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J. Appell, G. Porte, A. Khatory, F. Kern, S. Candau. Static and dynamic properties of a network of wormlike surfactant micelles (cetylpyridinium chlorate in sodium chlorate brine). *Journal de Physique II*, 1992, 2 (5), pp.1045-1052. 10.1051/jp2:1992104 . jpa-00247690

HAL Id: jpa-00247690

<https://hal.science/jpa-00247690>

Submitted on 4 Feb 2008

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Classification

Physics Abstracts

47.15 — 51.20 — 78.35 — 82.70

Static and dynamic properties of a network of wormlike surfactant micelles (cetylpyridinium chlorate in sodium chlorate brine)

J. Appell ⁽¹⁾, G. Porte ⁽¹⁾, A. Khatory ⁽²⁾, F. Kern ⁽²⁾ and S. J. Candau ⁽²⁾

⁽¹⁾ Groupe de Dynamique des Phases Condensées (*), Université des Sciences et Techniques du Languedoc, 34095 Montpellier Cedex 05, France

⁽²⁾ Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes (**), Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

(Received 4 November 1991, revised 28 January 1992, accepted 10 February 1992)

Abstract. — The structure of solutions of cetylpyridinium chlorate micelles is studied by light scattering and found to be analogous to that of polymer solutions in good solvent and in the semi dilute range. In contrast the micellar solutions are found here to be very fluid and their measured rheological properties are strikingly different from that of polymer solutions. These rheological properties are not accounted for by the recently developed model for semi dilute solutions of equilibrium polymers which described well the properties of other similar wormlike micellar systems. We suggest that the existence of crosslinks rather than entanglement points in the network of wormlike micelles could be responsible for these unexpected properties.

Introduction.

In solution, surfactant molecules autoassociate to form aggregates. At low concentrations the aggregates are generally globular micelles [1]. In some systems these micelles grow upon an increase of surfactant concentration and/or upon addition of salt, alcohols etc... These micelles have been shown experimentally to grow to elongated more or less flexible rod-like micelles : the so-called sphere to rod transition [2-8]. Theoretical predictions on micellization [9, 10] suggest that, under appropriate conditions, the elongated micelles can grow very long. One then expects an analogy between solutions of flexible micelles (with a length larger than the persistence length characteristic of their flexibility) and solutions of polymers as suggested in [11]. In the last years much experimental evidence has reinforced this analogy to a certain extent [12-17]. It is important to stress at this point the transient character of surfactant

(*) URA du CNRS n° 233.

(**) URA du CNRS n° 851.

aggregates. In particular the wormlike micelles can break and recombine on a time scale which is dependent on the system and on the physico-chemical conditions.

This description leads to the idea [14] that solutions of wormlike micelles must be a good example of solutions of equilibrium polymers as opposed to solutions of « classical » polymers. In « classical » polymer solutions the molecular weight distribution is quenched and their properties have been thoroughly investigated both in the dilute and semi-dilute regime so that they are now well understood [18-20]. In solutions of equilibrium polymers, the linear polymers can break and recombine and this ensures that their molecular weight distribution is in thermal equilibrium. Examples of solutions of equilibrium polymers are end-functionalized polymers, liquid sulphur or selenium and certain surfactant assemblies (cylindrical microemulsions or elongated micelles). Tentative descriptions of the properties of solutions of equilibrium (or living) polymers have recently appeared [21, 22].

We then expect the solutions of semi dilute wormlike micelles to appear as identical to an entangled network of 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} . And 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 [23]) τ_{rept} of a micelle in the entangled network [18, 23]. In this frame, experimental results on the cetyltrimethyl ammonium bromide (CTAB)/KBr system are well accounted for [12-14, 24]. Similarly the rheological behavior of other viscoelastic surfactant systems are well accounted for in the range where the viscoelasticity increases quickly reflecting the huge increase in micellar length [5, 15, 17] 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 describe in this paper the properties of solutions of wormlike micelles in the system cetylpyridinium chlorate (CPClO₃) in 1 M sodium chlorate brine. A light scattering study of this system [16] indicates that, over the explored concentration range, the experimental results are well accounted for assuming an entangled network of giant wormlike micelles. Strikingly the rheological properties do not fit in this picture and are very different from that of the CTAB/KBr system mentioned above. The viscosity is much lower and it has a much weaker dependence on the volume fraction of micelles. Its response to stress is Newtonian over the entire range of shear rate explored, again in contrast to those measured for CTAB/KBr or other micellar systems.

