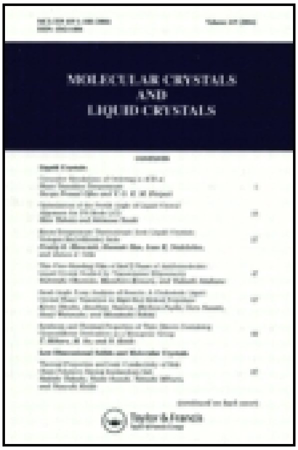

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N. M. Kimura [a], P. A. Santoro [a], S. L. Gómez [b] & A. J. Palangana [a]

[a] Departamento de Física, Universidade Estadual de Maringá, Maringá, PR, Brazil

[b] Departamento de Física, Universidade Estadual de Ponta Grossa, Ponta Grossa, PR, Brazil

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Nonlinear Refractive Index and Thermal Diffusivity Measurements Near the Reentrant Isotropic – Discotic Nematic Phase Transition

N. M. Kimura[1], P. A. Santoro[1], S. L. Gómez[2], and A. J. Palangana[1]
[1]Departamento de Física, Universidade Estadual de Maringá, Maringá, PR, Brazil
[2]Departamento de Física, Universidade Estadual de Ponta Grossa, Ponta Grossa, PR, Brazil

In this work we report on measurements, as a function of the temperature, of the nonlinear refractive indices parallel ($n_{2_\parallel}$) and perpendicular ($n_{2_\perp}$) to the nematic director near the reentrant isotropic – discotic nematic phase transition in a lyotropic mixture of potassium laurate, decanol and D_2O. Thermal diffusivities, parallel ($D_\parallel$) and perpendicular ($D_\perp$) to the director in this reentrant isotropic–discotic nematic phase transition, were also obtained as a function of the temperature from Z-scan experiment and interpreted through a thermal lens model. The ratios $n_{2_\parallel}/n_{2_\perp}$ and $D\|/D_\perp$ are less than one in this nematic phase. These results are discussed in terms of structural changes in the micellar configuration which takes place in each nematic phase transition.

Keywords: discotic nematic; nonlinear refractive index; thermal diffusivity

INTRODUCTION

Lyotropic liquid crystals are anisotropic complex fluids formed in aqueous solutions of amphiphilic molecules under convenient temperature and concentration conditions. The basic units of these liquid crystals are anisotropic micelles. From the phase diagram reported by Yu and Saupe [1], two uniaxial nematics and one biaxial nematic

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Address correspondence to A. J. Palangana, Departamento de Física, Universidade Estadual de Maringa, Av. Colombo, 5790, Maringa, PR 87020-900, Brasil. E-mail: palanga@dfi.uem.br

phases were characterized. In addition, an isotropic phase (I) is observed at high temperature as well as one reentrant isotropic phase (I_{RE}) which takes place at a lower temperature. The uniaxial nematic lyotropic phases are known as prolate (calamitic N_C) and oblate (discotic N_D) micellar aggregates [2] depending on whether the director **n** is oriented parallel or perpendicular to the magnetic field **H**. When a laser beam passes through these materials the absorbed energy is converted into heat and nonlinear phenomena can be induced. At milliseconds (*ms*) time range, the nonlinear optical response is expected to be of thermal and orientational origin [3,4]. In this context, the Z-scan technique was conceived as being a simple and efficient method to measure the nonlinear optical response of a medium material [5]. In this work, we report on nonlinear refractive index (n_2) and thermal diffusivity (D) measurements [6,7] through the use of Z-scan technique in a I_{RE}-N_D-I phase transitions, as a function of the temperature, in a lyotropic mixture of potassium laurate, decanol and D_2O. It is well known that in liquid crystal materials the nonlinear refractive index and thermal diffusivity are anisotropic parameters [8,9]. In this way, this study requires the measurements of nonlinear refractive indices, $n_{2_\parallel}$ and $n_{2_\perp}$, and thermal diffusivities, $D_\parallel$ and $D_\perp$. These parameters can be obtained from an experimental configuration as a laser beam travels in the nematic medium with polarization parallel or perpendicular, respectively, to the director of the nematic sample. The experimental results are analyzed according to the thermal lens model (TLM) as described in Ref. [10]. By applying that procedure the nonlinear birefringence, $\Delta n_2 = n_{2_\parallel} - n_{2_\perp}$, and thermal diffusivity anisotropy, $\Delta D = D_\parallel - D_\perp$, have been found to be positive and negative, respectively, in the discotic nematic phase [6,7]. These data are discussed in terms of structural changes in the micellar configuration which takes place in each phase transition.

