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Evidence for Local Orientational Order in Salt-Free Worm-Like Micelles: A Transient Electric Birefringence Study

R. Oda (*), F. Lequeux and E. Mendes

Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes (**), (L.U.D.F.C),
4 rue Blaise Pascal, 67070 Strasbourg Cedex, France

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Abstract. — Transient electric birefringence experiments were performed on a aqueous dispersions of salt-free charged giant micelles of a recently introduced gemini surfactant (referred as 12-2-12). In the dilute regime, the system consists of small rod-like micelles, while at higher concentrations (semi-dilute region) the micelles are semi-flexible and entangled. For concentrations far from c^* , either dilute or semi-dilute regime, the birefringence has the same sign suggesting that the micelles align with the electric field in the same direction in both dilute and entangled regime. For concentrations close to c^* , an anomalous signal with an opposite sign is observed. For the entire surfactant concentration range studied here, we show that the static signals of the electric birefringence can be split into three different components with very different characteristic times, each component being associated to specific orientational mechanism: 1) a parallel alignment to the applied electric field after free rotation in the dilute regime, or confined rotation of small segments in the semi-dilute regime, 2) an alignment perpendicular to the field that appears near c^* , and interpreted as the result of pre-smectic ordering as recently proposed by Cates, 3) a parallel alignment after disentanglement occurring in the semi-dilute regime.

1. Introduction

Surfactant molecules dissolved in various solvents can self-assemble reversibly into spatially organised structures forming associations which are physically and not chemically bound. Under certain conditions, they form long flexible worm-like micelles of size depending strongly on temperature, surfactant and salt concentrations [1]. Most of the study concerning structural and dynamic behaviours of these worm-like micellar solutions were focused on systems with presence of a large amount of salt [2]. However, during the last few years, new surfactant systems have been introduced [3, 4], and it is now possible to obtain the worm-like micellar phase in the absence of added salt for some ionic surfactants [5]. This allows us to investigate the electrostatic interactions which strongly influence the structures and the dynamics of the surfactant self-assemblies. The surfactant used here is the ethylene-bis (dodecyldimethylam-

(*) Author for correspondence (e-mail: reiko@fresnel.u-strasbg.fr)

(**) Laboratoire associé au C.N.R.S., URA 851

monium bromide) shortly called as "12-2-12" introduced by Zana *et al.* [4], where the direct evidence for the existence of long cylindrical micelles had been obtained by cryo-TEM. It has been shown [6, 7] that, in the dilute regime, (for the studied system, less than $c^* \equiv 0.9\%$ (wt)) these charged surfactants assemble in rigid rods, their size being limited by electrostatic repulsion. Beyond the overlapping concentration, c^* , the micelles become entangled, and grow exponentially with concentration due to the screening of intermicellar electrostatic interaction. In this semi-dilute regime, they behave similarly to polyelectrolyte polymers [2].

Time resolved electric birefringence allows one to probe the angular dynamics of suspended assemblies in solution. Those techniques have recently been applied to the study of polyelectrolytes [8] and worm-like micellar solutions [9] by Hoffmann's group, where they brought to evidence an anomalous behaviour for concentrations near c^* . A theoretical interpretation of such an anomaly was developed by Cates [10]. He proposed that, when an external electric field is applied to a polyelectrolyte solution near c^* , the chains tend to align perpendicular to the field due to local pre-smectic ordering.

In the work presented here, we report results on the rotational dynamics of 12-2-12 micellar solutions using transient electric Birefringence (TEB). In the absence of salt, we have investigated solutions in dilute and semi-dilute regimes, as well as around the overlap concentration, c^* , where an anomalous behaviour was found as in another worm-like micellar system [8, 9]. We also report below the dependence of the TEB signal as a function of the temperature for some surfactant concentrations. Moreover, we were able to split the signal into three contributions which originate in three different orientational mechanisms. This allows us to give a complete interpretation of the quite complex dynamic behaviour of the micelles probed by the TEB experiments.