In the last part of this paper we will discuss a possible explanation of this striking behavior : the possible crosslinking of the wormlike micelles leading to a multiconnected rather than to an entangled network. Such a possibility was initially considered in the sequence of morphologies expected in surfactant aggregation [25] and its occurrence was further suggested as an explanation to the observed phase separation in wormlike micellar solutions. A statistical description of the occurrence of crosslinks *versus* entanglements in giant micellar semi-dilute solutions has recently been proposed [26]. The fact that a multiconnected network can be less viscous than an entangled network is not evident at first sight. We can 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 crosslinks along the micelles through the viscous flow of the surfactant molecules. This is in fact reminiscent of the highly fluid L₃ (sponge) phase [27-29] which consist of multiconnected fluid membranes and for which a similar explanation has been given [30]. The second mechanism is related to the transient character of crosslinks : when a micellar thread collides with the network it forms a transient crosslink and recombines on the other side of the encountered micelle ; this can relax the stress by a « ghostlike » crossing.

Experimental.

The cetylpyridinium chlorate (CPClO₃) is obtained by recrystallization from a solution of purified [3] cetylpyridinium bromide (CPBr) in concentrated sodium chlorate brine [4, 11]. The samples are prepared by weight in 1 M sodium chlorate brine.

For light scattering measurements the sample is filtered through 0.22 μm Millipore filter into the cylindrical light scattering cell. Static and dynamic light scattering are performed on a standard set up (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 (quasi elastic 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.

Results.

From a small angle neutron scattering study of solutions of CPClO₃ micelles we have recently ascertained the local structure of these micelles [31] which is essentially identical to that found previously for CPBr micelles [32]. The micelles are locally cylindrical with a circular cross section; the radius of the paraffinic core equals to $20 \pm 1 \text{ \AA}$, taking into account the polar heads this leads to a micellar diameter of 50 Å. The micelles are very flexible: the persistence length characterizing their flexibility is found equal to $170 \pm 50 \text{ \AA}$.

LIGHT SCATTERING. — The complete analysis of light scattering results has been described, at length, previously [16]. The CPClO₃ solutions have been studied over a wide range of concentrations (from critical micellar concentration $\sim 0.00065 \text{ g/g}$ to 0.2 g/g). The obtained results point to the similarity of these solutions and of polymer solutions in the semi dilute regime.

For polymer solutions, the angular distribution of scattered light has been shown [17, 18] to be a universal function of a dimensionless parameter qL_c where L_c is the correlation length. The universal behavior of the scattering patterns in reduced units is shown over a broad qL_c region in figure 1 and is seen to coincide, within experimental errors, with the scattering pattern from polymer solutions. On the other hand L_c is expected to decrease as a power law of concentration with an exponent $= -0.77$. The exponent of the experimentally observed power law is equal to -0.75 ± 0.05 in excellent agreement with the predicted value. And the osmotic compressibility decreases as a power law with an exponent -0.35 ± 0.05 in agreement with the predicted value (-0.31).

Quasi-elastic light scattering probes different relaxation processes depending on the magnitude of qL_c . For $qL_c < 1$ the average decay rate $\bar{F} = \bar{D}q^2$ is typical of a pure diffusive process and \bar{D} the cooperative diffusion constant is found to scale as L_c^{-1} as expected [18, 19]. For $qL_c > 1$ the relaxations of the fluctuations of the refractive index are due to the internal modes of the individual micellar « blobs » and theory predicts [18-20] the average decay rate to be independent on micellar concentration and to be proportional to q^3 . Such a behavior has been observed [16] for solutions with $c < 0.01 \text{ g/g}$ where the condition $qL_c > 1$ holds.

