Nonlinear refractive index measurements of discotic and calamitic nematic lyotropic phases

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In this work, through the Z-scan technique, we report on measurements of the nonlinear refractive index (n_2) in discotic and calamitic nematic phases at room temperature in lyotropic mixtures of potassium laurate, decanol and D_2O. This technique presents high sensitivity when compared to conventional interferometry. The nonlinear optical birefringence (Δn_2) of these nematic phases was also determined. The sign and absolute value of this relevant nonlinear parameter are discussed in terms of structural changes in the micellar configuration which takes place in each nematic lyotropic phase.

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I. INTRODUCTION

In the field of complex fluids, the lyotropic liquid crystals (LLC) constitute one of the most interesting examples [1]. The basic units, named micelles, are anisotropic aggregates of amphiphilic molecules disperse in a solvent (usually water). The remarkable characteristics of LLC stimulated enourmous effort in both basic and applied research. Because of the vast number of different phases shown by LLC's, they were the subject of various works in the field of phase transition, statistical mechanics, and biological sensors [1,2]. In a classical paper, Yu and Saupe [3] reported the existence of biaxial nematic phase between two uniaxial nematic phases in a deuterated ternary lyotropic mixture. In this lyotropic system, the classical isotropic phase (I) at high temperature and also a re-entrant isotropic phase (I_{RE}) which takes place at lower temperature were observed. The uniaxial nematic lyotropic phases are composed by average prolate (calamitic N_C) or oblate (discotic N_D) micellar aggregates. Experimental data support that they are the macroscopical consequences of different orientational fluctuations of the micellar aggregates [4]. In the uniaxial nematic phases these orientational fluctuations are full rotations along the nematic director, and only small amplitude oscillations in the biaxial nematic phase (N_B). Linear optical techniques are usually used to study the nature of phase transitions. The linear birefringence can be connected to the order parameter and its measurement in the vicinity of critical points can improve the understanding of the collective behavior of the basic units. On the other hand, the nonlinear optical properties of LLC have received less attention than its linear optical ones. An elegant and simple method to measure the nonlinear optical response of a medium at different time scales is the single-beam Z-scan technique [5]. At milliseconds (ms) time range, the nonlinear optical response is expected to be of thermal and orientational origin [6–8]. The photothermal process, responsible for changes on the refraction index of the medium, leads to the formation of a lens-like element [9]. The Z-scan technique was recently used to study the thermal nonlinear optical properties of lyotropic liquid crystals on the ternary mixture of potassium laurate, 1-decanol, and water in the N_C, N_B, and isotropic (I) phases dopped with small amounts of ferrofluid [8,10,11]. It was shown that lyotropic liquid crystals [8] exhibit thermal nonlinear optical responses $\sim 10^{-2}$ times lower than thermotropic liquid crystals [12], depending on phase, temperature, and content of ferrofluid. In this paper, as far as we know, we report the first measurements of the nonlinear refractive index (n_2) in lyotropic mixtures of potassium laurate, 1-decanol and D_2O, in discotic and calamitic nematic phases.

II. FUNDAMENTALS

The lyotropic liquid crystals investigated in this work were mixtures of potassium laurate (KL), 1-decanol (DeOH), and D_2O with two different compositions in wt %: M_1[25.20/6.14/68.5] and M_2[24.80/6.24/68.96]. DeOH (>99% purity) and D_2O (>99% purity) are commercially avaliable from Aldrich. KL was synthetized in our laboratory from lauric acid via neutralization with potassium hydroxide and was further recrystallized with ethanol several times. The compounds for this synthesis come from Merck. By using a polarized-light optical microscopy and optical refractometry [13,14] the phase sequences, as a function of temperature, were determined as follows: sample M_1, $I_{RE}-N_C$ (11.6 °C) and N_C-I (52.4 °C), and sample M_2, $I_{RE}-N_D$ (12.1 °C) and N_D-I (36.3 °C), respectively. The nematic samples were conditioned in sealed planar glass cells (1 mm of light path) from Hellma. Uniform orientation of the samples were obtained using an electromagnet ($H \sim 1$ Tesla) for 24 h and checked by crossed polarizers. The laboratory frame axes are defined with the boundary surfaces parallel to the x-y plane and z is the axis normal to the biggest surface of the sample cell. The measurements were made at $T=25$ °C in a temperature controlled device stable at 10 mK. In the N_C phase, the direction of the magnetic field defines the director $\hat{n}$. The values of $n_{2\parallel}$ and $n_{2\perp}$ can be obtained by orientation of the director along two perpendicular directions, so the configurations between $\hat{n}$ and the polarization of the laser beam $\vec{E}$ are $\hat{n} \| \vec{E}$ and $\hat{n} \perp \vec{E}$, respectively. In the N_D oriented phase it is necessary to regularly rotate the sample around the z axis in the presence of a

