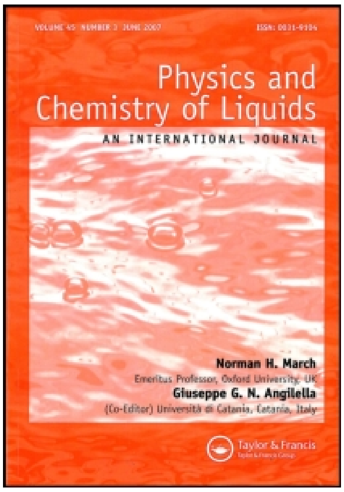

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Self-aggregation in aqueous TRITON X-100 solutions near CMC

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Experimental results are presented on the electric birefringence induced in aqueous TRITON X-100 solutions near critical micelle concentration (CMC). The results show the transition from anisotropic aggregates to spherical micelles and the changes that take place in the monomers' concentration.

Key words: Electric birefringence; Surfactant; Micelles; CMC

PACS: 78.20; 82.70

1. Introduction

Ionic and nonionic surfactants have a wide applicability from both biological and technological points of view [1]. The experimental sharp changes in such physical properties of the aqueous solutions of surfactants as surface tension, conductance, and scattered light intensities have been attributed to the formation of micelles in equilibrium with their monomeric species [2].

The critical micelle concentration (CMC) plays an important role in the description of the physical behavior of the surfactant solutions in such phenomena as adsorption and solubilization [3].

The forces controlling micellar structures are delicately balanced so that distortion of the shape may occur fairly easily. Any attempt to represent the structure can at best be a statement of the average shape over some discrete time interval. Following Aniansson [4] the exchange that occurs between monomer molecules and those in micelles occupies a time-scale of the order 1 to 10 μs.

Although a great number of attempts have been made to describe the mechanism of the formation of micelles, this problem has not been decisively solved as yet [5].

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In spite of many theoretical and experimental works, until the present time there are no detailed studies on the evolution of the structures for concentrations near CMC.

Standard techniques such as light scattering, electrical conductivity, viscosity, etc. do not allow us to observe in detail the structure evolution around the CMC.

On the other hand, we show that the technique of electric birefringence is sufficiently sensitive to follow the changes in the structure of the aggregates caused by small variations of the concentration. This technique is applied to TRITON X-100 aqueous solution.

The model that we use to interpret the experimental data is a very simple one. We assume that the surfactant molecules give place to rods with a certain number of monomers. We evaluate this number using the Kerr constant.

The grade of solvation of the rods is determined by their hydrodynamic properties, which can be estimated by means of birefringence relaxation times.

2. Experimental

TRITON X-100 (TX-100) is a *p*-(1,1,3,3-tetramethylbutyl) phenoxypolyoxyethylene glycol containing an average of 9.5 oxyethylene units per molecule. TX-100 were supplied by Malincroft (Lot 9263). Distilled and deionized water was used. All measurements were made at 25°C (±0.2°C).

The procedure is as follows: we prepare different concentrated TX-100 aqueous solutions. Samples are extracted and diluted with water until reaching the needed concentration value. The samples are shaken for 15 min and then are stabilized for 30 min before placing them in the measurement cell. The studied concentrations range between 0 and 1.2 mM.

The surface tension was measured by means of an equipment designed and made in our laboratory [6]. This equipment uses the maximum bubble pressure technique (MBP). With these data we can see that the CMC is approximately 0.28 mM, similar to that obtained by other authors [7].

Light-scattering experiments were conducted using an equipment made in our laboratory. We found that, for concentrations higher than CMC, the micelles are spherical with a mean aggregation number of 142 ± 20 and hydrodynamic radius of 3.7 ± 0.4 nm, which are in agreement with those obtained by other authors [8].

The equipment for electric birefringence measurement has been described elsewhere [9]. We tried pulses of different width (between 0.150 and 10 mseg) and voltage from 900 to 2000 V. We took special care in avoiding the heating of the sample.

In all the cases, the values of the Kerr constant obtained for the water correspond with reference values [10].

