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Flow birefringence experiments showing a shear-banding structure in a CTAB solution

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Abstract Experiments of flow birefringence have been performed on a concentrated solution of CTAB submitted to shear in a Couette cell. Qualitative observations of the flow in the annular gap of the Couette device let us clearly see that the flow is divided into two layers when the shear rate exceeds a critical value. This shear banding structure is shown on a set of photographs. The extinction angle χ and the retardation ϕ were measured as a function of the shear rate $\dot{\gamma}$ for different temperatures. The results are in agreement with the predictions of the shear banding theory.

Key words Cetyltrimethylammonium bromide (CTAB) – shear-induced structures – flow birefringence micelles

Introduction

Molecules of surfactants show the interesting property of forming large aggregates of molecules, called micelles, when put in solution. As the concentration of surfactant in the solvent is increased beyond the critical micellar concentration (CMC), the size and shape of the micelles will gradually change and take various shapes which depend on the concentration and type of surfactant [1]. This happens, for example, in aqueous solutions of CTAB which form spherical micelles in the concentration range of 9.10^{-4} to 0.3 mol/l and rodlike particles in the range 0.3 to 0.7 mol/l approximatively [2]. For concentration higher than 0.7 mol/l a liquid crystalline phase, made of very long threads, is expected to grow [3, 4]. This structure confers strong viscoelastic properties to aqueous solutions of these surfactant molecules.

We report, in this paper, the result of an experimental study performed on a solution of CTAB in water at the concentration of 0.6 mol/l close to the concentration at which a liquid crystalline phase is likely to form. The experiments we have realized consist of flow birefringence measurements performed as a function of the shear rate for various temperatures.

We have observed an unusual behavior of the extinction angle χ and of the birefringence intensity Δn when the solution is submitted to an increasing shear rate; we hope to give a satisfactory explanation of these results.

Experimental section

Materials and methods

The surfactant used in our experiments is commercially available from Johnson Matthey Gmbh D-7500 Karlsruhe; it is used as purchased without any purification. The solvent is water distilled twice in a quartz vessel.

Once the equilibrium state of the solution is reached, an experiment can begin and the solution is studied in a conventional Couette cell. The cell is built mainly from stainless steel with a few parts of glass and Teflon; its typical dimensions are 3 cm height and 4.7 and 5.0 cm respectively for the radius of the inner and outer cylinders.

At rest, the solution is optically isotropic and, consequently, when placed between crossed polarizer and analyzer, the extinction will be maintained. Under shear, two quantities of interest have to be determined: the angle of extinction χ which defines the orientation of the medium and the retardation ϕ induced by the flow. χ is the acute angle formed by the line of flow and a neutral line of the medium and is readily measured by rotating the pair polarizer–analyzer which remain crossed, until the extinction is realized again: in that case the direction of polarization will be the same as the direction of a neutral line. A quarter wave plate is added to measure the retardation ϕ according to the method of Senarmont. The birefringence intensity Δn is readily evaluated from the relation:

$$\Delta n = \frac{\phi \lambda}{2\pi e}, \quad (1)$$

where e is the thickness of the sample equal to the height of the Couette cell. χ and ϕ are measured as a function of the shear rate $\dot{\gamma}$ for different temperatures ranging from 29° to 35 °C.

The birefringence exhibited by these solutions is so strong that even a visual observation can lead to accurate measurements of χ and ϕ.

During the visual observations the sample is placed between crossed polarizers and submitted to shear; we were able to observe a bright line which takes the shape of the inner rotating wall of the Couette cell. Let the motion of the inner cylinder be stopped and the phenomenon fades out to disappear completely after a duration which can be as long as tens of seconds depending on the temperature of the solution. The emergence of this bright line corresponds very closely to a change in the curves showing the variations, with the shear rate $\dot{\gamma}$, of the extinction angle χ and of the birefringence intensity Δn of the micellar solution.

The method of measurements and the experimental device were described in detail in a previous paper [5]; we have only added a source of white light to illuminate the entire gap when we photograph the flow.

Qualitative observation of the flow birefringence

An aqueous solution of CTAB at the concentration of 0.6 mol/l was submitted to an increasing shear rate. The sample was looked at between crossed polarizer and analyzer and white light was used.

