Z-scan measurement of the nonlinear refractive indices of micellar lyotropic liquid crystals with and without the ferrofluid doping

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The laser-induced nonlinear optical response of micellar lyotropic liquid crystals in the nematic and isotropic phases is presented. The *Z*-scan technique is used to measure the amplitude and the sign of the nonlinear refractive indices of the lyotropic mixture. The amplitude of the nonlinear refractive indices ($\sim -10^{-6}$ esu) is two orders of magnitude smaller than the one observed in thermotropic liquid crystals. The effect of the ferrofluid doping is also discussed. [S1063-651X(99)14103-5]

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I. INTRODUCTION

In the field of complex and supermolecular fluids, liquid crystals [1] constitute one of the most interesting examples. Because of their physical-chemical properties, not only basic research but also many technological applications are available. Optical techniques are widely used to investigate the physical-chemical properties of liquid crystals. In particular, in the phase transition and critical phenomena physics, considerable work has been done in the last years. The linear birefringence can be directly connected to the order parameter [1] and its measurement in the vicinity the critical points can improve the understanding of the collective behavior of the building blocks (molecules in thermotropics or micelles in lyotropics) of the liquid crystals. Specially in lyotropic nematic liquid crystals, the linear birefringence measurements were used to study the uniaxial-to-biaxial phase transition [2–4]. In most of these experiments with lyotropics [4,5], ferrofluids [6] were used to improve the sample's orientation in low magnetic fields. Ferrofluids are colloidal suspensions of small magnetic grains (about 100 Å of typical dimension), coated with surfactant agents or electrically charged, and dispersed in a liquid carrier. Until now, as far as the linear optical properties are concerned [7], this doping does not modify the values of the index of refraction and birefringence of lyotropics.

Liquid crystals also exhibit large optical nonlinearities [8]. This is due to the particular spatial arrangement of the molecules in space and their characteristics [1]. The nonlinear optical response of thermotropic liquid crystals has been investigated in recent years [9–12]. Depending on the time scale [12], different mechanisms (electronic, thermal, reorientational) contribute to the optical nonlinear response of the liquid crystalline media. The nonlinear optical properties of thermotropics can have several causes. The electric field of a laser interacting with a liquid crystal can induce refractive index changes by different mechanisms. Due to the large dielectric anisotropy of the molecules, the optical field can interact strongly with them causing a local reorientation of the nematic director or give rise to a preferential direction in the isotropic phase. This effect produces a change in the refractive index probed by the laser beam. This realignment depends on the geometry of the interaction between the nematic director and the wave polarization [10]. It is possible to induce a nonlinear optical response in liquid crystals in two different ways besides the electric one: an increase in the sample's temperature induces a change in the density (thermoelastic effect); and, another process induces a change in the order parameter. This effects, however, have different time scales. The steady-state behavior of these nonlinear effects has been explored both theoretically and experimentally [10]. The amplitude and the sign of the nonlinear refractive index depend on the time scale considered [8,12], but the origin of this dependence is not yet well understood.

To our knowledge, the nonlinear optical properties of micellar lyotropic liquid crystals with and without the ferrofluid doping, have not yet been investigated. These materials are mixtures of amphiphilic molecules and a solvent (usually water), under proper temperature and relative concentrations conditions [13,14]. The basic units of lyotropic nematics (discotic, calamitic and biaxial, named N_D, N_C, and N_B, respectively) are micelles, which are aggregates of amphiphilic molecules.

In this paper, we report what we believe to be the first measurements of the nonlinear refractive indices of a lyotropic liquid crystal mixture in the uniaxial nematic and isotropic phases, with and without the ferrofluid doping, using the *Z*-scan technique [15].

II. EXPERIMENTAL SECTION

A. Samples

The liquid crystal investigated is a mixture of potassium laurate (KL), 1-decanol (DeOH) and water [16], with two different compositions in wt %: mixture M_1 with KL $=27.968$, DeOH$=7.102$, and water$=64.93$; M_2 with KL $=27.041$, DeOH$=6.409$, and water$=66.55$. The phase sequences as a function of the temperature *T*, obtained measuring the linear birefringence as a function of *T* and by x-ray diffraction technique are mixture M_1:

$$N_D 17\,°\mathrm{C}\ N_B\, 20\,°\mathrm{C}\ N_C\, 44\,°\mathrm{C}$$

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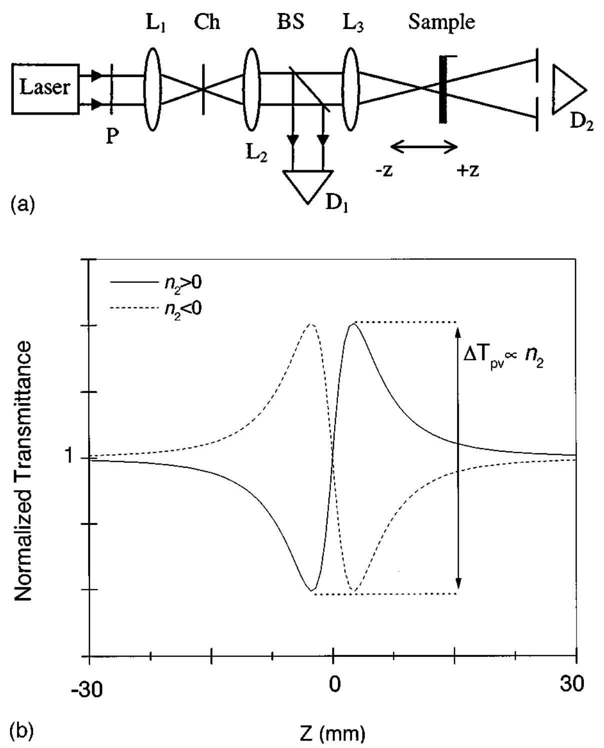

FIG. 1. (a) Sketch of the *Z*-scan apparatus. *P*, polarizer; Ch, chopper; L_1, L_2, and L_3, lens; BS, beam sampler; D_1 and D_2, detectors. (b) Theoretical behavior of the normalized transmittance as a function of the *z* position for two signs of the nonlinear refractive index n_2. The peak-to-valley distance ΔT_{pv} is proportional to n_2.

isotropic phase; mixture M_2: L (7.2 °C) isotropic (47.1 °CL), where L is a lamellar phase. All the measurements are performed at the temperature of 23 ± 1 °C. A small amount of a water-base ferrofluid [7] (3, 6, and 9 μl of ferrofluid per ml of the sample) is added to the doped mixtures. The magnetic fluid used a water base ferrofluid from Ferrofluidics Corp. (A01). The grains are made of Fe_3O_4 (concentration of 10^{15} gr/cm^3), with mean diameter of 154 Å (standard deviation of 94 Å); saturation magnetization $4\pi M=3.2$ G/cm^3, double coated with oleic acid. In the case of the sample M_1 the doping improves the sample's orientation (N_C phase) in a magnetic field. The liquid crystal is encapsulated in rectangular glass cells with two different sample thickness: 200 and 400 μm. Initially, the sample (N_C phase) is oriented in a static magnetic field in an electromagnet ($H_1\sim10$ kG), with $\mathbf{H}_1$ parallel to the largest dimension of the sample holder. In this configuration, the N_c nematic phase orients in a planar geometry (with the director **n** parallel to $\mathbf{H}_1$). After that, the sample is placed in the *Z*-scan apparatus, where a magnetic field (permanent magnets) of $H_2\sim1$ kG is present. This field, which keeps the same direction of the former $\mathbf{H}_1$, will maintain the sample's orientation during the measurements.

B. *Z*-scan technique

In general, a sample that presents a third-order nonlinearity has a refraction index $\overline{n}$ that may be written as $\overline{n}=n_o+(n_2/2)|E|^2$, where n_o, n_2, and E are the linear, the nonlinear refractive indices, and the electric field, respectively. The *Z*-Scan apparatus is the usual one described elsewhere [12,15,17]. Although many techniques have been developed to study nonlinear optical effects, the single-beam *Z*-scan technique is attractive because of its simplicity and sensitivity in measuring both the sign and the magnitude of the nonlinear refraction as well as the nonlinear absorption. In this technique a polarized Gaussian laser beam, propagating in the *z* direction, is focused to a narrow waist by using lens [Fig. 1(a)]. The sample is moved along the *z* direction through the focal point and the transmitted intensity is measured [Fig. 1(b)] in the far field using a photodiode behind a small iris, as a function of the *z* position. As the sample moves along the beam focus, self-focusing and defocusing modifies the wave front phase, thereby modifying the detected beam intensity. By measuring the transmittance, the value of the nonlinear refracted index is obtained. A continuous-wave Ar^+($\lambda=514.5$ nm) focused laser beam is used. A mechanical chopper provides the ms (between 10 and 50 ms) pulses incident on the sample. The beam waist at the sample is about 15 μm. The power illuminating the sample is 185 mW. A signal acquisition, with temporal resolution, is made to discard the linear effects [18]. In the case of anisotropic samples (such as the N_c phase), the setup allows the measurement of n_2 in different polarization conditions: with the electric field of the laser beam parallel (‖) and perpendicular (⊥) to the nematic director **n**.

