion coefficient Γ/q^2 (with Γ the relaxation rate at q) on q while in the second case, well inside the semidilute regime, the polydispersity of the micelles become irrelevant and the mean diffusion coefficient of the blobs is q -independent. This behavior is indeed observed as illustrated in Figure 4: Γ/q^2 varies linearly with q^2 up to $c = 1 \times 10^{-2}$ g/g while it is found constant at $c = 2 \times 10^{-2}$ g/g indicating that this concentration is well over the crossover region characterized by c^* . ξ_h the mean hydrodynamic length derived from the mean diffusion coefficient at $q = 0$ is plotted in Figure 2 together with ξ and is found to have a parallel evolution.

In the semidilute regime both ξ , ξ_h and $I(0)$ are expected to decrease as a power law of concentration. In 1 M brine we found that exponent for ξ and $\xi_h = -0.75 \pm 0.05$ and the exponent for $I(0) = -0.35 \pm 0.05$ in excellent agreement with the predicted values -0.77 and -0.31 .¹⁵⁻¹⁷ As can be

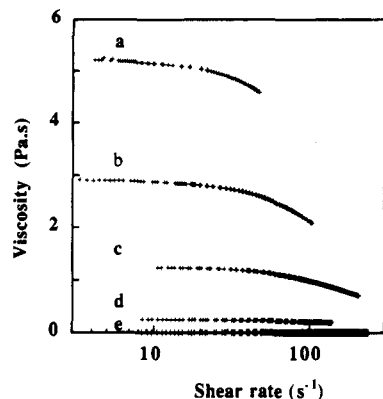


Figure 5. Viscosity as a function of shear rate in 0.1 M NaClO₃ brine with C_{CPClO_3} = (a) 0.2 g/g, (b) 0.15 g/g, (c) 0.1 g/g, (d) 0.05 g/g, and (e) 0.01 g/g.

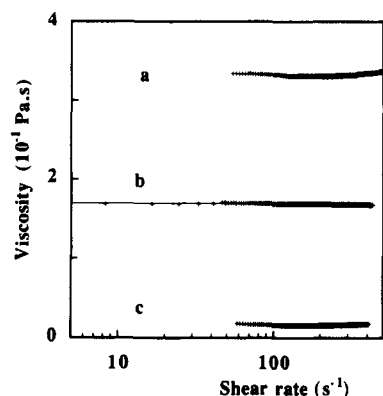


Figure 6. Viscosity as a function of shear rate in 1 M NaClO₃ brine with C_{CPClO_3} = (a) 0.2 g/g, (b) 0.1 g/g, and (c) 0.01 g/g.

seen in Figures 2 and 3 the curves for the system in 0.1 M brine tend to follow the same power laws above the crossover from the dilute to the semidilute regime.

Rheology. We have measured the viscosity as a function of shear rate between 35 and 50 °C. The results obtained for five concentrations in 0.1 M brine and at 35 °C are shown in Figure 5. The observed behavior of the solutions is clearly non-Newtonian; this implies viscoelastic relaxation times on the order of 10⁻¹ s. This contrasts with the behavior previously discussed of solutions in 1 M brine,¹¹ illustrated in Figure 6: in that case the viscosity is independent of shear rate in the explored range (0–600 s⁻¹) and this implies that the viscoelastic relaxation times are much shorter, i.e. smaller than 10⁻³ s. Furthermore the viscosity is higher by roughly a factor of 10 for the solutions in 0.1 M brine compared to that of solutions in 1 M brine.

The viscosity at zero shear rate is plotted as a function of c in Figure 7 for the solutions in 0.1 and 1 M brine.⁴¹ In both cases the viscosity increases very slowly at the lowest concentrations then, above a certain concentration, which presumably corresponds to the crossover from the dilute to the semidilute regime, it increased rapidly. We thus obtain $c^* = 1.5 \times 10^{-2}$ g/g and 7×10^{-3} g/g in 0.1 and 1 M, respectively. The viscosity increases more steeply in 0.1 M brine than in 1 M brine; this is reflected in the exponent of the observed power law, c^γ , with $\gamma = 2$ and 1, respectively. Both of these exponents are smaller than

(41) We note that the observed viscosity data for the 0.1 M NaClO₃ system are rather large in the dilute regime $c < c^*$. Nonoverlapping colloidal systems generally have a lower viscosity closer to that of the solvent. This is reminiscent of our previous observations in micellar solutions in pure water; cf. Porte, G.; Poggi, Y.; Appell, J.; Maret, G. *J. Phys. Chem.* 1984, 88, 5713.

