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Flow-induced birefringence in a lyotropic liquid crystal in the isotropic phase: An order diffusion approach

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The flow-induced birefringence produced by the movement of a plate in an isotropic lyotropic liquid crystal phase was theoretically treated as a diffusion problem. A characteristic length $l \sim 10^{-4}$ cm, which informs about the intermicellar correlation, was experimentally obtained. The diffusion coefficient measured in the middle of the isotropic phase is $D \sim 10^{-6}$ cm^2/s. The analysis of the results indicates that l and D increase near the isotropic-to-lamellar phase transition temperatures. [S1063-651X(97)03911-1]

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I. INTRODUCTION

Lyotropic liquid crystals are mixtures of amphiphilic molecules and water under proper temperature and relative concentrations conditions. The flow regime of this system is complex since the translational micellar motions are coupled to the orientational motions of the micelles. The isotropic (ISO) phase of lyotropic liquid crystals does not have long-range orientational ordering but it is possible to induce birefringence by flow. This flow-induced birefringence, however, is not an exclusive property of the isotropic phase, being observed in optically isotropic lyotropic sponge phases [1]. From the theoretical point of view, de Gennes predicted [2,3] the divergence of the flow-induced birefringence δn in the isotropic phase as the temperature approaches the transition temperature to the nematic phase, and the dependence of δn with the molecular (or micellar) velocity field gradient.

A large number of papers devoted to the study of the flow-induced orientational ordering in liquid crystals have been done with thermotropic nematics [4,5]. Usually optical techniques [6] were used. More recently [7,8], the dynamical properties of lyotropic micellar complex fluids have been investigated under shear flow.

In a recent paper [9] we presented experimental results of the flow-induced birefringence in the isotropic phase of the lyotropic mixture of potassium laurate (KL), decanol (DeOH), and water. This mixture has an ISO phase between two lamellar phases, as a function of the temperature. The shear flow produced by a perturbation in the isotropic phase induced a birefringent phase that relaxes back to ISO with a typical relaxation time $\tau \sim 10^{-2}$ s. These relaxation times increase as the temperature approaches the ISO-to-lamellar transition temperatures, and presented a maximum in the middle of the ISO domain. Assuming that τ is qualitatively a measurement of the intermicellar correlation, the existence of a maximum in the curve τ *versus* the temperature was interpreted as an indication of a virtual nematic phase. Changing a little the amphiphilic concentration of the mixture (less than 1% in weight), a calamitic nematic phase is observed at the same temperature where the maximum value of τ was found.

In this Brief Report we present a theoretical study of the flow-induced birefringence in the ISO phase of a lyotropic mixture. In this framework, the problem is treated as a diffusion of the tensorial order parameter inside the sample, originally produced by the velocity field gradient. The theory allows the determination of a characteristic length, as a function of temperature, which informs about the intermicellar correlation in the isotropic phase.

II. THEORY

The Landau–de Gennes theory [10] characterizes the equilibrium state of the macroscopic nematic system using a tensorial order parameter $\overleftrightarrow{Q}$.

According to the Landau hypothesis [11], the free energy of the system (F) can be represented as a function of a thermodynamic variable. In this framework, F can be expanded in terms of the invariants of $\overleftrightarrow{Q}$, and its gradients [2]:

$$F(T,Q)=F_0+\frac{1}{2}A(T)Q_{\alpha\beta}Q_{\beta\alpha}+\frac{1}{3}BQ_{\alpha\beta}Q_{\beta\delta}Q_{\delta\alpha}+\frac{c}{4}(Q_{\alpha\beta}Q_{\alpha\beta})^2+O(Q^5)+\frac{1}{2}d\left(\frac{\partial Q}{\partial z}\right)^2, \quad (1)$$

where T is the temperature, F_o is the free energy (for a given temperature and pressure) of the state with $Q=0$, $A(T)=a(T-T^*)$, a, B, c, and d are the Landau coefficients essentially temperature independent. Expression (1) represents the one-dimensional approximation, where the gradient is considered only along the z axis.