2. Experimental Section

The transient electric birefringence measurements were performed with a He-Ne laser ($\lambda = 6238 \text{ \AA}$), polarised at 45° with respect to vertical. The laser beam passed through a thermostated cell containing the solution between two steel electrodes which were placed parallel to each other with a separation of 2 mm. The electric field is applied perpendicular to the laser beam and parallel to the optical table. After the sample cell, a $\lambda/4$ plate and an analyser (crossed with the polariser) are placed before a photodiode. A part of the laser beam is taken before the polariser and used to analogically subtract the laser noise from the measurement. During the experiment, a square tension pulse, up to 900 V, can be applied on the electrodes. The applied tension changes sharply from 0 to 900 V (or from 900 V to 0) in a timescale of the order of $0.5 \mu\text{s}$. The overall time resolution of the set up is about $1 \mu\text{s}$.

The surfactant molecules were synthesised by Zana (Insitut Charles Sadron, CNRS, Strasbourg, France) [3], and the samples were studied in heavy water. Repetitive application of the electric pulses causes electroconvection, which leads to inhomogeneities as well as changes of index of refraction of the sample, which cause the shift of the baseline of the spectra before and after the pulse. Therefore each pulse was applied after at least 15 minutes interval, and samples were replaced frequently. Various concentrations were studied around the transition between dilute and semi-dilute regimes, starting from 0.4% and up to 1.8%(weight %). Samples were kept in the oven (40°C) for at least one day after the preparation before measurements to achieve complete thermal equilibrium, and measurements were performed within one month.

Fig. 1. — Four types of birefringence signals for high applied fields at 21 °C; for different surfactant concentrations: (a) 0.6%, (b) 0.8%, (c) 1.0%, (d) 1.8% (%weight).

3. Results and Discussion

We describe below the dependence of the static birefringence of 12-2-12 solutions in the concentration ranging from the dilute to the semi-dilute regimes, as well as its dependence on temperature.

3.1. DEPENDENCE OF THE BIREFRINGENCE ON SURFACTANT CONCENTRATION. — The TEB signals for different concentrations for $T = 21$ °C are shown in Figure 1. These static birefringence signals show a large variation, and as can be seen, they can be separated into three different components with different characteristic times.

(1) In the dilute regime, $c = 0.6\%$, the signal is positive where the characteristic time is of the order of $5 \mu\text{s}$.

(2) As the concentration increases, a negative component appears at the concentration about 0.8% . This negative signal is superimposed on the positive signal, and it has the typical characteristic time on the order of $50 \mu\text{s}$, ten times slower than the previous one.

(3) As the concentration is further increased, a third and positive signal, with a much longer characteristic time ($500 \mu\text{s}$ or longer) appears at concentrations which are around 1% . This very slow component is also superimposed on the previous ones. Let us remark that if the pulse is cut where the plateau of the second component is achieved, one might miss the rise of the third positive signal.

(4) With the further increase of the surfactant concentration, $c \geq 1.5\%$, the negative signal disappears, but the very fast first component and very slow one (both positive) remain observable.

Fig. 2. — Splitting of the birefringence signal into three components Δn_i ($i = 1, 2, 3$). This splitting procedure applies for any of the four different spectra shown in Figure 1.

Since the characteristic times of the three processes described above differ from each other by roughly an order of magnitude, the static signals can be directly split into three components. A typical decomposition is shown in Figure 2, where the static components of the Δn_i ($i = 1, 2, 3$) are defined. The indexes $i = 1, 2, 3$ correspond to the first, second and third components, respectively. Those three components are plotted separately in Figure 3 as a function of the square of the applied electric field, E^2 , for different surfactant concentrations. It has to be emphasised that this is different from extracting the plateau height with respect to the base line as classically done [8,9]. As can be seen in Figure 3, the dependence of the positive components of the static birefringence, Δn_1 , as a function of the electric field, E , follows Kerr's law, varying linearly with E^2 . However, both Δn_2 and Δn_3 exhibit a non-linear behaviour with E^2 . Δn_2 first increases with E^2 but saturates and decreases for higher values of the field. Δn_3 saturates for quite low values of E .