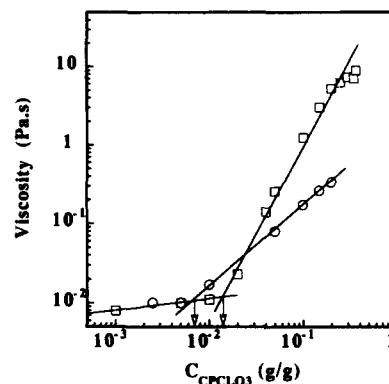


Figure 7. Viscosity as a function of the concentration of CPClO₃ (O) in 1 M NaClO₃ brine and (□) in 0.1 M NaClO₃ brine. The arrows indicate the corresponding approximate value of c^* in both cases. Above c^* the straight lines have slopes of 1 and 2, respectively.

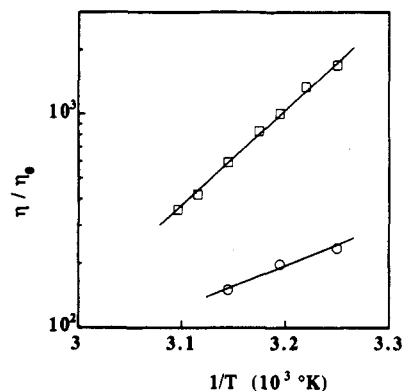


Figure 8. Evolution of the relative viscosity with 1/temperature for solutions of 0.1 g/g CPClO₃ (O) in 1 M NaClO₃ brine and (□) in 0.1 M NaClO₃ brine.

the exponent predicted by the model of reptation plus breaking and recombination developed by Cates^{12,13} as discussed below. Note that for the solutions in 0.1 M brine a slowing down of the viscosity increase is noticeable above $c = 0.2$ g/g; this is probably due to the proximity of a phase transition to a birefringent phase.

In Figure 8 the ratio of the viscosity of solutions ($c = 0.1$ g/g) to that of water is plotted as a function of the inverse of temperature. This ratio follows an Arrhenius law and we can deduce an activation energy $E_a = [17.8 \pm 0.2]kT$ for the solution in 0.1 M brine and $E_a = [6 \pm 0.5]kT$ for the solution in 1 M brine.

Fluorescence Recovery after Bleaching (FRAP). D_{self} has been measured at $T = 35$ °C for solutions in 0.1 and 1 M brine. The fluorescence recovery curves are exponential, meaning that the breakage-recombination times are shorter than the reptation times and that an average self-diffusion coefficient D_s is measured. D_s is independent of the fringe spacing i , as expected for a standard diffusion process (we do not observe accelerated diffusion as with CTAB micelles in the presence of large amounts of salt).¹⁰ The results are plotted in Figure 9. The curve observed for the system 0.1 M is very analogous to those observed for wormlike micelles of CTAB in brine or lecithine in isooctane⁹ with three successive regimes of variation; at very low concentrations D_{self} decreases slowly for increasing concentration up to 3×10^{-3} g/g, then it decreases more rapidly with increasing concentration up to $c = 6 \times 10^{-2}$ g/g, then it increases slightly. In the curve for the system 1 M the first regime is not observed, and after the rapid decrease with concentration up to $c = 1 \times 10^{-2}$ g/g, D_{self} becomes almost constant. The transition

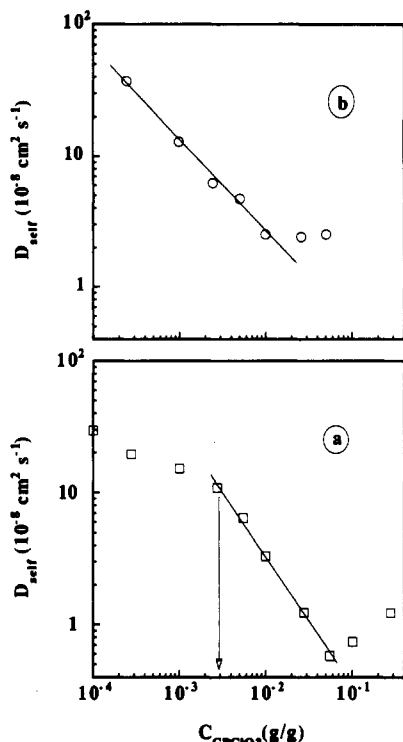


Figure 9. D_{self} as a function of c_{CPClO_3} (a) in 0.1 M NaClO_3 brine, where the arrow indicates the corresponding approximate value of c^* and (b) in 1 M NaClO_3 brine.

from regime 1 to regime 2 can be ascribed to the crossover from the dilute to the semidilute regime and it is noticeable only in the 0.1 M system (leading to $c^* \sim 3 \times 10^{-3}$ g/g). The transition from regime 2 to regime 3 is abrupt, as observed previously; its origin is still debated.