In the thermodynamics of irreversible processes [13] two types of parameters are defined to described these processes. One of them describes the force that produce the process and the other describes the response of the system to this force, called flux. The fluxes are consequences of the applied forces. One of these fluxes ($R_{\alpha\beta}$) is expressed by the time variation of the order parameter:

$$R_{\alpha\beta}=\frac{\partial Q_{\alpha\beta}}{\partial t}, \quad \alpha,\beta=1,2,3,\dots. \quad (2)$$

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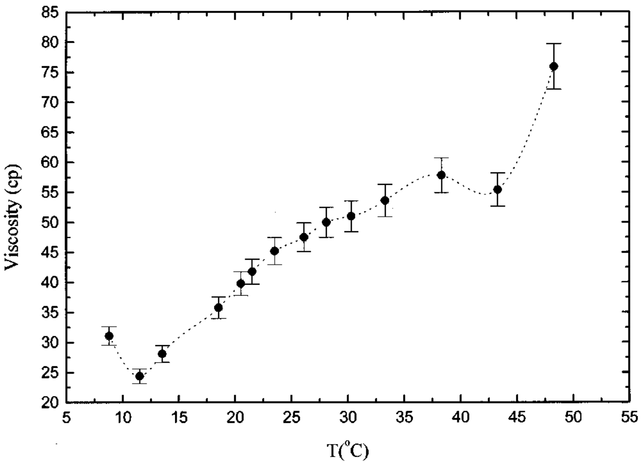

FIG. 1. Mean viscosity μ as a function of the temperature T. The dashed line is only a guide for the eyes.

The hydrodynamic flux tensor, which takes into account the velocity ($\mathbf{v}$) gradients, is written as

$$e_{\alpha\beta}=\frac{1}{2}\left(\frac{\partial v_\beta}{\partial x_\alpha}+\frac{\partial v_\alpha}{\partial x_\beta}\right), \tag{3}$$

In incompressible fluids $e_{\alpha\beta}=0$. The force associated with $Q_{\alpha\beta}$ is obtained from the free energy expression (1):

$$\phi_{\alpha\beta}=-\frac{\partial F}{\partial Q_{\alpha\beta}}=-A(T)Q_{\alpha\beta}. \tag{4}$$

Let us suppose a situation where the velocity gradients present in a sample vanish at the time $t=0$. The Onsager's relations in this particular situation give

$$\frac{\delta F}{\delta Q_{\alpha\beta}}=-\mu\frac{dQ_{\alpha\beta}}{dt}, \tag{5}$$

where $\delta F/\delta Q_{\alpha\beta}$ is a functional derivative, and μ is a mean viscosity.

Let us consider now an ISO phase where a velocity field gradient induces an orientational ordering of the micelles. We expect that the induced scalar order parameter is very small compared to its gradients. In this framework, expression (1) can be written as

$$F=F_o+\frac{1}{2}d\left(\frac{\partial Q}{\partial z}\right)^2. \tag{6}$$

Introducing expression (6) in expression (5), and using the fact that in the isotropic phase $\partial F/\partial Q=0$ one obtains

$$\frac{\partial Q(z,t)}{\partial t}=D\frac{\partial^2 Q(z,t)}{\partial z^2}, \tag{7}$$

which represents a diffusion equation for the scalar order parameter Q. $D=d/\mu$ is a diffusion coefficient [14].

Expanding $Q(z,t)$ into Fourier's integrals one gets

$$Q(z,t)=\int Q_z(t)\exp(ikz)dk, \tag{8}$$

where the expansion coefficients are

$$Q_z(t)=\frac{1}{2\pi}\int Q(z',t)\exp(-ikz')dz'. \tag{9}$$

Introducing expression (8) into (7) one obtains

$$\frac{\partial Q_z(t)}{\partial t}+Dk^2Q_z(t)=0, \tag{10}$$

which has the solution

$$Q_z(t)=Q_{0z}\exp(-Dk^2t). \tag{11}$$

Introducing expression (11) into (8), the solution of the diffusion equation (7) is obtained:

$$Q(z,t)=\sqrt{\frac{1}{4\pi Dt}}\int Q_0(z')\exp\left[\frac{-(z-z')^2}{4Dt}\right]dz'. \tag{12}$$

In Eq. (12) $Q_0(z')$ is the order parameter distribution function at $t=0$. At this point we assume a Gaussian shape to $Q_0(z')$:

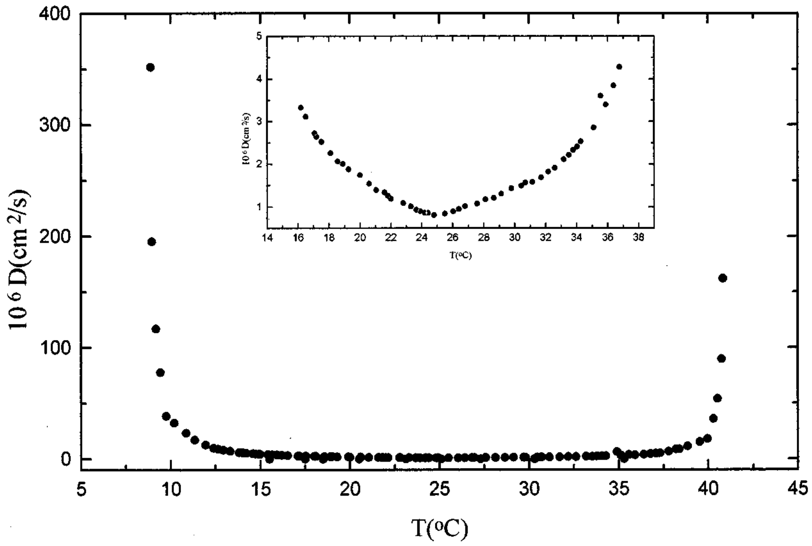

FIG. 2. Diffusion coefficient D as a function of the temperature T. The inset is a detail of the temperature range from 14 °C to 37 °C.

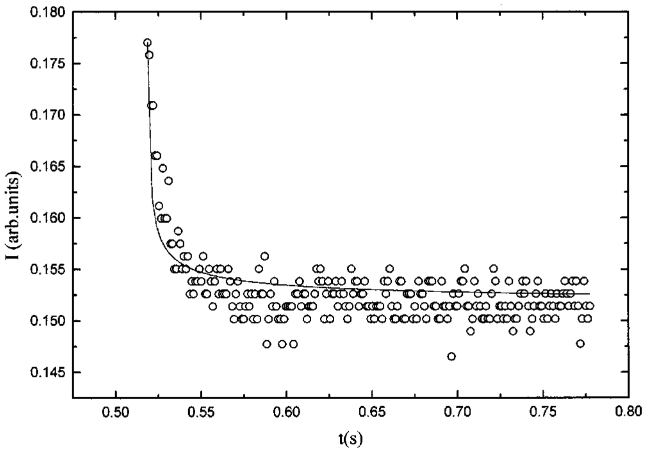

FIG. 3. Typical behavior of the transmittance in arbitrary units as a function of the time. Flow-induced birefringence produced by the movement of a plate inside the sample. The solid line is a fit of expression (15). $T=28.0$ °C.

$$Q_0(z')=Q_0\exp\left[-\left(\frac{z'}{l}\right)^2\right], \tag{13}$$

where $Q_0=Q(0,0)$ and l are constants, l being a characteristic length of the problem. The Gaussian shape was assumed because we are considering a one-dimensional velocity field gradient along the z axis. This function has the physical boundary conditions of the problem, i.e., it presents a maximum at $z=0$ and vanishes at $z\rightarrow\infty$, and allows an analytic integration of Eq. (12).

Using expression (13) in (12) one can write

$$Q(z,t)=\frac{Q_0 l}{\sqrt{4Dt+l^2}}\exp\left[-\frac{z^2}{(4Dt+l^2)}\right], \tag{14}$$

which is solution of the diffusion equation (7) for a given temperature. The optical transmittance $I(t)$ at a given temperature can be written [15] as a function of $[Q(z,t)]^2$, as will be discussed in the next section.

This situation can be experimentally produced [9] by the movement of a plate (in the x-y plane) along the x axis, placed inside a sample holder with a liquid crystal at the ISO phase.

III. DISCUSSION

In Ref. [9] the experimental data of $I(t,T)$ were presented. The samples used in that work were mixtures of potassium laurate (KL: 26.89 wt %), decanol (DeOH: 6.39 wt %) and water (66.72 wt %). The phase sequence as a function of the temperature is LAM (8.6 °C) ISO (48.5 °C) LAM, where LAM stands for the lamellar phase. The velocity field gradient was produced by a stainless steel square plate (placed in the x-y plane), which moved along the x axis.

The transmittance $I(t)$ at a given temperature is proportional to $[Q(z,t)]^2$, and can be written as

$$I(t)=C\sqrt{\frac{\pi}{8}}\,Q_0^2\frac{l^2}{(4Dt+l^2)^{1/2}}, \tag{15}$$

where C is a constant.