The results of our visual observations are represented by a set of five photographs taken at the temperature of 29.7 °C. In all five of them, the letter A is one the side of the inner rotating cylinder while the letter C shows the fixed wall of the Couette cell. The width of the annular gap is 1.5 mm. The first photograph (Photo 1) corresponds to the lowest value of the shear rate ($\simeq 2\ s^{-1}$) and represents what we usually observe with many birefringent solutions as long as the flow remains in its first stage, i.e., laminar concentric Couette flow. The dark part of the picture which is one arm of the cross of isocline is the locus of the points where one of the axes of the anisotropic medium is parallel to the direction of polarization of the incident light beam. The sides of this dark band are not parallel with the radius of the cylinders; the tilting that we can observe is a consequence of the variation of the shear rate in the annular gap which is not infinitely narrow [6]:

$$\dot{\gamma} = A - \frac{B}{r^2} \quad (2)$$

A, B are constants depending on the radius R_e and R_i of the outer and inner cylinders of the cell and on the angular velocity Ω of the rotating cylinder; r stands for the distance from the center of the cell to a point in the annular gap. We shall see later that the shear rate which exits in the solution can be quite different from $\dot{\gamma}$ when the shear banding

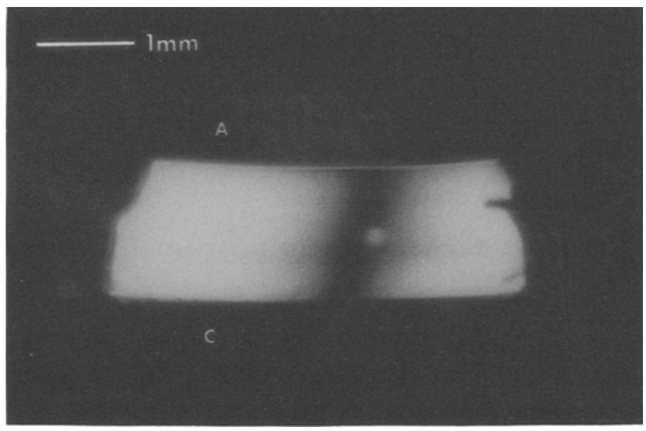
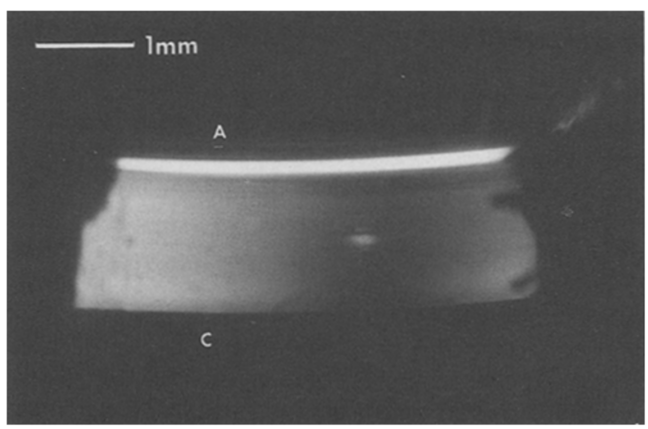


PHOTO 1



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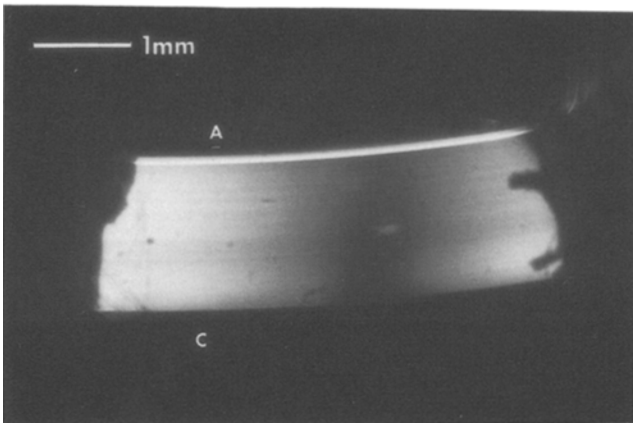

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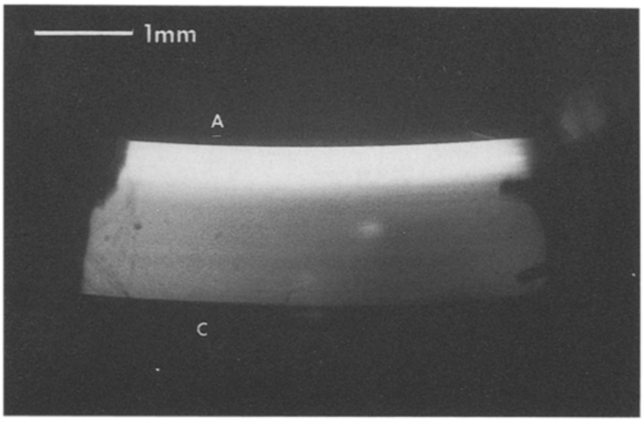