The fast decrease before the leveling off of D_{self} follows a power law with c : $c^{-\delta}$. δ is 0.75 in 1 M brine and 1 in 0.1 M brine; these values are close to but significantly smaller than those previously observed for other systems. For lecithine micelles⁹ the value obtained (1.35 ± 0.05) seems to agree with the description of tracer diffusion in living polymers given by Cates.¹² This is not the case for CTAB micelles where δ is larger than 1.35 for salt (KBr) concentrations smaller than 0.25 M⁸ and where, at larger salt concentrations, anomalous diffusion takes place¹⁰ unless temperature is raised. For example at $T = 55^\circ\text{C}$ and with 1 M KBr, δ is 1 ± 0.05 .

Discussion

Transition from the Dilute to the Semidilute Micellar Solutions. From a small angle neutron scattering study⁴² the micelles of CPClO_3 in NaClO_3 brine have been shown to be locally cylindrical with a micellar diameter of 50 Å. These micelles are highly flexible; their persistence length is equal to 170 ± 50 Å. This local structure is found to be insensitive to the salt concentration. The solutions of these long flexible micelles are expected to have properties similar to those of flexible polymers. We thus expect to observe, starting at low concentration with dilute solutions of wormlike micelles, a crossover to a semidilute regime where the wormlike micelles overlap more and more when the concentration increases. The crossover concentration c^* is well-defined in "classical" polymer solutions where the polymers have a narrow distribution of size independent of concentration. By analogy, we expect such a crossover to be observed in

wormlike micelles, but its definition can be obscured by the large size distribution and by its evolution with concentration as recently discussed by Carale and Blankstein.⁷ As already mentioned above we do indeed find a change of the properties measured in the solutions of wormlike micelles which must be indicative of the transition from the dilute to the semidilute regime.

We compare here the indications obtained from the three sets of experiments. It is well-known that the crossover region is quite broad and each measured property is expected to be sensitive to the change of regime somewhere within this region; furthermore we suspect that the weighting of small and large micelles varies from one experiment to the other. It is thus not surprising to obtain somewhat different values of c^* from the three experiments. In light scattering the crossover is in principle easy to detect as it is expected to lead to a maximum in the curves of characteristic lengths and zero angle scattered intensity as stated above. In rheology as in FRAP the task is more difficult as both the zero-shear viscosity and the self-diffusion coefficient vary monotonically; however the concentration dependence of these parameters is expected to be much stronger in the semidilute regime.

In the solutions in 0.1 M brine, all three experiments point to a crossover from the dilute to the semidilute regimes. $c^* \sim 8 \times 10^{-3}$ g/g in light scattering, $\sim 1.5 \times 10^{-2}$ g/g in rheology, and $\sim 3 \times 10^{-3}$ g/g in FRAP. If we turn to the solutions in 1 M brine, indication of a crossover is clearly perceptible only in the rheological experiment $c^* \sim 7 \times 10^{-3}$ g/g. From the observation that for 0.1 M the c^* values obtained from LS and FRAP are both significantly lower than that obtained from rheology, it is plausible that the corresponding c^* are virtual, i.e. below the range of concentration where micelles exist. This is confirmed by the evolution of the light scattering results with temperature⁴³ which indicates that the lowest concentration is close to the crossover as probed by LS. The size of the micelles is known to decrease with temperature,^{20,22,23} at the lowest concentration both ξ and $I(0)$ are found to decrease with increasing temperature as expected for dilute micellar solutions where the size of individual micelles is relevant, whereas they should remain constant well inside the semidilute regime.

The decrease of c^* with salt concentration is not surprising if we turn to the thermodynamical model for micellar growth as discussed below. The salt concentration is a triggering parameter for the elongation of micelles: wormlike micelles are thus longer at a given CPClO_3 concentration when the salt content increases, and thus c^* , which marks the concentration at which micelles begin to overlap, is lower.

Description of the Micellar Solutions in the Semidilute Regime. The description that can be made of the semidilute solutions of wormlike micelles in the two systems (0.1 and 1 M brine) is very different if one refers to the light scattering results which points to an analogy with solutions of polymers and with solutions of other micellar systems or to the dynamical results obtained from rheology or FRAP where striking differences with solutions of polymers and with solutions of other micellar systems are observed: the solutions are more fluid; the relaxation times are shorter; the variations with concentration are slower. This is true for the two systems examined here. Furthermore the two systems have the same behavior in their respective semidilute range as regards the static properties (LS results), but they differ in their dynamical properties (rheology and FRAP).

