Inversion in the change of the refractive index near the nematic-isotropic phase transition in lyotropic liquid crystal

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This work demonstrates the occurrence of dn/dT inversion from negative to positive near the nematic-isotropic phase transition in lyotropic liquid crystal. It is suggested that this effect is attributed to the sudden increase of the electronic polarizability due to a change in the micelles shape near this phase transition. It is also shown the formation of long lasting lens-like element within the sample when it is irradiated at moderately high laser powers. This permanent lens is erasable by increasing the temperature above the nematic-isotropic transition temperature.

Keywords: thermal lens, refractive index, lyotropic liquid crystal, phase transitions

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INTRODUCTION

Laser induced refractive index change has been widely employed in order to understand the fundamental properties of thermotropic liquid crystals. As a result of the sample-laser beam interaction several nonlinear processes are straightforwardly induced, depending on both the liquid crystals composition and their spatial orientation. Among these, Kerr effect, electrostriction, non-linear electronic polarization and thermal heating processes have been observed. The discrimination among these optically induced non-linear processes has been successfully achieved by changing the beam power and polarization, the experimental configuration and the time scale of the experiments.

Recently, we have reported on the use of Thermal Lens (TL) technique to the evaluation of the thermal diffusivity anisotropy of lyotropic liquid crystals. In this paper, we applied for the first time the TL technique to investigate the temperature dependence of the rate of change of the refractive index in lyotropic liquid crystal. In particular, we focus our attention to the temperature range from 48°C up to 52°C, where this material present a nematic-isotropic phase transition (N ↔ I).

EXPERIMENTAL

Lyotropic nematic liquid crystals are mixtures of amphiphilic molecules and a solvent (usually water), under adequate temperature and concentration conditions. The basic units of these systems are anisotropic micelles. The composition of the sample investigated in this work was: potassium laurate (29.4 wt%), decanol (6.6 wt%), water (64 wt%) The phase sequence was determined by optical microscopic and conoscopic observations: isotropic up to 50°C, calamitic nematic from 15 to 50°C and isotropic above 50°C again. The sample was placed in a quartz cuvette with thickness of L = 0.5 mm. The axes of the directors in the nematic phases were aligned for 15 hours in a magnetic field (1.5 T) for orientations both parallel and perpendicular to the side walls. After that, the sample was positioned inside a hot stage (MK200) device. For each orientation of the directors the measurements were performed as a function of the temperature in the range from 25°C to 54°C. The resolution of the hot stage is 0.01°C. The measurements were performed only when the temperature of the sample was stabilized to better than 0.1°C.

The thermal lens experiments were performed using the mode mismatched configuration as a function of the temperature. In this arrangement the probe beam spot size is higher than the excitation beam, improving the sensitivity of the technique when compared to the mode matched or single beam configuration. An Argon ion laser was used as the excitation beam (514.5 nm) and a He-Ne laser (632.8 nm) as the probe beam. The exposure of the sample to the excitation beam was controlled by a shutter. The output of the photo-diode was fed into a digital oscilloscope which was triggered by a second photo-diode. The data were transferred through a GPIB interface, and stored in a microcomputer for further analysis. Each scan resulted in 1000 measured points.

The experimentally observed time profile of the developing thermal lens, I(t), is described by Eq. 1 below, which is used for the determination of the thermo-optical properties of the sample:

\[
\frac{I(t)}{I(0)} = \frac{1 - \frac{\theta}{2} \tan^{-1} \left( \frac{2mV}{[(1+2m)^2 + V^2]^{1/2}(1/2t) + 1 + 2m + V^2} \right)}{(1+2m)^2 + V^2} \]

(1)

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where $dn/dT$ is the temperature coefficient of the sample refractive index at the probe beam wavelength, $\lambda_p$. Here one must observe that, depending on the sign of $dn/dT$, the propagation of the probe beam through the TL results in either a defocusing ($dn/dT<0$) or a focusing ($dn/dT>0$) of the beam center. The other quantities in the equations above are: excitation ($\omega_e$) and probe ($\omega_p$) beam radii at the sample; excitation beam power ($P_e$) and absorption coefficient ($A_e$); sample thermal conductivity ($k$) and diffusivity ($\alpha$).

It should be noted that the above theoretical model was developed for an isotropic medium, while in the present experiments, especially in the case of the planar geometry, the parameter $\theta$ has an effective value, defined as $\theta_{te}$. For the homeotropic alignment there is a radial symmetry in the thermal lens profile, which means that the values of the measured parameters are related to the perpendicular orientation of the director. Here we call $\theta$ as $\theta_p$.  