FUNDAMENTALS

In the Z-scan experiment a Gaussian laser beam (TEM_{00}) is focused on a narrow waist by a lens along the propagation direction of the beam defined as being the z axis [5]. 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 Figure 1. The experimental setup includes a diode laser Ventus MPC600 (from Quantum) with power output adjusted

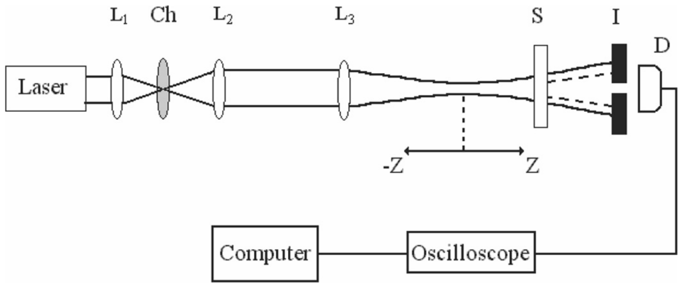


FIGURE 1 Sketch of the Z-scan apparatus. L_1, L_2, and L_3 are lenses; Chopper (Ch); Sample (S); Iris (I) and Detector (D).

to 47 mW. The beam waist radius ω_o is about 21.5 μm and a mechanical chopper (Standford SR540) provides laser pulses (33 ms) incident on the sample. Data acquisition with temporal resolution is made by an oscilloscope model TDS3012 (from Tektronix) and a GPIB board. The nonlinear parameters can be determined from fitting the spatial dependence on z and the temporal dependence via thermal lens model [11]. The normalized light transmittance (TN), as a function of z and time t, can be expressed by [10]

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

where $x = z/z_o$, z_o is the confocal parameter, $\theta = 2.303(-dn/dT)\alpha P/\lambda k$ is the phase shift [12], $t_{co} = \omega_o^2/4D$ is the characteristic thermal time, $D = k/\rho C_P$ is the thermal diffusivity, P is the power of the laser beam, λ is the wavelength of the laser, α is the linear optic absorption, dn/dT is the thermo-optical coefficient, k is the thermal conductivity, ρ is the density and C_P is the specific heat. The nonlinear refractive index (n_2) defined from Sheik Bahae model [5,10] is related to parameter θ (in esu units) by

$$n_2 = \frac{\lambda\omega_o^2 cn}{80 \times 0.406\pi dP}\theta, \tag{2}$$

where d is the optical path length of the nematic sample, n is the linear refractive index, and c is the light speed in the vacuum. The anisotropic parameters, $\theta_{\parallel}(\theta_{\perp})$, $n_{2_{\parallel}}(n_{2_{\perp}})$, $t_{co_{\parallel}}(t_{co_{\perp}})$ and $D_{\parallel}(D_{\perp})$, are defined in a direction parallel (perpendicular) to the director $\mathbf{n}$ of the nematic sample, so the configurations between $\mathbf{n}$ and the laser beam polarization $\mathbf{E}$ are $\mathbf{n}||\mathbf{E}$ and $\mathbf{n}\perp\mathbf{E}$, as indicated in Figure 2.

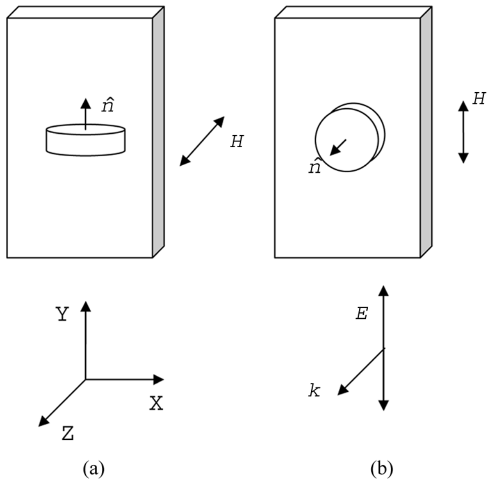
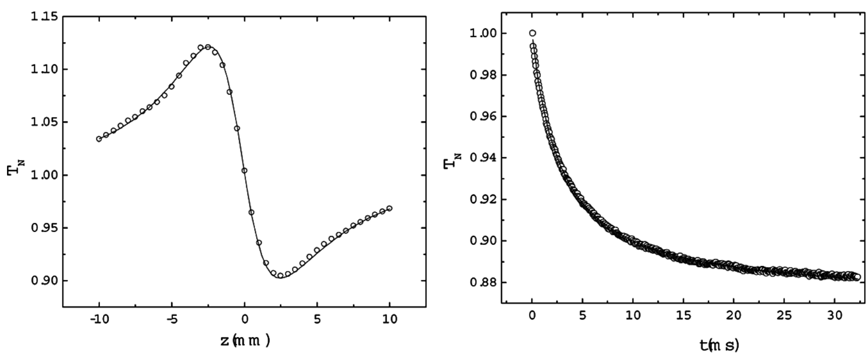


FIGURE 2 Experimental configuration of the nematic director, magnetic field and the laser beam polarization for thermal diffusivity measurements of (a) $n_{2_{\parallel}}(D_{\parallel})$ and (b) $n_{2_{\perp}}(D_{\perp})$ in the N_D phase.