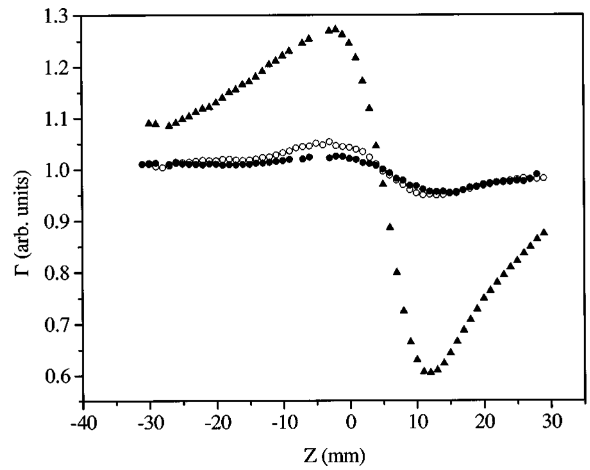

FIG. 2. *Z*-scan curves (normalized transmittance Γ as a function of the position *z*; 35 ms pulse, 185 mW power) of the lyotropic mixture M_2 at the isotropic phase, with different ferrofluid concentrations: (●) undoped sample; (○) ferrofluid-doped (3 μl/ml) sample; (▲) ferrofluid-doped (9 μl/ml) sample.

III. RESULTS AND DISCUSSION

A. Lyotropic without the ferrofluid doping

Figure 2 shows the typical *Z*-scan curve (normalized transmittance Γ as a function of the position *z*, 34 ms pulse) of the lyotropic mixture M_2 at the isotropic phase. In a first approach, the nonlinear refractive index n_2 can be determined from this measurement by fitting Eq. (1) [15]:

$$\Gamma(z)=1-\frac{4\Delta\phi_o(z/z_o)}{[1+(z/z_o)^2][9+(z/z_o)^2]}, \qquad (1)$$

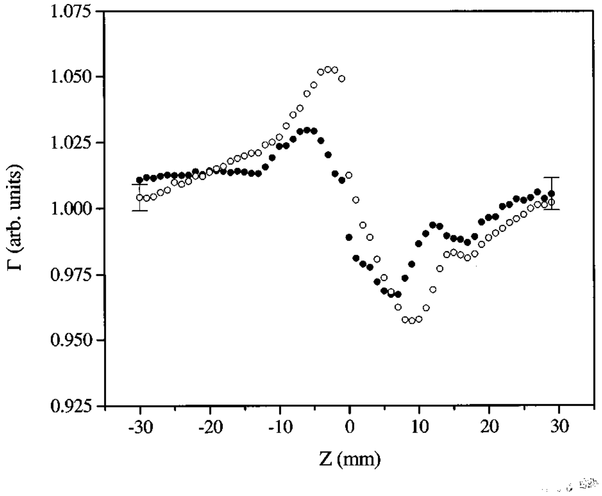

FIG. 3. Typical Z-scan result (normalized transmittance Γ as a function of the position z, 35 ms pulse; 185 mW power) with sample M_1 at the N_c phase. Electric field of the polarized laser beam perpendicular to **n**: (●) undoped sample; (○) ferrofluid-doped (3 μl/ml) sample. Typical error bars are shown.

with $\Delta\phi_o = k\,n_2 L\,I_o$, where k, L, I_o, and z_o are the wave vector, the sample thickness, the laser beam intensity at the focus, and the Rayleigh length of the beam, respectively.

The mean value of n_2 obtained from a series of independent experiments is $n_2 = -(3.8\pm 0.1)\times 10^{-6}$ esu. This error takes into account not only the fitting errors but also the reproducibility of the experiment. The order of magnitude of n_2 is 10^2 smaller than the values obtained with thermotropic liquid crystals [11,17]. The negative sign of n_2 indicates a *self-defocusing* effect of the lyotropic sample.