RESULTS AND DISCUSSION

Figure 1 shows the typical time resolved thermal lens signal for the director aligned parallel to the side walls for two different temperatures. It can be observed an inversion in the build up of the thermal lens at 48.8°C, (compare Fig. 1a at 34.5°C with Fig.1b at 48.8°C - in the isotropic phase, above 50°C, the former behavior is restored). The corresponding values of $\theta_{te}$ and $\theta_p$ (normalized to the laser power), obtained from the phase-shift signal data fitting to Eq. 1 are plotted in Figs. 2a and 2b, respectively, as a function of temperature. The data points in the isotropic phase in Fig. 2a and Fig 2b are represented by crosses. They were obtained through an average of the data from all measurements performed in this region. For the planar geometry the value of $\theta_{te}$ decreases from about 2 at 34°C to 0.04 at 48.3°C and becomes negative between 48.5°C and 49.3°C, returning to a positive value above 49.3°C. It follows from Eq. 3 that this inversion of the $\theta_{te}$ sign is a consequence of a change in $dn/dT$ from negative to positive. We note that this defocusing-self-focusing inversion was only observed for the planar geometry near the nematic-isotropic phase transition. We attribute this inversion to the rate of change of the refractive index with respect to the temperature, namely, $dn/dT$, since the probe beam polarization was parallel to the director orientation, while the pump laser beam was circularly polarized, thus preventing reorientation of the director.

Since $dn/dT$ is a function of the temperature coefficient of the electronic polarizability ($\varphi$) and of the thermal expansion coefficient ($\beta$), a possible mechanism driving the observed inversion of $dn/dT$ in the director orientation is the increase in the $\varphi$ values in the long axis of the micelles, resulting from their higher electronic polarizability near the nematic-isotropic phase transition as compared to the nematic and isotropic phases. This agrees with the observation that, in the nematic-isotropic phase transition the electronic polarizability is greatly enhanced in the axis parallel to the director. The $\varphi$ value is associated to the electronic polarizing power $Z/a^2$, where $a$ is the distance between the dipole charges $Z$. This, in turn, suggests that the observed inversion in $dn/dT$ results from a change in the micelles shape, decreasing the distance between the dipole charges. In other words, the inversion in $dn/dT$ reveals, from a microscopic point of view, a significant change in the spatial distribution of the charges in the sample induced by a modification on its basic units. This explanation is consistent with published X-ray diffraction measurements, showing the micelles shape change near the nematic discotic-isotropic phase transition in lyotropic liquid crystal.  

For the homeotropic configuration the $\theta_p$ values increase with increasing temperature presenting a peak at 50°C. In this sample alignment the thermal expansion coefficient, $\beta$, dominates the observed change in $dn/dT$ which is negative in the whole temperature range investigated in this work. We note that the temperature of the peak of $\theta_{te}$ for the planar alignment is smaller than that of the peak in Fig. 2b for the homeotropic geometry. This difference may be attributed to the fact that the electronic polarizability increases as the temperature value...
approaches the nematic-isotropic phase transition overcoming the possible changes in the thermal expansion values. After reaching the minimum at about 48.8°C, θ_{iso} moves into a region where their values increase until reaching the isotropic phase, indicating that in this temperature range the thermal expansion coefficient increases and dominates dn/dT. For the homeotropic geometry, as mentioned before, the thermal expansion coefficient dominates dn/dT in the whole temperature range and becomes maximum just before the isotropic phase.

The above results indicate that thermal lens measurements provide an alternative route for investigating the temperature dependence of dn/dT, with the advantage of allowing the measurements to be independently performed for each orientation of the director. We have next performed a second set of experiments using the same mode-mismatched thermal lens experimental set up, except that the two laser beams were used with the polarization parallel to the director orientation and the probe beam profile was projected on a screen. The sample was oriented in the planar geometry at a temperature close to the phase transition. The excitation beam power was increased up to 300 mW, when a permanent lens was induced, remaining unchanged during the one hour time of observation. We have also found that this process could be erased by increasing the sample temperature until their isotropic phase. We have also noted that the permanent lens was greatly enhanced when the sample was doped with ferrofluid. This memory effect is similar to the one observed by Khan,17 and Khoo and Normandin 18 in lyotropic liquid crystals, specially in the temperature range where phase transition occurs.

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