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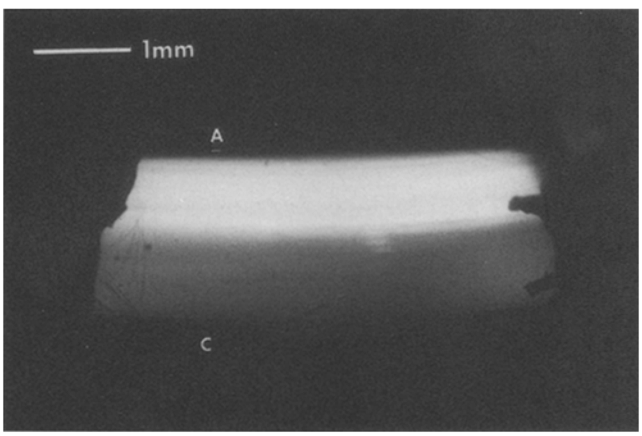


PHOTO 5

structure appears in the flow. It is well known that flow birefringence arises from a preferential orientation in the solution, therefore we can state that the micelles which are present in that part of the liquid which appears dark, have roughly the same orientation.

Everything else remaining constant or in the same position as far as optical devices are concerned, let us now slowly increase $\dot{\gamma}$. Photographs 2 to 4 show what we were able to observe directly in the Couette cell: two different zones can be observed in the annular gap of the latter. A bright thin line taking the shape of the inner cylinder appears in the gap when $\dot{\gamma}$ reaches a critical value ($\simeq 3\ s^{-1}$) called $\dot{\gamma}_c$ in the following (Photo 2). This region of the gap we shall call h-band for reasons that will be explained later. The arm of the cross of isocline mentioned previously and described on the first photograph still exists although it seems wider and a bit blurred; the layer containing this dark region is called l-band. The width of the bright line increases with $\dot{\gamma}$ to become a bright wide band extending over half the annular gap for $\dot{\gamma} \simeq 16\ s^{-1}$ for this temperature (Photos 3–5).

The decay of the birefringence in these layers happens on a completely different time scale at the cessation of the flow. When the temperature lies in the range [29.5°–30 °C], we have noticed by visual observation that the birefringence of the l-band disappears very quickly when we stop the motion of the inner cylinder while the h-band remains strongly birefringent for many seconds. These observations lead us to think that the organization of the particles or the structure of the solution is quite different in these layers and that in the h-band the particles could look like very long threads closely packed together to give a very strong birefringent medium.

Measurement of χ and ϕ

Quantitative measurements of the extinction angle χ and of the phase difference ϕ are performed with a thin beam of light of a low-power He–Ne laser crossing the solutions in the vicinity of the middle of the gap which is always in the l-band. We have not been able to perform measurements under shear in the h-band; for example, the extinction of the transmitted light which allows for the determination of the angle χ, cannot be achieved in this layer.

Figure 1 shows the behavior of χ as a function of $\dot{\gamma}$ for different temperatures. In the case of the highest temperature (35 °C, empty circles), χ decreases smoothly with $\dot{\gamma}$ as can be expected: the shear flow tends to orientate the structure formed by the particles more and more in the direction of the flow.

For the other temperatures, a sharp break is found in the curves $\chi(\dot{\gamma})$ which presents two parts roughly linear. The slope of the first part, corresponding to low shear rates, increases when the temperature decreases. The slope of the second part of each curve is to no extent comparable with the slope of the first one: χ decreases very slowly with $\dot{\gamma}$. The break in the different curves $\chi(\dot{\gamma})$ corresponds roughly with the emergence of the bright line mentioned before, the value of the shear rate which corresponds to these