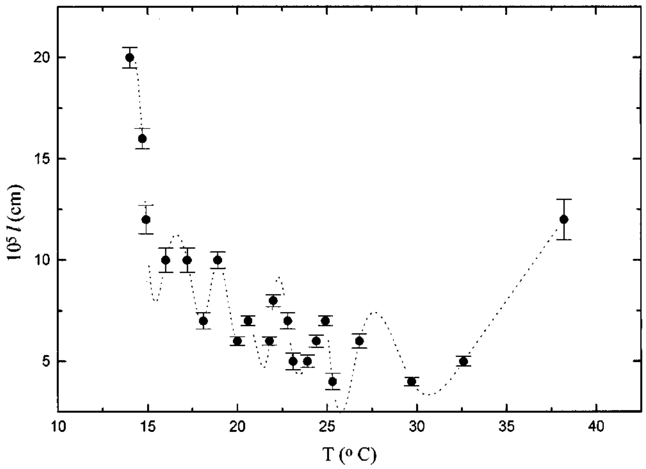

FIG. 4. Characteristic length l the flow-induced birefringence process as a function of the temperature T. The dashed line is only a guide for the eyes.

Expression (15) can be used to fit the experimental results of $I(t)$ at a given temperature.

The diffusion coefficient D is temperature dependent since μ and the elastic constants depend on T. The mean viscosity of the sample (the same of Ref. [9]) was measured as a function of T using a cone-plate rheometer (Brookfield LV-DVIII CP). Figure 1 shows μ versus T. μ increases as the temperature approaches the ISO-to-LAM phase transition at $T_C=48.5$ °C. A similar behavior was found [12] in a different lyotropic mixture, in a nematic phase near the nematic-to-lamellar phase transition. The errors presented in Fig. 1 are evaluated taking into account the reproducibility of the experiment. Our results do not clearly show an increase of μ at the ISO-to-LAM transition at the lower temperature. Only the first measured value indicates this tendency. The constant d is essentially an elastic constant [16] that, in the case of lyotropic nematics, is about 10^{-6} dyn [17]. The temperature dependence of d was evaluated taking the data of a similar lyotropic mixture [12], which presents a nematic-to-lamellar phase transition. Following this procedure, D can be obtained and its temperature dependence is shown in Fig. 2. The diffusion coefficient increase near the ISO-to-LAM transitions ($T_C=48.5$ °C and $T_C=8.6$ °C). The values of D in the middle (25 °C) of the ISO domain are about 10^{-6} cm^2/s, and increase, as a function of the temperature, near the ISO-to-LAM phase transitions. The value of D at 25 °C is about the same measured [18] for the diffusion of the glycose (or saccharose) in water.

Figure 3 shows a typical fit of Eq. (15) to the sample transmittance at 28.0 °C. The unique fitting parameter is l. This is a typical length characteristic of the flow-induced birefringence in the lyotropic mixture. l is expected to be a qualitative measurement of the intermicellar correlation. Figure 4 shows the behavior of l as a function of T. The error is evaluated taking into account the standard deviation of the fit and the reproducibility of the experiments. Different experiments were performed at the same temperature and the values of l obtained lie within the error bars evaluated. The order of magnitude of l is 10^{-4} cm. Taking into account that the typical dimension available per micelle [19] is about 10^2 Å (i.e., the micelle and the surrounding water), in l we have about 10^2 micelles. The increase of l near the upper and lower temperature transitions to the lamellar phases is clearly observed in Fig. 4. In the middle of the ISO range the values of l present a dispersion around 7×10^{-5} cm. The relaxation time of the flow-induced birefringence [9] ($\tau\sim10^{-2}$ s) *versus T* also increased near the ISO-to-LAM phase transition temperatures, and presented a maximum at about 25 °C. As pointed out before, observing the usual topology of the lyotropic nematic phase diagram [20,21] we notice that on increasing the water concentration, the nematic domain becomes smaller, always surrounded by an isotropic region. For a given critical water concentration, the nematic domain vanishes and only the isotropic domain remains. The mixture used in the present work is very near this critical concentration and the analysis of the parameter τ indicated [9] the tendency of the mixture to present a nematic phase. This behavior, with a local maximum at the middle of the ISO domain, was not observed in the measurements of l versus T (Fig. 4).

With the orders of magnitude of l, obtained in the present work ($\sim10^{-4}$ cm), and τ measured in Ref. [9] ($\sim10^{-2}$ s), we can calculate the order of magnitude of the diffusion coefficient D, to check the consistency of our approach. We find $D\sim10^{-6}$ cm^2/s, which agrees with the order of magnitude obtained before (d/μ).

IV. CONCLUSIONS

The flow-induced birefringence produced by a perturbation in an isotropic lyotropic phase was theoretically treated as a diffusion problem. An adjustable parameter l that informs about the typical length of this effect was experimentally obtained. This parameter also informs about the extent of the correlation properties among the micelles. The analysis of the results indicates that l increases near the isotropic-to-lamellar phase transition temperatures.

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