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Short Communication

S.A.N.S. Spectra and Elastic Plateau Modulus in a Charged Wormlike Micelles Solution: Effect of Salt

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Résumé. — Nous présentons les résultats de diffusion de neutrons et de module élastique au plateau obtenus pour une solution de micelles géantes cylindriques chargées, à différents taux de sel. Les spectres sont tout à fait semblables à ceux observés pour des solutions semi-diluées de polymères polyelectrolytes classiques. Le module au plateau, qui indique la portée des fluctuations élastiques, augmente avec la concentration en sel. Ainsi, nous déduisons que les répulsions electrostatiques induisent non seulement l'apparition d'un pic de corrélation statique marqué, mais encore qu'elles entraînent des corrélations à longue distance des fluctuations élastiques du système.

Abstract. — We present S.A.N.S. and elastic plateau modulus data obtained from semi-dilute wormlike micellar solutions, with small amounts of salt added. The spectra of these solutions are reminiscent of polyelectrolyte semi-dilute solutions. The plateau modulus, which is related to the correlation length of the fluctuations in strain, is increased by the addition of salt. The primary result is that the electrostatic interactions induce short-range correlations in the structure of the semi-flexible rod network, and this leads to a long-range correlation in the strain fluctuations.

It has long been known that wormlike micelles can be formed in various surfactant solutions [1]. These solutions have many properties reminiscent of semi-dilute polymer solutions. Moreover, the knowledge of semi-dilute polymer solutions has provided a good framework for the analysis of solutions of wormlike micelles with large amounts of added salt. Recently, Kern et al. reported on the properties of charged, unscreened wormlike micelle solutions [2]. One expects the properties of such solutions to be reminiscent of polyelectrolyte solutions. Unfortunately, the understanding of the structure of polyelectrolyte solutions is still in its early stage.

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clear rheological data on polyelectrolyte solutions. In this short communication, we investigate the effect of small amounts of salt on ionic surfactant semi-dilute wormlike micelles. We compare the information about correlations in the solution obtained from both S.A.N.S. and elastic plateau modulus measurements.

The surfactant used is the same as that in [2] and was provided by Zana. It is a dimeric surfactant, the ethanediyl-α, ω-bis (dodecyltrimethylammonium bromide), also called 12-2-12. The samples were prepared in deuterated water for both rheological and SANS experiments to allow comparison.

All the samples studied here have a surfactant concentration of 5.2 wt%. Thus there are clearly in the semi-dilute regime, the overlap concentration being about 1%. All the micelles are then cylindrical and very long. At this concentration, there is no more short micelle, as explained in [1]. This is caused by the natural distribution in wormlike micelles and amplified by the electrostatic interactions.

The rheological experiments have been performed using a strain imposed rheometer (RFS II of Rheometrics) in a Couette cell. The frequency range explored is $0.002 < \omega < 16 \text{ s}^{-1}$. Like screened micellar solutions, the salt free micellar samples exhibit at low frequencies a Maxwellian behavior [3] due to reversible scission processes. This very simple rheological behavior has been described theoretically by Cates and Turner [4] for screened micellar solutions based on the reptation model and including reversible scissions. In the frequency range $1/\tau_R < \omega < 1/\tau_{\text{Rouse}}$, where $\tau_R$ is the terminal time and $\tau_{\text{Rouse}}$ the Rouse time between two entanglements, entanglements lead to an elastic modulus which reaches a plateau value of $G'_\infty$. As shown by Kern et al. [2], the salt-free micellar solutions exhibit the same behavior and the addition of salt does not modify this behavior as shown in Figure 1. Figure 2 represents the

![Graph](image)

**Fig 1.** — Elastic (■) and loss modulus (Δ) versus frequency at 5.2% in surfactant, with no added salt, at 30 °C. The behavior is clearly Maxwellian and the plateau modulus is easy to estimate.
plateau modulus $G'_\infty$ as a function of salt concentration for a fixed surfactant volume fraction equal to 5.2%.