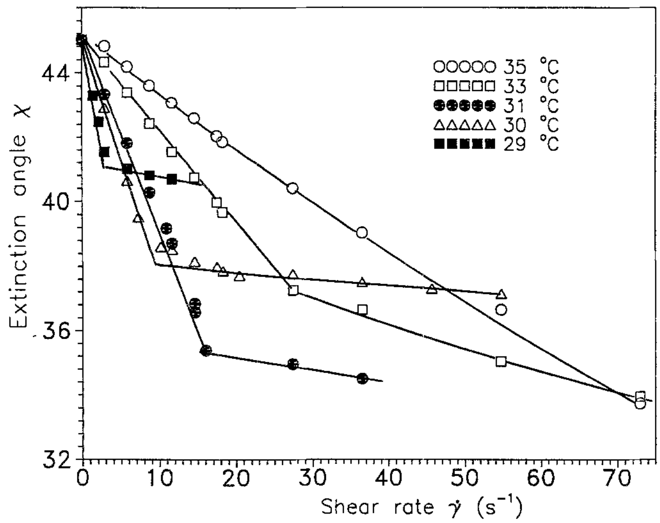
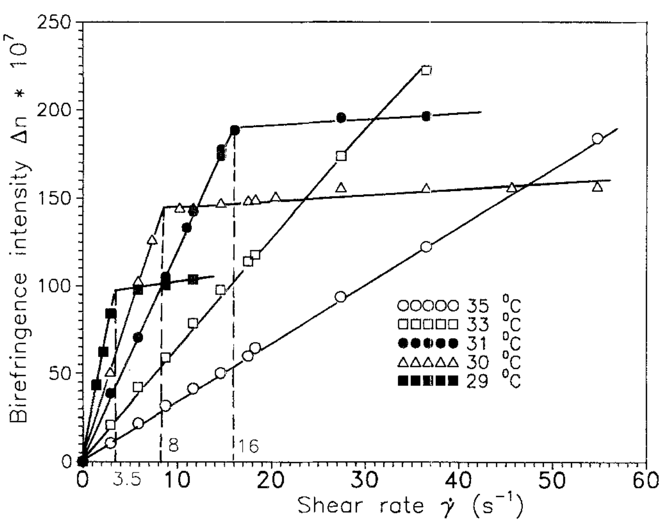


Fig. 1 Variation of the extinction angle χ versus the shear rate $\dot{\gamma}$ for different temperatures

breaks is therefore the critical shear rate $\dot{\gamma}_c$ introduced before.

The same phenomenon can be observed in the curves $\Delta n(\dot{\gamma})$ represented in Fig. 2. As $\dot{\gamma}$ is increased, the slope of the curve $\Delta n(\dot{\gamma})$ should gradually decrease towards zero and Δn should reach a saturation value which indicates that the orientation is fully realized. This kind of behavior is in fact observed in the case of the highest temperature (35 °C, empty circles), but has not been represented in Fig. 2 since it occurs for a shear rate well outside the shear rates were are interested in. When $\dot{\gamma}$ reaches the critical value $\dot{\gamma}_c$, the value of which depends on the temperature, Δn remains practically constant when $\dot{\gamma}$ is further increased.

Fig. 2 Variation of the birefringence intensity Δn versus the shear rate $\dot{\gamma}$ for different temperatures



As in the case of χ, both parts of the curves show a linear variation of Δn with $\dot{\gamma}$; for $\dot{\gamma} < \dot{\gamma}_c$ the slope of the straight lines increases when the temperature is lowered and for $\dot{\gamma} > \dot{\gamma}_c$, the curves are nearly parallel in the case of the three lowest temperatures, with a slope $\simeq 0$. This result indicates that the retardation ϕ has reached a maximum value at each temperature and that the shear rate in the l-band is nearly constant. For the lowest temperature, measurements become very difficult, this is the reason why only a few points appear on the curve for $\dot{\gamma} > \dot{\gamma}_c$.

As already mentioned, the disorientation process in the h-band is very long for the lowest temperature: the bright band induced by the shear remains visible for many seconds after the motion of the rotating cylinder has been stopped. Measurements of χ performed in the h-band at the cessation of the flow ($\dot{\gamma} = 0$) have shown that the value of the extinction angle is very near to zero and remains constant until the h-band has completely disappeared. This shows that the long thread-like particles are nearly parallel to the direction of the flow.

This particular orientation of the long particles was already noticed and measured when shear induced structures, named SIS, were studied by Hofmann and coworkers [7, 8].

The critical values of $\dot{\gamma}$ at which the break in the curves $\Delta n(\dot{\gamma})$ appears are measured in Fig. 2 and are gathered in the next table.

Discussion

The qualitative observations made on the photographs and the quantitative measurements fit quite well with several previously made theoretical attempts dealing with the dynamics of concentrated solutions of polymers or micelles.