Consider separately the dependence of each component, Δn_i ($i = 1, 2, 3$), of the static birefringence on surfactant concentration in the limit of small fields around the overlap concentration. Parallel rheological and light scattering measurements [4] have shown that the overlap concentration, c^* , was around $0.8 \sim 1.0\%$ (wt.) surfactant weight. Here, the concentration ranges from 0.4% (dilute) to 1.8% (semi-dilute). In Figure 4 Δn_i ($i = 1, 2, 3$) are displayed as a function of concentration for a fixed value of $E = 850$ V/m. Herein, the origin of each contribution is discussed separately.

• Δn_1 : The Rapid Positive Response to the Applied Field

This rapid ($\sim 5 \mu s$) positive signal was observed for the entire range of concentration studied here. For dilute samples at low fields, the signal increases linearly to the surfactant concentration, while for concentrations higher than 1% , this signal starts decreasing with increasing concentration. The micellar length at the critical concentration can be estimated by packing arguments to be about 50 nm if one assumes that the surfactant molecular length is ~ 2 nm

Fig. 3. — Variation of Δn_i ($i = 1, 2, 3$) as a function of the square of the applied field, E^2 .

Fig. 4. — Variation of Δn_i ($i = 1, 2, 3$) as function of surfactant concentration, for a small value of the electric field.

and that the average surface area per polar head is 0.65 nm^2 . Using crude thermodynamic estimation, it can be shown that micelles of length $\sim 30 \text{ nm}$ have a rotational time of $5 \mu\text{s}$. Therefore, for $c < c^*$, the signal Δn_1 can be associated to free rotation of isolated micelles. The increase of the signal Δn_1 with concentration corresponds to the fact that the signal is proportional to the density of micelles, as well as their length. This variation is small since the length of a micelle in the dilute regime varies only logarithmically with the surfactant concentration [6].

In the semi-dilute regime, for $c \geq c^*$, micelles are entangled, and most of them cannot rotate freely because of steric interactions (or entanglements). Two different mechanisms may be responsible for the Δn_1 signal in this regime. First, these long entangled micelles can still *partly* rotate before being sterically blocked by their neighbours. Secondly, because of the large polydispersity due to the breaking-recombining mechanism, there are always some micelles which are smaller than the mesh size. They can in principle rotate freely. However, as the concentration increases in the semi-dilute regime, the average length of micelles grows and the mesh size diminishes, leading to a decrease of the population of free micelles [7]. At the same time, because of the smaller mesh size, the local rotation of entangled micelles becomes even more restricted.

The combination of the effects described above leads to a maximum for Δn_1 around c^* . This effect is more clearly displayed in Figure 5a, where each component of the static birefringence is plotted separately.

• Δn_2 : The Slow Negative Response to the Applied Field

In Figures 4 and 5b, Δn_2 as a function of surfactant concentration is plotted at $T = 20^\circ\text{C}$. This negative contribution to the static birefringence exists only in a certain concentration range, around $c^* \sim 1.0\%$, and is observed neither for dilute nor semi-dilute regimes far from c^* . In Figure 6, the dependence of Δn_2 on E^2 is plotted for different temperatures for a fixed surfactant concentration 1.5% . Around this concentration, the amplitude of this negative birefringence increases linearly with E^2 for low fields. For certain temperatures, we can observe that it saturates (and decreases) at higher field values.