The SANS experiments have been performed in the Laboratoire Léon Brillouin in Saclay. The scattered intensities presented here are untreated, since the noise is negligible. In Figure 3, scattered intensities are plotted as a function of the scattering vector $q$, for 5.2% (gram per cm$^3$) surfactant solutions, at various added salt (NaCl) molarities. The scattering spectrum of the sample without added salt exhibits a clear peak. The wavevector $q^*$ corresponding to the peak varies like the square root of the surfactant concentration. Moreover, the distance $d^* = 2\pi/q^*$ calculated from the measured $q^*$ value is in good agreement with a crude estimate of the distance between neighboring rods. When salt is added, the peak intensity decreases and the peak gradually disappears, while the scattered intensity at small wavevectors increases.

These results show that the correlation peak is caused by the electrostatic repulsion between the wormlike micelles. In other words, the electrostatic repulsion induces a strong correlation between neighboring rods, which disappears in favor of a softer excluded volume interaction when the ionic charge is increased. This behavior is similar to that observed for classical polyelectrolyte solutions [6]. The plateau modulus gives somewhat different information.

The plateau modulus is related to a length $\xi$ which represents the correlation length of the strain fluctuations by:

$$G'_\infty = \frac{k_BT}{\xi^3}$$

For semi-dilute polymer solutions, this length is equal to 2.4 times the correlation length deduced from static light scattering [7]. For other wormlike micelle solutions, Berret et al. have measured a ratio decreasing from about 5 to 3.3 with increasing concentration [8]. However,
for the plateau modulus value, the authors take the osculating circle diameter in the Cole Cole representation. This leads to an overestimate of $\xi$, especially at low concentrations. Hence it is possible that, in this case, the ratio does not vary as much as estimated in [8]. Here, since we keep surfactant concentration constant, varying only the electrostatic screening, the variation of the length $\xi$ is then clearly significant. In our case, in the absence of salt, this length is surprisingly large, $\xi = 70$ nm compared to the static case of $d^* = 15$ nm. This length $\xi$ decreases first while the salt concentration increases and reaches the value of 27 nm at its minimum. This means that the strain fluctuation correlation length decreases with the range of the electrostatic interaction while the concentration, and hence the inter-rod distance, remains constant. Thus the electrostatic interaction leads not only to a short-range interaction, but also to a long range dynamical interaction.

This is in fact not very surprising. As strain (or orientational) fluctuations create disorder, they will have a free energy cost increasing with the quality of the packing at rest. More precisely, the free energy cost for a unit strain of a blob of diameter $d^*$ containing one piece of wormlike micelle is of the order of $k_B T$, whatever the interaction of the worm with its surroundings. In other words, an affine deformation does not much destroy the order. Actually, it is the gradient of strain fluctuation which destroys the quality of packing [9]. More rigorously, when the free volume is decreased, long-range interactions of an entropic nature appear, as shown in a recent simulation [10]. So electrostatic interactions essentially increase the range $\xi$ of the elastic fluctuations, which is simply of the order of the mesh size in normal semi-dilute polymers. Hence electrostatic interactions induce long-range elastic fluctuations which are responsible for the decrease of the modulus from its semi-dilute value.
For solutions with salt concentrations larger than \([NaCl] = 0.02\) M, the elastic modulus decreases and the solution phase separates. We presently do not have a clear explanation of this phase separation. It may be caused by an attractive dielectric interaction between the rods, or by branching [11]. However, in the vicinity of this phase separation, long range correlations probably appear. Thus, for similar reasons, this phase separation also leads to a decrease of the plateau modulus.

Finally, we observe that electrostatic interactions in these giant wormlike micelles lead to S.A.N.S. spectra very similar to those observed in classical covalent polyelectrolytes: a correlation peak appears when the ionic charge is decreased. In the same way, these interactions decrease the elastic plateau modulus, and this reveals long range correlations in strain fluctuations, induced by electrostatic interactions.

**Remark:** Addition of salt to the system leads to other effects: the length of the micelles increases, the ionization is modified, and the kinetics of the scission recombination mechanism varies. The viscosity is affected by the modulus, the micelle length, and the kinetic rate. Adding salt thus affects the viscosity in a complex way [12]. In our case, the viscosity decreases or exhibits a maximum while increasing the salt concentration, depending on temperature. In this short note, we have deliberately restricted our discussion to the plateau modulus in order to analyze a local (at the blob scale) quantity. The effect of temperature is also complex, however, because it modifies the ionization degree and in this way the magnitude of electrostatic repulsion.

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**References**