(42) Appell, J.; Marignan, J. *J. Phys. II* 1991, 1, 1447.

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Images of the network of large flexible micelles, existing in other systems of wormlike micelles, have recently been obtained by cryotransmission electron microscopy giving a strong support to the description of these micellar solutions.^{44,45} We once hoped to be able to obtain images of the 1 M system using freeze fracture electron microscopy which has been successfully used to obtain images of other phases formed in solutions of surfactants.⁴⁶ The attempts came to nothing, this is most probably due to the fact that the relaxation times are very short and do not allow the freezing of the structure.

The light scattering results point to a network of large flexible micelles analogous to the network of flexible polymers; the evolution of ξ and $I(0)$ as power laws of the concentration predicted and observed in semidilute solutions of the polymers are observed here as indicated above. However a noticeable difference between the two systems is observed; well above c^* , at a given micellar concentration one would expect to measure the same correlation length and the same $I(0)$. On the contrary, we find a significant difference. The values measured at 0.1 M are lower than those at 1 M (cf. Figures 2 and 3). This could be due to an effect of insufficient screening but it could as well reveal some structural differences between systems at high and low salt content as argued below.

The representation we have of the solutions of wormlike micelles is, to this point, that of a network of micelles for which we assume the same thermodynamical equilibrium than in dilute solutions. Then, as stated before, we can expect their dynamic properties to be that of entangled equilibrium polymer solutions^{12-15,18} for which two possible mechanisms for the relaxation of stress have been considered. One is the reptation of micellar chains identical to that described for classical polymers with a relaxation time τ_{rept} (taken as the reptation time of a micelle of mean length) and the other is the breaking and the recombination of micellar chains with a relaxation time τ_{break} . The dynamics of the solutions then depend upon the relative magnitude of τ_{rept} and τ_{break} .

If $\tau_{\text{rept}} < \tau_{\text{break}}$, reptation is the rate-determining step of stress relaxation; the dynamic properties vary with the concentration with the laws for classical polymer solutions^{15,17} modified so as to take into account the distribution of micellar length and its evolution with concentration.^{12,13} We can rule out this possibility in the present case. In that case both the viscosity and the coefficient of self-diffusion should scale with micellar concentration with exponents of 5.4 and -2.75 , respectively, i.e., should vary much more rapidly with concentration than has been observed here (see above).

If $\tau_{\text{rept}} > \tau_{\text{break}}$, then the second relaxation mechanism becomes operative and the dynamic properties are modified. In the limit $\tau_{\text{break}} \ll \tau_{\text{rept}}$, the system displays one viscoelastic relaxation time $T_R = [\tau_{\text{break}} \tau_{\text{rept}}]^{1/2}$.¹² The viscosity and the coefficient of self-diffusion are predicted to scale with micellar concentration with exponents ~ 3.6 and ~ -1.6 . Such a situation was only met in the systems CTAB/KBr at low salt concentration.^{1,3,8} But in the two CPClO₃ systems we find exponents that are significantly smaller as summarized in Table I and that decrease with increasing salt content. In fact further measurement on CPClO₃/NaClO₃ over a large range of salt concentration indicates a regular decrease of these exponents with salt

Table I. Comparison of the Properties Observed in Semidilute Solutions of CPClO₃ Solutions in 0.1 and 1 M NaClO₃ Brine

	static properties		viscosity $\eta \sim c^\gamma$	T_R , s	D_{self} $D \sim c^{-\delta}$
	$I(0) \sim c^{-\alpha}$	$\xi \sim c^{-\beta}$			
	α	β	γ		δ
entangled network	0.31	0.77	3.6 ^a		1.35 ^a
0.1 M	0.35 ± 0.05	0.75 ± 0.05	2	~0.1	1
1 M	0.35 ± 0.05	0.75 ± 0.05	1	<10 ⁻³	0.75

^a For equilibrium polymers with $\tau_{\text{break}} \ll \tau_{\text{rept}}$.

concentration and a similar situation is observed in the CTAB/KBr system.⁴⁷

In our investigation on the CPClO₃ solutions in 1 M brine,¹¹ we suggested that a structure which remained compatible with the picture given by the static results could be that of a network where a certain number of the entanglements are replaced by cross-links. From a geometrical point of view the cross-links and the entanglement points contribute equally to the crossings of the network, but it is sensible to expect that the proportion of cross-links and entanglement points will have a strong influence on the dynamic properties of the micellar networks.