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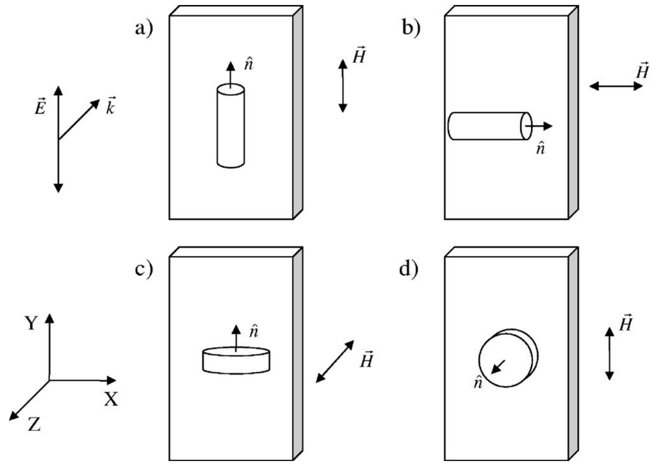

FIG. 1. Experimental configurations of the nematic director, magnetic field and polarization of the laser beam for nonlinear refractive index measurements of (a) $n_{2\parallel}$ and (b) $n_{2\perp}$ on the N_C phase; (c) $n_{2\parallel}$ and (d) $n_{2\perp}$ on the N_D phase.

magnetic field parallel to the x-y plane of the sample cell. So, the director $\hat{n}$ will be perpendicular to a plane determined by two nonparallel directions of the magnetic field $\vec{H}$ in the laboratory frame axes. A small quantity of ferrofluid (<0.04 wt. %) was added to the nematic samples in order to ensure a good quality alignment of the director in the N_C and N_D nematic phases. Figure 1 shows a scheme of the relative configuration of the nematic director, magnetic field, and polarization of incident laser beam for measurements of $n_{2\parallel}$ and $n_{2\perp}$ in the N_C and N_D phases.

Among the techniques developed to study nonlinear optical effects, the Z-scan technique stands up by its simplicity and sensitivity to measure the amplitude and sign of the nonlinear refraction index n_2 [5]. It is important to mention that ($n_2 \sim \chi^{(3)}$) is related with the linear refractive index (n_o) by $n=n_o+n_2I$ where n is the refractive index, I is the incident light intensity on the sample, and $\chi^{(3)}$ is the third-order electrical susceptibility [6]. In this experimental technique a Gaussian laser beam (TEM_{00}) is focused to a narrow waist by a lens along the propagation direction of the beam defined as being the z axis. The sample is moved through the focal plane along the z direction and the far-field transmittance of an iris centered along the beam propagation direction is measured as a function of the position z of the sample. As the sample moves along the beam focus, further focusing or defocusing modifies the wave front phase, thereby modifying the detected intensity. A sketch of the Z-scan setup is shown in Fig. 2. Our experimental setup includes a diode laser Quantum Ventus MPC600 from Quantum. The power of the incident laser was adjusted to 47 mW. A mechanical chopper (Standford SR540) provides ~30 ms pulses incident on the sample. The beam waist radius ω_o is about 21.5 μm. Data acquisition with temporal resolution is made by an oscilloscope (model TDS3012 from Tektronix) and general purpose interface bus (GPIB) board. The values of the nonlinear refractive indices for a thermal nonlinear optical response can be determined from fitting the spatial dependence on z and the temporal dependence, via thermal lens model [15], at

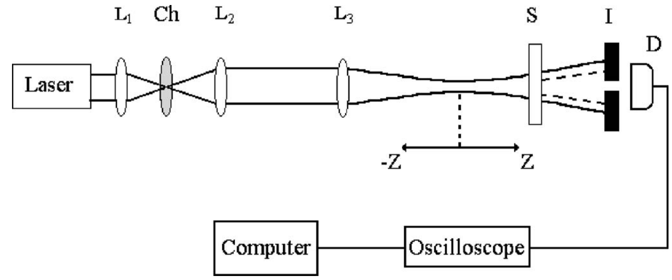

FIG. 2. Sketch of the Z-scan apparatus. L_1, L_2, and L_3 are lenses, chopper (Ch), sample (S), iris (I), and detector (D).