Figure 3 shows a typical Z-scan result with sample M_1 (N_c phase). The value of n_2 with the incident beam polarized perpendicular to **n** (35 ms pulse width), obtained from a series of independent measurements [Eq. (1)] is $n_{2\perp} = -(3.4\pm 0.1)\times 10^{-6}$ esu. n_2 increases with the pulse width, and reaches an almost constant value for widths larger than about 35 ms.

At this time scale, the nonlinear behavior of the lyotropic liquid crystal has a thermal origin and we can evaluate the order of magnitude of the pure thermal refractive index change using Eq. (2) [8]:

$$n_2 = \frac{\alpha\omega_o^2}{4\pi^2\rho_o C_v D}\left(\frac{dn}{dT}\right), \tag{2}$$

where α, ω_o, ρ_o, C_v, and D, are the linear absorption ($\simeq 10^{-3}$ cm^{-1}), the laser beam waist at the focus ($\simeq 15$ μm), the liquid crystal density ($\simeq 1$ g/cm^3), the specific heat ($\simeq 4.1\times 10^7$ erg/g K), and the diffusion coefficient $\simeq 10^{-6}$ cm^2/s), respectively. We also use $dn/dT \simeq -2.5\times 10^{-4}$ [2]. The value of n_2 obtained is -7×10^{-7} esu, in reasonable agreement with our experimental values.

As stressed before, our results of $n_{2\perp}$ are about 10^2 times smaller than the available results of thermotropic nematics (pulse width of 10 ms) [12]. In our case, n_2 is negative. In the case of the 5CB in the nematic and in the isotropic phase, the order of magnitude of n_2 is 10^{-4} esu, $n_{2\parallel} < 0$ and $n_{2\perp} > 0$. For the T15 (which differs from the 5CB only by the presence of an additional ring), the order of magnitude is the same but both indices are negative. In the case of the commercial ZLI-1538 and 2303, the order of magnitude is the same (10^{-4}), $n_{2\parallel} < 0$ and $n_{2\perp} > 0$. The comparison between these results of lyotropics and thermotropics, however, is not straightforward.

Taking into account the time scale involved (milliseconds), it is reasonable to consider that the main effect present in our measurements has a thermal origin. It is expected that the thermal response time depends on the laser pulse width. This time is mainly related to the Brownian and noncorrelated behavior of the micelles, which could induces some local modifications of ρ and S. The lyotropic mesophases present also a small diamagnetic susceptibility anisotropy $\Delta\chi_m$ ($\sim 10^{-8}$ cgs) [19]. The coupling between the magnetic field (associated with the laser beam) and the director **n**, taking into account the value of $\Delta\chi_m$, is smaller (10 times) than the Brownian thermal energy at $T \sim 23$°C. So, it is highly improbable that the nonlinear effect observed in lyotropics could be associated to variations in S due to the magnetic coupling. On other hand, variations in ρ and S could be due to the heating of the sample by the laser beam. The dielectric constant of a medium can be written as $\varepsilon_i(T) = \varepsilon_I(T) + C_i\Delta\varepsilon(T)$, where ε_I is the dielectric constant of the isotropic mesophase of the lyotropic liquid crystal ($T \gg T_c$ $\equiv$ temperature transition to the isotropic phase), $\Delta\varepsilon$ is the dielectric anisotropy and i states for $\parallel$ or $\perp$. These parameters, ε_I and $\Delta\varepsilon$, depend on the sample's density ρ [20]. Since the micelles have around them an electric double layer [21,22] formed by the counterions of the potassium laurate molecules, in the limit of high frequencies, the contribution of the micellar susceptibility is expected to be important.

B. Lyotropic with the ferrofluid doping

Figure 2 shows the typical Z-scan curve (normalized transmittance Γ as a function of the position z, 35 ms pulse) of the ferrolyotropic mixture M_2 at the isotropic phase (ferrofluid doping of 9 μl/ml). The mean value of n_2 obtained [Eq. (1)] from a series of independent experiments is: $n_2 = -(7.4\pm 0.1)\times 10^{-6}$ esu. The same experiment (at the same experimental conditions) performed with distilled and deionized water with the same concentration of magnetic grains gives $n_2 = -(1.3\pm 0.1)\times 10^{-6}$ esu. Without the ferrofluid doping no Z-scan signal is detected with pure water. The effect of the ferrofluid concentration on the Z-scan curves with sample M_2 at the isotropic phase is also shown in Fig. 2. The larger the ferrofluid concentration the bigger the nonlinear response of the sample. The values of n_2 obtained with the two doped samples presented in Fig. 2 are $-(1.0\pm 0.1)\times 10^{-6}$ and $-(7.4\pm 0.1)\times 10^{-6}$ esu, for the ferrofluid concentrations of 3 and 9 μl/ml, respectively.