Altogether light scattering results lead to the picture of solutions of entangled flexible micelles and to a straightforward analogy with solutions of polymers in good solvent and in

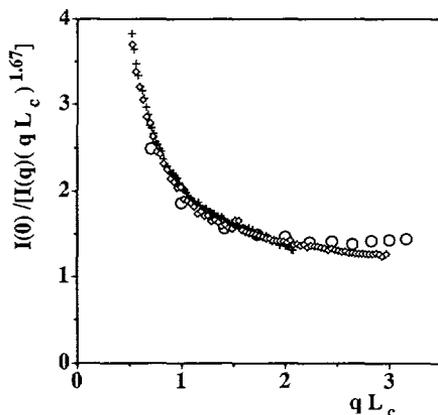


Fig. 1. — An illustration of the analogy between the light scattering patterns from micellar solutions and polymer solutions in the semi-dilute range. CPClO_3 solutions; (\diamond) $c = 0.0025$ g/g; (+) $c = 0.005$ g/g. (\circ) universal curve for polymer solutions derived from figure XV-25 in reference [19].

the semi dilute range. This is very similar to the results obtained in semi-dilute solutions of other wormlike micelles [12-14].

RHEOLOGY. — The main results in rheological measurements are very surprising in the frame of the above description of the micellar solutions.

Exploration of the rheological behavior as a function of shear rate indicates that all solutions (in the same concentration range as above) behave as Newtonian liquids. This is illustrated by the plot of viscosity *versus* shear rate shown in figure 2 for different concentrations. We have checked on one sample (cf. Fig. 2) that at very low strains the sample still displays Newtonian behavior. Furthermore a qualitative observation of all

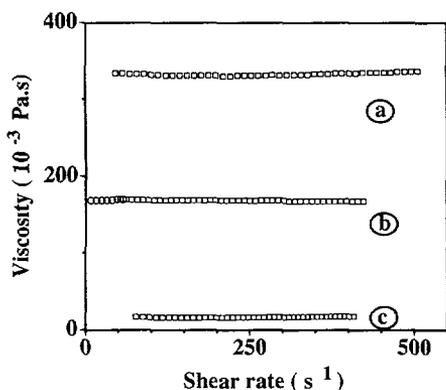


Fig. 2.

Fig. 2. — The viscosity of solutions of CPClO_3 micelles as a function of shear rate: a) $c = 0.2$ g/g, b) $c = 0.1$ g/g, c) $c = 0.01$ g/g at a fixed temperature $T = 35$ °C. In curve b the results obtained in a low shear experiment (\circ) are displayed illustrating the constancy of viscosity down to the lowest shear rates.

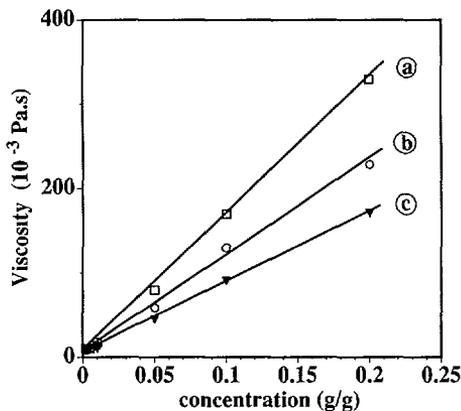


Fig. 3.

Fig. 3. — The viscosity of solutions of CPClO_3 micelles as a function of concentration and at three temperatures: a) $T = 35$ °C, b) $T = 40$ °C, c) $T = 45$ °C.

samples brought no evidence of any yield stress. The viscosity is independent of shear rate in the explored range up to 550 s^{-1} . This implies that the viscoelastic relaxation times are very short i.e. smaller than a millisecond at all concentrations. This is in strong contrast to the results obtained in the analogous system CTAB/KBr [13] where the longest viscoelastic relaxation times are larger by at least one order of magnitude.

In figure 3 viscosity *versus* concentration is plotted. Here again comparison with the results on the analogous system CTAB/KBr is instructive : the viscosity is here much smaller (two or more orders of magnitude) and it increases linearly with concentration in contrast to the steep increase observed in the CTAB/KBr system where viscosity varies as a power law of concentration with an exponent ~ 3.6 .