The lyotropic mixture investigated in this work was prepared with the following concentrations in weight percentage: potassium laurate (*KL: 24.80*), decanol (*DeOH: 6.24*) and D_2O (*68.96*). The phase sequence, determined by optical microscopy, digital image processing and refractive index measurements [13,14], is reentrant isotropic I_{RE} (12.1°C) – discotic nematic N_D (36.3°C) – isotropic I. The nematic sample was conditioned in sealed planar glass cells (1 mm of light path) from Hellma. The $x-y$ plane of the sample is defined with $x(y)$ axis parallel to the length (width) of the cells and z is the normal axis to the biggest surface of the sample holder. Homeotropic alignment of the discotic nematic phase was performed by a magnetic field of 10 kG parallel to the $x-y$ axis of the laboratory frame combined with rotations of the sample around z-axis. A small quantity of ferrofluid (<0.04 wt%) was added to the nematic sample in order to ensure a homeotropic uniform orientation of the N_D phase. The experimental data can be determined according to Eq. (1) by means of a self-consistent fitting procedure of θ and t_{co} parameters and Eq. (2). This procedure is the same utilized in Ref. [10]. In this way $n_{2_{\parallel}}(n_{2_{\perp}})$ and $D_{\parallel}(D_{\perp})$ are determined as a function of the temperature near the $N_D - I_{RE}$ and $N_D - I$ phase transitions.

RESULTS AND DISCUSSION

Figure 3(a) shows a typical Z–scan curve obtained for the discotic nematic phase at temperature $T = 35.7°C$ and Figure 3(b) exhibits the typical time dependence transmittance at a fixed z position. In this case, the nonlinear refractive index is negative ($n_2 < 0$) indicating a self-defocusing effect [5]. The experimental curves shown in these figures correspond to the N_D phase, for a laser beam traveling in the nematic medium with polarization parallel to the optic axis of the discotic nematic sample. Similar curves were obtained in a perpendicular direction to the optic axis of the N_D phase. In the N_D phase, extraordinary ($n_\parallel$) and ordinary ($n_\perp$) linear refractive indices were determined [14] through an Abbe refractometer with an accuracy of 2×10^{-4}. Taking the experimental values, $\lambda = 532\,\text{nm}$, $P = 47\,\text{mW}$, $d = 1\,\text{mm}$, $\omega_o = 21.5\,\mu\text{m}$, $n_\parallel(n_\perp)$ and $\theta_\parallel(\theta_\perp)$ fitting parameters into account we obtain, from Eq. (2), the parallel ($n_{2_\parallel}$) and perpendicular ($n_{2_\perp}$) nonlinear refractive indices. These data are plotted in Figure 4(a), as functions of the temperature near the $N_D - I_{RE}$ and $N_D - I$ phase transitions, respectively. Note that, near the $N_D - I_{RE}$ transition, $n_{2_\parallel}(n_{2_\perp})$ decreases (increases) as the temperature decreases until, in the I_{RE} phase, just one nonlinear refractive index is determined. This fact confirms the existence of the I_{RE} phase in accordance to the phase diagram reported by Yu and Saupe [1]. In Figure 4(b) we can observe that, near the $N_D - I$ transition, as the temperature increases, $n_{2_\parallel}(n_{2_\perp})$



(a) (b)

FIGURE 3 Typical curves of Z-scan measurements on the lyotropic mixture in the N_D phase, concerning the configuration $n \| E$. The solid line (a) corresponds to the fitting of Eq. (1) with $t \sim 10t_{co}$ for $\theta_\parallel = 1.213 \times 10^{-3}$. Typical time dependence transmittance (b) at fixed $z = 2.5\,\text{mm}$. The solid line corresponds to the fitting of Eq. (1) with $\theta_\parallel = 1.213 \times 10^{-3}$ for $t_{co_\parallel} = 2.47\,\text{ms}$.