each z position of the transmittance T in a Z-scan [16] measurement expressed by

$$\Gamma(z,t) = \left\{ 1 + \left[\frac{\theta}{1+(1+x^2)t_{co}/2t} \right] \frac{2x}{1+x^2} \right\}^{-1}, \quad (1)$$

where $x=z/z_o$, z_o is the confocal parameter, $t_{co}=\omega_o^2/4D$ is the characteristic thermal time, $D=k/\rho C_P$ is the thermal diffusivity, $\theta=2.303\,(-dn/dT)\alpha P/\lambda\kappa$ is the phase shift [10], P is the power of the laser beam, λ the wavelength of the laser, α the linear optical absorption, dn/dT is the thermo-optical coefficient, κ the thermal conductivity, ρ is the density, and C_P is the specific heat. It is important to mention that dn/dT, α, κ, and D are anisotropic parameters in liquid crystal samples. These parameters $dn_{\parallel}(n_{\perp})/dT$, $\alpha_{\parallel}(\alpha_{\perp})$, $\kappa_{\parallel}(k_{\perp})$, and $D_{\parallel}(D_{\perp})$ are defined in a direction parallel (perpendicular) to the director of the nematic sample. The experimental data are obtained according to Eq. (1) where θ and t_{co} are the fitting parameters. The procedure employed here is the same utilized by Palffy-Muhoray *et al.* [16]. The relationship between θ and the nonlinear refractive index in the Sheik Bahae's model [5] n_2, in esu units, is given by

$$n_2 = \frac{\lambda \omega_o^2 c n_o}{80 \times 0.406 \pi d P}\theta, \quad (2)$$

where d it is the optical path length of the sample, n_o the linear refraction index, and c the speed of light at vacuum. The nonlinear refractive index (n_2) will be determined by means of Eqs. (1) and (2), respectively.

III. RESULTS AND DISCUSSION

Figure 3 shows typical experimental curves of Z-scan measurements on deuterated lyotropic mixtures in the N_C and N_D nematic phases. For both samples and both configurations of nematic director and beam polarization, the nonlinear refraction index is negative ($n_2<0$) indicating a self-defocusing effect [5]. The curves of Z-scan experiments exhibited in Figs. 3(a) and 3(b) correspond to the N_C phase, for a laser beam traveling in the nematic medium with polarization parallel and perpendicular to the optic axis of the nematic sample, respectively. In the same way the curves shown in Figs. 3(c) and 3(d) were obtained for the N_D phase. In these lyotropic nematic phases, extraordinary ($n_{\parallel}$) and ordinary ($n_{\perp}$) linear refractive indices were performed through an Abbe refractometer (Atago-3T) with an accuracy of