Figure 3 shows a typical Z-scan result of sample M_1 doped with ferrofluid (N_c phase). The values of n_2 [using Eq. 1)] with the incident beam polarized parallel ($n_{2\parallel}$) and perpendicular ($n_{2\perp}$) to **n** are presented in Table I. n_2 increases with the pulse width, and reaches an almost constant value for widths larger than approximately 35 ms.

The nonlinear optical birefringence, $\Delta n_2 = n_{2\parallel} - n_{2\perp}$ is shown in Fig. 4. Δn_2 remains almost constant (approximately -10^{-7} esu), for all the pulse widths (Δt) used.

TABLE I. Pulse width in the Z-scan experiment and the nonlinear refractive indices $n_{2\parallel}$ and $n_{2\perp}$. Lyotropic nematic (N_C) liquid crystal at $T=23\,°C$. Ferrofluid doped (3 μl/ml) sample. $\Delta t=35$ ms.

Pulse width (ms)	$-n_{2\parallel}(10^{-6}$ esu)	$-n_{2\perp}(10^{-6}$ esu)
10	1.13±0.08	0.78±0.11
15	1.21±0.04	0.91±0.06
20	1.28±0.04	0.98±0.06
25	1.39±0.05	1.03±0.07
30	1.39±0.05	1.09±0.07
35	1.47±0.04	1.09±0.07
40	1.46±0.04	1.09±0.07
45	1.54±0.04	1.12±0.07
50	1.52±0.04	1.13±0.07

The values of n_2 obtained with doped samples are about 10 times larger than those obtained with undoped samples. A possible mechanism that could be present in the ferrolyotropic samples illuminated by the laser beam is the *indirect heating* of the sample *via* the ferrofluid grains. This mechanism (called hyperthermia) is well known in the biomedical application of magnetic fluids in the treatment of tumoral cells [23]. The usual mechanism of hyperthermia of living tissues in contact with ferrofluids consists of submiting the grains to a radiofrequency field. The energy absorbed by the grain increases its temperature and, by heat conduction, increases the tissue temperature. A similar mechanism seems to take place in ferrolyotropics. The grains absorb energy from the laser beam and heat the lyotropic matrix around them. This increase of temperature could modify the density of the lyotropic and increases its nonlinear response. The result obtained with water doped with ferrofluids corroborates this scenario.

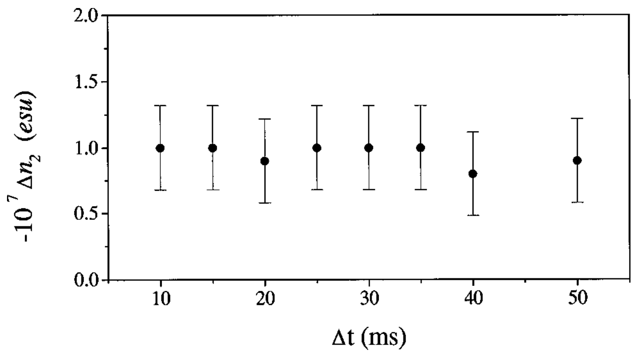

FIG. 4. Nonlinear optical birefringence, $\Delta n_2=n_{2\parallel}-n_{2\perp}$. Sample M_1 at the N_c phase. Ferrofluid-doped (3 μl/ml) sample.

IV. SUMMARY

Using the transmission Z-scan technique, we have measured the laser-induced nonlinear optical response of a micellar lyotropic liquid crystal in the calamitic nematic and isotropic phases, in time scales of millisecond laser pulses, with and without the ferrofluid doping. The order of magnitude of n_2 is 10^2 smaller than that measured in thermotropics. In the case of the lyotropic nematic, $n_{2\parallel}<0$ and $n_{2\perp}<0$, indicating the defocusing behavior of the sample. Considering the particularities of the lyotropic system and the time scale used, we suggest that the nonlinear response observed has mainly a thermal origin. The ferrofluid doping, even in small quantities, modifies the nonlinear response of the lyotropic phase.

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