In particular, Doi and Edwards [9, 10] have computed the theoretical expression of the shear stress $\tau(\dot{\gamma})$ which becomes a multi-valued function of $\dot{\gamma}$ when the shear stress $\tau > \tau_c$ indicating that instabilities can occur in the flow. Cates and co-workers [11] have shown that the steady shear flow in a Couette device could only be achieved if two layers or shear bands form. These layers are submitted to the same shear stress but the shear rate will be different in each layer. If we denote by $\dot{\gamma}_h$ the highest value and $\dot{\gamma}_l$ the

Table 1 Critical shear rates for different temperatures

Temperature in °C	29.50	30.20	31.20
Shear rate in s^{-1}	3.5	8	16

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lowest one, it can easily be shown that the volume fractions ϕ_l and ϕ_h of the layers exist in such a way that the shear rate $\dot{\gamma}$ obeys the law:

$$\dot{\gamma} = \dot{\gamma}_l \phi_l + \dot{\gamma}_h \phi_h \qquad (3)$$

Also of great interest is the theory developed by McLeish and co-workers [12, 13] for polymers melts flow in which they have shown that the normal stress as well as the shear stress are continuous at the interface of the layers. Let us now discuss our observations considering these theoretical results.

The curves $\chi(\dot{\gamma})$ and $\Delta n(\dot{\gamma})$ are divided into two parts according to the shear rate $\dot{\gamma}$ being smaller or greater than $\dot{\gamma}_c$.

When $\dot{\gamma} < \dot{\gamma}_c$, $\chi(\dot{\gamma})$ and $\Delta n(\dot{\gamma})$ are linear functions of $\dot{\gamma}$ as already mentioned. For a given value of $\dot{\gamma}$, the effect of the velocity field in the annular gap will be to give an average orientation to the micelles. The angle of extinction is a measure of this orientation and its variations with $\dot{\gamma}$ indicate that the micelles tend to align more and more in the direction of the flow as $\dot{\gamma}$ is increased. In the same range of shear rates Δn increases also linearly with $\dot{\gamma}$ and, for a given shear rate the absolute value of Δn decreases with the temperature. This can easily be understood when one knows that the length of the micelles decreases with an increase in the temperature and that the preferential orientation in a particular direction is more difficult to realize for smaller particles.

The unusual and interesting behavior of χ and Δn arises when the macroscopic shear rate reaches the critical value $\dot{\gamma}_c$ and is increased beyond this value. Due to the finite width of the annular gap, the shear rate $\dot{\gamma}$ is not constant in the gap but decreases slowly from the inner rotating cylinder to the outside wall at rest (see Eq. (2)). This is the reason why the bright band starts to grow from the inside of the cell since $\dot{\gamma}$ reaches its critical value $\dot{\gamma}_c$ at first near the moving wall. In this bright band it is likely that the long thread-like micelles pack together in a compact arrangement probably of nematic structure to form a highly birefringent liquid crystalline phase.

It can be seen on the photographs that the width l of the h-band increases with $\dot{\gamma}$. We have performed measurements of the width of this layer on a set of photographs taken at the temperature of 29.5 °C. Figure 3 shows the curve $l(\dot{\gamma})$: the variations are approximatively linear with $\dot{\gamma}$. The extrapolated value for $\dot{\gamma} = 0$ is the critical shear rate, this value is in good agreement with the value determined by the visual observation of the emergence of the bright band at this particular temperature ($\simeq 2\ s^{-1}$ in this case).

Figure 4 shows a sketch of the velocity profile in the annular gap for different angular velocities of the rotating cylinder; the magnitude of the tangential velocity is represented by an arrow: AB, for example, stands for the tangential velocity of a point A on the moving wall for the lowest angular velocity. For $\dot{\gamma} \leqslant \dot{\gamma}_c$, the envelope of the arrows is a single straight line and $\tan(\widehat{AOB})$ is $\dot{\gamma}$. Let the line OB represent the case $\dot{\gamma} = \dot{\gamma}_c$; χ and ϕ have then reached their extreme value and the bright fine band starts to grow in the flow.