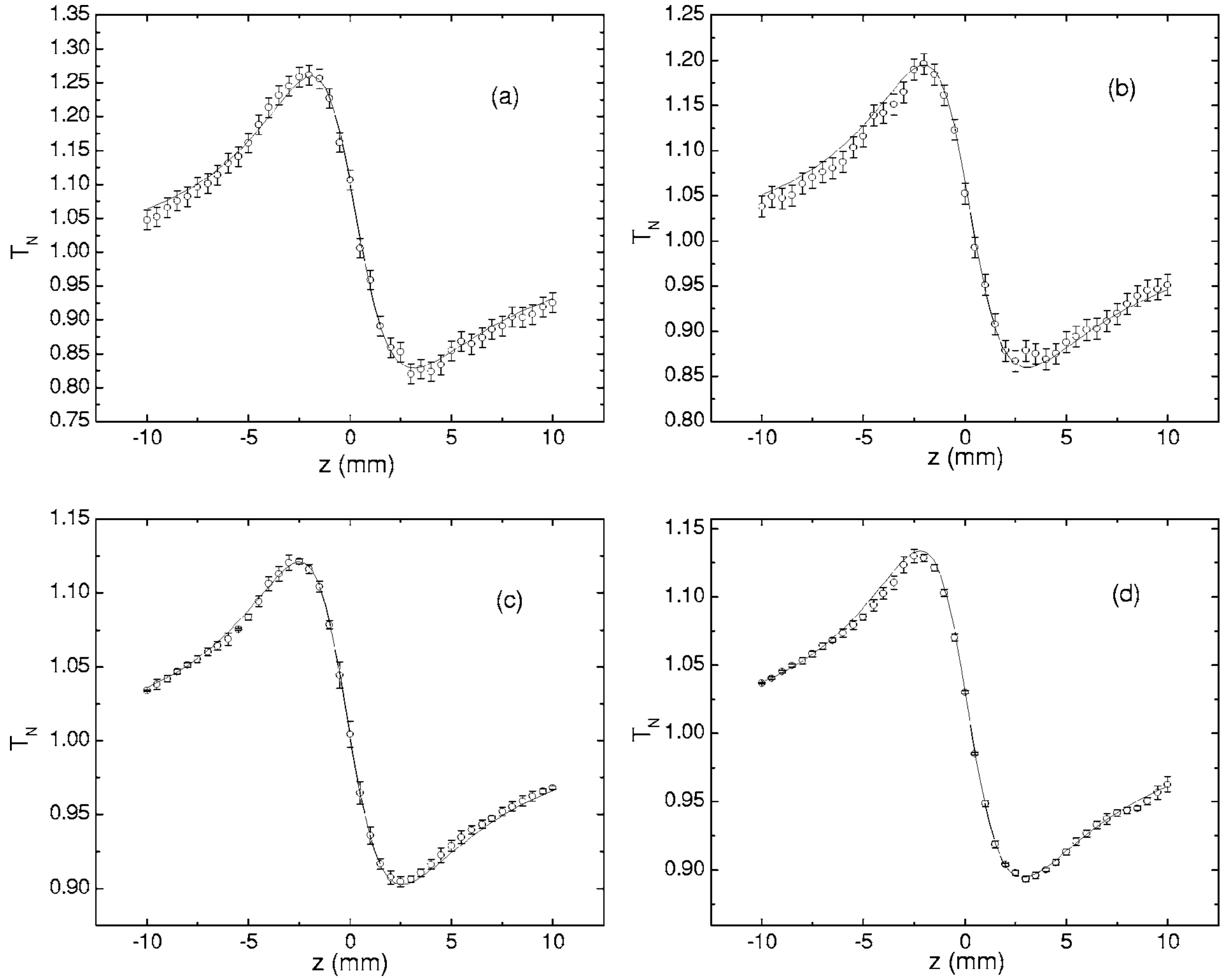

FIG. 3. Typical curves of Z-scan measurements on lyotropic mixtures for both configurations between the polarization of the laser beam and nematic director: (a) $\hat{n}||\vec{E}$ and (b) $\hat{n}\perp\vec{E}$ on the N_C phase; (c) $\hat{n}||\vec{E}$ and (d) $\hat{n}\perp\vec{E}$ on the N_D phase. The solid line corresponds to the fitting [16] of Eq. (1) with $t\sim 10\ t_{co}$.

2×10^{-4}. The sample temperatures were stable at 10 mK. The procedure for refractive index measurements is based on the internal reflection of light at an interface between the nematic samples and the surface of an optical glass prism. An optical polarizer was coupled to the Abbe refractometer to obtain the $n_{\parallel}$ and $n_{\perp}$ refractive indices [13]. Taking the experimental values, $\lambda=532$ nm, $P=47$ mW, $d=1$ mm, $\omega_o=21.5\ \mu$m, $n_{\parallel}(n_{\perp})$, and $\theta_{\parallel}(\theta_{\perp})$ anisotropic parameters into account, we obtain from Eq. (2) the values for the nonlinear refractive indices and the ratio $n_{2\parallel}/n_{2\perp}$. These important parameters are shown in Table I.

As can be seen in Table I, the nonlinear birefringence [11,18], $\Delta n_2=n_{2\parallel}-n_{2\perp}$, of N_C and N_D phases have opposite sign, being negative for the N_C phase and positive for the N_D phase and in absolute values $(\Delta n_2)_{N_C}>(\Delta n_2)_{N_D}$. It is worth to note that from Eq. (2) one can write

$$\Delta n_2=-An_{\perp}\left(\frac{n_{\parallel}}{n_{\perp}}\theta_{\parallel}-\theta_{\perp}\right), \tag{3}$$

where A is a constant. As the ratio $n_{\parallel}/n_{\perp}$ is approximately equal to the unit, we may conclude that the sign of nonlinear birefringence Δn_2 of N_C and N_D phases is due to the magnitude of phase shift θ produced in each phase. This important experimental result reflects a change of the symmetry of the micellar configuration as determined by the sign of the nonlinear birefringence and is in accordance with the linear optical birefringence measurements performed by several au-

TABLE I. Values of the linear refractive indices, phase shifts, nonlinear refractive indices (in esu units) and ratio of the nonlinear refractive indices of samples M_1 and M_2 at $T=25\ ^\circ$C.