3. Results

The birefringence is defined as:

$$\Delta n = n_{\parallel} - n_{\perp} = \lambda B E^2$$

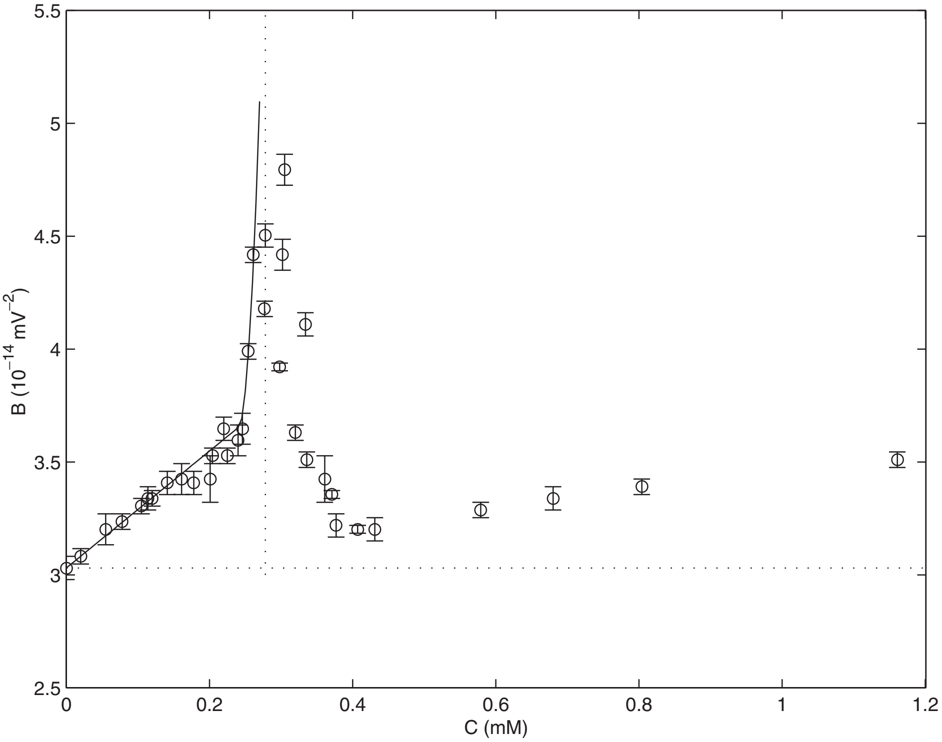

Figure 1. Experimental Kerr constant. The horizontal dotted line is the value obtained for the water. The vertical line indicates the CMC obtained previously by surface tension measurement. The full lines correspond to an adjustment of the experimental data in relation to the proposed model.

where $n_{\parallel}$ and $n_{\perp}$ are parallel and perpendicular refraction indices with respect to the direction of polarizing field E; B is the Kerr constant and the wavelength $\lambda = 632.8$ nm; in turn:

$$B = \lim_{E \to 0} \frac{\Delta n}{\lambda E^2}$$

In figure 1 we plot the Kerr constant data. One can note that the birefringence is proportional to the surfactant concentration until points near CMC.

We observe a maximum around 0.28 mM (that coincides with the CMC obtained by surface tension). After the observed maximum the birefringence reaches a minimum around 0.4 mM and then it increases in proportional form to the total surfactant concentration.

The Kerr constant of a system of two components (water and surfactant) can be expressed by:

$$B_{\mathrm{exp}} = B_{\mathrm{w}}(1 - \phi) + \phi B_{\mathrm{s}} \tag{1}$$

where ϕ is the surfactant volume fraction and B_{s} its specific average Kerr constant. If $M = 624\,\mathrm{g\,mol^{-1}}$ is the surfactant molar mass, $\rho = 1.06\,\mathrm{g\,cm^{-3}}$ the density, and C the molar concentration, then $\phi = MC/\rho$.