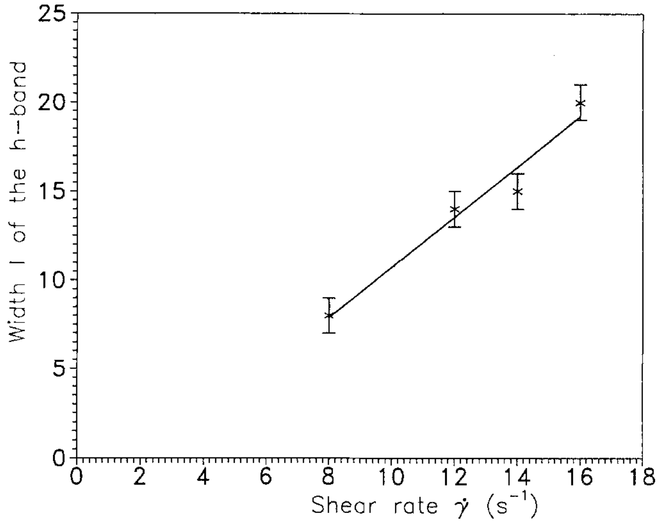

Fig. 3 Width l of the h-band as a function of the shear rate $\dot{\gamma}$ (in arbitrary units)

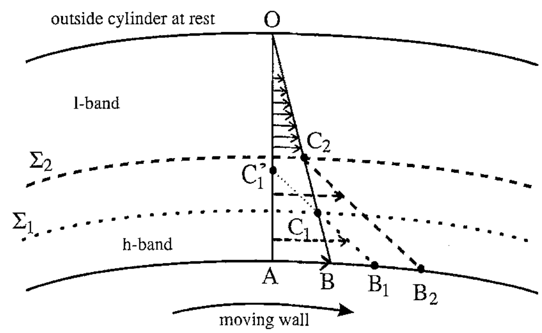

Fig. 4 Qualitative representation of the velocity profile in the annular gap of the Couette device

The angular velocity is then increased, the shear rate becomes equal to $\dot{\gamma}_1 > \dot{\gamma}_c$; the bright band grows wider and is separated from the l-band by the interface Σ_1. In the l-band, the experimental results show that χ and Δn remain practically constant indicating that the shear rate $\dot{\gamma}_l$, the shear stress τ and the viscosity η_l are also nearly constant: the velocity profile remains the same and the envelope OC_1 is superimposed to OB in the l-band. This is not the case in the h-band where the shear rate $\dot{\gamma}_h$ defined as $\tan(\widehat{AC'_1B_1})$ is greater than $\dot{\gamma}_l$. As a matter of fact, in the bright layer, the solution forms a liquid crystalline phase the viscosity of which is much smaller than the viscosity η_l of the solution in the other layer. Since the shear stress is continuous at the interface of the bands, as already stated, we have:

$$\eta_h \dot{\gamma}_h = \eta_l \dot{\gamma}_l \text{ or } \dot{\gamma}_h = \dot{\gamma}_l \frac{\eta_l}{\eta_h}, \quad (4)$$

and $\eta_h < \eta_l$ implies that $\dot{\gamma}_h > \dot{\gamma}_l$.

Let the macroscopic shear rate be further increased to $\dot{\gamma}_2 > \dot{\gamma}_1$, the interface moves to Σ_2, the volumic fraction ϕ_l and ϕ_h of each layer meet Eq. (3).

In the l-band, the velocity profile is the same as in the first case: the envelope OC_2 is superimposed to OC_1 and $\dot{\gamma}_l = \tan(\widehat{AOC_2})$.

In the h-band where a liquid crystalline phase exists, the increase of $\dot{\gamma}$ has probably little effect on the viscosity η_h of this phase, $\dot{\gamma}_h$ remains constant according to Eq. (4) and C_2B_2 is drawn parallel to C_1B_1.

Conclusion

We have shown that the shear in the annular gap of a Couette device is able to induce the formation of very long micelles which align in the direction of the flow. These particles pile up in a compact nematic structure, to form a highly birefringent layer which is a liquid crystalline phase.

Such transitions to a liquid crystal state have been recently studied in different concentrated systems: $CPClO_3/NaClO_3$ [15], CPCl/NaCl/Hexanol [16] mainly by SANS or rheological measurements and CTAB [17].

Flow birefringence observations and measurements allow for a direct observation of the phenomenon and have proved to be a useful tool for the study of the transition from an isotropic to a liquid crystalline phase. Further theoretical investigations will be necessary to relate the birefringence intensity to the shear stress or shear rate in order to bring a quantitative demonstrated of the plateau behavior of the curves $\chi(\dot{\gamma})$ and $\Delta n(\dot{\gamma})$. We are now investigating different systems of surfactants already studied by SANS and rheological measurements to derive an experimental corroboration of our optical results.

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