This anomalous signal was first observed by Hoffmann [8,9] in polyelectrolyte solutions and worm-like micellar solution. Recently, Cates [10] proposed an interpretation for the case of polyelectrolyte solutions in which the chains possess many statistical units and form rod-like assemblies. Although, unlike polyelectrolyte, micelles possess only few statistical units near c^* , due to their long persistence length, they themselves are rod-like around this concentration. The overall qualitative behaviour described by Cates can thus be applied to micellar systems. His argument states the following: at concentrations close to c^* , there would exist a strong local coupling between the orientation of neighbouring pairs of rod-like micelles. Non-entangled micelles are, therefore, likely to be parallel to one another and form disc-like clusters. Since, for the case of micelles, the nematic long-range ordering would be energetically unfavorable, a local disc-like ordering would be favoured. When the electric field is applied to such a "pre-smectic clustering" [10], in order not to break this local ordering, (which would require the energy) the macroscopic polarisability would be higher (while the energy would be lower) for the configuration where the induced dipole of each micelle is aligned perpendicular to the long axis of a micelle (in the plane of the "disc"). This would lead to a birefringence signal opposite in sign to the one found in the dilute regime. Thus, that we observed a negative contribution just around c^* is consistent with this argument: if the solution is too dilute, there is no more orientational interaction, and if the solution is concentrated above c^* , micellar length increases

Fig. 5. — Variation of a) Δn_1 b) Δn_2 c) Δn_3 as functions of the surfactant concentration. Two different temperatures are considered: 20 °C (■) and 30 °C (●).

rapidly with the concentration [6, 7], leading to the entanglement of micelles which become much longer than their persistent length. Therefore, the disk-like ordering does not exist for the concentrations far from c^* .

Using the Stokes-Einstein equation and the measured characteristic time for the anomalous component ($\sim 50 \mu\text{s}$ at 20 °C) one can estimate the dimension associated to such a domain (the radius of a disk) to be about 1100 Å. If we assume the aspect ratio of these micelles to be about 2 [10], at c^* ($L \sim 500$ Å), the number of micelles in such domain will be of the order of 15.

Conversely, as can be seen from Figure 6, Δn_2 tends to vanish as high electric fields are applied ($T = 20$ °C and 28 °C). This suggests that any domain or structure responsible for the anomalous signal is destroyed when the external field is strong enough. This observation is consistent with the pre-smectic ordering picture [10].

Fig. 6. — Variation of Δn_2 as a function of the square of the applied field, E^2 . Different temperatures are considered while the surfactant concentration is fixed at 1.5%.

• Δn_3 : The Very Slow Positive Response to the Applied Field

This very slow component of the birefringence, Δn_3 , also has a positive sign as Δn_1 , but with a much longer ($\geq 500 \mu s$) characteristic time. As shown in Figure 3d, in the semi-dilute regime, Δn_3 increases sharply in the weak fields and then saturates at stronger fields. The dependence of Δn_3 for a fixed small field ($E = 850 \text{ V/m}$) as a function of concentration is plotted in Figures 4 and 5c. This signal appears only for the entangled regime, $c \geq c^*$ and it is, therefore, related with the existence of the entanglements. One can interpret such a behaviour using the Edwards tube model [11], which describes usual semi-dilute solutions. The micelles, and hence the tubes, can be strongly oriented under the electric field, due to topological constraints between micelles. In fact, the long measured characteristic time ($\geq 500 \mu s$) for this component corresponds to tube renewal process coupled to collective rotation: Δn_3 can be associated with the dynamics of a temporary network formed by the entangled micelles.

Unfortunately, it was not possible to perform experiments for even higher concentrations in the semi-dilute regime, because of the high viscosity and the presence of electroconvection in the samples. Thus, the dependence of this long characteristic time on concentration could not be obtained in the semi-dilute regime.

3.2. TEMPERATURE DEPENDENCE OF THE BIREFRINGENCE. — In Figure 7, a typical set of spectra for the same surfactant concentration ($c = 1.8\%$) is plotted for different temperatures: 26.5 °C, 30 °C and 34 °C. For $c = 1.8\%$ at 26.5 °C, the system is in the semi-dilute regime and the birefringence can be split into two components, while for the same concentration at 30 °C three contributions to the birefringence are observed. Comparison with Figures 1c and 1d indicates that heating has a similar effect on the spectra as that of decreasing concentration. This fact is coherent with rheological measurements [4] which show that c^* is displaced towards higher surfactant concentrations as the temperature increases. Therefore, qualitative changes in the birefringence signals with temperature seem to be related to the displacement of c^* .