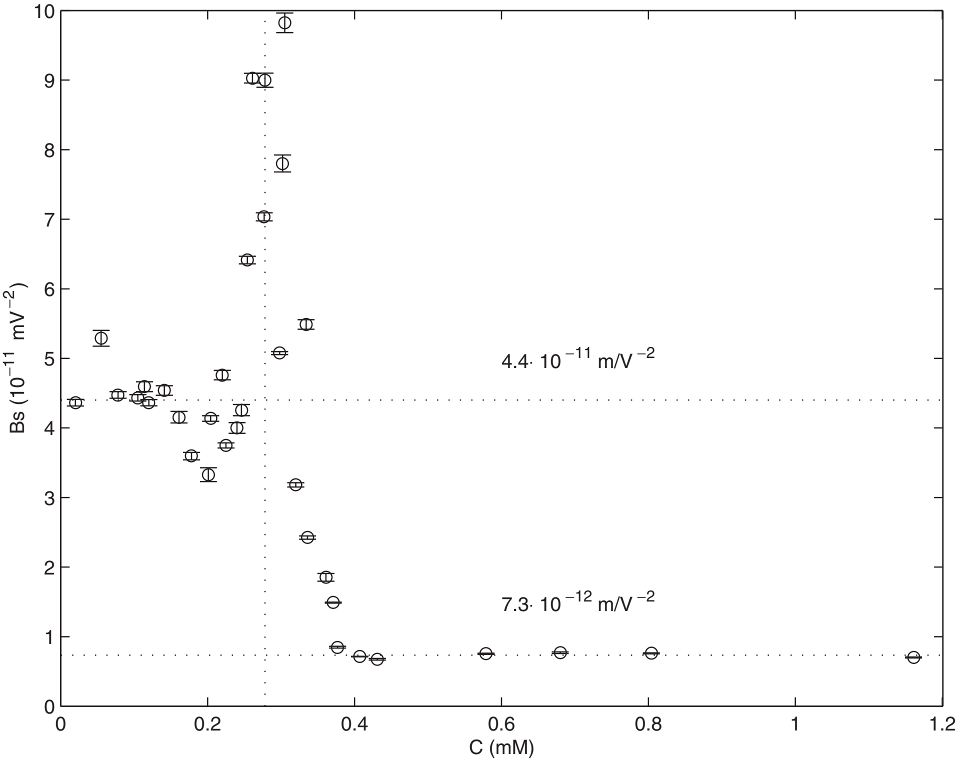

Figure 2. Specific Kerr constant of the surfactant *vs* surfactant concentration.

B_s is computed using the equation 1 and the values B_{exp} ($B_w = 3.06 \times 10^{-14}\,\mathrm{mV}^{-2}$). In figure 2 we show the results.

When the orientational field is switched off, the birefringence diminishes with a characteristic time that can be calculated as:

$$\langle \tau_{\mathrm{exp}} \rangle = \int_0^{\infty} \frac{\Delta n(t)}{\Delta n(0)} dt$$

According to figure 1, the value of the water Kerr constant is of the same order as those corresponding to the surfactant solution. On the other hand its characteristic time is much shorter than that of the solution. This allows us to calculate the time of relaxation of the whole surfactant ($\langle \tau_s \rangle$):

$$\langle \tau_s \rangle = \frac{B_{\mathrm{exp}}}{(B_{\mathrm{exp}} - B_w)} \langle \tau_{\mathrm{exp}} \rangle \tag{2}$$

In figure 3 the obtained values of $\langle \tau_s \rangle$ are presented. For concentrations lower than CMC, the relaxation of the birefringence cannot be detected by our equipment. The same thing happens when the concentration is bigger than 0.4 mM.

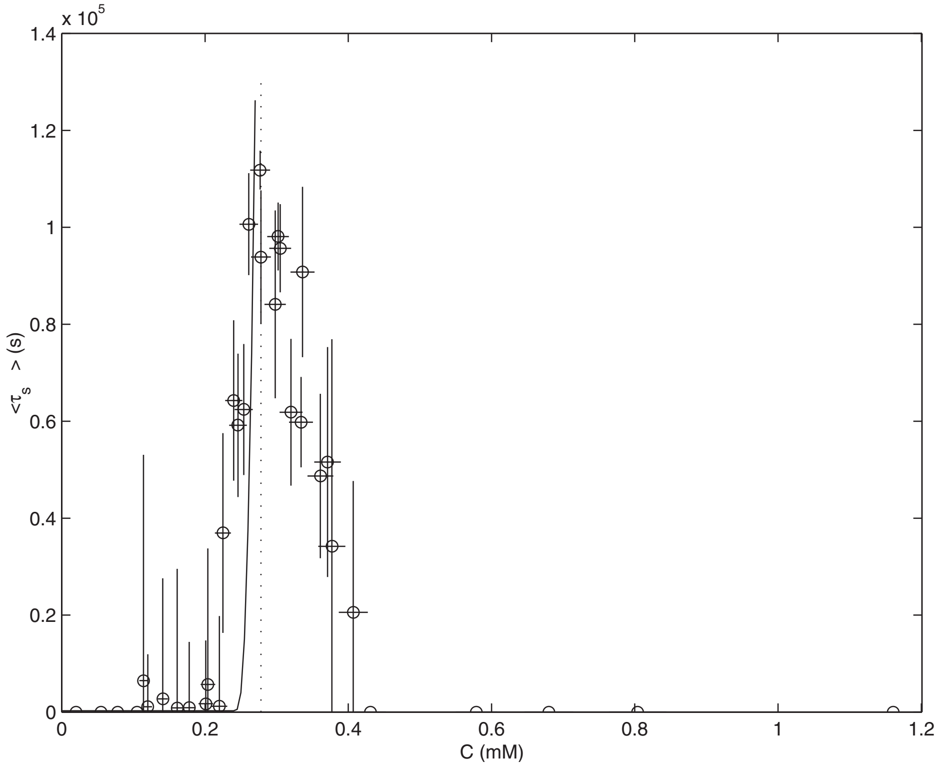

Figure 3. $\langle \tau_s \rangle$ for the aqueous solution of TRITON X-100 as a function of the surfactant concentration.