Phase	$n_{\parallel}(\pm 0.0002)$	$n_{\perp}(\pm 0.0002)$	$10^{-2}\ \theta_{\parallel}$	$10^{-2}\ \theta_{\perp}$	$10^{-6}\ (-n_{2\parallel})$	$10^{-6}\ (-n_{2\perp})$	$n_{2\parallel}/n_{2\perp}$
N_C	1.3771	1.3799	22.61±0.01	17.89±0.01	4.79±0.08	3.80±0.08	1.26
N_D	1.3763	1.3744	11.82±0.01	12.94±0.01	2.50±0.08	2.74±0.08	0.91

thors in similar lyotropic systems [13,14,17]. The sign of the Δn_2 for the N_C phase of the deuterated lyotropic mixture is the same as the one reported for a lyotropic liquid crystal at the N_C phase made with common water [8,10]. Negative nonlinear birefringence was also observed in some thermotropic liquid crystals for light pulses in the ms range [18]. Note that the ratio $n_{2\|}/n_{2\perp}$ for the N_C phase is greater than that determined for the N_D phase. From Eq. (2) and Table I $n_{2\|}/n_{2\perp} \sim \theta_\|/\theta_\perp = 1.26$ for the N_C phase. In this way, the ratio $\theta_\|/\theta_\perp$ can be connected with the linear optical absorption and thermal diffusivity by $\theta_\|/\theta_\perp \sim \alpha_\| D_\perp/\alpha_\perp D_\|$. Taking the experimental value of the ratio $D_\|/D_\perp \sim 1.2$ into account, for the same nematic phase in a similar system, determined by a related technique [19], we obtain $\alpha_\|/\alpha_\perp \sim 1.5$. The anisotropy, $\Delta\alpha = \alpha_\| - \alpha_\perp$, observed in this N_C phase has been also determined in nematic thermotropic [6] and confirms the reliability of our results. In the N_D phase, the ratio $n_{2\|}/n_{2\perp} \sim \theta_\|/\theta_\perp = 0.91$. This value pointed out for the $\alpha_\|/\alpha_\perp$ and $D_\|/D_\perp$ is smaller than 1. This result has not been found in nematic thermotropic phase [20]. Therefore, it is not so surprising as it may seem at a first glance since the micelles, in lyotropic systems, do not have a rigid structure and change the micellar shape configuration under temperature and concentration conditions of amphiphilic molecules present in the lyotropic mixture. In addition, the parallel and perpendicular thermal diffusivities can be determined, by means of parameter t_{co}, from time evolution of the curve fitting of Eq. (1). In this N_D phase, we obtain the ratio $D_\|/D_\perp = 0.93$. The data indicate that $D_\|/D_\perp$ can be associated, in a simple approximation, with the anisotropy shape of the micelles being proportional to the ratio $l_\|/l_\perp \sim 0.8$, obtained from x-ray diffraction measurements [17] in the same N_D phase studied in this work, where $l_\|$ is thickness and $l_\perp$ the diameter of the disks in the discotic nematic sample. In this context, as a consequence of these experimental results, we found the ratio, $\alpha_\|/\alpha_\perp < 1$ as expected in the N_D phase.

To sum up, we have carried out a nonlinear refractive index study in discotic and calamitic nematic phases of deuterated lyotropic mixtures (KL/DeOH/D_2O). To the best of our knowledge, this experiment presents the first investigation of these nonlinear parameters, particulary, in the discotic nematic phase. Our data, in terms of the signs of the nonlinear birefringences $\Delta n_2 > 0$ in N_D phase and $\Delta n_2 < 0$ in N_C phase, are consistent with the nature of anisotropy shape of micellar aggregates characteristic of each uniaxial lyotropic nematic phase. The ratio $n_{2\|}/n_{2\perp} < 1$ and as consequence $D_\|/D_\perp$ and $\alpha_\|/\alpha_\perp < 1$ obtained for N_D phase is an interesting result which has not been found in nematic phases.

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