The occurrence of such cross-links and the role of the added counterion (both in nature and in concentration) are a straightforward matter in the admitted description of the self-assembly of surfactants. This self-assembly into aggregates of different morphologies is explained in terms of a preferred curvature for the surfactant monolayer.^{27,38} Elongated micelles thus correspond to locally cylindrical aggregates, their two free ends are generally thought to be closed by globular endcaps and the driving force for the micellar growth is then the difference in the free energy of surfactants in the cylindrical or globular environment; a larger difference leads to longer micelles in order to diminish the number of surfactants in the "unfavorable" globular surroundings (with a larger curvature than the cylinder). This leads to micellar solutions having static and dynamic properties analogous to those of solutions of equilibrium polymers. One can figure out another way to suppress the free ends of locally cylindrical micelles: to connect the cylinders³⁰ in which case the unfavorable surroundings (the connection point) correspond to smaller curvatures than the cylinder. The solution adopted by a particular system will depend on the respective energies to form globular endcaps or connection points. If the increase of a given parameter (addition of salt, alcohol, etc.) triggers the elongation of micelles, it implies that it decreases the optimal curvature of the surfactant monolayer so that the formation energy of endcaps will increase and conversely the formation energy of connection points will decrease. Thus in a given system it is possible to imagine that the increase of such a parameter promotes the elongation of micelles with endcaps and upon further increase promotes the connection (cross-linking) of cylindrical micelles. This involved situation has been recently formalized³¹ in the limit of no free extremities. The distribution of real cross-links and entanglement points and its influence on some properties of the dilute micellar solutions have been discussed.

In a partially cross-linked network of micelles, the mechanism for the relaxation of stress will be largely dependent on the proportion of connections and entanglements points:

As long as the proportion of connections remains small the topological constraint remains large and the reptation

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of branched micelles must be considered. It was shown³⁷ recently that in that case the reptation time decreases because the curvilinear motion of the cylinders is accelerated by the possibility for the connections (which are not chemical bonds) to slide along the cylindrical parts of the micelles. This model does predict that the viscosity decreases with an increasing proportion of connections. The exact law for the variation of viscosity with micellar concentration remains to be established, but this model (assuming the breakage/recombination process to occur on a smaller time scale than the reptation) does predict a somewhat smaller increase of viscosity with concentration than in the model of reptation of wormlike micelles undergoing reversible scission.

If the proportion of connections increases so that the topological constraint due to the entanglements diminishes and eventually vanishes, then new mechanisms for the relaxation of stress can be assumed. We described previously¹¹ two plausible mechanisms. The first possible mechanism of relaxation is, in continuity with the preceding one, by sliding the connections along the micelles through the viscous flow of the surfactant molecules through the micellar network. Such a mechanism can allow for a very fluid solution and for a faster relaxation of stress than reptation of wormlike or even branched micelles. The second mechanism is relaxation of stress by a "ghostlike" crossing;^{11,36} the equilibrium properties of the micellar network, correspond to a transient character of the connections so that when a micellar thread collides with another one in the network, it can form a transient cross-link and the two threads separate on the other side.

A theoretical description of these mechanisms and of the resulting laws for dynamic properties, in a cross-linked network with a given proportion of connections, is still a challenge for theoreticians.

The results obtained for CPClO₃ solutions in 0.1 and 1 M brine can be interpreted in the light of the above arguments. ClO₃⁻ has indeed been found to be one of the most efficient counterions in promoting the elongation of micelles.²³ Increasing its concentration can then also promote more and more cross-links. In a network of wormlike micelles with an increasing proportion of cross-links, we can expect the new mechanisms of stress relaxation to come more and more into play so that one will observe a continuous evolution (cf. Table I) of the dynamic properties from that of a network of entangled wormlike micelles to that of a multiconnected network of cross-linked micelles. Although the static picture of an entangled or of a multiconnected network must be very similar, we must recall that a scattering experiment probes the intramicellar correlations screened by the other micelles, the presence of connections leads to a propagation over larger distance of these intramicellar correlations or, stated in other words, the presence of more connections acts as an effective attractive interaction thus increasing the osmotic compressibility ($I(0)$) and the screening length (ξ). This is indeed observed when comparing the static results in the semidilute range for the 0.1 and the 1 M systems as noted above.

Further works are currently in progress to ascertain and clarify the above description of semidilute solutions of more or less cross-linked wormlike micelles.