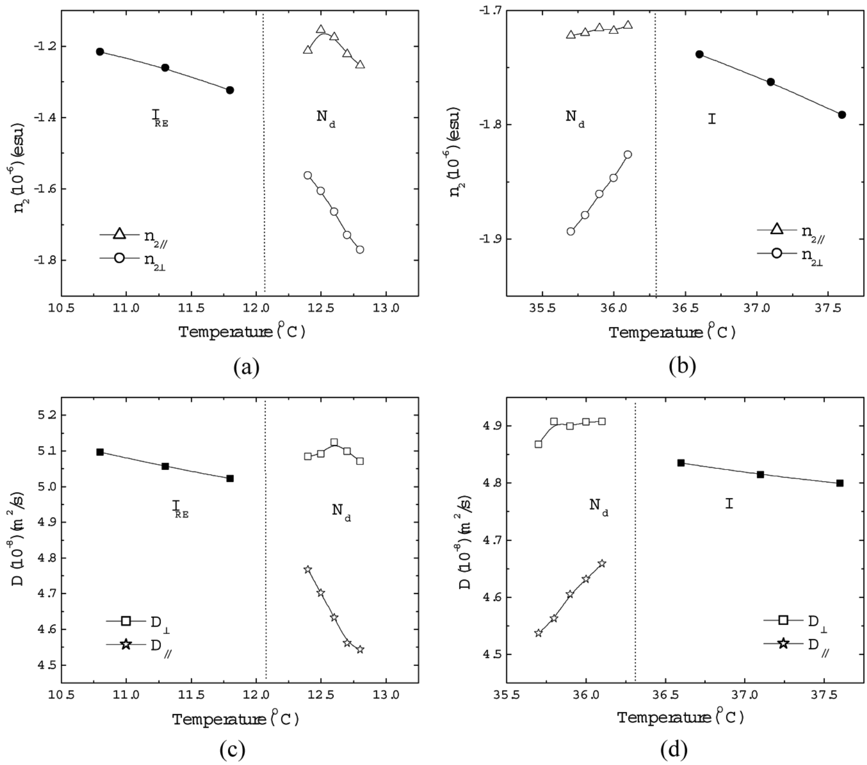


FIGURE 4 Nonlinear refractive indices and thermal diffusivities versus temperature; (a) and (c) near the discotic nematic – isotropic reentrant transition and (b) and (d) near the discotic nematic – isotropic transition; $n_{2_\parallel}(n_{2_\perp})$ and $D_\parallel(D_\perp)$ are the parallel (perpendicular) nonlinear refractive index and parallel (perpendicular) thermal diffusivity, respectively. The solid lines are only a guide to the eyes.

decreases (increases) and both indices trend to one nonlinear refractive index in the isotropic phase. From these experimental data one gets the nonlinear birefringence, $\Delta n_2 = n_{2_\parallel} - n_{2_\perp}$, which is positive in this discotic nematic phase. On the other hand, negative nonlinear birefringence is observed in a calamitc nematic phase and in some thermotropic liquid crystals for light pulses in the *ms* range [6,15]. It is important to mention that, from Eq. (2), the sign of Δn_2 is due essentially to the magnitude of phase shift θ produced in the N_D phase, since the ratio $n_\parallel/n_\perp$ is approximately equal to the unit [6].

In addition, parallel $(D_\parallel)$ and perpendicular $(D_\perp)$ thermal diffusivities can be determined from experimental data by using with $t_{co} = \omega_o^2/4D$

with $t_{co_{\parallel}}(t_{co_{\perp}})$ anisotropic parameters and $\omega_o = 21.5\,\mu\text{m}$. Figure 4(c) and 4(d) shows the $D_{\parallel}$ and $D_{\perp}$ parameters versus temperature near the $N_D - I_{RE}$ and $N_D - I$ phase transitions. Temperature dependence of $D_{\parallel}(D_{\perp})$ thermal diffusivities in the vicinities of these transitions is opposed to the $n_{2_{\parallel}}(n_{2_{\perp}})$ nonlinear refractive indices, and in this way both anisotropic parameters trend to one nonlinear refractive index or thermal diffusivity in the isotropic or isotropic reentrant phases. It is worth mentioning that the thermal diffusivity anisotropy, $\Delta D = D_{\parallel} - D_{\perp}$, is negative in this N_D phase and consequently the ratio $D_{\parallel}/D_{\perp}$ is smaller than one. This important result was recently discussed [7] by using a simple model [16] where this ratio was correlated to the micellar shape anisotropy [17]. Theoretical investigations are yet required to clarify this ratio $(D_{\parallel}/D_{\perp} < 1)$ determined in this work [18].

To sum up, we have carried out nonlinear refractive index and thermal diffusivity studies near the $N_D - I_{RE}$ and $N_D - I$ phase transitions of a lyotropic discotic nematic phase. The anisotropic parameters, $\Delta n_2 = n_{2_{\parallel}} - n_{2_{\perp}}$ and $\Delta D = D_{\parallel} - D_{\perp}$, determined in this work are positive and negative, respectively, in this N_D phase. These results are consistent with the nature of anisotropy shape of micellar aggregates characteristic of this phase. To the best of our knowledge, this experiment presents the first investigations of these anisotropic parameters in the vicinities of the $N_D - I(I_{RE})$ transitions and confirms the occurrence of the reentrant isotropic phase (I_{RE}) in accordance with the phase diagram reported in the literature.

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