Fig. 7. — Effect of temperature on the spectra of samples containing 1.8% of surfactant. At 26.5 °C, the solution is in semi-dilute regime.

Following [4], one can quantitatively estimate the dependence of c^* on temperature. The theoretical description for the growth of worm-like micelles gives us an estimate for the overlap concentration [6, 7] which is:

$$c^* \approx \left(\frac{k_B T l_B a \nu^2}{E_c} \right)^2 \quad (1)$$

where E_c is the end-cap energy, or the energy required to create two end caps from a cylinder. a is the radius of the cylindrical micelle and ν an effective charge per unit length, $\nu \approx l_B^{-1}$. $l_B = e^2/\epsilon kT$ is the Bjerrum length, where ϵ , the dielectric constant of the solution depends of the temperature, $\epsilon \approx T^{-3/2}$ [5]. Thus one gets $c^* \propto T/E_c^2$. For the present case, we consider $c^*(T)$ as the surfactant concentration at which the third slow signal corresponding to entangled micelles appears. We obtain:

c^* (weight fraction)	0.008	0.010	0.015	0.018
T (K)	293	299	303	307
c^*/T	2.7×10^{-5}	3.34×10^{-5}	4.95×10^{-5}	5.9×10^{-5}

It can be seen from the table that the obtained values for c^*/T increase with temperature thus the end-cap energy E_c decreases with temperature.

4. Conclusions

Using transient electric birefringence, we investigated the orientational dynamics of charged worm-like micelles in a concentration domain ranging from dilute to semi-dilute condition. We showed that for all studied concentrations the birefringence signal can be split into three different contributions, Δn_i ($i = 1, 2, 3$), each one with a very different characteristic time. This allowed us to separate the contribution of each component as a function of surfactant concentration. Two of those contributions, Δn_1 ($\tau \approx 5 \mu\text{s}$) and Δn_3 ($\tau \geq 500 \mu\text{s}$) have the same sign, and are related to different orientational mechanisms. The first one, Δn_1 , which is the only non-zero contribution in dilute conditions, is related to the orientation of free small micelles in the dilute case. In the semi-dilute regime, this component is also observed and it is related to the rotation of micelles which are smaller than the mesh size, as well as to partial rotation of entangled micelles. In a semi-dilute solution, a much slower component, Δn_3 , with the same sign as Δn_1 , is also present. This originates from a the release of entanglements between the micelles. A second component, Δn_2 , with an opposite sign was observed only in the vicinity of the overlapping concentration c^* .

One possible interpretation of the anomalous component, Δn_2 , has been recently proposed [10] for polyelectrolyte solutions. It states that in those systems a pre-smectic ordering could be present near c^* . The results presented above on worm-like micellar assemblies are consistent with this disk-like ordering model. The fact that the anomalous effect appears only in a small concentration range near c^* , the shift of such a concentration domain with temperature, as well as the disappearance of this anomalous signal with the application of very strong fields, seem to corroborate the picture of pre-smectic ordering. The concrete investigations about the relaxation time as well as more detailed signal dependence on the surfactant concentration around c^* will be needed.

The complex temperature dependence corresponds actually to the shift of the overlap concentration, c^* , [5] and a precise analysis of this shift shows that the end-cap energy is a decreasing function of the temperature.

The relaxation of the birefringence signal is in fact, rather intricate, as it presents the relaxation of the three different dynamics overlapped to each other. Also, deriving the Δn 's from the plateau values as it is done in this paper, the value we get is rather qualitative. In order to give a quantitative descriptions of this dynamics, one would need to perform the fitting of the relaxation curves. Nevertheless, we believe that the approach of separating the signals in three components would lead us to the correct understanding of dynamics of micelles under electric field around c^* . Also, further quantitative investigations of the variation of the anomalous component Δn_2 around c^* and its dependence on the applied electric field will be necessary. These subjects are presently under investigation and will soon be reported.

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