Discussion.

We are now faced with two sets of evidence.

On the one hand light scattering results are similar to those obtained for other micellar systems and for solutions of polymers in the semi dilute range. An important difference with other micellar systems is that the onset of the semi dilute regime is practically at the c.m.c. which corresponds to a very low micellar concentration. This implies an unusually steep micellar growth.

On the other hand rheological properties are strikingly different from the properties of polymer solutions in the semi dilute range and also from the properties of other micellar systems which show the same light scattering properties. The main differences are first the low viscosity and its slow evolution with micellar concentration and second the very short relaxation time.

Let us first examine these properties in the light of the description [18, 20, 22] of entangled equilibrium polymer solutions 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} and the other is the breaking and the recombination of micellar chains with a relaxation time τ_{break} .

* If reptation is the rate determining step of stress relaxation, the rheological properties vary with the concentration with the laws for classical polymer solutions [18, 20] modified to take into account the distribution of micellar length and its evolution with concentration [22]. We can rule out this possibility in the present case. First because the relaxation times for reptation of long micelles are certainly orders of magnitude larger than 10^{-3} s (which is the upper bound for the relaxation time in this system). And above all because, if the relaxation process was reptation, the viscosity should scale with micellar concentration with an exponent 5.4.

* When the second relaxation mechanism becomes operative then the rheological properties are modified. In the limit $\tau_{\text{break}} \ll \tau_{\text{rept}}$ the system displays one viscoelastic relaxation time $T_R = [\tau_{\text{break}} \tau_{\text{rept}}]^{1/2}$ [22]. And viscosity is predicted to scale with micellar concentration with an exponent ~ 3.6 . Such a situation was met in the system CTAB/KBr [13, 14]. In the CPClO_3 system T_R is at least an order of magnitude smaller than in CTAB/KBr. To explain such a small value of the observed relaxation time in the CPClO_3 system we must assume an important decrease of τ_{break} compared to its value in CTAB/KBr. Although this eventuality cannot be ruled out it seems contradictory to the experimental observation of much longer micelles in the CPClO_3 system. As explained below, this indicates that the unimolecular scission plus the formation of two endcaps request more energy in the present system, so that intuitively, we expect τ_{break} in CPClO_3 to be larger than in CTAB/KBr. The second observation, namely that the viscosity varies linearly with ϕ in complete disagreement

with the scaling law predicted above, is an even stronger reason to discard this second description as a possible one for the relaxation of stress in the CPClO₃ system.

We thus turn to seek other possible mechanisms for the relaxation of stress in a structure which must remain compatible with the picture given by the static results : locally cylindrical and flexible elongated micelles form a network analogous to the network formed by entangled polymers. In doing so we implicitly assume that under the strain applied to the system the structure of the micellar solution is retained. This seems a reasonable assumption if we recall, as stated above, the constancy of the viscosity over the explored range of stress.

Autoassociation of surfactants is known to give rise to a number of phases where the surfactant aggregates have different morphologies. This has been explained in terms of a preferred local structure or equivalently a preferred curvature for the surfactant monolayer [9, 33]. Elongated micelles thus correspond to locally cylindrical aggregates, their two free ends are generally thought to be closed by globular endcaps. 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). If the volume fraction of these micelles is sufficient they form an entangled network of equilibrium polymers which has been found to describe well the properties of a number of micellar systems. Another route to eliminate the free ends of locally cylindrical micelles is to branch the cylinders [25] in which case the unfavorable surroundings (the branch point) corresponds to smaller curvatures than the cylinder. If the volume fraction of such branched micelles is large enough they will form an entangled network of branched micelles. The solution adopted by a particular system will depend on the respective energies to form globular endcaps or branch 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 branch 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 branching of cylindrical micelles. This involved situation has been recently formalized [26] and the distribution of real crosslinks and entanglement points and its influence on some properties of the dilute micellar solutions have been discussed. From a geometrical point of view the branch points (crosslinks) and the entanglement points contribute equally to the crossings of the network, but it is sensible to expect that the proportion of crosslinks and entanglement points will have a strong influence on the dynamical properties of the micellar networks.