4. Discussion

The experimental results for the stationary regime allow us to distinguish three regions: $C < 0.24\,\mathrm{mM}$; $0.24\,\mathrm{mM} < C < 0.4\,\mathrm{mM}$ and $C > 0.4\,\mathrm{mM}$.

In the first zone ($C < 0.24\,\mathrm{mM}$), the birefringence grows lineally with the concentration and its characteristic time is inferior to the sensibility of our equipment. This is explained if we admit that the solution is formed by monomers in high dilution.

For this range of concentrations, the slope of the graphic B_{exp} *versus* C (figure 1) is $(2.59 \pm 0.32) \times 10^{-14}\,\mathrm{mV}^{-2}(10^{-3}\,\mathrm{M})^{-1}$ then from equation 1:

$$B_s = (4.4 \pm 0.5) \times 10^{-11}\mathrm{m\,V}^{-2} \tag{3}$$

In the second region ($0.24\,\mathrm{mM} < C < 0.4\,\mathrm{mM}$), both the Kerr constant and the relaxation time increase up to the CMC. Starting from this point a decrease of both magnitudes is observed, showing the existence of aggregates.

It is inferred that the anisotropy of the aggregates increases as we come closer to the CMC and then it diminishes until those acquire the spherical form as it could be proven by light scattering.

At this point it is interesting to know about the form of the aggregates around the CMC in the third region i.e. ($0.24\,\mathrm{mM} < C < 0.28\,\mathrm{mM}$).

We consider that the simplest answer to this question is to suppose that, in this region, the solution consists of particles whose structure is that of a lineal and rigid aggregates of k monomers ($1 \leq k$).

If C_k is the molar concentration of particles made by k molecules, the total molar concentration of surfactant is $C = \sum_{k=1}^{\infty} kC_k$ and the mean aggregation number is:

$$\overline{k}(C) = \frac{\sum_{k=2}^{\infty} k^2 C_k}{\sum_{k=2}^{\infty} kC_k} \tag{4}$$

To estimate $\overline{k}(C)$, we will suppose that the specific Kerr constant of the particles will be, in approximate form $B_k = k \cdot B_1$ [11], and that the density is independent of k ($\rho_1 = \rho_k$).

A polydispersed particles solution has a Kerr constant:

$$B_{\text{exp}} = B_{\text{w}}\left(1 - \sum_{i=1}^{\infty} \phi_i\right) + \sum_{i=1}^{\infty} \phi_i B_i \tag{5}$$

since $B_{\text{w}} \ll B_1$ (according to equation 3), simplifying we arrive at:

$$B_{\text{exp}} = B_{\text{w}} + \frac{M_1}{\rho_1} B_1 C_1 + \frac{M_1}{\rho_1} B_1 (C - C_1)\overline{k}(C) \tag{6}$$

Using the results of figure 1 we estimate that $1 < \overline{k}(C) < 14$; the maximum is obtained near CMC.

For $0.28\,\text{mM} < C < 0.4\,\text{mM}$, the additional surfactant gives place, seemingly, to spherical rigid micelles, with the corresponding disappearance of the rods. As the birefringence of the rigid spherical structures equals zero then it decreases and reaches a minimum value at 0.4 mM.

In the third region ($C > 0.4\,\text{mM}$), the birefringence again grows lineally with the total surfactant concentration and its characteristic time is lower to the sensibility of our equipment. This fact supports our hypotheses that we have a mixture of monomers and globular rigid particles. Therefore the birefringence is only produced by the monomers.

As it is shown in figure 2 the specific Kerr constant is:

$$B_{\text{s}} = (0.73 \pm 0.04) \times 10^{-11}\,\text{m}\,\text{V}^{-2} \tag{7}$$

Then, in this region, we estimate that the monomers' concentration is 17% of the surfactant total concentration.

5. Conclusions

The main purpose of this work has been to analyse the behavior of the Kerr constant and the relaxation time as a function of the surfactant concentration in diluted aqueous TX-100 solutions.

The experimental results reveal changes in the state of aggregation when the concentration is modified.

According to our experimental data we conclude that:

- For $C < 0.24\,\text{mM}$ the surfactant is found as isolated monomers.
- For $0.24\,\text{mM} < C < 0.4\,\text{mM}$ there is a mixture of monomers and anisotropic structures (seemingly rods).
- For $C > 0.4\,\text{mM}$ there is a mixture of monomers and rigid spherical micelles. The relative concentration of monomers is about 17%.

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