Our suggestion is that a network of crosslinked cylindrical micelles that is a multiconnected rather than an entangled network could allow for the observed facts. Such a network is identical from the neutron and light scattering point of view to an entangled network. Its rheological properties could however be considerably different : new mechanisms for the relaxation of stress become possible. The first possible mechanism of relaxation is by sliding the crosslinks along the micelles through the viscous flow of the surfactant molecules through the micellar network as sketched in figure 4a. Such a mechanism can allow for a very fluid solution and for a faster relaxation of stress than disentanglement or breaking of wormlike micelles, in qualitative agreement with the present results. An analogy can be drawn here with the highly fluid L₃ (sponge) phase where an infinite multiconnected fluid membrane separates two identical subspaces of solvent [25-27]. A model has been successful in describing the rheological properties of the L₃ phase in different systems [29]. In this model, the relaxation of stress occurs through the simple viscous flows of the surfactant in the fluid membrane and of the solvent in its subspace. The second mechanism is relaxation of stress by

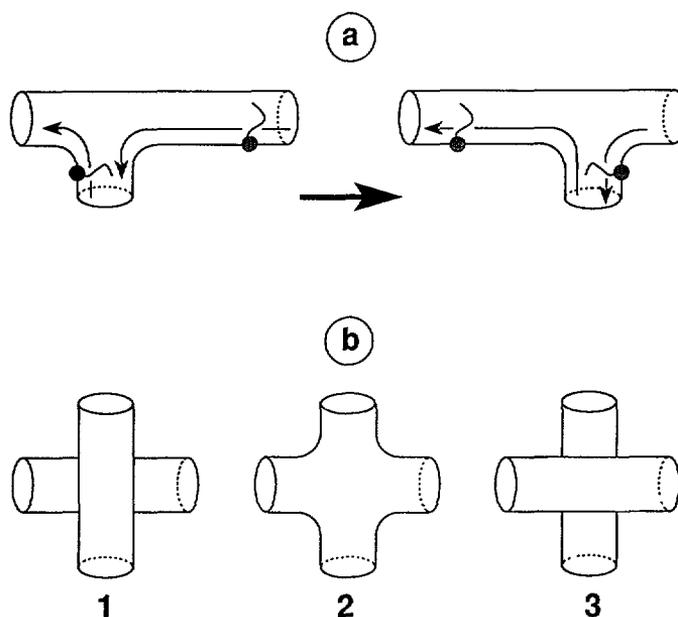


Fig. 4. — a) Sliding, here from left to right, of a crosslink along a micellar thread through the viscous flow of the surfactant molecules along the micellar network. b) A ghostlike crossing : 1) encounter of the two micellar threads ; 2) a transient crosslink ; 3) separation of the two micellar threads.

a « ghostlike » crossing as illustrated in figure 4b. The equilibrium properties of the micellar network corresponds to a transient character of crosslinks so that when a micellar thread collides with another one in the network it can form a transient crosslink and the two threads separate on the other side. A theoretical description of both mechanisms in a crosslinked network and of the resulting laws for rheological properties is yet a challenge for theoreticians.

A last point to be discussed is the difference in the rheological properties between the two systems $\text{CPClO}_3/\text{NaClO}_3$ and CTAB/KBr , since they appear at first sight chemically very close. From the above discussion this difference must be due to the occurrence of crosslinks in the first system only. We have shown and discussed previously [4] the specificity of counterions to induce the elongation of micelles and found in this study that ClO_3^- was, by far, the most efficient in promoting this elongation compared to Br^- . This was ascribed to the adsorption equilibrium of counterions on the micelles which modified the ionic environment of the micelles and modified the local curvature. As stated above if a given parameter 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 branch points will decrease. It is then reasonable to assume that the occurrence of crosslinks in the CPClO_3 system is due to the higher efficiency of the counterion ClO_3^- to decrease the local curvature.

Acknowledgements.

We are grateful to M. E. Cates for communicating his theoretical work on crosslinked networks prior to its publication.

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